

# Effect of Different Cooling Modes on Crystal Size Distribution in a Batch Cooling Crystallizer for DL-Malic Acid

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The effects of various cooling modes such as natural cooling mode, linear cooling mode, and controlled cooling modes type A and B in a batch cooling crystallizer on crystal size distribution (CSD) as well as the mean crystal size have been studied for DL-malic acid. The natural cooling mode was found to yield crystals in the range of 250 to 1000  $\mu$ m, whereas the linear cooling mode was found to yield larger crystals, in the range of 800 to 1600  $\mu$ m. The mean crystal size was found to increase in the order of natural cooling mode. Since linear cooling mode A, controlled cooling mode B, and linear cooling mode. Since linear cooling mode was found to yield larger ger mean crystal size, the effect of operating parameters such as the seed concentration and agitation rates on CSD was assessed using the linear cooling mode. The increase in seed concentration from 0.5 to 1% resulted in a larger mean crystal size; while an increase from 1 to 2% reduced the mean crystal size. An agitator rate of 90 rpm was found to yield larger mean crystal size than agitation rates of 60 and 120 rpm.

Keywords batch cooling crystallizer, DL-malic acid, crystal size distribution (CSD)

#### Introduction

Crystallization is one of the well-known unit operations and an important processing technique in several industries that can be performed either in batch or continuous mode. Crystallization from solution retains importance as an industrial process because many materials continue to be marketed in crystalline form. The appearance and size range of the crystalline products are significant since customer acceptance largely depends on this (Bamforth, 1965). Crystallization's uses are two-fold: crystals formed from impure solutions are pure in nature and crystallization affords a practical method of obtaining pure chemical substances in a satisfactory condition for packaging and storing (McCabe et al., 1993).

Address correspondence to C. Srinivasakannan, School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Pulau Penang, Malaysia. E-mail: chkannan@eng.usm.my The crystals obtained as a final product should be strong, non-aggregated, uniform in size, and non-caking in the package. If the crystals are to be further processed, reasonable size and size uniformity are desirable for filtering, washing, reacting with other chemicals, transporting, and storing. For these reasons, crystal size distribution (CSD) must be under control, which is the prime objective in the design and operation of a crystallizer. A uniform and narrow CSD with a large mean crystal size is often desired.

A batch cooling crystallizer is commonly used in the production of fine chemicals, pharmaceuticals, biochemicals, and products that are difficult to handle, such as toxic and highly viscous materials. In a batch cooling crystallizer, the solution is cooled for achieving supersaturation, which is essential for crystallization (Jones, 1974). In many cases, only a batch crystallizer can produce the required crystal form, size distribution, or purity. It has the advantage of being simple and flexible, requiring less investment, minimizing encrustation on heat exchanger surface, and generally involving less process development (Tavare et al., 1990). Batch processes are also preferred if the production rate is low or the equipment must be used to produce several different products (Mersmann, 2000).

A crystallizer often incorporates controlled cooling, since uncontrolled cooling leads to poor crystal quality (Mullin, 1997). This is due to the formation of a large number of crystal nuclei that cannot grow to the desired size if the cooling rate in the initial stage of the process is too high. To get large crystals, the temperature should be reduced slowly in the early stages of the process and more rapidly as the temperature of the solution decreases (Mullin & Nyvlt, 1971).

Earlier research results on batch crystallizers were mostly focused on the control of cooling rate and seed concentrations in order to maintain supersaturation within the so-called metastable zone to control crystal size distribution. Jagadesh et al. (1999) compared the crystal size distribution for the three types of cooling modes, namely, controlled cooling mode, linear cooling mode, and natural cooling mode for potassium sulfate. They reported that the linear cooling mode yielded crystals of larger mean size. However, the natural cooling mode was selected as the mode to operate the crystallizer as it does not require any temperature control. Natural cooling mode corresponds to the case where coolant to the jacket of the crystallizer is supplied at constant temperature. Appropriate seeding was found to arrest the formation of fresh nuclei resulting from the high levels of supersaturation created under natural cooling mode. A decrease in supersaturation levels with increase in the seed concentration ratio simulating conditions of controlled cooling was reported. Further, a bimodal-type of crystal size distribution was observed in all the cooling modes at lower seed concentration, and a critical seed concentration was identified to eliminate the bimodal CSD. The seed concentration required for attaining uni-modal crystal size distribution is much lower than the seed concentration required for attaining ideal growth curve.

Mohameed et al. (2002) reported that the linear cooling mode yielded a larger mean crystal size for potassium chloride than the controlled cooling mode for unseeded crystallizer. The linear cooling mode is found to have higher supersaturation levels initially, which aids the formation of fresh nuclei, which have sufficient time to grow to a larger mean crystal size. The supersaturation levels in controlled cooling mode were lower during early stages of crystallization than those of the linear cooling mode, but higher than those of the linear cooling mode during the later stages of crystallization. This was attributed to the formation of fresh nuclei at later stages, resulting in a lower mean crystal size. While comparing the utilization of natural cooling mode for operation of crystallizers, its requirement of high seed concentration to control supersaturation to attain ideal growth curve leads to higher loads on the downstream processing, thereby increasing processing cost. Moreover, the utilization of higher seed concentration limits the mean crystal size of the crystals due to mass balance constraint. Since control of the cooling rate is not difficult with the use of modern process control, the goal was to study the effect of different cooling modes on crystal size distribution for a uni-modal crystal size distribution of DL-malic acid with seeding, since it is a common practice in industry to seed the crystallizer in order not to cross the so-called metastable zone to avoid showering of nuclei.

DL-malic acid is one of the fine chemicals, otherwise called apple acid, that finds wide application in preparation of flavoring extracts, confections, soft drinks, and effervescent salts; acidifiers; dispersing agents; medicines; and acidulants, and antioxidants in foods. Crystallization is the bottleneck of the process, due to high solubility and low growth rate resulting in large holdup of the magma. The specific objectives were to study the effect of different cooling modes in order to identify the cooling mode that is best suited for production of narrow CSD as well as higher mean crystal size and to assess the effect of operating parameters such as the seed concentration and rate of agitation under the preferred cooling mode.

### **Experimental Design**

Experiments were carried out in a five-liter jacketed crystallizer made of stainless steel 316 grade with a dished bottom, and a mild steel jacket for heating and cooling purposes. The schematic diagram of the experimental setup is shown in Figure 1. The crystallizer consists of an agitator, thermocouple, jacket, jacket fluid inlet, jacket fluid outlet, and outlet valve. The diameter of the crystallizer was 180 mm with a height of 220 mm. The experimental setup comprised a circulation bath



Figure 1. Schematic diagram of batch cooling crystallizer; (1) agitator, (2) thermocouple, (3) jacket, (4) jacket fluid inlet, (5) jacket fluid outlet, (6) outlet valve.

Temperature °C	Grams of malic acid/100 g of water
0	89
10	105
20	126
40	180
60	270
80	460

**Table 1.** Solubility data for malic acid-water system

with provision to either cool to  $-50^{\circ}$ C or heat to  $250^{\circ}$ C. An anchor agitator was used for mixing that was kept at a height of 20 mm from the bottom of the crystallizer. The span or diameter, height, and width were 90 mm, 80 mm, and 10 mm respectively.

Desired temperature in the crystallizer was achieved by setting the appropriate temperature in the control unit of the circulation bath. The temperature sensor in the control unit refers to the temperature in the crystallizer bath and accordingly manipulated the temperature of coolant to achieve the required temperature. Based on the solubility data (Table 1) a saturated solution of malic acid was prepared at a



Figure 2. Different temperature cooling modes.

temperature of 60°C by dissolving the required amount in three liters of distilled water. Commercially available food-grade malic acid obtained from the market (source: TCL, India) was utilized for the study. After the malic acid was dissolved, the stirrer speed was adjusted to the desired level. The experiments were started by cooling the solution following different cooling modes as shown in Figure 2. The seeds were added to the crystallizer under supersaturated conditions at required seed concentration. Seed concentration was expressed as the mass percentage of seeds taken to the theoretical yield of crystals obtained from the solubility curve by cooling from 60° to 10°C. Preliminary experiments were conducted to ensure that uni-modal crystal size distribution was obtained at the seed concentration used in the present study. The total suspension was withdrawn at the end of the experiment and filtered in a Buckner funnel under vacuum. The product was dried in an air oven and subjected to sieve analysis. The crystal size distribution was obtained and the mean size was calculated. Experiments were conducted to assess the effect of different cooling modes, shown in Figure 2, on the crystal size distribution to identify the cooling profile that provided a larger mean crystal size, further to assessing the effect of operating parameters such as the seed concentration and agitation rate under the linear cooling mode.

Each experiment was repeated twice to ensure the repeatability of the obtained data. It was observed that 90% of the data obtained on crystal size distribution varied within only  $\pm 3\%$ . The range of operating parameters covered is given in Table 2. The seed concentration was in general observed to range within 0 to 2% for most of the crystallization studies reported in literature, hence a seed concentration of 0.5 to 2% was chosen to study the effect of seed concentration on crystal size distribution. Preliminary experiments were carried out to ensure that the crystal size distribution followed a uni-modal distribution at 0.5% seed concentration. Similarly, a choice of agitation rate in the range of 60 to 120 rpm was chosen based on the preliminary experiments. An agitation rate less than 60 rpm was found to be insufficient for keeping the solids in suspension during crystallization, hence an agitation rate of 60 rpm was chosen as the lower limit, and the agitation rate was doubled to fix the upper limit of 120 rpm.

Referring to Figure 2, the natural cooling mode corresponds to cooling of magma in the crystallizer with a constant coolant temperature or, in other words, a rapid cooling in which the desired temperature is achieved at a much faster rate compared to other cooling modes. Linear cooling mode corresponds to linear variation of temperature of the magma in the crystallizer with respect to time, controlled cooling mode A corresponds to cooling the magma faster during the initial stages of the crystallization and slower during the later stages, and controlled cooling mode B

Parameters	Range
Temperature	60 to 10°C
Seed concentration, %	0.5, 1, 2
Experimental time	10 hours
Agitator speed	60, 90, 120 rpm
Seed size	150 µm

Table 2. Details of parameters studied

corresponds to cooling the magma slower during the initial stages of the crystallization and faster during the later stages. All experiments were carried out for 600 minutes, except the natural cooling mode, in which the desired temperature is achieved in 300 minutes.

### **Results and Discussion**

The different temperature profiles (Figure 2) correspond to different levels of supersaturation, which is the mass transfer driving force for crystal formation and growth, during the various stages of crystallization. Figure 3 compares the CSD corresponding to various modes of cooling shown in Figure 2. As expected the CSD of controlled cooling mode B is better than that of controlled cooling mode A. This can be attributed to the generally agreed upon fact in crystallization that a larger mean crystal size can be obtained by reducing the temperature slowly during early stages of crystallization and faster during later stages of crystallization (Mullin & Nyvlt, 1971). Reducing temperature slowly during the early stages of crystallization results in good control of the supersaturation and in turn the nucleation rate, while faster cooling during the initial stages leads to showering of a large number of nuclei, resulting in a lower mean crystal size.

The CSD of the linear cooling mode is found to be better than that of controlled cooling mode B contrary to the common belief, although this has been also validated in some recent work (Jagadesh et al., 1999; Mohameed et al., 2002). Since the supersaturation in controlled cooling mode B is better controlled during the early part of crystallization, one would expect better control of the nucleation rate and hence promotion of growth on existing crystals, leading to a larger mean



Figure 3. Effect of different cooling modes on CSD.

crystal size. However, the higher levels of supersaturation during the later stages of crystallization would lead to nucleation during later stages of crystallization, which give crystals less time to grow, leading to a reduction in the mean size of the crystals. This argument can be validated also from the measurement of the supersaturation by Mohameed et al. (2002) wherein the supersaturation peak for the linear cooling mode appears earlier than that of controlled cooling mode B and the peak is higher than that of controlled cooling mode B, as expected. But as the crystallization progresses the supersaturation level created never exceeds a limit and is lower than the supersaturation levels created by controlled cooling mode B. This is to confirm the possibility of creation of fresh nuclei during later stages of crystallization in controlled cooling mode B as compared to the linear cooling mode.

Further, as expected, the natural cooling mode yielded crystals of smaller mean size because of high levels of supersaturation created due to the fast cooling, which could have caused nuclei showering. Although this is a well-known fact, it can also be substantiated by the supersaturation measurements of Mohameed et al. (2002) and Jagadesh et al. (1999). Additionally Mersmann (2000) stated that rapid cooling usually caused a greater crystal density and corresponding smaller size. Hence, linear cooling was selected as the mode of operation of the crystallizer to understand the effect of operating parameters such as the seed concentration and rate of agitation on CSD.

The crystals obtained were non-transparent, a strong individual white mass more or less spherical in shape. The product corresponds to the commercially



Figure 4. Effect of seed concentration on CSD.

available material, although a much larger mean crystal size was obtained using controlled cooling modes.

From Figure 4 it can be observed that an increase in seed concentration from 0.5 to 1% results in increase of the mean crystal size, while a further increase in the seed concentration to 2% results in reduced mean crystal size. As the seed concentration is increased until the optimum seed concentration is reached, the magnitude of the reduction in the formation of fresh nuclei is significant compared to the number of additional crystals introduced due to increase in seed concentration, thereby resulting in a larger mean size of the crystals. However, when the seed concentration crosses an optimum point, the reduction of the formation of fresh nuclei with increase in seed concentration becomes insignificant, wherein the number of additional crystals introduced due to increased seed concentration causes the supersaturation to be distributed on more crystals, leading to a reduction in the mean crystal size. This was evident from the results showing an increase in mean crystal size when the seed concentration was increased from 0.5 to 1% and a reduction with further increase in seed concentration from 1 to 2%. The possible presence of an optimal seed concentration had been identified in the range of 1 to 2%, and more experiments are needed to pinpoint the optimum seed concentration. The current work identifies the reversal/reduction in mean crystal size beyond the optimum seed concentration.

Figure 5 compares the effect of the agitation rate on CSD. A larger mean crystal size was obtained at an agitation rate of 90 rpm than at agitation rates of 60 and



Figure 5. Effect of agitation rates on CSD.

120 rpm. With the increase in agitation rate from 60 to 90 rpm it was observed that the solids are kept well in suspension all through the course of crystallization. This could be the reason for a larger mean crystal size at 90 rpm than at 60 rpm, apart from the enhancement of the rate of crystallization due to the reduction in the mass transfer resistance for migration of the solute molecules to the surface of the crystals due to increased agitation rate. However, a decrease in mean crystal size was observed at an agitation rate of 120 rpm, which could be attributed to the intensity of mixing that leads to crystal breakage, resulting in secondary nucleation causing a reduction in the mean size of the crystals. The attribution of reduction in mean crystal size to the intensity of mixing is based on physical observation of the mobility of the crystals in the crystallizer.

#### Conclusion

A simple, straightforward study to understand the effect of different cooling modes such as the linear cooling mode, natural cooling mode, and controlled cooling modes A and B on the CSD for pL-malic acid was undertaken. It was found that the linear cooling mode yielded crystals of larger mean crystal size than the other three modes of cooling in concurrence with the work of Jagadesh et al. (1999) and Mohameed et al. (2002). The effect of operating parameters such as seeding ratio and agitation rate were studied utilizing the linear cooling mode. An increase in seed concentration from 0.5 to 1% resulted in an increase in mean crystal size, while a further increase from 1 to 2% resulted in reduction of mean crystal size. This was explained on the basis of mass balance constraints at higher seeding concentration. An agitation rate of 90 rpm was found to produce crystals of larger mean size than agitation rates of 60 and 120 rpm produced. The lower agitation rate of 60 rpm was found to be insufficient to keep the solids in suspension all through the course of crystallization, while the agitation rate of 120 rpm was found to be very intense, resulting in secondary nucleation leading to smaller mean crystal size.

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