Parameter Estimation for Crystallization Processes using Taylor Method

Yi Cao∗ Vinay Kariwala∗∗,1 Zoltan K. Nagy***

* School of Engineering, Cranfield University, Cranfield, Bedford MK43 0AL, UK (e-mail: y.cao@cranfield.ac.uk)
** School of Chemical & Biomedical Engineering, Nanyang Technological University, Singapore 637459 (e-mail: vinay.kariwala@in.abb.com)
*** Department of Chemical Engineering, Loughborough University, Leicestershire LE11 3TU, UK (e-mail: z.k.nagy@lboro.ac.uk)

Abstract: A high-order Taylor series based parameter estimation method is proposed for crystallisation processes. The process is represented using a moment model with unknown kinetic parameters associated with nucleation and growth phenomena. For the nonlinear least-squares problem related to parameter estimation, Taylor method is developed to calculate the residuals and the associated Jacobian matrix. Simulated and experimental case studies related to cooling crystallization of inorganic salts are used to evaluate the performance of the proposed method. These studies show that the predicted moments and concentration profiles obtained using Taylor method match the measured counterparts satisfactorily. Furthermore, the proposed method is found be computationally more efficient and numerically more accurate than traditional ODE solver based approaches.

Keywords: Automatic differentiation, Crystallization, Dynamic simulation, Method of moments, Particulate processes, Parameter estimation, Population balance equations.

1. INTRODUCTION

Crystallization is a key unit operation that finds extensive applications in pharmaceutical, food and fine chemicals industries [Mullin, 2001]. The operating conditions of the crystallization process have a direct effect on the purity, size distribution, shape and polymorphic form of the crystals. These properties in turn affect the efficiencies of the downstream operations such as filtration, drying and formulation, and product effectiveness such as dissolution rate, bio-availability and toxicity [Winn and Doherty, 2000]. Therefore, batch-to-batch uniformity of the crystal properties are important from a consumer and regulatory point of view [Shekunov and York, 2000].

On the other hand, most of the industrial crystallization processes are operated based on recipes found using extensive trial-and-error experimentation. Such operational policies are not able to cope with variations in solution thermodynamics and kinetics induced by contaminants, non-ideal mixing and unexpected polymorphic phase transformations. Improved control of crystallization processes offers possibilities for better crystal product quality, shorter process times, and the reduction or elimination of compromised batches [Fujiwara et al., 2005].

Recent advances in online measurement devices and process analytical technology (PAT), particularly in pharmaceutical industries [Barrett et al., 2005], has renewed the interest in model-based control of crystallization processes [Fujiwara et al., 2005, Nagy et al., 2008, Nagy, 2009]. Naturally, a prerequisite for the use of these control strategies is the availability of a model. Under reasonable assumptions, a crystallization process can be modelled using population balance equations (PBEs) coupled with mass/energy balances and kinetic equations. While the functional form of the model is well-established, the kinetic parameters of the model related to growth and nucleation phenomena, need to be estimated using experimental data.

Rigorous parameter estimation methods have been applied for identification of crystallization model parameters. Among all the available techniques, posing the estimation as an optimization problem has been regarded as most relevant [Rawlings et al., 1993]. Palwe et al. [1985] used three different methods, including polynomial fitting, initial derivatives, and optimization procedure, to determine the growth rate kinetics of ammonium nitrate. They noted that the least-squares error optimization procedure is potentially the most accurate and precise. When several measurements with different scales or reliability are used, weighted least squares approach is often employed with the weights estimated using e.g. maximum likelihood estimation. Methods based on the Fisher Information Matrix and bootstrapping can be used to estimate the confidence intervals related to the estimated parameters [Beck and Arnold, 1977]. The computation of parameter sensitivities and the repeated solution of the model equations in the optimisation problem generally require considerable computational effort for problems with the simultaneous estimation of several parameters.
According to automatic differentiation (AD) theory, high-order Taylor coefficients of any smooth nonlinear function can be obtained recursively and accurately [Griewank, 2000]. The recursive Taylor expansion approach can be directly applied to solve ordinary differential equations (ODEs) with high precision [Barrio, 2005]. Recently, the Taylor method has been further developed to calculate the dynamic sensitivity against control input for nonlinear model predictive control [Cao, 2005] and against model parameters for recurrent neural network training [Al-Seyab and Cao, 2008a,b]. Applications in industrial processes [Atwuonwu et al., 2010], crystallization processes [Kariwala et al., 2012], agriculture systems [Demmers et al., 2010] and satellite systems [Cao and Chen, 2009] have demonstrated that the Taylor method is computationally more efficient and numerically more accurate than the traditional ODE solver based approaches.

In this work, the recursive Taylor method is applied to solve the parameter estimation problem for the crystallization processes. The population balance model is first converted into a set of ODEs using the method of moments [Hulburt and Katz, 1964]. The parameter estimation problem is then formulated as a nonlinear least-squares problem, for which a Taylor method is developed to calculate the residuals and the associated Jacobian matrix. This enables a direct application of the efficient Levenberg-Marquardt algorithm [Marquardt, 1963] to solve the problem. Both simulated and experimental case studies are provided to explain the usage and demonstrate the superiority of the new approach.

2. MODEL DEVELOPMENT

We consider 1-D crystallization process with growth and nucleation phenomena, where the dimension refers to the number of independent characteristic lengths needed to describe the crystals. A well-mixed crystallizer with constant volume can be modelled using the following PBE:

$$\frac{\partial n(L, t)}{\partial t} + \frac{\partial (G(L, t)n(L, t))}{\partial L} = B_0(t)\delta(L - L_0)$$  \hspace{1cm} (1)

where \(n(L, t)\) is the crystal size distribution (CSD), \(L\) is the characteristic length of the crystals, \(L_0\) is the size of nuclei, \(G(L, t)\) is the growth rate, \(B_0(t)\) is the rate of nucleation and \(\delta\) is the Dirac delta function. In (1), it is assumed that there is no crystal aggregation or breakage. For cooling crystallization, as considered in this paper, the driving force is the supersaturation level of the solution. The growth rate is usually modelled as [Abegg et al., 1968]

$$G(L, t) = k_g S^p(t)(1 + \gamma L)^p$$  \hspace{1cm} (2)

where \(k_g\) and \(g\) are the kinetic parameters, and \(\gamma\) and \(p\) dictate the dependence of crystal size on the growth rate. Due to their larger surface area, in general, the larger crystals grow faster than the smaller crystals, \(i.e.\ \gamma \geq 0\). In (2), \(S(t)\) is the relative supersaturation defined as

$$S(t) = \frac{C(t) - C_{sat}(T(t))}{C_{sat}(T(t))}$$  \hspace{1cm} (3)

where \(C(t)\) is the solution concentration, \(C_{sat}(T(t))\) denotes the saturated solution concentration and \(T(t)\) is the solution temperature.

It is considered that the dominant mechanism for nuclei formation is secondary nucleation, which occurs due to fluid shear and the collision of crystals among themselves and with the wall of the crystallizer. The following empirical relationship is used to model the rate of secondary nucleation [Nyvlt et al., 1985]:

$$B_0(t) = k_b V(t)S^\theta(t)$$  \hspace{1cm} (4)

where \(k_b\) and \(b\) are kinetic parameters, and \(V(t)\) is the volume of the crystals in the system. We assume that the nuclei have negligible size and thus the consumption of material due to nucleation is negligible. Under this assumption, the mass balance equation for the liquid phase, which accounts for the depletion of material from solution due to crystal growth, is given as

$$\frac{\partial}{\partial t}C(t) = -3\rho_c k_v \int_0^\infty G(t)L^2 dL$$  \hspace{1cm} (5)

where \(\rho_c\) is the crystal density and \(k_v\) is the volumetric shape factor.

Although many methods [Ramkrishna, 2000, Gunawan et al., 2004, Majumder et al., 2010] are available for directly obtaining \(n(L, t)\) by solving the model in (1)- (5), these methods are computationally expensive. For parameter estimation, it suffices to simplify the model using a moment transformation, where the \(r\)th moment of the distribution, \(\mu_r\), is given by:

$$\mu_r = \int_0^\infty n(L)L^r dL$$  \hspace{1cm} (6)

After the moment transformation, the PBE in (1) is represented by the following set of ODEs in terms of the moments [Hulburt and Katz, 1964]:

$$\dot{\mu}_0(t) = B_0(t)$$  \hspace{1cm} (7)

When \(p = 1\), \textit{i.e.} the crystal growth rate depends linearly on the crystal size, the moment equations in (7) close and are solvable using an ODE solver. When \(p \neq 1\), to overcome the closure problem, a quadrature approximation of the moments can be used, which gives rise to differential algebraic equations [McGraw, 1997, Kariwala et al., 2012]. In this paper, we focus on the case, where \(p = 1\), for which (7) can be simplified as [Hulburt and Katz, 1964]

$$\dot{\mu}_0(t) = B_0(t)$$  \hspace{1cm} (8)

$$\dot{\mu}_1(t) = k_g S(t)^p(\mu_0(t) + \gamma \mu_1(t)) + B_0(t)L_0$$  \hspace{1cm} (9)

$$\dot{\mu}_2(t) = 2k_g S(t)^p(\mu_1(t) + \gamma \mu_2(t)) + B_0(t)L_0^2$$  \hspace{1cm} (10)

$$\dot{\mu}_3(t) = 3k_g S(t)^p(\mu_2(t) + \gamma \mu_3(t)) + B_0(t)L_0^3$$  \hspace{1cm} (11)

$$\dot{C}(t) = -3\rho_c k_v k_g S^\theta(t)(\mu_2(t) + \gamma \mu_3(t))$$  \hspace{1cm} (12)

This simplified model is used to identify the following set of parameters from the data

$$\theta = [\gamma \ b \ k_b \ g \ k_g]^T$$  \hspace{1cm} (13)

3. TAYLOR METHOD

In this section, an efficient and accurate Taylor method is presented for parameter estimation. The Taylor method is
based on the principle of recursive Taylor expansion, which is introduced first.

3.1 Recursive Taylor Expansion

Consider a nonlinear smooth function, \( z(t) = f(x(t)) \) where \( x(t) \in \mathbb{R}^n \) and \( z(t) \in \mathbb{R}^m \). Assume that \( x(t) \) can be approximated by the truncated Taylor series up to order \( d \) as \( x(t) = \sum_{i=0}^{d} x[i]t^i \). Then, \( z(t) = \sum_{i=0}^{d} z[i]t^i \), where the \( k \)th Taylor coefficient, \( z[k] \), can be recursively determined from \( x[0], x[1], \ldots, x[k] \) as follows:

\[
z[k] = f[k](x[0], x[1], \ldots, x[k])
\]

(14)

<table>
<thead>
<tr>
<th>Table 1. Taylor Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>( z = x \pm y )</td>
</tr>
<tr>
<td>( z = xy )</td>
</tr>
<tr>
<td>( z = x/y )</td>
</tr>
<tr>
<td>( dz/dt )</td>
</tr>
</tbody>
</table>

For simple arithmetical functions, the Taylor coefficients can be derived directly, as shown in Table 1. Furthermore, for most elementary functions, \( z = f(x) \), the Taylor coefficients can be derived through differentiation, \( \hat{z} = f'(x)\hat{x} \), where \( f'(x) = \partial f(x)/\partial x \); see Table 2 for examples. It can be readily proven that the sensitivity of \( z[k] \) against \( x[j] \) is only dependent on up to \( (k-j) \)th order Taylor coefficients of \( x \) [Christianson, 1992]. Thus,

\[
\frac{\partial f[k]}{\partial x[j]} = \frac{\partial f[k-j]}{\partial x[0]} = A[k-j](x[0], x[1], \ldots, x[k-j])
\]

(15)

According to this property, \( z[k] \) is linearly dependent on \( x[j] \) for \( j > k/2 \), because the sensitivity \( A[k-j] \) is independent of \( x[j] \) for \( 2j > k \) or \( j > k-j \). Furthermore, \( A[k] \) is the \( k \)th Taylor coefficient of the Jacobian matrix \( \partial f(x)/\partial x \), i.e. \( f'(x) = \sum_{i=0}^{n} A[i]t^i \).

<table>
<thead>
<tr>
<th>Table 2. Taylor coefficients derived through differentiation</th>
</tr>
</thead>
<tbody>
<tr>
<td>( z = ax )</td>
</tr>
<tr>
<td>( z = x^2 )</td>
</tr>
<tr>
<td>( e^x )</td>
</tr>
<tr>
<td>( \ln x )</td>
</tr>
</tbody>
</table>

3.2 Taylor Method for Differential Equation

The recursive Taylor expansion approach can be applied to solve an ODE of the form

\[
\dot{x} = f(x, \theta), \quad x(t_0) = x_0
\]

(16)

where \( \theta \in \mathbb{R}^n \) is the parameter of the model. By applying the recursive Taylor expansion described in Section 3.1, the Taylor coefficients of the solution, \( x(t) \), can be recursively obtained as

\[
x[k+1] = \frac{1}{k+1} f[k](x[0], x[1], \ldots, x[k]), \quad x[0] = x_0
\]

(17)

Then, the value of \( x \) at \( t_1 = t_0 + h \) can be obtained as

\[
x(t_1) = \sum_{i=0}^{d} x[i]h^i, \quad h \text{ is the integration step.}
\]

This procedure is repeated at \( t_1 \) by letting \( x[0] = x(t_1) \) so that the solution at all the sampling points, \( t_1, t_2, \ldots, t_f \), can be iteratively calculated.

The solution accuracy depends on the order of Taylor series, \( d \) and integration step, \( h \). For a given \( d \), to achieve the required accuracy, \( \delta, h \) needs to satisfy [Cao, 2005]

\[
h \leq \left( \frac{\delta\|x[d-1]\|_{\infty}}{\|x[d]\|_{\infty}} \right)^{1/(d+1)}
\]

(18)

The sensitivities of solutions, \( x(t_1), x(t_2), \ldots, x(t_f) \) against the initial states, \( x_0 \) and the parameter, \( \theta \) are derived next. According to (15) and (17), the following recursive equations can be derived.

\[
B_x[k+1] := \frac{dx[k+1]}{dx_0} = \frac{1}{k+1} \sum_{i=0}^{k} A_x^i B_x[k-i]
\]

(19)

\[
B_{\theta}[k+1] := \frac{dx[k+1]}{d\theta} = \frac{1}{k+1} \left( A_{\theta}^k + \sum_{i=0}^{k} A_{\theta}^i B_{\theta}[k-i] \right)
\]

(20)

where \( A_x^k = \frac{\partial f[k]}{\partial x_0} \) and \( A_{\theta}^k = \frac{\partial f[k]}{\partial \theta} \). At every time step, these recursive calculations are initialised by \( B_x[0] = \frac{dx[0]}{dx_0} \) and \( B_{\theta}[0] = \frac{dx[0]}{d\theta} \). For \( t = t_0, B_x[0] = I \) and \( B_{\theta}[0] = 0 \), whilst for other time points, \( t_{j+1} = t_j + h_j \), these initial sensitivities are cumulated from previous steps as

\[
B_x[j+1] = \sum_{i=1}^{d} B_x[i] h_j^i, \quad B_{\theta}[j+1] = \sum_{i=1}^{d} B_{\theta}[i] h_j^i
\]

(21)

where \( B_{x,j} = B_x(t_j) \) and \( B_{\theta,j} = B_{\theta}(t_j) \).

3.3 Taylor Method for Parameter Estimation

Assume that the parameter, \( \theta \) in the differential equation system (16) is unknown and needs to be determined from the measured data, \( y = g(x) \). Then the parameter estimation problem can be cast as the following nonlinear least-squares problem:

\[
\min_{\theta} E^T E \quad \text{subject to} \quad \dot{x} = f(x, \theta)
\]

(22)

where \( e = g(x) - y, E = Q [e_1^T \cdots e_f^T]^T \) with \( Q \) being a weighting matrix and \( e_j = e(t_j) \). This problem can be efficiently solved using the Levenberg-Marquardt algorithm [Marquardt, 1963] as

\[
\theta_{k+1} = \theta_k + (J_k^T J_k + \mu_k I)^{-1} J_k^T E_k
\]

(24)

where the subscript represents the iteration step, \( J \) is the Jacobian matrix of \( E \) against \( \theta \), and the scalar, \( \mu \) is determined by the algorithm to ensure convergence.

To derive an expression for \( J \), let \( e_j^{[k]} \) and \( x_j^{[k]} \) be the \( k \)th Taylor coefficients of \( e \) and \( x \) at sample time \( t_j \), respectively. Then,

\[
e_j^{[0]} = g[0](x_j^{[0]}) - y_j, \quad e_j^{[k]} = g[k](x_j^{[0]}, \ldots, x_j^{[k]})
\]

(25)
The Taylor coefficients of the sensitivity of $e_j$ are
\[ D_j^{[k]} := \frac{d e_j^{[k]}}{d \theta} = \sum_{i=0}^{k} \frac{C_{ij}^{[i]}}{B_{j}^{[k-i]}} \] (26)
where $C_{ij}^{[k]} := \frac{d C_j^{[k]}}{d x_j}$. Since $e_{j+1} = \sum_{i=0}^{d} e_i^{[i]} h_j^{[i]}$, the Jacobian of $e_{j+1}$ against $\theta$ is $F_{j+1} = \sum_{i=0}^{d} D_j^{[i]} h_j^{[i]}$ and $J$ can be constructed as
\[ J = Q \left[ F_1^T \cdots F_{j}^T \right]^T \] (27)

4. SIMULATION STUDY

We consider seeded batch cooling crystallization of potassium nitrate (KNO$_3$) from water [Miller and Rawlings, 1994, Gunawan et al., 2004]. For this process, the saturated solution concentration is
\[ C_{sat}(t) = 1.721 \times 10^{-4}T^2 + 5.88 \times 10^{-3}T + 0.1286 \] (28)
The following temperature profile is used
\[ T(t) = 32 - 4(1 - e^{-t/1860}) \] (29)
which corresponds to a slow cooling profile. The initial distribution of the crystal is given as
\[ n(L, 0) = -3.48 \times 10^{-4}L^2 + 0.136L - 13.3 \] (30)
where $180.5 \mu m \leq L \leq 210.5 \mu m$ and zero otherwise. The expression for $n(L, 0)$ in (30) can be analytically integrated using (6) to get the initial values of the moments. The initial concentration is 0.493 g/g of water. The volumetric shape factor $k_v$ and the size of nuclei $L_0$ are taken as 1 and 0.25 $\mu m$, respectively. The crystal density is considered to be $2.11 \times 10^{-12} \ g/\mu m^3$. The true value of the kinetic parameters are shown in Table 3.

Table 3. True [Miller and Rawlings, 1994] and Estimated values of kinetic parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>True value</th>
<th>Taylor Estimated</th>
<th>ODE45 Estimated</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>$b$</td>
<td>1.78</td>
<td>1.45</td>
<td>1.22</td>
</tr>
<tr>
<td>$k_b$</td>
<td>$4.64 \times 10^{-7}$</td>
<td>$4.43 \times 10^{-7}$</td>
<td>$1.12 \times 10^{-7}$</td>
</tr>
<tr>
<td>$g$</td>
<td>1.32</td>
<td>1.33</td>
<td>1.33</td>
</tr>
<tr>
<td>$k_g$</td>
<td>116</td>
<td>125.22</td>
<td>119.53</td>
</tr>
</tbody>
</table>

For estimation of these parameters, it is considered that the solution concentration $C$ is measured using ATR-FTIR spectroscopy and the CSD is measured using online laser diffraction techniques. Based on the measured CSD, the moments $\mu_1 - \mu_3$ can be calculated, which are used for parameter estimation. For this purpose, $\mu_0$ is not used, as its accurate measurement is usually difficult. The accuracy level of the measurement of $C(t)$ is assumed to be $\pm 3\%$ of the change of $C(t)$ during the batch duration, whereas the moments are assumed to be measured with an accuracy of $\pm 5\%$.

The parameter estimation problem is thus formulated as the nonlinear least-squares problem with the residual defined as follows,
\[ E(\theta) := \left[ E_1^T \cdots E_{I}^T \right]_{I=00}^{T} \] (31)
where $\beta = 0.01$ is the weight for the parameters and $E_i$ is the residual at $i$th sampling point, defined as
\[ E_i = \left[ \frac{\mu_1(i)}{\mu_2(i)} - 1 \quad \frac{\mu_2(i)}{\mu_3(i)} - 1 \quad \frac{\mu_3(i)}{\mu_4(i)} - 1 \quad \frac{C(i)}{C(\bar{C})} - 1 \right]^T \] (32)

<table>
<thead>
<tr>
<th>Method</th>
<th>CPU Time (s)</th>
<th>$\mu_1$</th>
<th>$\mu_2$</th>
<th>$\mu_3$</th>
<th>$C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Taylor</td>
<td>12.92</td>
<td>0.0037</td>
<td>0.0065</td>
<td>0.0059</td>
<td>$4.79 \times 10^{-8}$</td>
</tr>
<tr>
<td>ODE45</td>
<td>66.05</td>
<td>0.0037</td>
<td>0.0065</td>
<td>0.0065</td>
<td>$4.72 \times 10^{-8}$</td>
</tr>
</tbody>
</table>

where $\mu_j(i)$, for $i = 1, 2, 3$ and $C(i)$ are the $i$th measured moments and concentration, respectively.

The parameter estimation problem is solved through Levenberg-Marquardt algorithm [Marquardt, 1963] given in (24). For comparison, the ODEs and the sensitivities are calculated through the Taylor method described in Section 3 and a traditional ODE solver, ODE45 of Matlab. Parameters estimated by both methods are compared in Table 3. It can be seen that both methods are able to provide reasonably accurate estimation of all parameters. In particular, for $b$ and $k_b$, the Taylor method based approach gives better estimation, whilst for $k_g$, the estimation obtained using ODE45 is slightly better than that estimated by the Taylor method.

The computation time and norm of residual of these two methods are compared in Table 4. Table 4 indicates that the Taylor method is about 3 times faster than the ODE45 based approach, whilst the prediction using the parameters estimated by Taylor method is slightly more accurate than that using the ODE45 based estimation. This is also demonstrated in the relative prediction error along the time, as shown in Figure 1.

![Fig. 1. Relative prediction error comparison (a) $\mu_1$, (b) $\mu_2$, (c) $\mu_3$ and (d) C, Solid line: Taylor method, Dashed line: ODE45](image)

5. EXPERIMENTAL STUDY

This section presents an experimental study to apply the high-order Taylor method to estimate model parameters of a batch crystallisation process.

5.1 Materials and Methods

Potash alum (Potassium aluminium sulphate dodecahydrate with purity $>99.95\%$ from Fisher Bio Reagents) with de-ionised water as solvent were used in the experiments, which were conducted in a 0.5 L jacketed glass vessel with temperature control using a Pt100 thermocouple and a Huber VPC CC3 450 thermostat. An overhead
stirrer with a four-blade pitch type impeller was used to agitate the system at 350 rpm. The concentration was measured in-situ using a conductivity probe. Conductivity (voltage) measurements were obtained using a CM 35 meter with WPA-35 conductivity probe using a calibration model following the methodology described in [Nagy et al., 2011]. The CSD was measured on-line every second using a Malvern Mastersizer 2000 laser-diffraction equipment connected with the crystallizer. A peristaltic pump was used to circulate the slurry (solids with solvent) between the crystallizer and the Mastersizer. A supersaturation controlled experiment was designed to generate information rich data for the estimation of nucleation and growth kinetics. After the seed addition first higher supersaturation was generated to trigger nucleation providing suitable data for the estimation of nucleation kinetics. This initial step was followed by a constant supersaturation part where the crystallisation was controlled at a lower supersaturation where the dominating phenomenon was the growth, providing data suitable for the estimation of the growth kinetics. The supersaturation profile and the corresponding temperature trajectory are shown in Figure 2.

![Fig. 2. Supersaturation controlled crystallization experiment to generate data suitable for estimation of nucleation and growth parameters](image)

5.2 Parameter Estimation Using Experimental Data

Experimental data for two hours were collected for every 5 seconds for measurements of concentration and the Sauter mean diameter (i.e. $\mu_3/\mu_2$) as well as the de Brouckere mean diameter (i.e. $\mu_4/\mu_3$). The same model described in equations (8) – (12) with $\gamma = 0$ and $L_0 = 0$ was adopted for the experimental process. Four parameters, namely, $k_g$, $g$, $k_b$, and $b$ as well as the initial conditions of the 5 moments were estimated to fit the experimental data collected using the Taylor method presented in Section 3. The final estimated parameters are $k_g = e^{26.747}$, $g = 4.256$, $k_b = e^{3.558}$, $b = 4.757$. The measurements and the corresponding values predicted using the estimated model parameters are shown in Figure 3. Note that due to uncertainty in the measurement data it is often important to estimate the initial conditions together with the dynamic experimental data for adequate fit of the model parameters. It can be seen that the concentration and the ratio of $\mu_4/\mu_3$ are fitted well. The discrepancy in the ratio $\mu_3/\mu_2$ is due to the fact that CSD measurements using laser diffraction are generally subject to artefacts affecting the smaller moments owing to the presence of impurities and measurement errors. Therefore it is recommended to use besides the concentration, CSD properties based on higher order moments (e.g. the de Brouckere mean diameter, i.e. $\mu_4/\mu_3$).

![Fig. 3. Experimental data fitting performance with the estimated model parameters](image)

6. CONCLUSIONS

A new high-order Taylor expansion based parameter estimation approach is proposed for crystallisation processes. The proposed method is computationally more efficient and numerically more accurate than traditional ODE solver based approaches. The results of simulated and experimental case studies presented in the work demonstrate the merits and applicability of the approach for the efficient estimation of crystallisation kinetics. The experimental study also shows that it is possible to combine parameter estimation with state estimation using the proposed approach. Based on recent developments reported by Kariwala et al. [2012], future work will extend the proposed approach to more sophisticated crystallisation processes e.g. with nonlinear growth kinetics, where the governing model is in the form of differential algebraic equations (DAE) instead of ODE.

REFERENCES
