Numerical Simulation of Particle Size Distribution in Large-Scale Purified Terephthalic Acid Crystallization Process

On-line Number 154

Yoshinori Matsuo1, Shin-ichiro Kajikawa1, Kazuhiko Kato2, Ken-ichiro Sotowa3
1 Material Science Laboratory, Mitsui Chemicals, Inc., 580-32 Nagaura, Sodegaura-shi, Chiba 299-0265, Japan
2 Process Technology Laboratory, Mitsui Chemicals, Inc., 1-2 Waki 6, Waki-cho, Kuga-gun, Yamaguchi 740-0061, Japan
3 Department of Chemical Science and Technology, Tokushima University, 2-1 Minami-Josanjimacho, Tokushima 770-8506, Japan

ABSTRACT

In this paper, we present an application of particle size distribution (PSD) simulation technique to the crystallization process in a large-scale Purified Terephthalic Acid (PTA) plant. The crystallization process in the PTA plant employs a multistage continuous crystallizer. Each stage is a stirred tank crystallizer, which is modeled using several compartments. The flow rates between compartments and mean velocity in each compartment were estimated from computational fluid dynamics (CFD) simulation of fluid flow in the crystallizers. The primary and secondary nucleation and size independent crystal growth were modeled while agglomeration and breakage were neglected. The parameters in the nucleation and growth rate equations were determined from the plant data. The model developed takes into account different crystallizer configurations (crystallizer scale, feed and withdrawal position, etc) and different operating conditions (feed rate, mean residence time, pressure, etc).

KEYWORDS

Compartment model, Particle size distribution, Industrial crystallizer, Purified Terephthalic Acid

INTRODUCTION

Supersaturation and particle size distribution (PSD) are not usually uniform in continuous crystallizers. To understand the behavior of crystallizers, therefore, it is important to develop a technique for predicting the spatial distribution of these variables. Recently, a number of studies on simulation of PSD in crystallizers on the basis of population and mass balances have been published (Lee and Saleeby 1994, Eek et al. 1995, Litster et al. 1995, Naito et al. 1998, Sotowa et al. 1998). Compartmental framework is a common technique for describing the spatial distribution of supersaturation and PSD (Kramer et al. 1999, Bermingham et al. 1999, Neumann et al. 1999, Hamamura et al. 2001, Ma et al. 2002, Sha and Palosaari 2002). However, there are few applications of such models to large-scale industrial processes (Semlali et al. 2001).

In this paper, we present an application of PSD simulation technique to the crystallization process in a large-scale Purified Terephthalic Acid (PTA) plant. The crystallization in the PTA plant is carried out in a multistage continuous crystallizer. Each stage is a stirred tank crystallizer, which is modeled using
several compartments. Flow rates between compartments and mean velocity in each compartment are estimated from computational fluid dynamics (CFD) simulation of fluid flow in the crystallizers. The primary and secondary nucleation and size independent crystal growth are modeled while agglomeration and breakage are neglected. The parameters in the nucleation and growth rate equations are determined from the plant data. The model can be applied to different crystallizer configurations (crystallizer scale, feed and withdrawal position, etc) and different operating conditions (feed rate, mean residence time, pressure, etc).

PROCESS DESCRIPTION

PTA is obtained by selective crystallization of Terephthalic Acid in a multi-stage crystallizer. Each stage is a stirred tank crystallizer. Both the pressure and temperature are high before the first stage, and they are gradually reduced by means of staged flash. Production capacity per plant is several hundred thousand tons per year.

MODELING AND SIMULATION METHOD

In this paper, we simulate PSD using a compartment model in order to take into consideration the non-ideal mixing in each crystallizer.

Prior to building a compartment model, the followings must be determined:

• Number of compartments, their location and size.
• Flow rates between compartments.

These factors must be determined very carefully so that the effect of non-ideal mixing can be described with sufficient accuracy. However, there are no well-established methods to determine them. Each compartment must have sufficiently small supersaturation and temperature gradients, because each compartment is treated as a perfectly mixed tank in simulation. Often it is difficult to judge whether the perfect mixing assumption is satisfied for a given compartment configuration. Bermingham et al. (1998) proposed that the size and location of compartments should be decided in such way that the half life time for supersaturation decay is one order of magnitude larger than the residence time in the compartment.

In this paper, the number of compartments, their location and size were determined by comparing residence time distribution calculated from compartment model to CFD results. The flow rates between compartments were determined from the result of CFD simulation. CFD simulation was conducted by using a commercial CFD package RFLOW (RFLOW Co., Ltd.). The model was developed under the following assumptions:

• Each crystallizer is isothermal.
• Agglomeration and breakage are negligible.
• Crystal growth rate is independent of crystal size.
• Vaporization due to flash is finished before the entrance. (There is no vaporization in the crystallizers.)
Model Development

The compartment model for PTA crystallization process was developed using the result of CFD simulation. The schematic diagram of the compartment model is shown in Figure 1. The characteristic properties of this model are as follows:

1. Two dimensional configuration
   The model is two dimensional and axi-symmetric, but the model has special compartments near the feed point to describe the influence of high supersaturation region.

2. Vapor independent crystallization
   It was assumed that the nucleation and crystal growth rates are not affected by the presence of the vapor phase.

The CFD simulations were used to obtain the following data for PSD computations:

- Time averaged flow rate between compartments.
- Weighted mean velocity in each compartment used in calculating secondary nucleation rate.

Basic Equations for Particle Size Distribution Simulation

The basic equations (material and population balance equations) used in this study are shown below (Hamamura et al. 2001):

<Particle Balance>
\[
V_{c_i} \frac{d[1-\varepsilon_i(t)]}{dt} = \sum_j \left[ Q_{j,i} \left[1-\varepsilon_j(t)\right] \right] - \sum_k \left[ Q_{i,k} \left[1-\varepsilon_k(t)\right] \right] + Q_{in} \left[1-\varepsilon_i(t)\right] - Q_{out} \left[1-\varepsilon_i(t)\right] + \frac{\psi_i}{\rho_p},
\]

<Solute Balance>
\[
V_{c_i} \frac{d[\varepsilon_i(t)C_i(t)]}{dt} = \sum_j \left[ Q_{j,i} \varepsilon_j(t)C_j(t) \right] - \sum_k \left[ Q_{i,k} \varepsilon_k(t)C_k(t) \right] + Q_{in} \varepsilon_i(t)C_i(t) - Q_{out} \varepsilon_i(t)C_i(t) - \psi_i,
\]

>Total Material Balance>
\[
V_{c_i} \frac{d[\varepsilon_i(t)\rho_{sol} + \left[1-\varepsilon_i(t)\right]\rho_p]}{dt} = \sum_j \left[ Q_{j,i} \varepsilon_j(t)\rho_{sol} + \left[1-\varepsilon_j(t)\right]\rho_p \right] - \sum_k \left[ Q_{i,k} \varepsilon_k(t)\rho_{sol} + \left[1-\varepsilon_k(t)\right]\rho_p \right] + Q_{in} \varepsilon_i(t)\rho_{sol} + \left[1-\varepsilon_i(t)\right]\rho_p - Q_{out} \varepsilon_i(t)\rho_{sol} + \left[1-\varepsilon_i(t)\right]\rho_p,
\]

<Population Balance>
\[
V_{c_i} \frac{\partial n_i(t,L)}{\partial t} + V_{c_i} G_i \frac{\partial n_i(t,L)}{\partial L} = \sum_j \left[ Q_{j,i} n_j(t,L) \right] - \sum_k \left[ Q_{i,k} n_i(t,L) \right] + Q_{in} n_i(t,L) - Q_{out} n_i(t,L),
\]
where $V_c$, $e$, $Q$, $\rho$ are the volume of compartment, the volume fraction of the solution, the volumetric flow rate of slurry, and the density. $C$, $n$, $G$, $t$, and $L$ are the concentration, population density, crystal growth rate, time and crystal size, respectively. The subscripts $i$, $j$, $k$ denote compartment number, and $sol$ and $p$ denote solution and particles, respectively. Mass production rate due to crystal growth $\psi$ is expressed in the following form:

$$\psi_i = 3\rho_p k_v G \int_0^\infty L^2 n_i(t, L) dL,$$

where $k_v$ is the volume shape factor of the particles.

For describing the particle size distribution, it is necessary to model nucleation and growth rates appropriately. New particles occur due to two different nucleation mechanisms. One is primary nucleation, which is expected to be dominant in the high supersaturation region (near the feed point). The other is secondary nucleation. There are several different mechanisms for secondary nucleation. Collision of particle with the impeller, collision of a particle with other particles, and shear stress acting upon the particle surface are the most important mechanism for secondary nucleation. In the present study, three different nucleation rate equations were employed (Eqs.(6)-(8)). Both Eqs.(6) and (7) were used to calculate overall nucleation rates in each compartment. For calculating secondary nucleation rate in the impeller region, Eq.(8) was used instead of Eq.(7). Eq.(9) is the growth rate equation used in this study.

<Primary Nucleation Rate>

$$B_{p,i} = k_{b_p} \Delta C_i^{b_p}(t),$$  

<Secondary Nucleation Rate>

$$B_{s1,i,j} = k_{b_s} M_{T,j} \tau(t) v_i^{\mu} \Delta C_i^{b_s}(t),$$  

<Secondary Nucleation Rate (in impeller region only)>

$$B_{s2,i,j} = k_{b_s} M_{T,i} \tau(t) V_{TIP}^{\nu} \Delta C_i^{b_s}(t),$$  

<Crystal Growth Rate>

$$G_i = k_g \Delta C_i^{g}(t),$$

where $k$, $\Delta C$, $M_T$, $v$ and $V_{TIP}$ are the rate constant, supersaturation, magma density, weighted mean velocity in compartment and impeller tip speed, respectively.

The parameters in Eqs.(6)-(9) were determined from the operation data of the commercial plant, which produces several hundred thousand tons of PTA per year.

The population balance Eq.(4) was discretized by the finite difference method. An explicit algorithm was used for integration of Eqs.(1)-(4) with time.

**RESULTS AND DISCUSSION**

To examine the validity of the model developed, simulations were carried out for various operating conditions of the actual plant. The conditions selected were different from those used for fitting kinetic parameters.

Measured and simulated mean particle sizes for 10 sets of operating conditions are plotted in Figure 2.
Both measured and simulated values in the graph and the table in this paper are shown as percentage differences from a reference condition.

Since it was difficult to obtain samples at the exit of final stage crystallizer, samples were collected after the post-process. The mean particle size and the weight fractions of large and small particles were measured by sieving techniques and were averaged over a number of samples.

The calculated mean particle sizes shown in Figure 2 were values at steady state. State of the particles after the post-process were calculated assuming that both the mean particle size and the weight fraction of large particles decrease at constant rates, and the weight fraction of small particles increases at a constant rate.

It can be seen from Figure 2 that, with one exception, the error of the predicted mean particle size was less than ±10%. The operating condition was changed to a large extent in this study; almost any customer specifications can be met within the range of operating condition. It was found that the model also estimated trends in the amount of large and small particles correctly.

Table 1 presents the calculated mean particle size $L_w$, the weight fraction of large particles $W_L$ and that of small particles $W_S$ for 10 sets of operating conditions. The label “Large particles” denotes the weight fraction of particles 124% larger than the mean particle size for the reference condition, and “Small Particles” denotes the weight fraction of particles that are 66% smaller than the reference mean size. According to the results, $W_L$ increases monotonically with increasing $L_w$, whereas, $W_S$ does not decrease monotonically (case4 and case5). It seems that $W_L$ is correlated with $L_w$, but $W_S$ could be changed independently of $L_w$ by controlling operating conditions. Therefore, the calculation results indicate that the width of PSD can be regulated by appropriate control of operating conditions.

![Figure 2. Calculated vs Measured Mean Particle Size (Dashed Lines Denote ±10% Error Bounds.)](image)

<table>
<thead>
<tr>
<th>Deviation from the reference condition [%]</th>
<th>Mean Particle Size</th>
<th>Large Particles</th>
<th>Small Particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>case1</td>
<td>case2</td>
<td>case3</td>
<td>case4</td>
</tr>
<tr>
<td>Mean Particle Size</td>
<td>-21.0</td>
<td>-17.6</td>
<td>-8.9</td>
</tr>
<tr>
<td>Large Particles</td>
<td>-83.3</td>
<td>-76.9</td>
<td>-55.3</td>
</tr>
<tr>
<td>Small Particles</td>
<td>+57.0</td>
<td>+32.8</td>
<td>-4.4</td>
</tr>
</tbody>
</table>
CONCLUSIONS

We have developed a simulation model that predicts the particle size in PTA crystallization process. It was based on a compartment model, and PSD was estimated by solving population balance equation considering primary nucleation, secondary nucleation and size independent crystal growth. It was verified that the model could predict the mean size of particles produced in the large-scale actual plant within ±10% error in 9 cases out of 10.

Moreover, the calculation results indicate that the width of PSD can be regulated by appropriate control of operating conditions.

Currently, the experiments in actual plant are being performed to validate the results above. In future, we plan to investigate the influence of individual operating variables and crystallizer configurations, e.g., pressure, working volume, impeller position, feed and withdrawal position, on PSD by using the model.

REFERENCES