*Mathematical Model*

The population balance equation is:

Multiplying *Li* and integrating both sides with respect to *dL*, the RHS becomes:

Multiplying *Li* to the first term in the LHS we get the following:

The second terms in the LHS can be integrated by parts (assuming size independent growth rate) to give the following:

*B0* is the flux of particles entering at *L = 0* or also the nucleation rate.

Combining all the above equations, the moment transformation of the PBE becomes:

If the crystallizer volume is not constant (as in the cases of batch reactors), then the equation can be rewritten as:

The mass balances can be written separately for the solid and the liquid phase as:

To find out the value of *MC*, we multiply the equation for the third moment on both sides by *σVρSVR* and some rearrangement (regardless of crystallizer volume being constant or not), we get the following equation:

It is useful to recognize that, *σVM3* = ε. The first term in the RHS is the mass transfer to the crystals and the second term is the inflow and outflow due to convection. Hence, when we compare the above equation to the equation for mass balance of solid phase, we can get the relation for the mass transfer to crystals as:

The mass balance equation for the dissolved solids can be written as:

The heat balance can be written as:

Multiplying mass balance of the dissolved solid’s phase by *CpTref*:

Multiplying mass balance of solvent phase by *CP,LTref* and adding the resulting equation into the above equation, we get the following relation independent of *Tref*:

Similarly for the solid phase we have:

Adding the above equations to the original energy balance equation, we are left with the following relation independent of *Tref*:

This can also be written as:

Where

The only thing that is unknown in the above equations is how to account for the unknown outlet velocity. The following section deals with handling the unknown outlet velocity.

It should be noted that the

Differentiating w.r.t *t* we get:

Now there are two simplifying assumptions we can make to proceed from here.

***Constant liquid phase density assumption***

Assuming a constant density, the above equation for velocity directly translates into:

***Density linearly varying with solute concentration***

Differentiating the dissolved solute mass:

It should be noted that for the linearly varying density and constant density, the outlet volumetric flow rate may still be obtained explicitly and does not need to be solved simultaneously.

*Batch Mode*

For the case of a batch reactor, instead of solving for the outlet velocity, we will have to solve for the crystallizer volume instead.

Differentiating w.r.t *t* we get:

Setting , we get:

Again as before, there are two simplifying assumptions we can make to proceed from here.

***Constant liquid phase density assumption***

***Density linearly varying with solute concentration***

Differentiating the dissolved solute mass:

Setting , we get:

To complete the formulation of this problem, we have to write the initial conditions:

|  |  |
| --- | --- |
| **Variable** | **Unit** |
|  | #/ m3 |
|  | (#-m)/ m3 |
|  | (#-m2)/ m3 |
|  | (#-m3)/ m3 |
|  | (#-m4)/ m3 |
|  | kg |
|  | kg |
|  | - |
|  | K |

Table 1: Initial conditions required for each crystallizer unit

For multiple tanks in series the above equations can be written as:

And for non-constant volume as:

***Constant liquid phase density assumption***

***Linearly varying density assumption***

*Dimensionless Equations*

Equation for Liquid mass

Or for non-constant volume as:

***Constant liquid phase density assumption***

***Linearly varying density assumption***

*Batch Mode*

***Constant liquid phase density assumption***

***Density linearly varying with solute concentration***

*Reference values*

The values for the reference variables need to be defined. It helps to make intelligent choices for the reference values as that would be helpful in making more generalized insights for the system. The first reference variable we encounter is *Lref*. For *Lref*, in the present study we will define as the target particle size for the crystallization. This would be a user defined value. The second variable we encounter is *Vref*. It is convenient to define *Vref* as directly the volume of the reactor. The third variable is *M0,ref*. We will define *M0,ref* as the number of particles of target size which will be formed, if the total solute mass inside the reactor (operated in batch mode) is crystallized. So, the total solute mass inside the reactor (operated in batch mode) can be found out as:

So, we have:

The reference time can be defined as the residence time and can directly be written as:

, are taken to be same as the liquid phase properties. is defined as the inlet temperature. The reference concentration is simply defined as the inlet solute concentration.

|  |  |  |
| --- | --- | --- |
| **Symbol** | **Meaning** | **Unit** |
|  | Target particle size | m |
|  | Total volume of the crystallizer | m3 |
|  | Maximum total number of target sized particles that can be formed | # |
|  | Crystallizer residence time / Batch time | s |
|  | Pure liquid phase density | kg/m3 |
|  | Specific heat of pure liquid phase | J/kg-K |
|  | Inlet temperature taken as reference | K |
|  | Maximum possible extent of super saturation | kmol/m3 |

Table 2: Reference values for obtaining dimensionless form of equations

|  |  |  |
| --- | --- | --- |
| **Symbol** | **Meaning** | **Unit** |
|  | Target particle size | m |
|  | Total volume of the crystallizer | m3 |
|  | Maximum total number of target sized particles that can be formed | # |
|  | Unit crystallizer residence time / Batch time | s |
|  | Pure liquid phase density | kg/m3 |
|  | Specific heat of pure liquid phase | J/kg-K |
|  | Inlet temperature taken as reference | K |
|  | Maximum possible extent of super saturation | kmol/m3 |

The final form of the equations can thus be written as follows:

For non-constant crystallizer volume:

***Constant liquid phase density assumption***

***Linearly varying density assumption***

*Batch Mode*

***Constant liquid phase density assumption***

***Density linearly varying with solute concentration***

*Constitutive laws*

**Crystal growth**

**Primary Nucleation**

**Secondary Nucleation**

Auxiliary Equations

**Solubility**

**Concentration**

**Density**

Considering mass weighted average,

**Specific Heat**

Considering mass weighted average,

|  |  |  |
| --- | --- | --- |
| **Symbol** | **Meaning** | **Unit** |
|  | Number density distribution | #/(m3-m) |
|  | Particle size co-ordinate – taken here as particle diameter | m |
|  | Growth rate of particle | m |
|  | Volumetric flow rate | m3/s |
|  | Volume of crystallizer unit | m3 |
|  | Flow time | s |
|  | *ith* moment of the number density distribution | (#-mi)/ m3 |
|  | Nucleation rate | #/(m3-s) |
|  | Mass of liquid phase in crystallizer unit | kg |
|  | Density of liquid phase in crystallizer unit | kg/ m3 |
|  | Solid volume fraction | - |
|  | Rate of mass transfer from liquid phase to solid phase in the form of crystal growth | kg/s |
|  | Mass of solid phase in crystallizer unit | kg |
|  | Density of solid phase in crystallizer unit | kg/ m3 |
|  | Shape factor | - |
|  | Mass fraction of solute phase dissolved in solvent | - |
|  | Specific heat | J/(kg-K) |
|  | Temperature | K |
|  | Heat of crystallization | J/kg |
|  | Jacket side universal heat transfer coefficient | J/K |
|  | Environment side universal heat transfer coefficient | J/K |
|  | Dimensionless form of variable *X* | - |
|  | Concentration of solution | kmol/m3 |
|  | Solubility concentration as a function of temperature | kmol/m3 |
|  | Molecular weight of solute | kg/kmol |

Table 3: Symbols and notation used for derivations

|  |  |
| --- | --- |
| **Subscript** | **Meaning** |
|  | Liquid phase |
|  | Solid phase |
|  | Inlet stream |
|  | Mixture |
|  | *kth* tank in tanks in series model |
|  | Jacket |
|  | Environment |
|  | Reference variable |

Table 4: Subscripts used for derivations

*Inputs for Solver*

|  |  |  |
| --- | --- | --- |
| **Symbol** | **Meaning** | **Unit** |
|  | Pre-exponential constant for solubility expression | (kmol/m3) |
|  | Exponential constant for solubility expression | K-1 |
|  | Pre-exponential constant for growth rate | (m/s)(kmol/m3)-g |
|  | Activation energy | J/(kmol-K) |
|  | Universal gas constant | J/kmol |
|  | Growth rate exponent | - |
|  | Constant for primary nucleation rate expression | #/(m3-s)(kmol/ m3)-n1 |
|  | Exponent for primary nucleation rate expression | - |
|  | Constant for secondary nucleation rate expression | 1/(( m2-s)(kmol/ m3)-n2) |
|  | Exponent for secondary nucleation rate expression | - |
|  | Heat of crystallization | J/kg |

Table 5: Crystallization kinetic parameters

|  |  |  |
| --- | --- | --- |
| **Symbol** | **Description** | **Unit** |
|  | Total volume of crystallizer | m3 |
|  | Volume of crystallizer unit | m3 |
|  | Inlet volumetric flow rate | m3/s |
|  | Inlet temperature | K |
|  | Inlet 0th moment | #/ m3 |
|  | Inlet 1st moment | (#-m)/ m3 |
|  | Inlet 2nd moment | (#-m2)/ m3 |
|  | Inlet 3rd moment | (#-m3)/ m3 |
|  | Inlet 4th moment | (#-m4)/ m3 |
|  | Inlet dissolved solute mass fraction | - |
|  | Shape factor | - |
|  | Constant for liquid phase density relation | kg/m3 |
|  | Constant for liquid phase density relation | kg/m3 |
|  | Density of solid phase | kg/m3 |

Table 6: System Properties

|  |  |
| --- | --- |
| **Variable** | **Unit** |
|  | #/ m3 |
|  | (#-m)/ m3 |
|  | (#-m2)/ m3 |
|  | (#-m3)/ m3 |
|  | (#-m4)/ m3 |
|  | kg |
|  | kg |
|  | - |
|  | K |

Table 7: Initial conditions for each crystallizer unit

|  |  |  |
| --- | --- | --- |
| **Symbol** | **Description** | **Unit** |
|  | Specific heat of pure liquid phase | J/(kg-K) |
|  | Specific heat of pure solid phase | J/(kg-K) |
|  | Jacket temperature (can be programmed) | K |
|  | Jacket side universal heat transfer coefficient | J/K |
|  | Ambient temperature | K |
|  | Environmental side universal heat transfer coefficient | J/K |

Table 8: Heat transfer variables for each crystallizer unit

|  |  |  |
| --- | --- | --- |
| **Symbol** | **Description** | **Unit** |
|  | Number of tanks in series (Default = 1) | - |
|  | Starting time for simulation | s |
|  | Ending time for simulation | s |
|  | Reporting time for simulation | s |
|  | Absolute error tolerance | 1e-6 |
|  | Epsilon for detecting batch or non batch | 1e-12 |

Table 9: Solver settings

|  |  |  |
| --- | --- | --- |
| **Symbol** | **Formula** | **Physical Meaning** |
|  |  | Maximum possible hold up in crystallizer unit |
|  |  |  |
|  |  |  |
|  |  |  |
|  |  |  |
|  |  |  |
|  |  | Ratio of maximum possible growth rate to ideal growth rate |
|  |  |  |
|  |  | Ratio of maximum possible primary nucleation rate to ideal nucleation rate |
|  |  | Ratio of maximum possible secondary nucleation rate to ideal nucleation rate (expression simplified) |
|  |  |  |

Table 10: List of non-dimensional groups