Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Reactive Crystallization: A Review

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Supplemental Material – Simulation Details

A reactive crystallization system has been simulated for the simple batch reaction A ⇌ B and B crystallizes. A population balance model was used to account for nucleation and growth phenomena. The equations that follow constitute the material balances, reaction rates, growth rate, nucleation rates, and boundary conditions for the model. The method of lines is used to solve the PBM.[1] The solution is implemented in MATLAB.

The suspension density (M_T) is defined as

$$M_T = k_V \rho \mu_3 \qquad \backslash * \text{ MERGEFORMAT (S.1)}$$

where k_V is the volumetric crystal shape factor, relating the actual volume of a crystal to the length of its characteristic dimension, ρ is the crystal density, and μ_3 is the third moment of the crystal size distribution (see Equation S.11).

The supersaturation (σ) is defined as

$$\sigma = \frac{c_B - c_B^*}{c_B^*} \qquad \backslash * \text{ MERGEFORMAT (S.2)}$$

where c_B is the concentration of B and $c_B{}^*$ is the saturation concentration.

The growth rate (G), primary (J), and secondary nucleation (B_{sec}) rates are defined as

$$G = k_G \sigma^g \qquad \backslash * \text{ MERGEFORMAT (S.3)}$$

$$J = k_J \exp\left(\frac{-B_0}{\ln^2(\sigma + 1)}\right) \qquad \backslash * \text{ MERGEFORMAT (S.4)}$$

$$B_{\sec} = k_B \sigma^s M_T{}^m$$ * MERGEFORMAT (S.5)

where k_G, k_J, and k_B are rate constants, g, s, and m are power law orders, and B_0 is a grouped constant accounting for the energy required to create a nucleus.

The population balance is formulated below for a crystal population density function, n, and the boundary conditions indicate crystals of zero size, $L = 0$, are formed by nucleation and no crystals are present initially, $t = 0$.

$$\frac{\partial n(L,t)}{\partial t} = -\frac{\partial G(t) n(L,t)}{\partial L}$$ * MERGEFORMAT (S.6)

$$\frac{\partial n(0,t)}{\partial t} = J + B_{\sec}$$ * MERGEFORMAT (S.7)

$$n(L,0) = 0$$ * MERGEFORMAT (S.8)

The kinetics of the reaction A ⇌ B along with mass balances on A and B lead to the following differential equations for the changing concentrations (c_A, c_B) of the solutes

$$\frac{dc_A}{dt} = k_R c_B^{n_R} - k_F c_A^{n_F}$$ * MERGEFORMAT (S.9)

$$\frac{dc_B}{dt} = k_F c_A^{n_F} - k_R c_B^{n_R} - 3k_V \rho G \mu_2$$ * MERGEFORMAT (S.10)

where k_F and k_R are the forward and reverse reaction rate constants, n_F and n_R are the forward and reverse reaction orders, and μ_2 is the second moment of the crystal size distribution.

The moments of the crystal size distribution are defined as follows:

$$\mu_i(t) = \int_0^\infty L^i n(L,t) dL$$ * MERGEFORMAT (S.11)

All of the parameter values used in the simulations for Figure 3 in the main text are listed in Table S.1. The order of each process (i.e. the exponents in equations S.3, S.5, S.9-10) are held constant when varying the reaction and crystallization rates.

Table S.1. Summary of the parameter values used in equations S.1 - S.11 to simulate different reactive crystallization batches, with either slow and fast relative reaction and crystallization kinetics. The units are arbitrary. The values of the crystal volumetric shape factor and density were arbitrarily set to $k_V = 1$ and $\rho = 2$ g/cm^3, respectively.

			k_R	a	k_G	g	k_J	B_0	k_B	s	m
Fast Crystallization	Slow Rxn	Baseline	1	1	500	1	5×10^8	1	5×10^9	1	1
		Fast Nucl.			400		1×10^9		1×10^{10}		
		Slow Nucl.			633		2×10^8		2×10^9		
	Fast Rxn	Baseline	5	1	500	1	5×10^8	1	5×10^9	1	1
		Fast Nucl.			453		1×10^9		1×10^{10}		
		Slow Nucl.			625		2×10^8		2×10^9		
Slow Crystallization	Slow Rxn	Baseline	1	1	100	1	1×10^8	1	1×10^9	1	1
		Fast Nucl.			79.2		2×10^8		2×10^9		
		Slow Nucl.			126		5×10^7		5×10^8		
	Fast Rxn	Baseline	5	1	100	1	1×10^8	1	1×10^9	1	1
		Fast Nucl.			79.6		2×10^8		2×10^9		
		Slow Nucl.			126		5×10^7		5×10^8		

References

1. W. E. Schiesser and G. W. Griffiths, *A compendium of partial differential equation models: method of lines analysis with Matlab*, Cambridge University Press, 2009.