A Study on Crystallization of Oxalic Acid in Batch Cooling Crystallizer

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Profesional paper
Received: December 19, 2001
Accepted: April 25, 2002

A study on batch cooling crystallizer, to assess the effects of various cooling modes on the crystal size distribution, is attempted for oxalic acid. The linear cooling mode is found to give narrow crystal size distribution and higher crystal size as compared to controlled cooling modes. The effect of various operating quantities such as the seed ratio, type of agitator, agitation rates, are carried out with linear cooling mode. The increase in seed ratio is found to reduce the mean crystal size. For turbine type agitator, increase in the agitation rate beyond 140 rpm is found to widen the crystal size distribution and lower the mean crystal size, where as for anchor type agitator, agitation rate beyond 100 rpm is found to decrease mean crystal size.

Key Words:
Batch crystallization, oxalic acid, crystal size distribution.

Introduction

Batch cooling crystallizers are commonly used in the production of fine chemicals, pharmaceuticals and bio-chemicals. Crystallization from solution is an industrially important unit operation due to its ability to provide high purity separation. Batch processes are preferred, if the production rate is low or the equipment must be used to produce several different products. Batch cooling crystallizers present the advantage of being simple, flexible, require less investment and, generally, involve less process development.[1] However as compared to continuous process the batch process yield poor quality product with smaller crystal size.

The crystal size distribution is an important quantity in the production of high quality product and for determining the efficiency of downstream operations, such as filtration and washing, reaction with other chemicals, transportation and storage of crystals. If the crystals are to be marketed as a final product, customer's acceptance requires individual crystals to be strong, non-aggregated, uniform in size and non-caking in the package. For these reasons, crystal size distribution must be under control and it is the prime objective in the design and operation of crystallizer. A uniform and narrow crystal size distribution with a large mean crystal size is often desired.

In a batch cooling crystallizer, solution is cooled for achieving the supersaturation essential for crystallization.[2] Crystallizers often incorporate cooling control, since uncontrolled cooling leads to poor quality product.[3] This is caused by the formation of large number of crystal nuclei, which cannot grow to the desired size, if the cooling rate in the initial stages of the process is too high.[4] In order 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.[3,4] When the batch crystallizer is refrigerated with coolant of constant flow rate and temperature leads to wide size distribution and small size crystals.[9]

The earlier research on batch crystallizers were mostly focused on the control of cooling rate and seed ratios in order to maintain supersaturation within the so-called metastable zone to control crystal size distribution.[2,4–8] *Jagadesh* et al.,[9] have highlighted the use of natural cooling mode, as it does not require any temperature control. Sufficient seeding can 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 ratio simulating conditions of controlled cooling, was reported. Further a bimodal type of crystal size distribution observed in all cooling modes was eliminated at higher seed ratio. The seed ratio required for attaining uni-modal crystal size distribution is much lower as compared to seed ratio required for attaining ideal growth curve. Although increase in seed ratio leads to attaining ideal growth curve, due to mass balance constraint, the mean crystal size reduces rapidly. Moreover the use of high seed ratio, to control supersaturation and to attain ideal growth curve, leads to higher loads on the downstream processing, thereby increasing the processing cost.

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Since the control of cooling rate is quite easy with use of modern process control, the present study attempts to study the effect of different cooling modes on crystal size distribution for a uni-modal crystal size distribution of oxalic acid. The effects of various operating quantities on crystal size distribution for the best identified cooling mode, has been studied.

Experimental

Experiments are carried out in a five liter jacketed crystallizer made of stainless steel 316 Grade, with mild steel jacket for heating and cooling purpose. The schematic diagram of the experimental set up is shown in Figure 1. The crystallizer consists of agitator (1), baffles (2), jacket (3), jacket fluid inlet (4), jacket fluid outlet (5), and outlet valve (6). The diameter of the crystallizer is 180 mm with a height of 240 mm. The experimental set up comprises of a circulation bath with provision to either cool to –50 °C or heat to 250 °C. Six blade pitched turbine and anchor agitators are used in the present study. The agitator is placed 20 mm from the bottom of the crystallizer. The diameter of turbine as well as anchor agitator is 90 mm. Two baffles of 23 mm are installed opposite to each other to avoid vortex formation and for better mixing only in the case of turbine agitator.

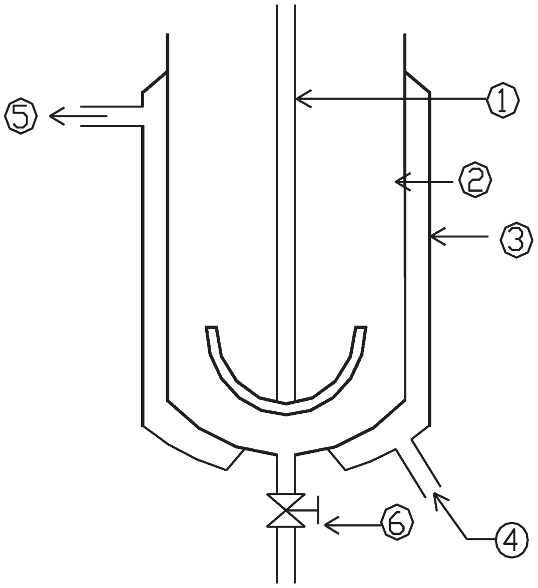

Fig. 1 – *Schematic diagram of experimental setup (1) Agitator, (2) Baffles, (3) Jacket, (4) Jacket fluid inlet, (5) Jacket fluid outlet, (6) Outlet valve.*

Desired temperature in the crystallizer is achieved by setting appropriate temperature in the control unit of circulation bath. Temperature sensor in the control unit refers to the temperature in the crystallizer bath and accordingly manipulates the temperature of coolant to achieve the required temperature. Based on the solubility data (Table.1) a saturated solution of oxalic acid is prepared at a temperature of 60 °C by dissolving required amount of oxalic acid in three liters of distilled water. After dissolving the stirrer speed is adjusted to the desired level. The experiments are started by cooling the solution at different cooling rates as required for the experiment. The seeds are added to the crystallizer under supersaturated conditions at required seed ratio. Seed ratio is defined as the mass of seeds taken to the theoretical yield of crystals taken from solubility curve by cooling from 60 to 10 °C. Preliminary experiments are conducted to ensure that uni-modal crystal size distribution is obtained at the seed ratio used in the present study. The total suspension is withdrawn at the end of the experiment, filtered in a Buckner funnel under vacuum. The product is dried in an air oven and subjected to sieve analysis. The crystal size distribution is obtained and the mean size is calculated. The experiments are conducted covering different temperature profiles as shown in Figure 2. The details of various quantities covered in the present study are detailed in Table 2.

Table 1 – *Solubility Data for Oxalic Acid – Water System*

Temperature °C	g of oxalic acid / 100 g of water
0	3.0
10	6.0
20	9.5
30	14.5
40	21.6
60	44.3
80	84.4

Table 2 – *Details of qualitities and their range covered in the present study*

Quantities	Range	Unit
Type of Agitators	Six Blade turbine, Anchor	
Temperature	60 to 10	°C
Seed Ratio	1, 3	
Batch time	130, 300	min.
Agitator speed	100, 140, 180	rpm
Seed size	80	μm

Results and discussion

In order to assess the crystallization characteristics of crystallizer, experiments are carried out with linear cooling mode and different controlled cooling modes. The effect of operating quantities such as agitation rates, type of agitator and seed ratio, are performed for the best identified cooling mode.

Figure 2 shows different cooling modes adopted for experimentation. Curve controlled cooling mode A, corresponds to slower cooling rate during the initial stages and faster cooling in the later stages. Curve controlled cooling mode B corresponds to faster cooling rate during the initial stages and slower cooling during the later stages. Curve linear cooling mode corresponds to constant rate of cooling from the beginning to end. However all the experiments are carried out for 300 minutes. Curve controlled cooling mode C corresponds to the case in which final temperature of the magma is reached at much faster rate as compared to other cooling modes. The final temperature of 10 °C is attained with in 130 minutes.

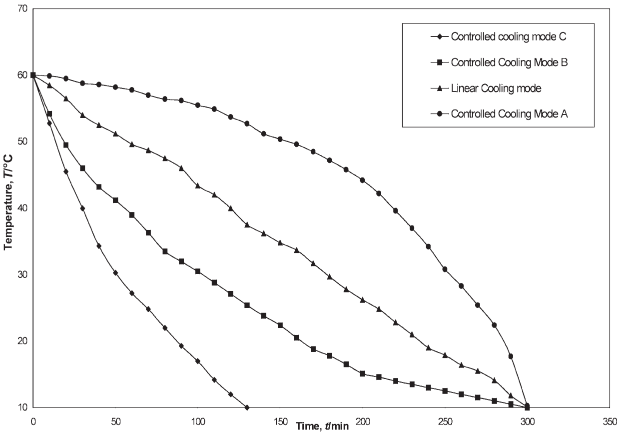

Fig. 2 – *Plot of crystallizer temperature with respect to time observed for various cooling modes*

The different temperature profiles correspond to different levels of supersaturation during various stages of crystallization. Figure 3 compares the crystal size distribution of all the above different modes of cooling. It can be observed, that a narrow crystal size distribution and higher mean size is obtained for linear cooling mode, as compared to controlled cooling mode A. This is contrary to the belief, as the supersaturation levels are maintained lower during the initial stages in controlled cooling mode A, as compared to linear cooling mode. This may be due to the secondary nucleation, which sets in at later stages of cooling due to higher levels of supersaturation, has lesser time to grow resulting in wider crystal size distribution and lower mean size. On the other hand in the case of linear cooling mode the small amount of nucleation that sets in during the initial stages of cooling has ample time to grow resulting in a narrow size distribution and higher mean size.

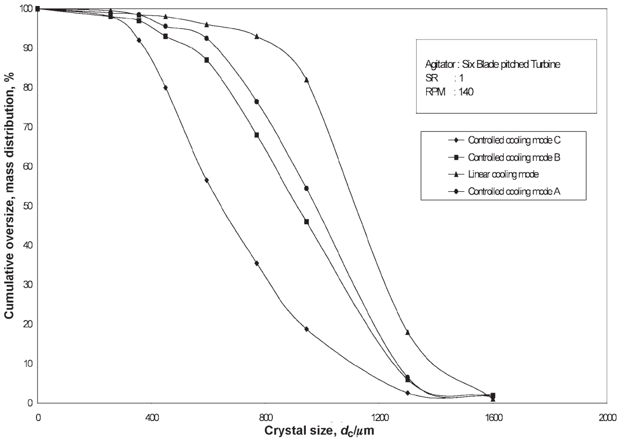

Fig. 3 – *Effect of different cooling modes on crystal size distribution*

The crystal size distribution due to controlled cooling mode B is inferior to the linear cooling mode and controlled cooling mode A (Fig. 3). This may be due to high levels of supersaturation in the initial stages, which leads to higher initial nucleation, leading to lower mean crystal size and wider crystal size distribution.

It can be observed from Figure 3 that the crystal size distribution due to controlled cooling mode C is inferior as compared to other cooling modes. Since the rate of cooling in controlled cooling mode C, as compared to other cooling modes is much faster leading to exposure of the seeded crystal to much higher levels of supersaturation, results in high amounts of initial nucleation and leads to wider size distribution and low mean crystal size.

The effects of operating quantities such as the seed ratio, type of agitator, agitation rate, are carried out following linear cooling mode with 300 minutes crystallization duration.

Figure 4 shows a reduction in the mean crystal size with the increase in seed ratio, although, there is no significant change in the crystal size distribution. The reduction in mean size of the crystals is due to the mass balance constraint. With the increase in number of seed crystals, the solute is distributed on higher number of seeds, and hence the size increase is limited. The increase in seed ratio on one hand reduces the initial nucleation in linear cooling profile and on the other hand promotes growth of the seeded crystals, on the other hand due to mass balance constraints the size enlargement is limited.

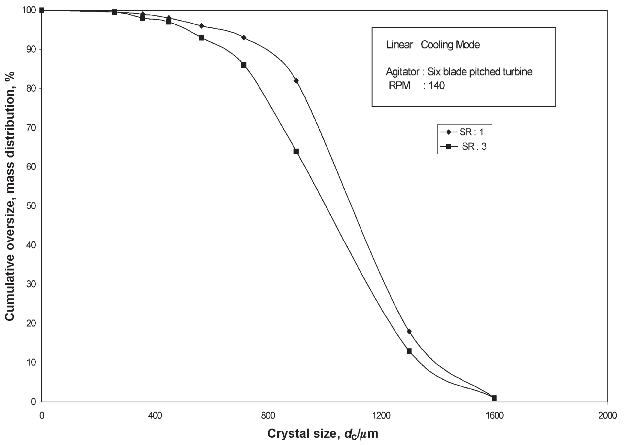

Fig. 4 – *Effect of seed concentration on crystal size distribution*

Figure 5 compares the crystal size distribution for turbine agitator and anchor agitator at 140 rpm. A higher mean crystal size and narrow crystal size distribution is obtained for turbine type agitator as compared to anchor type agitator. It could be, because of the intense mixing in anchor agitator, as compared to turbine agitator leading to formation of secondary nucleation due to attrition, contributing to fresh nuclei, results in lower mean size and wider crystal size distribution.

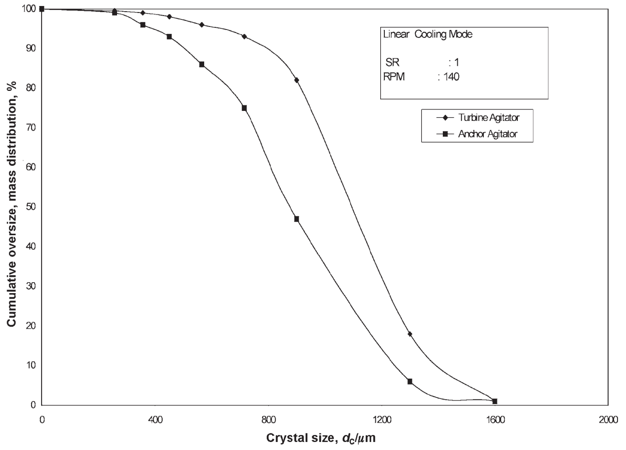

Fig. 5 – *Effect of type of Agitator on crystal size distribution*

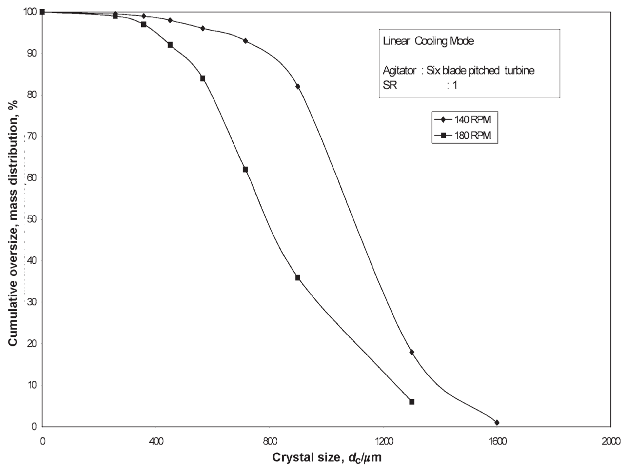

Fig. 6 – *Effect of different Agitation rate with turbine agitator on crystal size distribution*

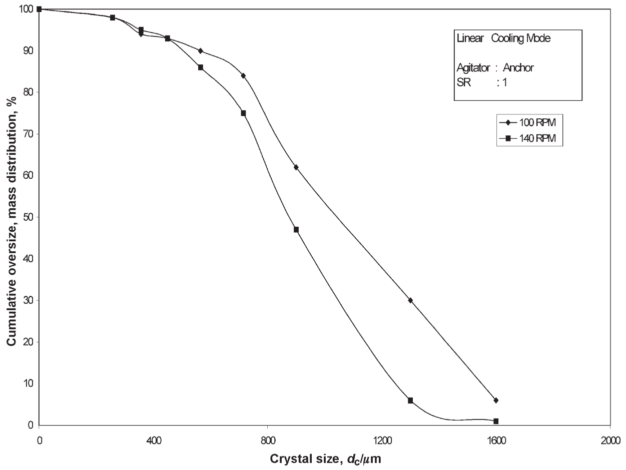

Fig. 7 – *Effect of different Agitation rate with Anchor agitator on crystal size distribution*

It can be evidenced from figure 6 that a higher mean crystal size and narrow crystal size distribution is obtained at 140 rpm as compared to 180 rpm with turbine type agitator. At 180 rpm the mixing is more intense leading to formation of fresh nucleation due to attrition resulting in poorer product quality. Similarly figure 7 shows a higher mean crystal size at 100 rpm as compared to 140 rpm for anchor agitator. In the case of anchor agitator since the mixing is observed to be better than the turbine agitator, 100 rpm is sufficient to keep the solids in suspension without aiding formation of fresh nuclei due to attrition.

Conclusions

A detailed study in batch cooling crystallizer covering different cooling modes is carried out and it is found that a linear temperature profile with 300 minutes cooling cycle is found to provide narrow crystal size distribution and higher mean crystal size. The effects of various quantities such as the seed ratio, type of agitator, agitation rate are assessed under linear cooling mode. The increase in seed ratio is found to decrease the mean crystal size due to mass balance constraints. The turbine agitator is found to have narrow crystal size distribution and higher mean crystal size at 140 rpm as compared to anchor agitator. This is attributed to the intense mixing with anchor agitator, which leads to secondary nucleation due to attrition. Similarly 140 rpm is found to give higher mean size and narrow size distribution as compared to 180 rpm with turbine agitator. With anchor agitator 100 rpm is found to give higher mean crystal size as compared to 140 rpm. An agitation rate of 100 rpm is sufficient to keep the solids in suspension with anchor agitator, whereas 140 rpm is required in the case of turbine agitator.

List of Symbols

SR – Seed Ratio, m_s/m_{th}
m – mass of crystal
m_s – mass of sead crystals
m_{th} – theoretical mass of crystal
d_c – crystal diameter, μm
t – time, h
T – temperature, °C

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