DEVELOPMENT OF MATHEMATICAL MODELS FOR THE DYNAMIC GROWTH OF CRYSTALS IN A COOLING BATCH CRYSTALLIZER

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Abstract: This research is aimed at developing mathematical models for the dynamic growth of crystals in a cooling batch crystallizer. Using mass, energy and population balance, three model equations which characterized the dynamic of the concentration of the solute in the crystallizer, the response of temperature of the solution and cooling water, and the crystal size distribution were developed. The models were solved using moment technique. In this method, the partial differential equation in the model was transformed to set of ordinary differential equations (in form of moment equations). The model developed can be used for any solution whose solubility increases with increase in temperature. In addition, it can be used to control or maintain the solute concentration within the metastable zone and to study the effect of super saturation and cooling rate on crystal growth.

Keywords; Crystals, Mathematical Modelling, Nucleation, Supersaturation

1.0 INTRODUCTION

Crystallization is the formation of solid particles within a homogeneous phase, it may occur as the formation of solid particles in a vapour, as in snow; as solidification from liquid melt, as in the manufacturing of large single crystals, or as crystallization from liquid solution (McCabe, 2005). Crystallization is rank as one of the oldest unit operations and a major processing technique in chemical industry (Mullin 2001). It differs from most unit operations because of the presence of solid product.

The main advantages of crystallization are high purity in one process step, a low level of energy consumption and relatively mild process condition. Application of crystallization can be found in producing inorganic materials such as paraxylene (raw material for polyester) as well as in industries producing product like pharmaceuticals (Oherek *et al*., 2021). Whether a vessel is called an evaporator or a crystallizer depends primarily on the criteria used in arriving at its sizing, in an evaporator of the salting out type, sizing is done on the basis of vapour release. In a crystallizer, sizing is normally done on the basis of the volume required for crystallization or for special features required to obtain the proper product size (Perry, 1997).

Maximizing profits by operating the most efficient process is the primary goal of all industrial operations. To help create efficient operations, chemical processing industries use process simulation, which is the application of a range of software tools to analyse complete processes, not just single unit operations. Process engineers and scientists use simulation models to investigate complex and integrated process operations, without the need for extensive experimentation (Potticary *et al*., 2021).

Crystallization from solution can be thought of as a two-step process. The first step is the phase separation, or birth of new crystals. The second step is the growth of these crystals to larger sizes. These two processes are known as nucleation and crystal growth, respectively. Analysis of industrial

crystallization process requires knowledge of both nucleation and crystallization.

The condition of supersaturation or super cooling alone is not sufficient cause for a system to begin to crystallize. Before a crystal can develop, there most exist in the solution a number of minute solid bodies, embryos, nuclei, or seed that act as the centre of crystallization. The formation of these new crystalline materials is termed nucleation. The driving force for nucleation is supersaturation, which is defined as the difference in chemical potential. The next step in crystallization process after nucleation is the growth of small sized particle formed during the nucleation process. In the absence of agglomeration and breakage, growth, together with nucleation, determine the final particle size distribution of the crystal population. In addition, the rate of crystal growth has a significant impact on the product purity and the crystal habit. The driving force for crystal growth is again supersaturation. Crystal growth is a process of mass transfer, surface integration and heat transfer. The mass transfer steps involve the diffusion of growth units such as ions, atoms or molecule toward the crystals surface. Next, orientation and absorption of the crystals unit takes place in the surface integration step Heat transfer occurs simultaneously with both steps and is usually not rate-limiting apart from melt crystallization (Yu *et al*., 2021).

The external shape of a crystal is determined by the crystal structure, that is, the internal order of the individual building blocks as determined by the space group symmetry. The crystal faces expressed by the macroscopic crystal always map a lattice plane defined by the microscopic unit cell. Nonetheless, crystals of the same chemical species with the same crystal structure can exhibit different habits. This is due to the fact that growth rates of individual crystal faces, and therefore their relative morphological importance, are subject to supersaturation effects and the influence of solvent and impurity molecules.

A mathematical model of a process is a system of equations whose solutions, given specified input data, is a representation of the response of the process to a corresponding set of input. Three methods are used by engineers and scientist to develop equations for the mathematical models: fundamental, empirical and analogy (Tong *et al*., 2020). Fundamental modelling uses fundamental physical and chemical laws such as law of conservation of mass, energy and momentum to develop model equations. Empirical and analogy modelling on the other hand use data obtained from experiment and equations describing the system that is believed to be analogous to the physical system understudy respectively to develop model equations (Denn, 2001). Mathematical models are obtained to enable the prediction of the expected behaviour of a process for a range of inputs and conditions. The particular prediction to be done depends on the application.

2.0 METHODOLOGY

2.1 Materials

A HP Laptop computer (Compaq 6735 s, 160 GB hard disc, 2 GHz processor, and 1,024MB RAM), MATLAB Version 7.0 numerical software package, Cooling crystallizer parameters reported for potassium sulphate (warranne *et al*, 2008) and Design procedures, tables, charts etc. obtained from standard chemical engineering textbooks, handbooks, journals, etc.

2.2 Methodology

This research deals with modelling and simulation of the dynamic growth of crystals

in a cooling crystallizer using MATLAB version 7.0. The following steps are adopted during the course of the research: Development of the model, simulation of the developed model using MATLAB 7.0 and validation of the model.

2.3 Model Development

In this work, mass balance equation for the crystallizer solute, energy balance equation for the system and population balance equation for the crystals were used to describe the dynamics of the crystallization process. The following simplifying assumptions were considered in the development of the model for the dynamic's growth of crystals in the cooling crystallizer.

i. The suspension density of the crystals and the supersaturation are homogeneous in all part of the crystallizer.

ii. Crystal can be characterized by a linear dimension L.

iii. Crystals of different sizes have the same crystal habit or shape (uniform crystal shape)

iv. Crystal breakage or agglomerations are negligible except for attrition, which result in minute particles of near nuclei size with no measurable reduction in the size of the parent crystal.

v. All new crystals are formed at nominal size

vi. No growth rate dispersion.

vii. Overall growth rate is size-independent

viii. There is thermal equilibrium between the vapour and the solution.

ix. Absence of fines dissolution, clear liquor overflow and nuclei generation due to primary nucleation.

x. Simplified form of enthalpy in which $h = C_pT$ for liquid and $h = C_pT + \gamma$ for gas is applicable.

2.4 Mathematical Model

The model equation was developed using the mass, energy and population balance together with some constitutive equations. These were grouped into model equation one, model equation two, model equation three and model equation four.

Consider a batch cooling crystallizer shown schematically in Figure 1 in which the supersaturation is achieved by cooling using a colder fluid in the jacket.

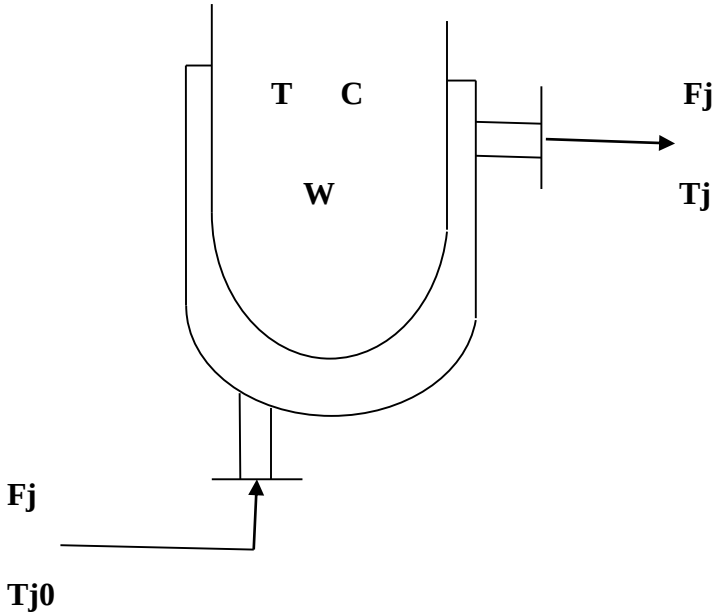

Figure 1: schematic of a cooling crystallizer

2.5 Model equation one

The model equations one was developed to describe the change in the mass of the solute concentration with respect to time and the detail of the mathematical model development is shown below

$$\begin{bmatrix} Time\ rate\ of\ change \\ of\ mass\ inside\ system \end{bmatrix} = \begin{bmatrix} Mass\ flow \\ into\ system \end{bmatrix} - \begin{bmatrix} Mass\ flow \\ out\ of\ system \end{bmatrix} \quad (1)$$

Carrying out mass balance for the solute we have

$$\begin{bmatrix} Time\ rate\ of\ change \\ of\ mass\ inside\ system \end{bmatrix} = \frac{d[W[c(t)+Mc(t)]]}{dt} = W\frac{d[[c(t)+Mc(t)]]}{dt} \quad (2)$$

$$\begin{bmatrix} Mass\ flow \\ into\ system \end{bmatrix} = 0 \quad (3)$$

$$\begin{bmatrix} Mass\ flow \\ out\ of\ system \end{bmatrix} = 0 \quad (4)$$

Substituting equations 2, 3 and 4 into equation 1 we have for the solute balance

$$\frac{d[[c(t)+MC(t)]]}{dt} = 0 \quad (5)$$

Equation c5 on simplification by differentiating and using the relation

$$M_c(t) = \rho_c k_v M_3(t) \quad (6)$$

reduces to

$$\frac{d[c(t)]}{dt} = \frac{d[Mc(t)}{dt} \quad (7)$$

Since the mass of solvent is constant and

$$\frac{d(M3(t))}{dt} = 3G(t)M_2(t) \quad (8)$$

The equation gives

$$\frac{d[c(t)]}{dt} = -3\rho_c k_v G(t)M_2(t) \quad (9)$$

Equation 7 represents the model equation for solute balance

2.6 Model equation two

Model equation two was developed to describe the change in temperature of the suspension with respect to time and the detail of the mathematical model development is shown below

The principle of conservation of energy says

$$\begin{bmatrix} Time\ rate\ of\ change \\ of\ energy\ inside\ system \end{bmatrix} =$$

$$\begin{bmatrix} Energy\ flow \\ into\ system \end{bmatrix} - \begin{bmatrix} Energy\ fflow \\ out\ of\ system \end{bmatrix} \pm \begin{bmatrix} Energy\ added\ or\ removed \\ from\ the\ system\ by \\ convection, conduction, \\ reaction\ and\ radiation \end{bmatrix} \pm$$

$$\begin{bmatrix} Work\ done\ on\ the\ system \\ or\ by\ the\ system\ on \\ the\ sorrounding \end{bmatrix} \quad (10)$$

$$\begin{bmatrix} Energy\ flow \\ into\ system \end{bmatrix} = \begin{bmatrix} Work\ done\ on\ the\ system \\ or\ by\ the\ system\ on \\ the\ sorrounding \end{bmatrix} = \begin{bmatrix} Energy\ fflow \\ out\ of\ system \end{bmatrix} = 0 \ldots\ldots\ldots\ldots\ldots (11)$$

$$\begin{bmatrix} Energy\ added\ or\ removed \\ from\ the\ system\ by \\ convection, conduction, \\ reaction\ and\ radiation \end{bmatrix} = -\Delta H_c \frac{d(WMc(t))}{dt} - UA(T\text{-}T_j) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (12)$$

$$\begin{bmatrix} Time\ rate\ of\ change \\ of\ energy\ inside\ system \end{bmatrix} = \frac{d[WCpT]}{dt} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (13)$$

Where C_p is the specific heat capacity of the solution

Substituting c9, c10 and c11 into c8 we have

$$WC_p\frac{d[T]}{dt} = -UA(T - T_j)\, 3W\rho_C k_v M_2(t)G(t)\Delta H_C \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (14)$$

Simplifiying equation c12 we obtain

$$\frac{d[T]}{dt} = -\frac{UA}{WCp}(T - Tj) - 3\rho_c k_v M_2(t) G(t) \frac{\Delta Hc}{Cp} \quad \ldots\ldots\ldots\

$$\begin{bmatrix}\text{number of crystal in}\\ \text{the size range L and } L + dL\\ \text{accumulated in the system}\end{bmatrix} = \frac{\partial[\mathrm{Wn(L,t)}}{\partial \mathrm{t}} = \mathrm{W}\frac{\partial[\mathrm{n(L,t)}]}{\partial \mathrm{t}} \quad \text{..... (18)}$$

$$\begin{bmatrix}\text{net number of crystal entering}\\ \text{the size range by growth}\end{bmatrix} = \frac{\partial[WG(t)n(L,t)}{\partial l} = WG(t)\frac{\partial[n(L,t)}{\partial l} \quad \text{.....} \quad (19)$$

$$\begin{bmatrix}\text{number of crystals entering}\\ \text{the size range by birth(agglomeration,}\\ \text{abration)}\end{bmatrix} = \begin{bmatrix}\text{number of crystals leaving the}\\ \text{size range by birth (agglomeration,}\\ \text{abrasion, breakage, dissolution}\end{bmatrix} =$$

$$\begin{bmatrix}\text{net range of crystal entering}\\ \text{the size range through}\\ \text{inflow and outflow}\end{bmatrix} = 0 \quad \text{..... (20)}$$

$$\frac{\partial[n(L,t)]}{\sigma t} = G(t)\frac{\partial[n(L,t)}{\partial l} \quad \text{..... (21)}$$

Transforming the population balance equation (21) into moment equation by multiplying both sides of the equation by L^j dL and then integrating over the entire size range (Rohani, 2001) we have

$$\frac{d[Mj(t)]}{dt} = 0^j B + Jm_{J-1}(t)G(t) \quad \text{.....(22)}$$

$$MJ(t) = \int_0^\infty Ljn°(L,t)dL \quad \text{..... (23)}$$

For j = 0….. 3 we have

$$\frac{d[Mo(t)]}{dt} = n^0G(t) = B^0 \quad \text{.....(24)}$$

$$\frac{d[M1(t)]}{dt} = M_0(t)G(t) \quad (25)$$

$$\frac{d[M2(t)]}{dt} = 2M_1(t)G(t) \quad (26)$$

$$\frac{d[M3(t)]}{dt} = 3M_2(t)G(t) \quad (27)$$

Thus equation 24, 25 and 27are moment equation representing the transform population balance equation.

2.8 Model Equation Four

Model equation four comprises of sets of constitutive equations associated with the

$$G = k_g\, exp(-EG/RT)\, S^g \quad (28)$$

Where

$$S = \left(\frac{C(t)-Cs(T)}{Cs}\right) \quad (29)$$

$$Cs(T) = a + bT + Ct^2 \quad (30)$$

Where S and Cs (T) represent the degree of supersaturation and temperature dependency of the solubility respectively

Nucleation rate

$$B^0 = k_b\, exp\left(\frac{-Eb}{RT}\right) S^j\, M_3 \quad (31)$$

2.9 Numerical solution

The mathematical model equations developed consist of non-linear equation, ordinary differential equation and partial differential equations. An analytical solution for such a system does not exist. The ordinary differential equations so developed were solved using finite difference method for a solution of concentration that would be within the metastable limit and the saturation concentration.

2.10 Numerical Algorithm

In applying the finite, the finite difference method, grid points were spread through the domain for which solution is to be provided. The unknown, here f(t), at a grid point t_i is assigned the symbol $f(i) = f(t_i)$. The finite difference method can be derived easily by using a Taylor expansion of the solution about this point. An expression for the derivative is truncated at the first term to give:

moment, mass and energy balance. Constitutive equations give the relationship between the characterizing dependent variables and are needed for the entire model to be consistent. The equations are given below crystal growth

$$\frac{df}{dt} = \frac{fi-fi-1}{\Delta t} \quad (32)$$

Simplifying the equation gives

$$f_i = f_{i-1} + \left(\frac{df}{dt}\right) \text{ x } \Delta t \quad (33)$$

The time space-size Δt was taken as 1, a value that is small enough to give a good estimate of the variables C, T, T_J, m0, m1, m2 and m3 using the relations:

$$C(i) = c(i-1) + \left(\frac{dc}{dt}\right) \times \Delta t \quad (34)$$

$$T(i) = T(i-1) + \left(\frac{dT}{dt}\right) \times \Delta t \quad (35)$$

$$m0\ (i-1) + \left(\frac{dm0}{dt}\right) \times \Delta t \quad (36)$$

3.0 RESULTS AND DISCUSSION

3.1 Model Equations

Equations 37-40 show the result obtained for the model equation one, model equation two and model equation three respectively.

$$\frac{d[c(t)]}{dt} = -3\rho_c\, k_v G(t) M_2(t) \quad (37)$$

$$\frac{d[T]}{dt} = -\frac{UA}{WCp}(T - Tj) - 3\rho_c\, k_v\, M_2(t)\, G(t)\, \frac{\Delta Hc}{Cp} \quad (38)$$

$$\frac{d[Tj(t)]}{dt} = \frac{UA}{\rho jvjCpj}(T(t) - Tj)) + \frac{fj}{vj}(Tjo - Tj(t)) \quad (39)$$

$$\frac{\partial[n(L,t)]}{\sigma t} = -G(t)\, \frac{\partial[n(L,t)}{\partial l} \quad (40)$$

Equation 41, equation 42 and equation 43 shows the result obtained for the transformed form of equation 44

$$\frac{d[Mo(t)]}{dt} = B(t) \quad (41)$$

$$\frac{d[M1(t)]}{dt} = M_0(t)G(t) \quad (42)$$

$$\frac{d[M2(t)]}{dt} = 2M_1(t)G(t) \quad (43)$$

$$\frac{d[M3(t)]}{dt} = 3M_2(t)G(t) \quad (44)$$

Equation 4.1 is the mass balance model equation. It describes how the concentration of the solute changes with time and consequently the growth and nucleation rate which depends on the liquid phase property.

The solution temperature profile affects the super saturation profile which has a strong effect on the final crystal size distribution via the nucleation and growth of the crystal. The temperature profile is described by equation 4.2 and it predicts how the temperature of the solution changes with respect to time. The variation in the temperature of the cooling water with respect to time is described by equation 4.3. It represents the dynamics of the cooling jacket.

Equation 4.4 is the population balance equation. It describes the crystal size distribution and is necessary to quantify growth and nucleation rate. The transformed form of equation 4.4 which are shown in equation 4.5equation 4.6 and equation 4.7 represent the dynamics of the zeroth, first second and third moment of crystal size distribution. The zeroth moment indicates the total number of crystals grown nuclei in the suspension. The first moment of the crystal size distribution on the other hand indicates the total length of the crystal when placed side by side. The second and the third moment indicate respectively the total area and the total volume of the crystals generated.

4.0 CONCLUSION

A model for the dynamic growth of crystals was successfully developed based on the principle of mass, energy and population balance. The partial differential equation of the population balance was transformed to set of moment equations and the resulting ordinary differential equations were solved using MATLAB source code written for finite difference method. Based on the result obtained, the following conclusions are drawn.

i. The effect of variation of operation parameter on product quality could be systematically investigated by modeling and simulation.

ii. The model can be used for any solution whose solubility increases with an increase in temperature.

iii. It can also be used to control or maintain the solute concentration within the metastable zone and to study the effect of supersaturation and cooling rate of crystal growth.

iv. The dynamic response of a crystallizer containing a supersaturated solution of potassium sulphate of concentration 0.1743 g solute/g solute at a temperature of 323 K and using a cooling water of temperature 293 K was studied.

v. The effect of variation of cooling water temperature on growth and nucleation rate was found to decrease with increase in temperature.

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