# Mathematical design of continuous, isothermal crystallizers with homogeneous nucleation: a simplified approach

by F. XAVIER MALCATA

Escola Superior de Biotecnologia, Universidade Católica Portuguesa
Rua Dr. António Bernardino de Almeida, 4200 Porto, Portugal

A simplified, systematic approach to the mathematical simulation of crystallizers is attempted by using the fundamental principles of mass conservation, via a population balance to the solid phase and a solute balance to both solid and liquid phases. A continuous, isothermal and isochoric crystallizer is assumed to be described by the MSMPR model under transient operating conditions with complete micromixing. The birth and death functions are assumed nil. Homogeneous nucleation is considered at a rate which is independent of the solution supersaturation. The growth rate of the crystals is described by McCabe's law. The possibility of solving the population balance and the mass balance independently is explored, and the conditions of validity for such an approach are found. The maximum linear dimension of crystal and the liquor concentration profile as functions of time are obtained. The approximation is found to be generally good for a period of time right after start-up of the crystallizer. A much wider range of time ensuring a satisfactory approximation is possible provided that the system and operation-dependent parameter takes small values.

## 1. Introduction

Crystallization, which consists in the recovery of a solute from a liquid solution in solid, purified form, is one of the most important unit operations in the chemical industry. Traditionally, crystals have been obtained by various methods, from batch reservoirs via cooling by natural convection to multistage systems via forced cooling/vaporization in the presence of ellutriation and recycling devices. Crystallization possesses some advantages in terms of energy requirements when compared with other separation processes [1].

Extensive progress has taken place encompassing the fundamental knowledge of the physicochemical phenomena on the molecular scale which are associated with crystallization. Such progress has made it possible to model some types of crystallizers on the basis of involved systems of partial derivative equations [2–9]; although the integration of such equations demands powerful numerical methods, some typical parameters relating to the crystallization process may be efficiently determined from experimental data [10, 11]. Since in the predesign steps of pilot scale or plant scale crystallizers the MSMPR type (i.e. mixed suspension, mixed product removal) [10, 12] is frequently used, one will consider this model here for the sake of mathematical simplicity [6, 13, 14]. In its simpler form, the modelling of crystallizers using first principles consists of a balance to the population of crystals

of different size and an independent balance to the solute in the liquor and solid phases [12]. In this fashion, a system of two coupled equations is obtained, where the former is a partial derivative equation and the latter is an ordinary differential equation with an improper integral. The solution requires simultaneous numerical integration with two independent variables as well as an error estimating procedure.

The purpose of this communication is to attempt the uncoupling of the aforementioned two equations leading to sequential solution, a process which allows one to resort to the numerical integration of a single first order ordinary differential equation. An *a posteriori* test of the accuracy of the procedure will also be provided. This reasoning will lead to the natural definition of two (dimensionless) design parameters, the product of which may be directly employed in the predesign steps of crystallizing equipment.

## 2. Theoretical development

In the case of a MSMPR crystallizer, the ellutriation phenomena inside the unit are negligible and the composition of the outlet stream at any time is equal to the composition of the mother liquor remaining in the crystallizer. In this study, the feed is considered exempt of crystals of any kind, and the birth and death functions of the crystals are considered nil. The operation is furthermore assumed to take place at constant volume under isothermal conditions, and the crystals are assumed to retain geometric similarity throughout their growth process. Using these postulates, the population balance can be written as

$$Qn + V\frac{dn}{dt} = 0 \tag{1}$$

where $Q$ is the volumetric flow rate through the crystallizer, $V$ is the volume of the crystallizer, $n$ is the population density, and $t$ is the time elapsed since start-up of the crystallizer. The total differential $(dn/dt)$ may in turn be calculated through

$$\left(\frac{dn}{dt}\right) = \left(\frac{\partial n}{\partial t}\right)_L + \left(\frac{\partial n}{\partial L}\right)_t \left(\frac{dL}{dt}\right) \tag{2}$$

where $L$ is the linear dimension of the crystal.

The material balance to the solute in the liquid and solid phases may be written as

$$\frac{dC}{dt} = \frac{Q}{V}(C_{in} - C) - \rho \Phi G \int_0^\infty n\{L, t\}L^2 \, dL \tag{3}$$

where $C$ is the solute concentration in the solution, subscript in denotes inlet conditions, $\rho$ is the mass density of the crystals, $G$ is the growth rate of the crystals, and the area factor associated with the crystals, $\Phi$, is defined as

$$\Phi \equiv \frac{A\{L\}}{L^2} \tag{4}$$

(For hypothetical crystals with spherical shape, $L$ would represent the radius of the crystals, and hence $\Phi$ would be equal to $4\pi$.)

The rate of growth of the crystals is assumed to follow McCabe's law, namely

$$G \equiv \frac{dL}{dt} = K(C - C_s) \tag{5}$$

where $C_s$ is the saturation concentration and $K$ is a constant.

For the sake of using the chain differentiation rule, the population density, $n \equiv n\{L, t\}$, can be written as $n \equiv n\{L, t, C\}$, thus yielding

$$\frac{dn}{dt} = \left(\frac{\partial n}{\partial t}\right)_{L,C} + \left(\frac{\partial n}{\partial C}\right)_{L,t}\left(\frac{dC}{dt}\right) + \left(\frac{\partial n}{\partial L}\right)_{t,C}\left(\frac{dL}{dt}\right) \tag{6}$$

If the time constant associated with the variation of the concentration of solute in the solution is small when compared with the time constant associated with the variation in the population density, i.e. if the following condition is satisfied

$$\left(\frac{\partial n}{\partial C}\right)_{L,t}\left(\frac{dC}{dt}\right) \ll \left(\frac{\partial n}{\partial t}\right)_{L,C} + \left(\frac{\partial n}{\partial C}\right)_{L,t}\left(\frac{dC}{dt}\right) + \left(\frac{\partial n}{\partial L}\right)_{t,C}\left(\frac{dL}{dt}\right) \tag{7}$$

and if this result is applied to equations (1) and (2), on obtains

$$n^* + \left(\frac{\partial n^*}{\partial t^*}\right)_{L^*,C^*} + C^*\left(\frac{\partial n^*}{\partial L^*}\right)_{t^*,C^*} = 0 \tag{8}$$

where the dimensionless variables are defined as

$$n^* \equiv \frac{n}{n_{in}} \tag{9}$$

$$L^* \equiv \frac{LQ}{VK(C_{in} - C_s)} \tag{10}$$

$$t^* \equiv \frac{tQ}{V} \tag{11}$$

and

$$C^* \equiv \frac{C - C_s}{C_{in} - C_s} \tag{12}$$

The solution of equation (8) can be obtained under the assumption of a pseudo steady-state for the solute concentration in the liquor. The strategy is then: (i) solve the population balance using equation (8) and obtain $n^* \equiv n^*\{L^*, C^*, t^*\}$; (ii) solve the mass balance using the dimensionless counterpart of equation (3) and obtain $C^* \equiv C\{L^*, t^*\}$; (iii) use $C^* \equiv C\{L^*, t^*\}$ in equation (8) and obtain $n^* \equiv n^*\{L^*, t^*\}$; and finally (iv) test the approximation criterion as given by equation (7).

In order to complete the solution, a boundary condition and an initial condition are still required. In order to do so, one will consider homogeneous nucleation. Such an assumption is based on the hypothesis of formation of temporary aggregates of solute molecules when these molecules collide in their random movements, some of which will eventually acquire regular spacing and thus form a new (crystal) phase. The rate of homogeneous nucleation is considered independent of the concentration of solute in the liquor. This fact may be mathematically expressed by the following initial condition,

$$t^* = 0, L^* \geq 0, n^* = \delta\{L^*\} \tag{13}$$

(where $\delta$ is the Dirac pulse function), coupled with the following boundary condition

$$L^* = 0, t^* \geq 0, n^* = 1 \tag{14}$$

Equation (8) may be solved in the Laplace domain together with equations (13)

and (14) using the appropriate integral transform [16]. The final solution then takes the form:

$$n^* \equiv n^*\{L^*, C^*, t^*\} = \exp\left\{-\frac{L^*}{C^*}\right\} H\left\{t^* - \frac{L^*}{C^*}\right\} \tag{15}$$

where $H$ denotes the Heaviside step function. Using equation (15) in equation (3) one obtains, after integration by parts,

$$\frac{dC^*}{dt^*} = 1 - C^* - 2\, Si\, Op^4\, C^{*4}\left(1 - \left(\frac{t^{*2}}{2} + t^* + 1\right)\exp\{-t^*\}\right) \tag{16}$$

Parameters $Si$ and $Op$ are defined as

$$Si \equiv \Phi L_{ref}^3 \frac{\rho\, n_{in}\, L_{ref}}{C_{in} - C_s} \tag{17}$$

and

$$Op \equiv \frac{KV(C_{in} - C_s)}{Q L_{ref}} \tag{18}$$

respectively. The physical significance of the aforementioned parameters is as follows: $Si$ is a characteristic parameter of the system, being proportional to the ratio of the total mass concentration of crystals with (arbitrarily defined) reference linear dimension $L_{ref}$ contained in a crystallizer and the supersaturation of the inlet mother liquor, assuming that the population density with the reference linear dimension is equal to the density of homogeneous nuclei (the proportionality constant is given by the product of the shape factor by the cube of the linear reference dimension); $Op$ is a parameter characteristic of the system and equipment, and is equal to the increase in the linear dimension of crystals during a time interval equal to one residence time in the crystallizer (assuming that the supersaturation at the inlet stream remains constant throughout the crystallization process), normalized by the reference linear dimension.

Since equation (16) is not integrable analytically, an initial-value numerical method has been employed from the following initial condition:

$$t^* = 1 \qquad C^* = 1 \tag{19}$$

to obtain the variation of the concentration of solute $C^*$ in the mother liquor with time $t^*$; the results therefrom are depicted in Figure 1(a) for five orders of magnitude of the lumped design parameter $Si\, Op^4$. The associated variation with time of the maximum linear dimension of crystal, i.e. $L^*_{max} = C^* t^*$, is plotted in Figure 2 for the same values of the design parameter $Si\, Op^4$.

The size distribution in steady state may be obtained from the asymptotic form of equation (15) for large time intervals:

$$n^*_{ss}\{L^*\} \equiv \lim_{t^* \to \infty} n^*\{L^*, t^*\} = \exp\left\{-\frac{L^*}{C_{ss}}\right\} \tag{20}$$

whereas equation (3) becomes, under steady-state conditions,

$$1 - C^*_{ss} - Si\, Op^4\, C^{*4}_{ss} \int_0^\infty n^*_{ss}\left\{\frac{L^*}{C^*_{ss}}\right\}\left(\frac{L^*}{C^*_{ss}}\right)^2 d\left(\frac{L^*}{C^*_{ss}}\right) = 0 \tag{21}$$
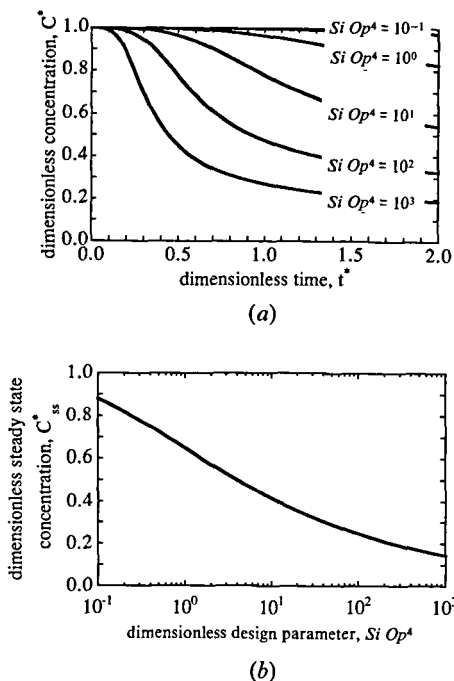
(a)



(b)

Figure 1. (a) Variation of the normalized concentration of solute with the dimensionless time for various values of the design parameter. (b) Variation of the normalized steady-state concentration of solute with the dimensionless design parameter.

Combination of equations (20) and (21) yields, after suitable integration,

$$2 \, Si \, Op^4 \, C_{ss}^{*4} + C_{ss}^{*} - 1 = 0 \qquad (22)$$

Equation (22) cannot be solved in an exact fashion; however, implementation of a Newton method from the starting estimate $C_{ss}^{*} = 1$ converges in less than ten iterations (using a maximum error estimate of 0·005); the variation with $Si \, Op^4$ of the steady-state value $C_{ss}^{*}$ thus obtained is available in Figure 1(b).

The goodness of the approximation based on equation (7) can be tested *a posteriori* through the evaluation of the dimensionless average error $R$ defined as
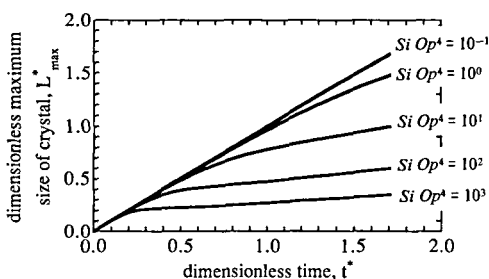


Figure 2. Variation of the normalized maximum linear dimension of crystal with the dimensionless time for various values of the design parameter.
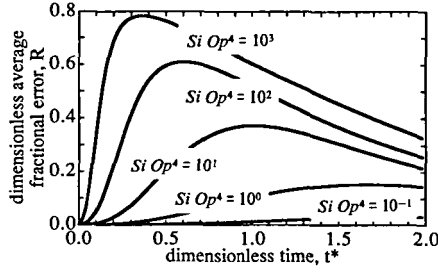
Figure 3. Variation of the average dimensionless error implicit in the approximation developed with the dimensionless time for various values of the design parameter.

$$R \equiv \frac{\int_0^\infty \left(\frac{\partial n^*}{\partial C^*}\right)_{L^*,t^*} \left(\frac{\mathrm{d}C^*}{\mathrm{d}t^*}\right) \mathrm{d}L^*}{\int_0^\infty \left(\left(\frac{\partial n^*}{\partial t^*}\right)_{L^*,C^*} + \left(\frac{\partial n^*}{\partial C^*}\right)_{L^*,t^*} \left(\frac{\mathrm{d}C^*}{\mathrm{d}t^*}\right) + \left(\frac{\partial n^*}{\partial L^*}\right)_{t^*,C^*} \left(\frac{\mathrm{d}L^*}{\mathrm{d}t^*}\right)\right) \mathrm{d}L^*} \tag{23}$$

Recalling the definition of a Dirac pulse (i.e. $\delta\{x\} = 0$ for $x \neq 0$ and the integral of $\delta\{x\}$ between zero and infinity equal to one), the fact that $\mathrm{d}H\{x\}/\mathrm{d}x = \delta\{x\}$, and the definition of the dimensionless variables, equation (23) becomes

$$R = \frac{\left(1 - \exp\{-t^*\} + t^* \exp\{-t^*\}\left(\frac{1}{C^*} - 1\right)\right)\left(\frac{\mathrm{d}C^*}{\mathrm{d}t^*}\right)}{\left(1 - \exp\{-t^*\} + t^* \exp\{-t^*\}\left(\frac{1}{C^*} - 1\right)\right)\left(\frac{\mathrm{d}C^*}{\mathrm{d}t^*}\right) - C^*(1 - \exp\{-t^*\})} \tag{24}$$

The validity of the approximation plotted as $R$ versus $t^*$ for various values of $Si\,Op^4$ is depicted in Figure 3. In industrial practice, the value of parameter $Si\,Op^4$ is of the order of unity [10, 11].


## 3. Discussion

The growth of a crystal tends to occur through the deposition of a series of layers [15]. According to a theory due to Frank [16], the growth takes place through cyclic, spiral-shaped preferential paths. However, the utilization of the classical theories of crystal growth allows a simpler, yet sufficiently accurate approach to the problem. The use of the double film theory allows one to write balances to the solute in the laminar layer next to the crystal surface [17] and in the turbulent layer from the bulk of the solution to the solid/liquid interface [18]. The combination of these two equations, coupled with the assumption that the shape of the crystal does not change throughout growth (which is a consequence of Gibbs-Wulff's theorem [10] on the assumption that the surface energy remains virtually unchanged from surface to surface of the crystal), allows one to conclude that the rate of increase of the crystal mass depends only on the degree of supersaturation of the solution, as first derived by McCabe and coworkers [19–21]. This law is valid for low levels of supersaturation. During the above theoretical development, it was assumed that the rate of growth is not a strong function of the size of the crystal when $C_{in} - C_s$ is unconstrained [12].

The assumption of homogeneous nucleation is a simplification of the simulation of the crystallization process which, in particular, requires the absence of impurities

within the bulk of the solution [10]. However, the existence of an activation energy controlling the nucleation process as suggested by Tammann [22] for not too high degrees of supersaturation places a system within the validity conditions referred to previously provided that not too high temperatures are employed.

The shape of the curves of the variation of the dimensionless concentration with dimensionless time are similar to each other, as apparent from inspection of Figure 1(*a*): they all start from unit $C^*$ (for $t^* = 0$), with zero derivative, exhibit a decrease (which is larger as the parameter $Si\,Op^4$ increases), and level off to a non-zero asymptotic value when $t^*$ tends to infinity. This asymptotic value, $C_{ss}^*$ (which can be obtained from Figure 1(*b*)), is closer to unity for smaller $Si\,Op^4$. Such a behaviour is expected because smaller $Si\,Op^4$ correspond to smaller residence time, nucleation rate, crystal growth rate or level of supersaturation, and hence the changes undergone by the solution are less important.

The curves which represent the variation in the maximum linear dimension of crystals with time start from zero, go through a transient which corresponds to the time interval when the concentration decreases significantly, and tend, after this period, to straight lines which retain the slope they had at the end of the transient period (see Figure 2). For low values of parameter $Si\,Op^4$, the transient does not virtually exist, and hence the line is a straight line with unit slope.

The decreasing exponential for the distribution of crystal sizes under steady-state conditions as given by equation (20) is expected because the size of a crystal at a given time depends on its residence time in the crystallizer since its formation by homogeneous nucleation, and it is known that the residence time distribution of a perfectly mixed reservoir is described by a decreasing exponential [23].

The mathematical design of a MSMPR crystallizer using the equations derived from first principles becomes greatly simplified whenever the equation describing the population balance can be solved before solving the mass balance equation. For short dimensionless times elapsed from the time at which the crystallizer is started the approximation is valid (the initial range of validity is extended with decreasing $Si\,Op^4$); this permits a good simulation of the crystallizer in the start-up region (see Figure 3). In general, though, the approximation is reasonable (i.e. leads to an average error not above, say, 15%) in the whole range of operation times when $Si\,Op^4$ is of the order of unity or smaller (which is also the range of higher practical interest); in this situation, the approximation may become always valid until steady-state conditions are reached. Due to these reasons, the uniparametric theoretical development reported here acquires special interest (not only in educational but also in practical terms) for the simulation of MSMPR isothermal crystallizers whenever the crystallization process is due to supersaturation of the inlet mother liquor.

*Nomenclature*

$C$    = concentration of solute (mol.m$^{-3}$)
$G$    = growth rate of crystals (m.s$^{-1}$)
$H$    = Heaviside step function ( − )
$K$    = McCabbe's constant (m$^4$.mol$^{-3}$.s$^{-1}$)
$L$    = linear characteristic dimension of the crystals (mol.m$^{-3}$)
$n$    = population density (m$^{-4}$)
$Op$    = dimensionless parameter characteristic of the system and equipment
$Q$    = volumetric flow rate through the crystallizer (m$^3$.s$^{-1}$)
$R$    = average dimensionless fractional error of the approximation

$Si$   = dimensionless parameter characteristic of the system
$t$    = time elapsed after startup of crystallizer (s)
$V$    = volume of the crystallizer (m$^3$)

*Subscripts*
in    = inlet conditions
ref   = reference value
s     = saturation conditions
ss    = at steady state conditions

*Superscripts*
*     = dimensionless

*Greek letters*
$\delta$   = Dirac's delta function
$\rho$     = mass density of crystals (kg.m$^{-3}$)
$\Phi$     = area factor associated with the crystals

## References

[1] COULSON, J. M., RICHARDSON, J. F., BACKHURST, J. R., and HARKER, J. H., 1978, *Chemical Engineering* (Oxford: Pergamon Press).

[2] RANDOLPH, A. D., and LARSON, M. A., 1971, *Theory of Particulate Systems* (New York: Academic Press).

[3] RANDOLPH, A. D., and LARSON, M. A., 1962, *A.I.Ch.E.J.*, **8**, 639.

[4] RANDOLPH, A. D., 1965, *A.I.Ch.E.J.*, **11**, 424.

[5] MURRAY, D. C., and LARSON, M. A., 1965, *A.I.Ch.E.J.*, **11**, 728.

[6] SAEMAN, W. C., 1956, *A.I.Ch.E.J.*, **2**, 107.

[7] PERRY, R. H., and CHILTON, C. H. (eds), 1973, *Chemical Engineers' Handbook* (New York: McGraw-Hill).

[8] PALERMO, J. A., and LARSON, M. A. (eds), 1969, *Chem. Eng. Progr. Symp. Series*, **65**, 95.

[9] LARSON, M. A., 1978, *Chem. Eng.*, **85**, 90.

[10] McCABE, W. L., and SMITH, J. C., 1976, *Unit Operations of Chemical Engineering* (New York: McGraw-Hill).

[11] BENNETT, R. C., FIELDELMAN, H., and RANDOLPH, A. D., 1972, *Chem. Eng. Progr.*, **69**, 86.

[12] FOUST, A. S., WENZEL, L. A., CLUMP, C. W., MAUS, L., and ANDERSEN, L. B., 1980, *Principles of Unit Operations* (New York: Wiley).

[13] RANDOLPH, A. D., and LARSON, M. A., 1962, *A.I.Ch.E.J.*, **8**, 639.

[14] RANDOLPH, A. D., and LARSON, M. A., 1971, *Theory of Particulate Processes* (New York: Academic Press).

[15] BUTLER, R. M., 1950, *Factors affecting the rate of growth of crystals from aquaous solutions*, Ph.D. thesis, University of London.

[16] FRANK, F. C., 1949, *Discuss. Faraday Soc.*, **5**, 48.

[17] NOYES, A. A., and WHITNEY, W. R., 1987, *J. Amer. Chem. Soc.*, **19**, 930.

[18] BERTHOUD, A., 1912, *J. Chem. Phys.*, **10**, 624.

[19] McCABE, W. L., 1929, *Ind. Eng. Chem.*, **21**, 30.

[20] McCABE, W. L., and ROBINSON, C. S., 1924, *Ind. Eng. Chem.*, **16**, 478.

[21] TAI, C. Y., McCABE, W. L., and ROUSSEAU, R. W., 1975, *A.I.Ch.E.J.*, **21**, 351.

[22] TAMMANN, G., 1926, *The States of Aggregation* (Constable).

[23] HILL, C. G., 1977, *An Introduction to Chemical Engineering Kinetics and Reactor Design* (New York: Wiley).