Sequential crystallization parameter estimation method for determination of nucleation, growth, breakage and agglomeration kinetics.

Atul H. Bari and Aniruddha B. Pandit

Department of Chemical Engineering, Institute of Chemical Technology,
Mumbai-40019, India

Supporting information:

Application of gPROMS parameter estimation tool for analytical cases:

The PBE can be solved using fixed pivot technique of discretization and gPROMS parameters estimation tool can be employed for parameter estimation. The efficacy of this approach is checked for some analytical cases. Although these cases may or may not have any physical significance, they are capable of representing (mathematically) the type of equations governed by respective processes. Thus, we would get an enough idea about any solution technique or a computational tool employed for solving, optimizing or parameterizing the PBE's indicating the physics of these processes.

Case 1: Pure growth

Analytical solution for temporal change of the first moment for pure growth with size independent growth rate is given as:

$$\mu_1(t) = \mu_1(0) + G\mu_0(0)t$$

Since here no other phenomena is considered, there won't be any death or birth of particles, thus zeroth moment will be constant.

$$\mu_0(t) = \mu_0(0)$$

Since the growth rate is constant, all the points on the solution profile will move at the same speed $G(x) = G$. If $n_0(x)$ is the initial solution, then the time evolution of number density is given by

$$n(x,t) = n_0(x - Gt)$$

Thus for initial number density given by $n(x,0) = sin(x)$, the time evolution of number density is given by $n(x,t) = sin(x - Gt)$. For this case the initial conditions and parameter considered are given in table S1. This is one of the simplest PBE which can be solved quite easily with linear discretization, considering the size range involved. As our intention is to check the efficacy of gPROMS parameter estimation and not to identify the method to solve PBE, different techniques are employed for different cases. Later in the case 3, i.e of pure agglomeration, the reason of employing different methods is elaborated.

Table S1. Conditions for pure growth process and estimated parameter.

Initial condition; $n(x,0)$		$sin(x)$
μ_0		6.366×10^3
$\mu_1(0)$		3.183×10^5
Growth parameter G	Theoretical	1
	Estimated	1

As it is clear that the total number of particles i.e μ_0 for pure growth is going to be constant, the time evolution of μ_0 won't be helpful. Instead, profile of μ_1 was used to estimate the kinetic parameter. The estimated kinetic parameter is exact with that of analytical. Also, it can be seen from the figure S1 that the estimated profile matches well with the analytical profile. The estimated CSD profile for this case is shown in figure S2. As expected, it can be seen from figure that the CSD is moving with a constant rate as time progresses.

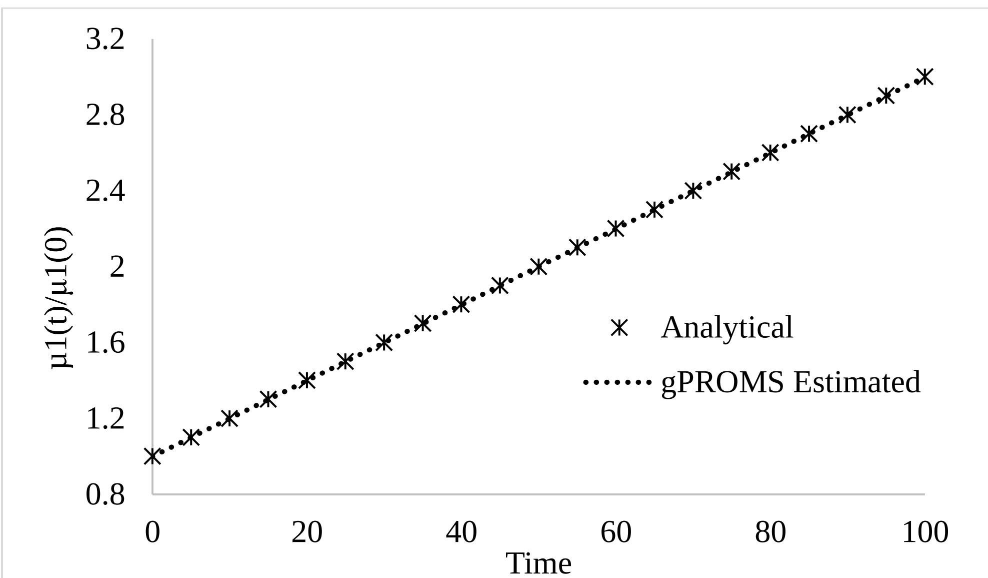

Figure S1 Analytical and estimated 1st moment profile for pure growth problem.

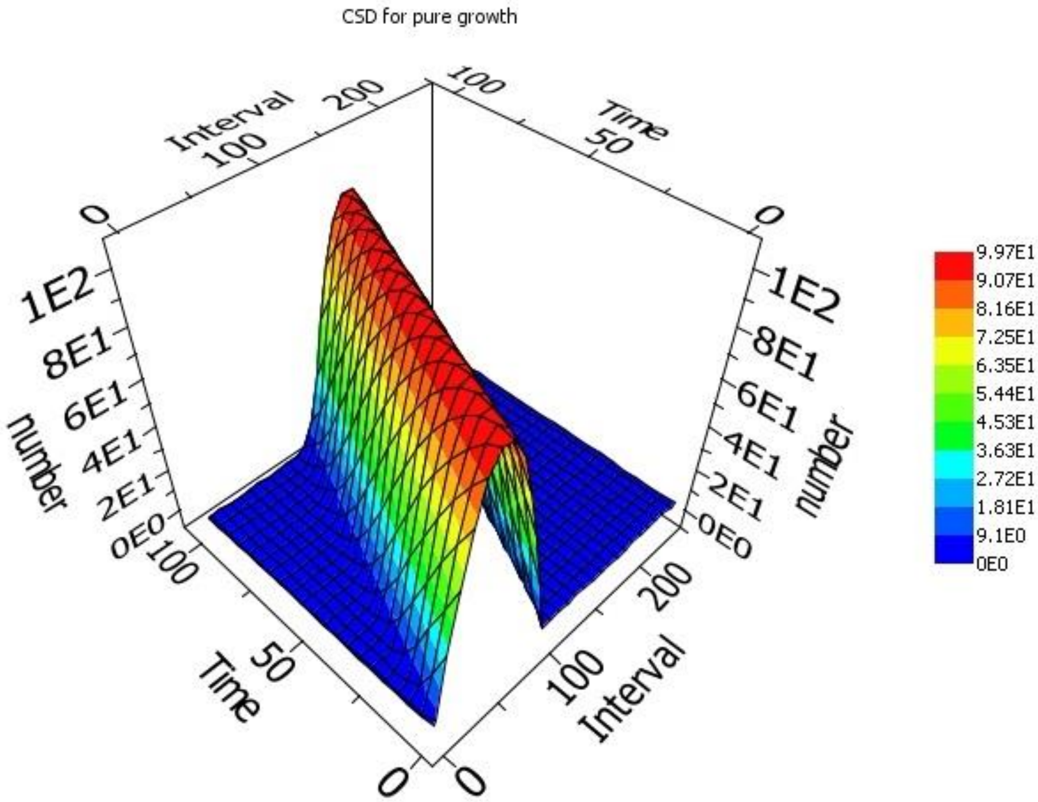

Figure S2 Time evolution of CSD for pure growth problem.

Case 2: Pure breakage

Ziff and McGrady (1985) had given analytical solutions for various cases of pure breakage process. The two such cases are considered here and are given in table S2. For the two cases considered, given in Table S2, breakage rate can be given as $S(v) = av^m$, and simulations were carried out to estimate kinetic parameters a and m. Instead of PSD, values of the 0^{th} moment, i.e., the number of particle at different time interval, was used as known data. The analytical values of the 0^{th} moment for these two cases were calculated by integrating equation for size distribution, i.e., $n(v,t)$ over the entire size domain. The results obtained were quite good and within acceptable error limits. This also suggests that we can estimate two parameters related to one process precisely. Figure S3 shows the comparison of the analytical 0^{th} moment with the simulated moment using estimated kinetic parameters for both cases given in Table S2.

Table S2 Initial conditions and estimated parameters for pure breakage process.

Case	n(v,0)	b(v,v')	S(v)	Analytical solution $n(v,t)$	Theoretical		Estimated	
					a	m	A	m
1	$exp(-v)$	$\frac{2}{v'}$	v	$exp[-v(1+t)](1+t)^2$	1	1	1.02	0.99
2	$exp(-v)$	$\frac{2}{v'}$	v^2	$exp(-tv^2-v)\times [1+2t(1+v)]$	1	2	1.01	1.97

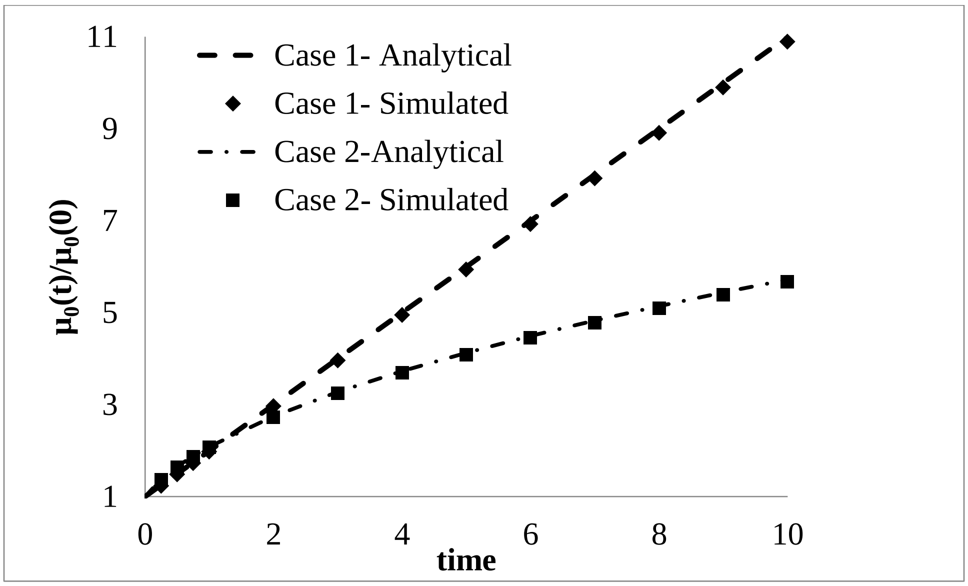

Figure S3. Variation of 0th moment with respect to time for breakage process with available analytical solutions

Case 3: Pure agglomeration

Scott (1968) provided number of solutions for a variety of initial conditions and different types of agglomeration kernel. Here we are considering the case with exponential initial distribution and constant agglomeration kernel. The analytical solution is for initial condition:

$$n(v,0) = \frac{N_0}{v_0} exp\left(\frac{-v}{v_0}\right)$$

here v_0 is mean size and N_0 is total number of initial particles.

The analytical solution is given by:

$$n(v,t) = \frac{4N_0}{v_0(N_0K_0t+2)^2} exp\left(\frac{-2\frac{v}{v_0}}{N_0K_0t+2}\right)$$

Where K_0 is constant agglomeration kernel.

The initial conditions and parameter for this case is given in figure S3.

Table S3 Initial conditions and estimated parameters for pure agglomeration.

<table>
<tr><td colspan="2">Initial condition; $n(x,0)$</td><td>$\frac{N_0}{v_0} exp\left(\frac{-v}{v_0}\right)$</td></tr>
<tr><td colspan="2">N_0</td><td>1×10^{3}</td></tr>
<tr><td colspan="2">v_0</td><td>20</td></tr>
<tr><td rowspan="3">Agglomeration parameter K_0</td><td>Theoretical</td><td>1.97×10^{-6}</td></tr>
<tr><td>Estimated fixed pivot</td><td>2.17×10^{-6}</td></tr>
<tr><td>Estimated Cell average</td><td>1.99×10^{-6}</td></tr>
</table>

For solving PBE of agglomeration, fixed pivot technique was used. The parameter estimation was carried by using gPROMS with 0^{th} moment profile. The estimated parameter was good within 10% of error, which is acceptable for engineering applications. However, it is necessary to identify if this error is associated with the method of solving PBE (Fixed pivot) or with gPROMS parameter estimation. Hence simulation were carried out with K_0 = 2×10^{-6} using fixed pivot technique. It can be seen from figure S4 that fixed pivot technique does not predict 0^{th} exactly. Although it does tells the inefficiency of fixed pivot technique, accuracy of gPROMS parameter is still questionable. Hence we need to employ better method for solving PBE of agglomeration. Cell average technique (Kumar et al, 2006) which is modified form of fixed pivot technique, has been considered a better option for agglomeration problem. Parameter estimation was also carried by solving PBE using Cell average technique. It is evident that the estimated parameter matches quite well with the theoretical parameter, confirming the accuracy of cell average technique as well as the efficiency of gPROMS parameter estimation tool. Henceforth for all the analytical cases with agglomeration, cell average technique is employed to solve the PBE.

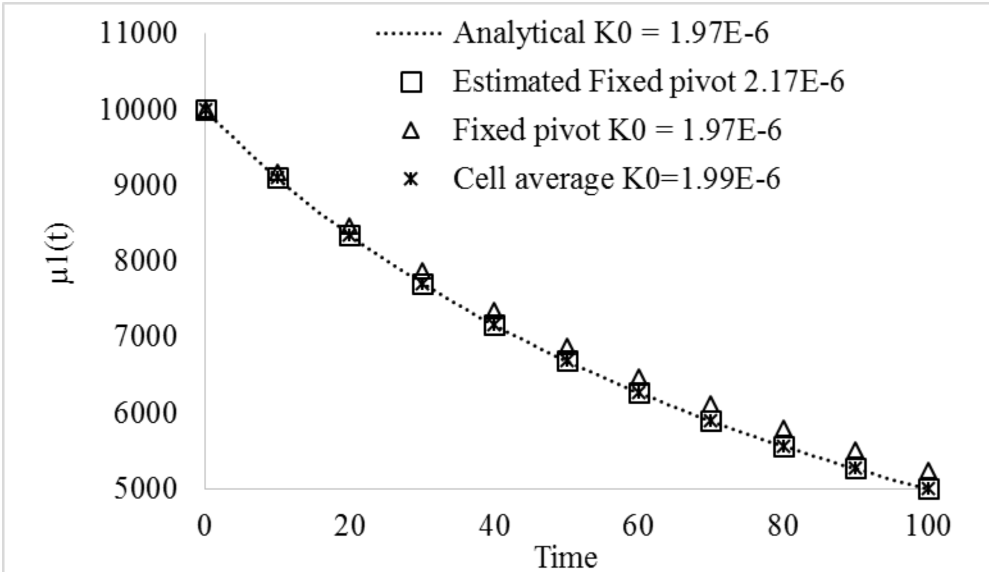

Figure S4 Analytical and estimated 0th moment profile for pure agglomeration problem.

Case 4: Simultaneous Growth and nucleation

For this case, continuous population balance takes the following form:

$$\frac{\partial n(v_i)}{\partial t} + \frac{\partial [G(v_i) n(v_i)]}{\partial v} = B_{nuc}(v_i)$$

Hounslow (1990) solved this equation for constant growth rate ($G(v_i) = G_0$ and mono-disperse nuclei $B_{nuc}(v_i) = B_0 \delta(v_i - v_0)$ of zero size ($v_0 = 0$) with initial condition $n(v_i, 0) = 0$. The analytical solution is given as:

$$n(v_i, t) = \frac{B_0}{G_0} U\left(t - \frac{v}{G_0}\right)$$

Where U is unit step function.

Since, in this case there is no other process causing crystal birth other than nucleation and no process responsible for death of crystals, the 0th moment is given as $\mu_0(t) = B_0 t$. Thus, nucleation rate can be found out by the 0th moment profile. However, since we are interested in checking the capabilities of gPROMS parameter estimation, we would not prefer to estimate individual parameters. Instead, we will try to estimate the parameters simultaneously from 1st moment profile.

The profile for 1st moment is given by;

$$\mu_1(t) = \mu_1(0) + G_0 B_0 \left(\frac{t^2}{2}\right) + B_0 v_0 t$$

The profile of μ_1 was used to estimate the both parameters G_0 and B_0. Since growth and nucleation are simpler process, linear discretization was used to solve PBE. Theoretical and estimated parameters are given in table S4. The estimated parameters are exactly same as that of theoretical parameters. Also, the analytical and estimated profile of μ_1 is shown in figure S5. It is clear from this case study that we can estimate parameters of two processes comprehensively using gPROMS.

Table S4 Theoretical and estimated parameters for simultaneous nucleation and growth process.

Theoretical	G_0	1.5
	B_0	5
Estimated	G_0	1.5
	B_0	5

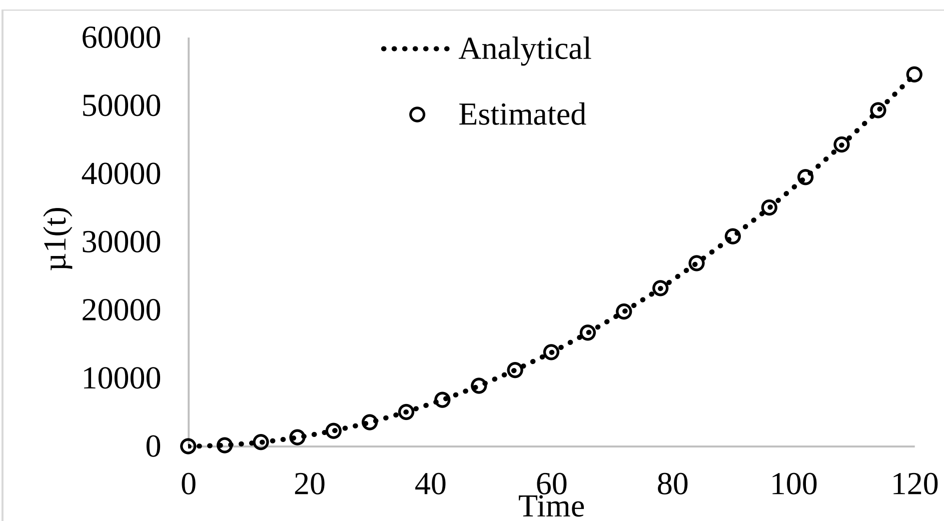

Figure S5 Analytical and estimated 1st moment profile for simultaneous growth and nucleation problem.

Case 5: Simultaneous nucleation and agglomeration

The continuous population balance equation in this case is given as

$$\frac{\partial n(v_i)}{\partial t} = \frac{1}{2}\int_0^\infty K(v_{i-j}, v_j) \times n(v_{i-j}) \times n(v_j) \times dv_j$$
$$- n(v_i)\int_0^\infty K(v_i, v_j) \times n(v_j) \times dv_j + B_{nuc}(v_i)$$

Analytical solutions are given for moments by considering the zero initial population with a constant aggregation kernel K_0 and a constant nucleation rate B_0. Alexopoulos and Kiparissides (2005) gave analytical solution for the first two moments;

$$\mu_0 = \hat{b}\tanh\left(\frac{\hat{b}\tau}{2}\right)$$

$$\mu_1 = \sigma\tau$$

where;

$$\sigma = B_0/\left(K_0 {N_0}^2\right)$$

$$\tau = K_0 N_0 t$$

$$\hat{b} = \sqrt{(2\sigma)}$$

In this case also, two parameters were estimated simultaneously using profile for 1st moment. For this case PBE is solved using Cell average technique since it is a case of agglomeration. Theoretical and estimated parameters are given in table S5. It is clear that the estimated parameters are in excellent agreement with the theoretical parameters; which once again confirms the capability of gPROMS to simultaneously estimate parameters involving multiple processes. The analytical and estimated profile for both 0th moment and 1st moment are shown in figure S6.

Table S5 Theoretical and estimated parameters for simultaneous nucleation and agglomeration process.

Theoretical	N_0	1
	B_0	0.1
Estimated	N_0	1.01
	B_0	0.1

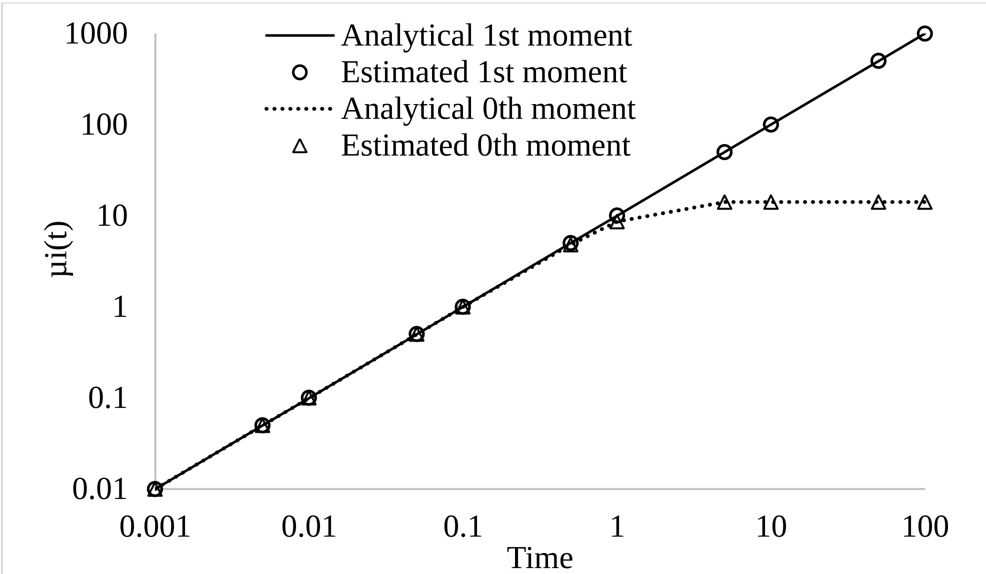

Figure S6 Analytical and estimated 1st moment profile for simultaneous nucleation and agglomeration problem.

Case 6: Simultaneous agglomeration and breakage

Patil et al. (1998) provided an analytical solution for the PBE with simultaneous breakage and agglomeration for a special case where the total number of particles is constant. They considered the following form of PBE;

$$\frac{\partial n(v_i)}{\partial t} = \frac{1}{2}\int_0^\infty K(v_{i-j}, v_j) \times n(v_{i-j}) \times n(v_j) \times dv_j \; - n(v_i)\int_0^\infty K(v_i, v_j) \times n(v_j) \times dv_j$$

$$+ 2\int_v^\infty b(v_i, v_j) \times S(v_j) \times n(v_j) dv_j - S(v_i) \times n(v_i)$$

With agglomeration kernel, breakage rate and distribution function given by;

$K(v_i, v_j) = \; K_0$

$S(v_i) = S_0 V_i$

$b(v_i, v_j) = \dfrac{1}{v_j}$

The analytical solutions are obtained for the following initial conditions

$$n(v, 0) = N_0 \frac{N_0}{\mu_1} \exp\left(-\frac{N_0}{\mu_1} v\right)$$

They prove that the steady state is achieved for the parameters satisfying:

$$\sqrt{2S_0\frac{\mu_1}{K_0}} = N_0$$

Thus, with parameters satisfying above condition, the analytical solution is given by:

$$n(v,t) = N_0\frac{N_0}{\mu_1}\exp\left(-\frac{N_0}{\mu_1}v\right)$$

In this case, we have multiple solutions with different pairs of specific breakage rate S_0 and agglomeration kernel K_0. Hence the simultaneous estimation of two parameters i.e S_0 and K_0 is not worthy. Instead, the parameter estimation was carried out for the esimaton of one parameter, with specifying other parameter. The initial condition and parameters satisfying above equation which are considered here, are given in table S6.

Here also the PBE are solved using Cell average technique. The estimation was carried for the two conditions: (1) With known breakage parameter estimation of agglomeration parameter (2) With known agglomeration parameter estimation of breakage parameter. The parameter estimation results are given in table S6. Simultaneous breakage and agglomeration is the most complex process considered so far (having analytical solution). It is clear from the table that gPROMS parameter estimation can estimate parameters for for this process also. The CSD profile obatined using the estimated kinetic parameters is shown in figure S7. It can be seen from the figure that the CSD profile is steady.

Table S6 Initial conditions and parameters for simultaneous agglomeration and breakage process.

Initial conditions (variables)		N_0	10^4
		μ_1	2×10^5
Parameters		S_0	0.5
		K_0	2×10^{-3}
Parameter estimation	Known parameter	S_0	0.5
	Estimated parameter	S_0	0.499
	Known parameter	K_0	2×10^{-3}
	Estimated parameter	K_0	2.01×10^{-3}

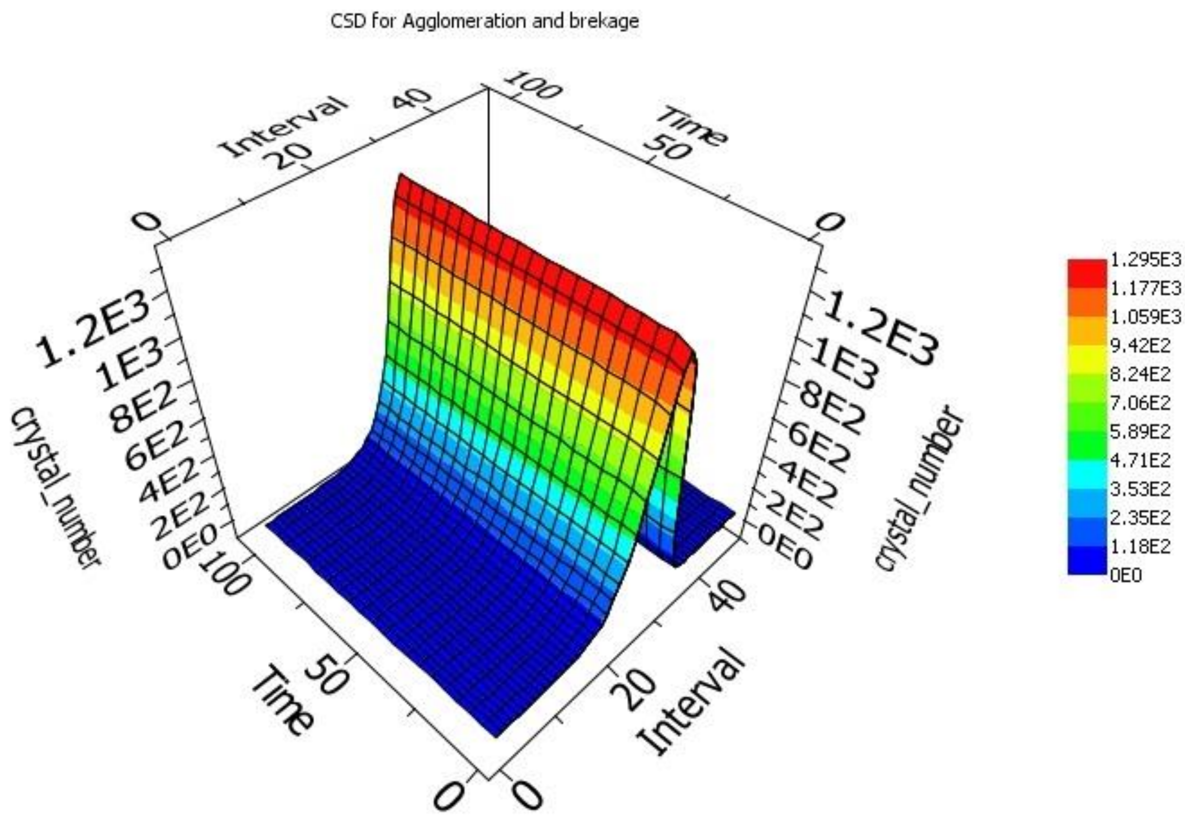

Figure S7. CSD for agglomeration and breakage with estimated parameters.