Modeling batch crystallization processes: Assumption verification and parameter estimation

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Abstract

In this work, experimental data of different batches was used for estimation of the kinetic parameters for the secondary nucleation framework of Gahn and Mersmann [Gahn, C. and Mersmann, A., 1999. Brittle fracture in crystallization processes. Chem. Eng. Sci. 54, 1273–1292].
An empirical experiment design procedure was used to design an informative batch experiment through optimization of the seed quality, size and mass and process conditions at seeding. The parameters estimated using the data of the designed experiment showed smaller magnitudes of the confidence ellipsoids and standard deviations as compared to those obtained by using the data of conventional (un)seeded batch experiments. It was shown that the designed experiment allowed reducing uncertainty in the initial conditions.
It was also demonstrated that the main reason for the model/process mismatch was the origin of nuclei. Dynamic experimental data could be described better if the state of the crystals forming the crystallization system corresponded to the assumptions of the used kinetic model. This work was published in Chem Eng. Sci. 66, 4867–4877.

1. Experimental

A fed-batch evaporative crystallization of ammonium sulfate from water was carried out in a 75-l draft-tube crystallizer (Fig. 1) operated at the impeller frequency of 450 *rpm* and the heat input of 120 kW/m^3.

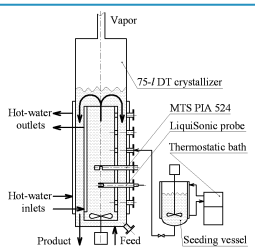

Fig. 1: Crystallization set-up

Table 1: Description of experiments

Code	Origin of seed crystals	Seed mass, *g*	Initial super-saturation σ_0	Residence time of seeds τ, *min*
DT_c19	unseeded	–	0.01743	–
DT_c31	Ground, 90–125 μm	600	0.01627	57
DT_c34	Product of DT_c33	±1000	0.01442	97
DT_c46	Product of DT_c45	±200	0.00668	78

2. Modeling in gPROMS

The crystallizer was modeled using compartmental modeling approach
– a single compartment for a well-mixed crystallizer body *and*
– a zero-volume compartment for the impeller – source of nuclei.

The CSD dynamics was modeled using the population balance concept.

Process kinetics was described by the secondary nucleation framework of Gahn and Mersmann with two kinetic parameters:
– surface related energy increase Γ_S [$J/m/mol$];
– rate coefficient for surface integration k_r [$m^4/mol/s$].

3. Parameter estimation in gPROMS

Two-step parameter estimation procedure:
– estimation of initial conditions (ε_0 & σ_0)
– estimation of kinetic parameters.

Results for each experimental data set:
– correlation and large uncertainty (Fig. 2);
– lack of fit with experimental data (Fig. 3).
Assumption: crystal surface state changes
Verification: relaxation of time invariance

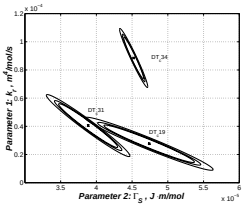

Fig. 2: Confidence ellipsoids for estimation with different experimental data sets

Estimation of time-varying parameters as an optimization in gPROMS:

$$\min_{k_{r,j};\,\Gamma_{S,k};\,\Delta t_i \in [0\ \ t_f];\,i=1,\ldots,n_{int};\,\sum_{i=1}^{n_{int}}\Delta t_i = t_f} \sum_{j=1}^{n_y} \frac{\int_0^{t_f} \left(\hat{\mathbf{y}}_j(t) - \mathbf{y}_j(t)\right)^2 dt}{\int_0^{t_f} dt}$$

Experimental data points were approximated by 5th-order polynomial functions of time **y**(t) (Fig. 3).

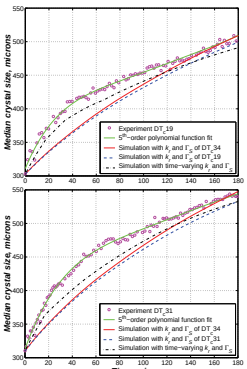

Fig. 3: Data fit for median crystal size of DT_c19 (above) & DT_c31 (below)

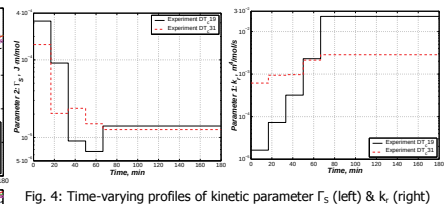

Fig. 4: Time-varying profiles of kinetic parameter Γ_S (left) & k_r (right)

Results for the same experimental data sets:
– parameters change the most in the first half of the batch (Fig. 4);
– data fit improved (Fig. 3) especially in the beginning of batches;
– behavior of primary nuclei & ground seed crystals still differs from strain-free crystals.

Assumption: strain-free crystals will behave in line with assumptions made in the kinetic model of Gahn and Mersmann
Verification: experiments with product crystals as seeds at process conditions maximizing growth and detection of attrition fragments

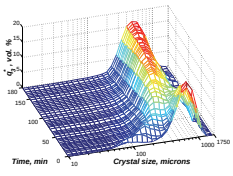

Fig. 5: CSD during batch DT_c34

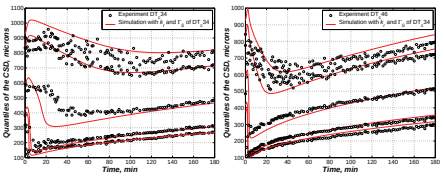

Fig. 6: Data fit for quantiles of DT_c34 (left) and control batch (right)

Results of parameter estimation with data of batch DT_c34:
– less uncertain, but still highly correlated set of parameters (Fig. 3);
– better fit of not only X_{50}, but also CSD (Fig. 5) & quantiles (Fig. 6);
– good prediction of process behavior at different initial conditions (Fig. 6, control batch DT_c46, see also Table 1).

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