Empirical trajectories for batch crystallization control with constraints*

Hsiang-Feng Hsieh and Jeffrey D. Ward

Abstract— Optimization of batch crystallization is studied with tight constraints on the maximum rate of change of batch temperature or maximum rate of evaporation. It is observed that under tight constraints, the constraint has the greatest effect on the shape of the batch trajectory. Three crystallization systems are simulated for different values of the batch time and crystal yield. The resulting temperature or evaporation rate trajectories are plotted in dimensionless coordinates and fit to an empirical equation. The empirical equation performs similar to other convex trajectories recommended in the literature and much better than the linear trajectory.

I. INTRODUCTION

Control and optimization of batch crystallization has been the subject of extensive study in the literature\textsuperscript{1–13} and several review papers.\textsuperscript{14–16} An operating recipe for a batch crystallization process must specify how the temperature, rate of evaporation or rate of anti-solvent addition changes with time during the batch. Previous researchers have used heuristics and optimization to determine such trajectories. Some trajectories, particularly those based on optimization, require rapid changes in the temperature or the rate of evaporation during part of the batch, but these may be difficult to achieve due to limited space area for heat transfer and may result in the metastable zone being exceeded during batch operation.\textsuperscript{2,11} In this contribution the effect of tight constraints on the maximum rate of heat transfer in batch crystallization is studied explicitly using simple process models. It is found that the temperature constraint is the dominant factor affecting the shape of the optimal trajectory. Empirical trajectories for batch process operation are developed by fitting data for several different crystallization processes for different values of batch time and crystal yield. The empirical trajectories perform similarly to other convex trajectories proposed in the literature and much better than the linear trajectory.

II. Mathematical Models and Optimization

A. Crystallization Process Model

In this work the method of moments is used to solve the population balance. The \( i \)th moment of the crystal size distribution is defined as:

\[
\mu_i = \int_0^\infty L^i f(L) dL
\] (1)

For the case of size-independent growth, no growth-rate dispersion, no breakage, aggregation or agglomeration and a well-mixed batch crystallizer, the moments of the crystal size distribution change with time according to:\textsuperscript{18,19}

\[
d \mu_{0,0} / dt = B
\] (2)

\[
d \mu_{a,i} / dt = i \mu_{a,i-1} \quad i > 1
\] (3)

\[
d \mu_{b,0} / dt = B
\] (4)

\[
d \mu_{b,i} / dt = i \mu_{b,i-1} \quad i > 1
\] (5)

Where the subscripts \( a \) and \( s \) designate nucleus-grown and seed-grown crystals respectively.

For cooling crystallization, the solution concentration is given by

\[
d C / dt = -3g \rho_s \kappa_s \mu_s
\] (6)

and evaporative crystallization it is given by

\[
C(t) = \left( C_0 + \mu_{h,0} \rho_s \kappa_s \right) \left( m_n(0) / m_n(t) \right) - \mu_n(t) \rho_s \kappa_s
\] (7)

B. Nucleation and growth kinetics

For pentaerythritol,\textsuperscript{20} the nucleation rate is given by

\[
B = 4.1151 \times 10^7 \Delta T \text{C}^{3.5}
\] (8)

and the growth rate is given by

\[
G = 6.4913 \times 10^{-5} \exp(-40/T) \Delta T \text{C}^{5.9}
\] (9)

For potassium nitrate,\textsuperscript{17} the nucleation rate is given by

\[
B = 4.64 \times 10^{11} S^{1.78} \mu_i
\] (10)

and the growth rate is given by

\[
G = 1.61 \times 10^{-4} S^{3.32}
\] (11)

For succinic acid,\textsuperscript{21} the nucleation rate is given by

\[
B = 5.61 \times 10^7 \Delta T \text{C}^{4.01} M_r N^{2.28}
\] (12)

and the growth rate is given by

\[
G = 1.04 \times 10^{-6} \Delta T \text{C}^{0.05} N^{0.63}
\] (13)

*Research supported by the Taiwan Ministry of Science and Technology. Hsiang-Feng Hsieh and Jeffrey D. Ward (phone: +886-2-3366-3037; fax: +886-2-2362-3040; e-mail: jeffward@ntu.edu.tw) are with the Department of Chemical Engineering, National Taiwan University, Taipei 106 Taiwan.
C. Solubility relationships

For pentaerythritol, the solubility is determined by

\[ \log C_{sat} = 0.01377 \times 10^{-7} T^{-2} + 5.88 \times 10^{-3} T + 0.1286 \]

For potassium nitrate, the solubility is given by

\[ C_{sat} = 1.721 \times 10^{-7} T^{-2} + 5.88 \times 10^{-3} T + 0.1286 \]

For succinic acid, the solubility is given by

\[ C_{sat} = 1.7797 \times 10^{-7} T^{-3} - 4.7631 \times 10^{-5} T + 0.1286 \]

D. Seed properties

For all cases, the seed crystal size distribution was assumed to be parabolic

\[ f_b(L) = \begin{cases} 0 & L > L_a \\ K(L - L_a)(L - L_b) & L_a < L < L_b \\ 0 & L < L_b \end{cases} \]

where where \( L_a = L_0 \times (1 + w) \), \( L_b = L_0 \times (1 - w) \), \( L_0 = \mu_4 / \mu_3 \) is initial seed average size (µm), \( w \in [0, 1] \) is the width of seed CSD, and \( K \) is a coefficient that determines the total number or total mass of seeds.

E. Batch parameters

Each case study system was simulated for a certain value of the seed mass and seed mean size and for different values of the batch time and change in temperature (cooling crystallization) or solvent mass (evaporative crystallization). The values of these parameters are given in Tables I and II.

\[ \text{solubility relationship} \]

\[ \text{nucleation and growth kinetics} \]

\[ \text{batch conditions} \]

F. Optimization

Batch conditions for evaporative crystallization

The objective function used in this work is the minimization of the ratio of the nucleated mass to the total crystal mass:

\[ J = \frac{\mu_{3,n}}{\mu_3} \]

Therefore, for cooling crystallization, the optimization problem can be stated as:

\[ \min J = \frac{\mu_{3,n}}{\mu_3} \]

\[ \text{s.t. (2) (6), (17)} \]

solubility relationship nucleation and growth kinetics batch conditions

For evaporative crystallization, the optimization problem can be stated as:

\[ \min J = \frac{\mu_{3,n}}{\mu_3} \]

\[ \text{s.t. (2) (5), (7), (17)} \]

solubility relationship nucleation and growth kinetics batch conditions

The optimization is solved by fitting the control variable to a linear spline and adjusting the points sequentially as described previously.22

III. Results

A. Dimensionless trajectories

Figure 1 shows representative results for the batch cooling crystallization of potassium nitrate from 32°C to 22°C in a batch time of 150 minutes. As was found in all cases, the unconstrained optimum trajectory (labeled “initial” in the figure) showed a very rapid drop in temperature towards the end of the batch. When constraints are imposed (represented by the dashed lines) the constrained optimal trajectory approaches the constraint asymptotically.

![Figure 1. Representative results for cooling crystallization of potassium nitrate.](image-url)
Figure 2 shows the optimization results for cooling crystallization for all three crystallization systems for different values of the batch time and crystal yield.

In the figures, the x axis is dimensionless time
\[ x = t/t_f. \]  
(21)
and the y axis is dimensionless temperature
\[ y = \left( T - T_f \right) / \left( T_0 - T_f \right). \]  
(22)

From the definitions of \( x \) and \( y \), a constraint on the maximum rate of change of temperature with time \( |dT/dt|_{\text{max}} \) is within a multiplicative constant of a constraint on the maximum rate of change of \( y \) with respect to \( x \) \( |dy/dx|_{\text{max}} \). (Since the batch is cooled, all slopes are negative, and therefore constraints are expressed in terms of absolute values.) Furthermore, for feasible process operation, \( |dy/dx|_{\text{max}} \) must be greater than one, since \( |dy/dx|_{\text{max}} = 1 \) corresponds to the case where the final temperature can just be reached by operating on the constraint during the entire batch. The three panels in Figure 1 correspond to \( |dy/dx|_{\text{max}} \) being equal to 1.5, 2, and 2.5.

It is clear from the figure that it is the value of the constraint, and not the chemical system, batch time or product yield, that has the greatest effect on the shape of the optimal trajectory. All optimal trajectories start with a relatively gradual decrease in temperature; the magnitude of the slope increases and approaches the constraint towards the end of the batch. When the constraint is more restrictive (panel (a) where \( |dy/dx|_{\text{max}} = 1.5 \)), the constraint is reached earlier.

In order to develop a heuristic expression for the temperature trajectory, the data in Figure 1 were fit to the following empirical relationship:
\[ y = \frac{ax^2 + bx}{cx^2 + dx + e}. \]  
(23)

The values of the parameters \( a - e \) that best fit the data and the value of the correlation coefficient \( R^2 \) for each constraint are given in Table III.
Table III. Correlation parameters for cooling crystallization

| $|\text{d}y/\text{d}x|_{\text{max}}$ | 1.5 | 2 | 2.5 |
|-----------------------------|-----|---|----|
| $a$                         | $-0.578$ | 0.366 | 1.516 |
| $b$                         | $3.115$ | 0.237 | 0.356 |
| $c$                         | $2.308$ | 0.538 | 1.66 |
| $d$                         | $-2.115$ | $-0.078$ | 0.025 |
| $e$                         | $2.367$ | 0.147 | 0.187 |
| $R^2$                       | 0.9989 | 0.9974 | 0.9949 |

Figure 2 shows the optimization results for evaporative crystallization for all three crystallization systems for different values of the batch time and crystal yield. In this figure, the variable $x$ retains its meaning (dimensionless time) but $y$ in this figure is the dimensionless solvent mass:

$$y = \left( m_{w} - m_{w,f} \right) / \left( m_{w,0} - m_{w,f} \right).$$

The values of the parameters $a$–$e$ that best fit the data and the value of the correlation coefficient $R^2$ for each constraint are given in Table IV.

Table IV. Correlation parameters for evaporative crystallization

| $|\text{d}y/\text{d}x|_{\text{max}}$ | 1.5 | 2 | 2.5 |
|-----------------------------|-----|---|----|
| $a$                         | 0.21 | 1.678 | 1.884 |
| $b$                         | 4.174 | 0.65 | 0.258 |
| $c$                         | 3.106 | 1.632 | 1.52 |
| $d$                         | $-1.759$ | 0.316 | 0.484 |
| $e$                         | 3.034 | 0.361 | 0.113 |
| $R^2$                       | 0.9988 | 0.9962 | 0.9929 |

B. Comparison of trajectories

In order to compare the empirical trajectories developed in this work to other empirical or semi-empirical trajectories developed previously for batch crystallization, each case was simulated using the proposed empirical trajectory (Empr) and three other trajectories: the cubic trajectory (Cubic)

$$T(t) = T_0 - \left( T_0 - T_f \right) \left( t/t_f \right)^3.$$
or
\[ m_m(t) = m_m(0) - \left( m_m(0) - m_m(t) \right) \left( t/t_f \right)^3. \]  

(26)

the linear trajectory (Linear)

\[ T(t) = T_0 - (T_0 - T_f) \left( t/t_f \right). \]  

(27)

or
\[ m_m(t) = m_m(0) - \left( m_m(0) - m_m(t) \right) \left( t/t_f \right). \]  

(28)

and the Mullin-Nyvlt trajectory (MN):

\[ C_{sw} = C_f + (C_0 - C_f) \left( 1 - \frac{(1 + at)^3 - 1}{(1 + a)^3 - 1} \right). \]  

(29)

where \( t' = t/t_f \) and

\[ a = \left( 1/m'_t + 1 \right)^{1/3} - 1. \]  

(30)

Table V. Average deviation of four different trajectories for cooling crystallization

<table>
<thead>
<tr>
<th>dydt max</th>
<th>Empr</th>
<th>Cubic</th>
<th>MN</th>
<th>Linear</th>
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<tr>
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<td>1.71</td>
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<td>3.80</td>
<td>21.16</td>
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Table VI. Average deviation of four different trajectories for evaporative crystallization

<table>
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<tr>
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<th>Cubic</th>
<th>MN</th>
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<tr>
<td>1.5</td>
<td>1.22</td>
<td>9.80</td>
<td>1.12</td>
<td>957.24</td>
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</tbody>
</table>

Potassium nitrite

2.5 | 4.30 | 2.68 | 6.59 | 88.72 |
2   | 11.99| 1.51 | 5.77 | 85.99 |
1.5 | 13.04| 1.17 | 4.77 | 78.61 |

Pentaerythritol

2.5 | 6.89 | 2.64 | 17.13 | 179.62 |
2   | 7.39 | 3.59 | 13.15 | 167.51 |
1.5 | 3.75 | 10.59| 9.38  | 140.31 |

Succinic acid

2.5 | 3.59 | 0.91 | 2.76  | 70.74  |
2   | 2.95 | 2.38 | 1.44  | 65.84  |
1.5 | 2.03 | 6.38 | 2.34  | 54.53  |

IV. Conclusions

In this work, optimization of three crystallization systems with tight constraints on the rate of change of temperature or solvent mass was studied. The results showed that the constraints played a major role in determining the shape of the final trajectory. Dimensionless trajectories for several different values of batch time and crystal yield for each system were regressed to develop an empirical trajectory which depends only on the value of the constraint. The empirical trajectory performs similarly to other convex trajectories that have been considered previously and much better than the linear trajectory.
References


