D_b = drop diameter
D_g = diameter of ballotini
D_e = diameter of restriction in two-dimensional model
E = net force on drop
g = gravitational acceleration
h = differential head on drop giving buoyancy force
R_1 = radius of leading surface of distorted drop
R_2 = radius of lower surface of distorted drop

Greek Letters

γ = interfacial tension
$\Delta\rho$ = difference in density between phases
ϕ = drop-void diameter ratio
θ = angle between packing elements and spherical cap of drop
ψ = angle between packing element and spherical base of drop

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Self-Generated Oscillations in Continuous Crystallizers:

Part I. Analytical Prediction of the Oscillating Output

The theory of nonlinear oscillations should provide a useful tool for studying both forced and self-generated oscillations in continuous crystallizers. The application of the theory is described in this paper for the case of self-generated oscillations in a MSMPR (mixed-suspension, mixed product removal) isothermal crystallizer. Although the process parameters do not correspond to typical industrial conditions, the results indicate that for the Class I system studied higher yields sometimes can be obtained from the periodic process than the steady state design. Thus, there may be some situations where oscillatory operation is advantageous.

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SCOPE

Chemical processes, such as crystallizers, sometimes produce oscillating outputs, and in certain situations it may be desirable to predict the behavior of the oscillating system. In this paper it is shown that the theory of nonlinear oscillations gives reasonable analytical solutions for the periodic outputs. The theory is applied to the simplest kind of crystallizer model, that is, an isothermal, mixed suspension-mixed product removal unit for a Class I system where high degrees of supersaturation are possible. The focus of the study is on an evaluation of the method of analysis rather than the practical aspects of crystallization.

CONCLUSIONS AND SIGNIFICANCE

The results demonstrate that the theory of nonlinear oscillations provides an additional tool that can be used to study periodic operation of crystallizers. However, the theory is tedious to apply, so that future work should be directed toward the development of simpler approximate models. An interesting feature of the particular system studied was that the time-average yield of crystals produced by the oscillating system exceeded the predicted steady state value, although the design parameters considered were outside the normal range of industrial operating conditions.

It has been known for many years that industrial crystallizers sometimes produce periodic outputs (Miller and Saeman, 1947), but oscillatory operation has seldom been observed in the laboratory (Nyvlt and Mullin, 1970). Recent research results indicate that for most industrial processes (primarily Class II systems), the observed oscillatory operation is caused by fines removal, product classification, and secondary nucleation effects (Randolph et al., 1973; Randolph and Beckman, 1974). However, most of the theoretical studies of the periodic operation of crystallizers have been limited to simpler cases (Hulburt and Katz, 1964; Sherwin et al., 1967, 1969; Lei et al., 1971). An interesting feature revealed in a few of these studies is that for Class I systems the total yield of crystals obtained from an oscillating unit may sometimes exceed the expected steady state design value.

Since there may be some situations where an improved crystallizer performance could be obtained with periodic operation, including both forced oscillations and self-generated oscillations, a preliminary attempt has been made to evaluate the application of the theory of nonlinear oscillations (Minorsky, 1962) to crystallization problems. The theory is rigorous only for very simple systems, that is, a set of two first-order ordinary differential equations, similar to those studied by Nývlt and Mullin (1970), or for certain classes of higher-order plants, but it has been useful in predicting the behavior of more complicated chemical reactor processes.

A Class I system in an MSMPR crystallizer was chosen for the study (because it is the simplest crystallization process to describe mathematically), and the case of self-generated oscillations was considered (because they are the most difficult to treat theoretically). Analytical procedures for estimating the effect of forced oscillations or parametric pumping on the crystallizer performance (similar to those discussed by Ritter and Douglas, 1970) should be easier to apply than those discussed below, whereas the treatment of self-generated oscillations for Class II systems will be more algebraically tedious.

Of course, it should be kept in mind that the deliberate design of a periodic process requires a consideration of the operation of the units downstream from the crystallizer. Thus, additional surge capacity may be needed to damp out the oscillations, filtration may be more difficult, etc. Moreover, if the product quality specifications require a narrow crystal size distribution, then oscillatory operation may be disadvantageous. Still, there may be situations where the improvements gained by a periodic design, such as in yield for Class I systems and perhaps in energy savings for Class II systems, are sufficient to overcome any additional costs.

SYSTEM EQUATIONS FOR A MSMPR CRYSTALLIZER

A complete derivation of the equations which can be used to describe the behavior of a simple crystallizer was published by Hulburt and Katz (1964). If we assume that the crystal shape does not change during growth (so that the crystal size can be characterized by a single variable L and the volume of a crystal is $K\,L^3$), that the crystal growth rate G is proportional to the degree of supersaturation of the solution

$$G = K_1\,(c - c_s) \tag{1}$$

and that the nucleation rate for new crystals is described by Volmer's model

$$B = K_2 \exp\left[\frac{-K_3}{(\ln c/c_s)^2}\right] \approx K_2 \exp\left[\frac{-K_3}{[(c/c_s) - 1]^2}\right] \tag{2}$$

(a similar analysis for a power law nucleation model is discussed in Part II of the paper), then a particle balance for a continuous, perfectly mixed crystallizer gives

$$\frac{\partial n}{\partial t} + G\frac{\partial n}{\partial L} = \epsilon\, B\, \delta(L - 0) - \frac{n}{\theta} \tag{3}$$

and a solute balance gives

$$\frac{dc}{dt} = \frac{c_0 - c}{\theta} - (\rho - c)\, 3GK\int_0^\infty L^2\, n\, dL \tag{4}$$

where $\epsilon = 1 - K \int_0^\infty L^3\ n\ dL$ = fractional volume which is the liquid phase, and δ is the Dirac delta function [so that the term $\delta(L - 0)$ indicates that new crystals are formed only at zero size].

Since these equations are difficult to solve, it is common practice to consider the moments of the size distribution m_j rather than the distribution function n. The moments are defined by

$$m_j = \int_0^\infty L^j\, n\, dL \tag{5}$$

so that if we multiply Equations (3) and (4) by L^j and integrate, the first four moment equations and the solute balance become

$$\begin{aligned}
\frac{dm_0}{dt} &= (1 - K\, m_3)\, B - \frac{m_0}{\theta}\\
\frac{dm_1}{dt} &= G\, m_0 - \frac{m_1}{\theta}\\
\frac{dm_2}{dt} &= 2\, G\, m_1 - \frac{m_2}{\theta}\\
\frac{dm_3}{dt} &= 3\, G\, m_2 - \frac{m_3}{\theta}\\
(1 - m_3)\,\frac{dc}{dt} &= \frac{c_0 - c}{\theta} - (\rho - c)\, 3\, G\, K\, m_2
\end{aligned} \tag{6}$$

Expressions for the higher-order moments can also be obtained, but it is easy to show that they only depend upon the lower-order moments, that is, m_0 to m_3, so that the closed set of equations above contain all the important information about the system stability and dynamics. For the sake of convenience, these equations are often written in dimensionless form by letting

$$\begin{gathered}
x_j = m_j/\overline{m}_j,\ R_o = (1 - \overline{\epsilon})/\overline{\epsilon},\ y = (c - c_s)/(\overline{c} - c_s)\\
g = (c_0 - \overline{c})/\overline{\epsilon}(\overline{c} - c_s),\ b/g = 2K_3/[(\overline{c}/c_s) - 1]^2,\\
\tau = t/\theta
\end{gathered} \tag{7}$$

where an overbar represents the steady state value, so that the system equations become

$$\begin{aligned}
\frac{dx_o}{d\tau} &= \left(\frac{1}{\overline{\epsilon}} - R_o\, x_3\right) \exp\left[\frac{1}{2}\,\frac{b}{g}\left(1 - \frac{1}{y^2}\right)\right] - x_o\\
\frac{dx_1}{d\tau} &= yx_o - x_1\\
\frac{dx_2}{d\tau} &= yx_1 - x_2\\
\frac{dx_3}{d\tau} &= yx_2 - x_3
\end{aligned} \tag{8}$$

$$[1-(1-\bar{\epsilon})\,x_3]\,\frac{dy}{d\tau}=(\bar{\epsilon}g+1-y)$$
$$-\,(1-\bar{\epsilon})\left(\frac{g}{R_o}+1-y\right)yx_2$$

With the equations in this form, the solution depends only on three parameters, $\bar{\epsilon}$, g, and b/g. The steady state solutions are obtained by setting the time derivative terms in the various equations above equal to zero. The results are

$$\begin{aligned}
\bar{n} &= \frac{\bar{\epsilon}\,\bar{B}}{\bar{G}}\exp\left(-\frac{L}{\theta\,\bar{G}}\right)\\
\bar{c} &= \frac{c_o-6\,K\,\bar{B}\,\theta^4\,\bar{G}^3\,\bar{\epsilon}\,\rho}{1-6\,K\,\bar{B}\,\theta^4\,\bar{G}^3\,\bar{\epsilon}}=\frac{c_o-\rho(1-\bar{\epsilon})}{\bar{\epsilon}}\\
\bar{m}_0 &= \bar{\epsilon}\,\theta\,\bar{B}\\
\bar{m}_1 &= \bar{\epsilon}\,\theta^2\,\bar{B}\,\bar{G}\\
\bar{m}_2 &= 2\bar{\epsilon}\,\theta^3\,\bar{B}\,\bar{G}^2\\
\bar{m}_3 &= (1-\bar{\epsilon})\,/K=6\bar{\epsilon}\,\theta^4\,\bar{B}\,\bar{G}^3
\end{aligned}\qquad(9)$$

SYSTEM STABILITY

To determine the stability of a steady state solution, we first linearize the moment equations around a steady state solution to obtain the set of linear equations

$$\begin{aligned}
\frac{dx_o'}{d\tau} &= -\,x_o'-R_o\,x_3'+\frac{b}{g}\,y'\\
\frac{dx_1'}{d\tau} &= x_o'-x_1'+y'\\
\frac{dx_2'}{d\tau} &= x_1'-x_2'+y'\\
\frac{dx_3'}{d\tau} &= x_2'-x_3'+y'\\
\frac{dy'}{d\tau} &= -\,g\,x_2'-(1+g)\,y'
\end{aligned}\qquad(10)$$

where the primed quantities represent deviations from the steady state conditions. For a stable system we require that all the eigenvalues of this set of equations are negative and real or have negative real parts. The characteristic equation is

$$(\lambda+1)(\lambda^4+a_1\,\lambda^3+a_2\,\lambda^2+a_3\,\lambda+a_4)=0\qquad(11)$$

where

$$a_1=4+g,\ a_2=6+4g,\ a_3=4+6g,$$
$$a_4=1+3g+b+R_o\qquad(12)$$

so that if we apply the Routh-Horwitz criterion, we can find the range of parameters where we expect to obtain stable, steady state solutions. Results of this type were obtained by Sherwin et al. (1967, 1969), and an illustration of a stability plot is shown in Figure 1.

As can be seen from Figure 1, in order to achieve unstable conditions, which we assume correspond to oscillatory operation, it is necessary to have values of b/g greater than 11 to 21, depending on the value of g. For most industrial crystallizers, ϵ is greater than 0.5, g falls in the range from 100 to 1000 (Sherwin et al., 1967), and b/g is approximately 3 or less, although in one case it was reported as large as 9. Thus, as mentioned earlier, the simple theory described above is not adequate to predict the oscillations observed in commercial processes (see Randolph et al., 1973; Randolph and Beckman, 1974). However, from an inspection of Equation (7) we see that it should be possible to obtain large values of b/g and thereby design an oscillating crystallizer for a Class I system merely by choosing the design conditions such that $\bar{c}/c_s \approx 1$. In other words, it should be relatively easy to experimentally verify the simple theory, although the experimental operating conditions will not be in the range of industrial interest. An experiment of this type is described in Part II of this paper.

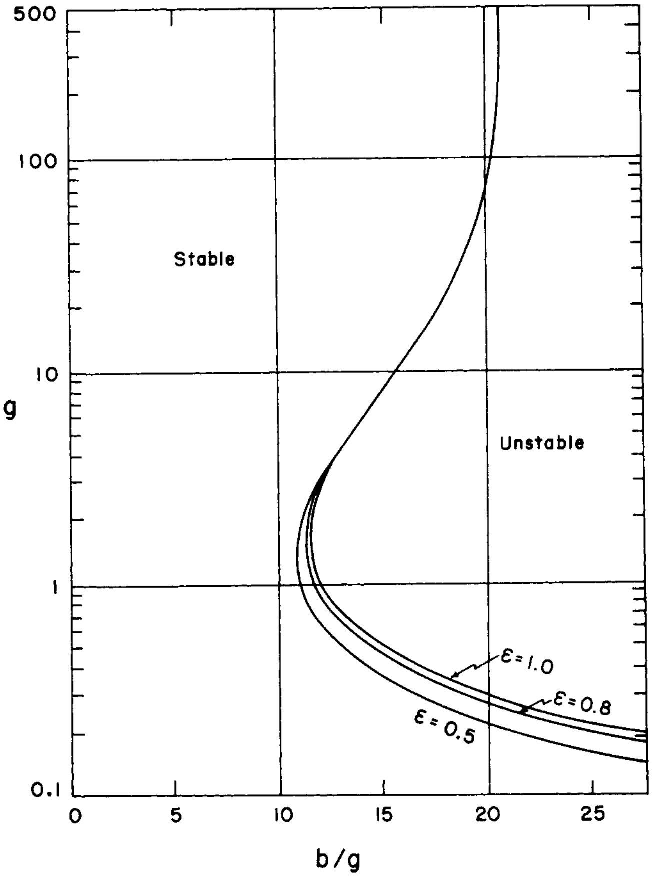

Fig. 1. Stability limits.

OSCILLATORY CONDITIONS

If the analysis above indicates that a crystallizer design is unstable, it is common practice to add a feedback control system in an attempt to stabilize the process [Gupta and Timm (1971) and Han (1969)]. However, it is of interest to determine the dynamic characteristics of an unstable system in case the controller should fail. Sherwin et al. (1967, 1969) and Lei et al. (1971) numerically solved the set of nonlinear moment equations, Equations (6), for unstable plants and found that the crystallizer produced a periodic output; that is, the moments and the solute concentration were periodic functions of time. Another interesting feature of their results is that it appears that the solids yield obtained from the oscillating system exceeds the predicted steady state value.

The periodic behavior of the process is due to a competition between the nucleation and the growth rates. In other words, a small increase in concentration causes a shower of nuclei to form, and then these nuclei grow, supplying such a large area for growth that the solute concentration decreases significantly. The decreasing concentration causes the nucleation rate to decrease until the removal of crystals (and therefore area for growth) by the convective flow and the addition of more solute in the feed stream alter the conditions to a point where another shower of nuclei occurs. Thus the system generates self-sustained oscillations even when the feed conditions are maintained constant. Obviously, a steady state design analysis cannot be used to predict the behavior of a system of this type, and therefore we would like to develop a procedure for estimating the performance of an oscillating system.

APPROXIMATE SOLUTIONS FOR THE PERIODIC PROCESS

One approach that can be used to develop a simple approximate solution for an oscillating crystallizer has been described by Nývlt and Mullin (1970). However, as an alternate procedure, we propose to use the theory of nonlinear oscillations (Minorsky, 1962; Douglas, 1972) because it has proved to be useful in understanding the nature of self-generated oscillations in reactors, and it should be possible to extend the analysis to the more complicated set of equations used to describe a simple crystallizer, Equation (8). There is no guarantee that we will obtain meaningful results, because we cannot rule out the possibility that multiple limit cycles, or some type of limiting surface, might be obtained for this complex system. However, the numerical solutions of the moment equations mentioned above give us hope that the theory may be applicable. Thus, an outline of the method is presented below.

$$\dot{\mathbf{y}} = \begin{bmatrix} \dot{y}_1 \\ \dot{y}_2 \\ \dot{y}_3 \\ \dot{y}_4 \\ \dot{y}_5 \end{bmatrix} = \begin{bmatrix} -\gamma & -\beta & 0 & 0 & 0 \\ \beta & -\gamma & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & \alpha & \omega_0 \\ 0 & 0 & 0 & \omega_0 & \alpha \end{bmatrix} \begin{bmatrix} y_1 \\ y_2 \\ y_3 \\ y_4 \\ y_5 \end{bmatrix} \tag{17}$$

so that it is an easy matter to solve the equations.

For most sets of parameters in the unstable region that we investigated, we found that there were two pair of complex conjugate roots, one pair having a negative real part $-\gamma$ and the other pair having a positive real part α. This positive value of α means that small deviations from steady state will tend to grow so that the system will not operate at steady state conditions. As we mentioned before, we expect to obtain a periodic output for this case.

Of course, if we want to find a periodic solution of the nonlinear equations, Equation (8), it seems reasonable to start with a periodic solution of linearized equations. If the value of α in Equation (17) were equal to zero, the expressions for y_4 and y_5 are equivalent to a harmonic oscillator. Since y_4 and y_5 are linear combinations of the moment variables, see Equations (10) and (15), the sinusoidal variations in y_4 and y_5 would appear as oscillations in the moments. Thus, to develop an approximate solution for the periodic system, we partition the coefficient matrix in Equation (17) as

$$\dot{\mathbf{y}} = \mathbf{\Lambda}_\omega \mathbf{y} + \mathbf{\Lambda}_\alpha \mathbf{y} \tag{18}$$

where

$$\mathbf{\Lambda}_\omega = \begin{bmatrix} -\gamma & -\beta & 0 & 0 & 0 \\ \beta & -\gamma & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -\omega_0 \\ 0 & 0 & 0 & \omega_0 & 0 \end{bmatrix} \quad \mathbf{\Lambda}_\alpha = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \alpha & 0 \\ 0 & 0 & 0 & 0 & \alpha \end{bmatrix} \tag{19}$$

We start our analysis by making a canonical transformation of the linearized equations in order to uncouple them. If we write Equation (10) in matrix form as

$$\dot{\mathbf{x}} = \mathbf{A}\,\mathbf{x} \tag{13}$$

where

$$\mathbf{A} = \begin{bmatrix} -1 & 0 & 0 & -R_0 & b/g \\ 1 & -1 & 0 & 0 & 1 \\ 0 & 1 & -1 & 0 & 1 \\ 0 & 0 & 1 & -1 & 1 \\ 0 & 0 & -g & 0 & -(1+g) \end{bmatrix} \tag{14}$$

we can apply a linear transformation to Equation (13)

$$\mathbf{x} = \mathbf{P}\,\mathbf{y} \tag{15}$$

and if we choose the columns of the transformation matrix **P** to be the right-hand eigenvectors of **A**, we will obtain a set of equations that are completely uncoupled

$$\dot{\mathbf{y}} = \mathbf{\Lambda}\,\mathbf{y} \tag{16}$$

where $\mathbf{\Lambda}$ is a diagonal matrix having the eigenvalues of the system as its diagonal elements. Unfortunately, if some of the eigenvalues are complex quantities, the y variables will also be complex. However, there is another standard transformation that can be used to avoid this difficulty. Thus, if we employ standard matrix transformation techniques, we find that we can write our equations in the canonical form

Moreover, we expand the set of nonlinear equations representing the behavior of the system, Equation (8), in a Taylor series around a steady state solution and retain all terms up to fifth order (third order would be adequate), so that the equations have the form

$$\dot{\mathbf{x}} = \mathbf{A}\,\mathbf{x} + \boldsymbol{\varphi}(\mathbf{x}) \tag{20}$$

where $\boldsymbol{\varphi}(\mathbf{x})$ is a vector of polynomial functions corresponding to the higher-order terms in the Taylor series expansion of each expression in Equation (8). Now, if we introduce the canonical transformation, Equation (15), into Equation (20), partition the $\mathbf{\Lambda}$ matrix as shown by Equation (19), and arbitrarily introduce a parameter ν in front of certain terms, we can write

$$\mathbf{y} = \mathbf{\Lambda}_\omega\,\mathbf{y} + \nu\,[\mathbf{\Lambda}_\alpha\,\mathbf{y} + \mathbf{P}^{-1}\,\boldsymbol{\varphi}\,(\mathbf{P}\,\mathbf{y})] \tag{21}$$

Clearly, if ν were equal to zero, the solution of Equation (21) would be a harmonic oscillator (along with some damped transient terms). However, we know that actually $\nu = 1$ because of the way it was introduced into the equations. Nevertheless, if the term in brackets in Equation (21) that is multiplied by ν is very small, we might epect that we could develop a periodic solution of Equation (21) using perturbation theory. In other words, by bringing the quantities which cause positive real parts of the characteristic roots, and therefore an unstable system, together with the nonlinear terms, which are important only when there are large deviations from steady state conditions, we hope that their sum will be small and

Table 1. Comparison of Analytical and Numerical Solutions

$$x_3' = \frac{m_3 - \bar{m}_3}{\bar{m}_3}, \; y' = \frac{c - \bar{c}}{\bar{c} - c_s}$$

				Frequency		Amplitude of x'_3		D.C. shift of x'_3		Amplitude of y'		D.C. shift of y'	
ϵ	b/g	g	ω_0	Num. solu.	Anal. solu.	Num. solu.	Anal. solu.	Num. solu.	Anal. solu.	Num. solu.	Anal. solu.	Num. solu.	Anal. solu.
0.5	11.5	1	1.43	1.17	1.42	0.22	0.17	0.028	0.042	0.18	0.17	−0.037	−0.057
0.5	11.5	2	1.65	1.32	1.63	0.13	0.10	0.020	0.032	0.21	0.20	−0.049	−0.073
0.5	13.0	4	1.88	1.57	1.87	0.063	0.051	0.012	0.008	0.19	0.20	−0.054	−0.083
0.5	17.0	7	2.13	1.68	2.04	0.065	0.072	0.010	0.235	0.35	0.51	−0.076	−1.65
0.8	12.0	1	1.42	1.29	1.41	0.15	0.19	0.016	0.060	0.14	0.19	−0.017	−0.065
0.8	12.0	2	1.65	1.48	1.63	0.096	0.12	0.010	0.052	0.18	0.25	−0.021	−0.11
0.8	14.0	3	1.83	1.68	1.77	0 075	0.10	0.013	0.080	0.22	0.31	−0.041	−0.24
0.8	16.0	6	2.07	1.80	2.00	0.039	0.054	0.006	0.062	0.21	0.32	−0.036	−0.38

cause only a minor deviation from the periodic solution of the modified linear equations.

The details of the analysis are developed by assuming that the solution has the form

$$\begin{aligned} \mathbf{y} &= \mathbf{y}_o + \nu \, \mathbf{y}_1 + \nu^2 \, \mathbf{y}_2 + \ldots \\ \omega_o &= \omega + \nu \, \omega_1 + \nu^2 \, \omega_2 + \ldots \end{aligned} \tag{22}$$

Substituting this assumed solution into Equation (21), then collecting terms having equal powers of ν, and setting each of these terms equal to zero, we get a set of differential equations describing the process. The first set of these equations is just

$$\dot{\mathbf{y}}_o = \boldsymbol{\Lambda}_\omega \, \mathbf{y}_o \tag{23}$$

and if we solve these equations with the boundary conditions

$$y_{01} = y_{02} = y_{03} = 0, \quad y_{04} = A_0, \quad \dot{y}_{04} = 0 \tag{24}$$

we will find that the solution is a harmonic oscillator. Unfortunately, the amplitude of the oscillation A_o and the frequency correction term ω_1 which appear in this solution are unknown quantities, so that it is also necessary to consider the equations for the first correction function $\mathbf{y}_1$:

$$\dot{\mathbf{y}}_1 = \boldsymbol{\Lambda}_\omega \, \mathbf{y}_1 + \boldsymbol{\Psi}(\mathbf{y}_o) \tag{25}$$

Here the vector function $\boldsymbol{\Psi}(\mathbf{y}_o)$ includes up to fifth-order polynomials in $\mathbf{y}_o$. When this set of equations is solved with zero boundary conditions [since the boundary conditions for $\mathbf{y}$ are matched by $\mathbf{y}_o$, Equation (22) required that all the boundary conditions for the other correction functions are equal to zero], we normally obtain secular terms in the particular integral; that is, we encounter terms having the form $(t \cdot \sin \omega t)$ and $(t \cdot \cos \omega t)$. The appearance of these terms would destroy the periodic nature of the solution, and therefore we require that the coefficients of these terms are equal to zero. Forcing these coefficients to be equal to zero imposes two restrictions on the solution, and fortunately these constraints allow us to calculate the oscillation amplitude and the frequency correction term. The algebra is too lengthy to repeat here, but additional details are available elsewhere, see Yu (1971). With this procedure we can obtain an approximate analytical solution for the periodic behavior of the nonlinear system.

It is also possible to develop an approximate analytical solution for the crystal size distribution function n by applying the perturbation procedure to the original set of equations, Equations (1) through (4), rather than the moment equations. After this set of equations has been linearized around a steady state solution, the same characteristic equation (11), is obtained from a conventional stability analysis. For the perturbation procedure, we want to modify the linearized system equations so that the characteristic equation will have a pair of imaginary roots with no real part. It appears as if there are several ways that this can be accomplished. Thus, if the original system equations are expanded in a Taylor series around a steady state and all terms up to fifth order are retained, then, the nonlinear terms and those linear terms leading to a positive real part of complex conjugate roots in the characteristic equation are lumped together and multiplied by an artificial small parameter ν, and a series solution is sought as a power series in ν. This gives a set of equations which can be solved analytically. The removal of secular terms from the equations for the first correction functions will fix the amplitude of the oscillations and the frequency correction term. A complete treatment has been given by Yu (1971).

NUMERICAL STUDY

In order to assess the validity of the approximate analytical solutions, the nonlinear equations for the moments, Equation (8), were solved numerically (either a digital or an analogue computer can be used) for several cases where the system was expected to exhibit periodic behavior. Some of the results are presented in Table 1 and Figures 2 through 5. Both the tabulated and the graphical

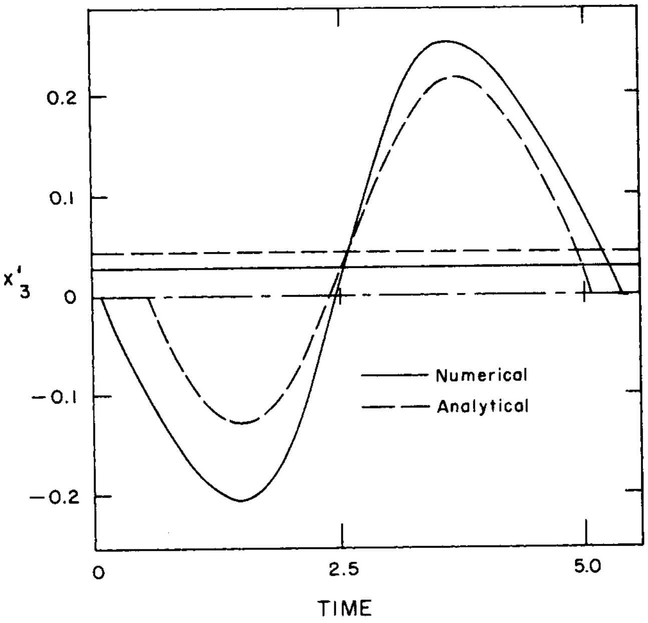

Fig. 2. Periodic behavior of x'_3, with $\epsilon = 0.5$, $g = 1$, $b/g = 11.5$.

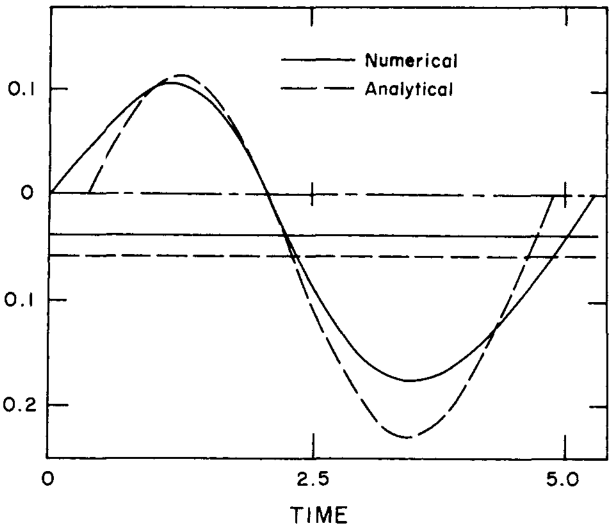

Fig. 3. Periodic behavior of y', with $\epsilon = 0.5$, $g = 1$, $b/g = 11.5$.

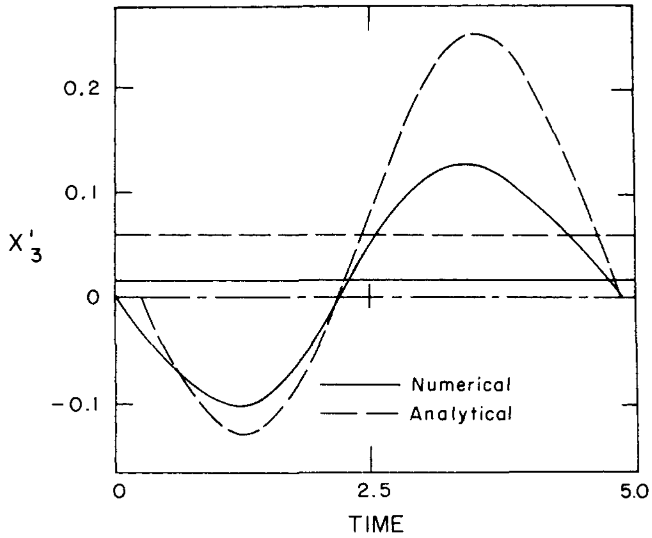

Fig. 4. Periodic behavior of x'_3, with $\epsilon = 0.8$, $g = 1$, $b/g = 12$.

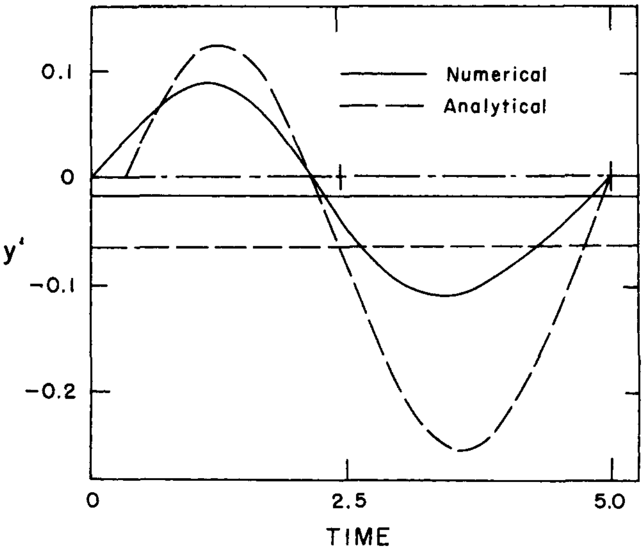

Fig. 5. Periodic behavior of y', with $\epsilon = 0.8$, $g = 1$, $b/g = 12$.

results indicate that the theory of nonlinear oscillations gives reasonable estimates of the oscillating behavior. The accuracy of the analytical procedure is fairly good for system parameters close to the boundary between stable and unstable operation, see Figure 1. However, the predictions are only qualitatively correct when the crystallizer is highly unstable, that is, for system parameters in the unstable region far away from the stability boundary, because in this region the limit cycles are very large and deviate significantly from the sinusoidal functions used as the generating solutions. Unfortunately, the cases of greatest interest would correspond to these highly unstable systems, where we expect large deviations of the time average outputs from the steady state values.

It should be noted that in some situations the analytical procedure gave incorrect results, that is, it predicted imaginary amplitudes for the oscillations, which did not agree with the numerical solutions. A similar problem has been encountered when the theory of nonlinear oscillations has been applied to simple reactor problems, see Beek (1972), Dorawala and Douglas (1971), Douglas and Gaitonde (1967), and Gaitonde and Douglas (1969), and it seems to be caused by the introduction of spurious singular points into the system equations when the Taylor series approximations are introduced. For example, there may be only one steady state solution of Equation (8), but when the right-hand sides of these equations are approximated by third- or fifth-order polynomials, then multiple steady states may exist. Unfortunately, these spurious steady state solutions have a significant effect on the topology of the system in the area away from the original singular point, which is the region where the real limit cycle would be observed. However, some trial-and-error computations revealed that this difficulty can be avoided by dropping some of the third- and fifth-order terms in the Taylor series expansion, so that the steady state characteristics of the approximate equations agree with those of the original nonlinear system Equation (9).

Another point of major interest is that both the analytical solutions and the numerical results indicate that more total solids can be obtained from the oscillating crystallizer than the corresponding steady state design, that is, the D.C. shift in x_3 is positive and that in y is negative. This observation, which is also implied by the earlier work of Sherwin et al. (1967, 1969), means that in some cases it may be possible to design an unsteady state crystallization process which has a better performance than the corresponding steady state design. However, it should be noted that the process parameters were selected such that they did not correspond to normal industrial operating conditions.

The approximate analytical solution describing the self-generated oscillations is complicated, and the algebra required to develop the solution is tedious. Thus, from a practical standpoint, if a designer only wants to get some feel for the nature of the self-generated oscillations by examining one or two sets of system parameters, then the simplest approach is to solve the nonlinear equations numerically. On the other hand, if an attempt is being made to design an oscillating crystallizer so that a great number of cases must be considered in order to determine the process economics and to integrate the oscillating crystallizer with the units downstream, then it is probably a more efficient approach to use the approximate analytical solution to obtain an order-of-magnitude estimate of the optimum design conditions.

OTHER POTENTIAL APPLICATIONS OF THE THEORY

If an attempt is made to develop a complete, approximate solution for a more complicated process, including fines removal, product classification effects, etc., then all the algebra must be repeated. There may be a host of cases, however, where the idea of unsteady state operation can be studied on a more intuitive basis. For example, if we consider crystallization operations where heat transfer is important (either vessels containing a cooling coil or a heater to evaporate solvent instead of the salting out process we studied), then it is necessary to add an energy balance to Equation (8) and to describe the temperature dependence of the nucleation and growth rate kinetics (for an evaporation process, an extra mass balance expression describing the evaporation rate also is required). For these systems, it may be possible to select design parameters such that a direct coupling between the energy equation and the temperature-dependent kinetic terms in either the zeroth moment expression or the equation for the solute composition, that is, either the first or last expression in Equations (6) or (8), leads to an unstable process. For an approximation of this type, the other state variables in these equations would be considered to be constants. With this approach, it may be possible to make very quick estimates (only second-order systems are considered) of the possible improvements obtained with periodic processing. Of course, eventually it will be necessary to verify that the estimates of stability, as well as the increased solids yield and/or lower energy requirements, are indeed valid for the complete set of system equations.

Some other situations where a careful assessment of the crystallizer equations coupled with the intuitive notions of periodic processing may prove to be fruitful are the use of positive feedback control systems to make stable crystallizers become unstable to generate periodic outputs, the deliberate periodic manipulation of an input variable to obtain an oscillatory output or to further amplify the effects of self-generated oscillations, and an attempt to design the mixing conditions in a crystallizer such that the outputs appear to be constant despite the existence of oscillating conditions within a portion of the system. A start on the problem of positive feedback control can be made by combining the ideas of Han (1969) and Gupta and Timm (1971) with those of Gaitonde and Douglas (1969) and Dorawala and Douglas (1971). The effect of periodic inputs on stable, or unstable, crystallizers can be estimated by using the procedure described by Ritter and Douglas (1970) and Dorawala and Douglas (1971), or by combining the ideas presented there with the analysis presented in this paper. A very interesting discussion of the mixing problem as applied to an Exxon patent for a periodic polymerization reactor has recently been published by Lee and Bailey (1974).

CONCLUDING REMARKS

The fundamental studies on crystallization in the last decade (see Randolph and Larson, 1971) have provided a much improved understanding of conventional crystallization operations. In some cases, however, the operation of a periodic crystallization process may be superior to a conventional steady state design. This paper describes an initial attempt to establish a methodology for studying oscillating crystallizers. Even if the periodic operation of crystallizers should prove to be impractical from an economic viewpoint, laboratory studies of periodic crystallization may still be worthwhile because they probably will provide more information than is available from conventional steady state experiments. An illustration of the differences between steady state and dynamic experiments is presented in the next paper.

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NOTATION

B = nucleation rate, see Equation (2)
b = system parameter, see Equation (7)
c = solute concentration
c_0 = feed concentration
c_s = saturation concentration
G = growth rate, see Equation (1)
g = system parameter, see Equation (7)
K = shape factor
K_1, K_2, K_3 = kinetic constants
L = crystal size
m_j = j^{th} moment, see Equation (5)
n = fraction of crystals per unit volume having a size between L and $L + dL$; $\dfrac{\text{number}}{(\text{mm length})(\text{mm}^3 \text{ of volume})}$
n^0 = number of crystals of zero size
R_0 = system parameter, see Equation (7)
t = time
V = crystallizer volume
W = feed rate
x_j = $m_j/\overline{m_j}$
y = $(c - c_s)/(\overline{c} - c_s)$

Greek Letters

δ = dirac delta function
$\bullet$ = $1 - K \int_0^\infty L^3\, n\, dL$ = fractional volume which is liquid phase
θ = V/W = drawdown time
τ = t/θ
ω_0 = frequency of linear oscillator

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Part II. An Experimental Study of an Isothermal System

An experimental study was undertaken to verify the theoretical predictions that for a certain range of operating conditions an isothermal crystallizer would produce oscillating outputs even when the inputs were maintained constant. An interesting feature of the results is that even though a power-law model and Volmer's model for nucleation kinetics provided equivalent descriptions of the steady state data, predictions of transient responses based on Volmer's equation were much better than the power-law results, and the observed behavior of the oscillating system was described well with Volmer's expression, whereas the power-law equation predicted that the system would not oscillate.

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SCOPE

In recent years there have been significant advances in the theories used to predict the behavior of continuous crystallizers. Most of these studies have been concerned with steady state operation of the process or transient behavior between two steady states. In this study, a laboratory-scale crystallizer was designed to produce oscillatory outputs by use of the theory described in Part I of this paper. Only the simplest kind of continuous crystallizer was considered, that is, an isothermal, mixed-suspension, mixed-product removal (MSMPR) unit for a Class I system where high degrees of supersaturation are possible. Even for this simple process, the predictions of the existence of oscillatory operation are strongly dependent on the functional form chosen for the nucleation kinetics, that is, Volmer's model or a power-law model, and theoretical predictions indicate that oscillatory experiments are more sensitive to the magnitude of kinetic parameters than are steady state experiments.

CONCLUSIONS AND SIGNIFICANCE

Self-generated oscillations around the normal, steady state, exponential crystal size distribution were observed in a laboratory MSMPR crystallizer. The experimental values of the oscillatory output agreed very well with theoretical predictions based on steady state measurements of the growth rate and nucleation rate kinetic parameters, which is a very severe test of the elementary theory. For the very low range of suspension densities considered in the study, which does not correspond to normal industrial operation, Volmer's model provided an excellent description of the nucleation kinetics, whereas a power-law nucleation model failed to predict the existence of oscillations.

Even though self-generated oscillations have been observed for many years in industrial crystallizers (Miller and Saeman, 1947), they have seldom been encountered in laboratory studies (Nývlt and Mullin, 1970). Actually, there are two regions where oscillatory operation can occur (Randolph, et al., 1974). For high-order cycling, the instability occurs because the nucleation rate decreases much faster than the growth rate as the supersaturation driving force is lowered, and the system oscillates around the MSMPR exponential population distribution. For low-order cycling, the instabilities are caused by fines removal, product classification, and secondary nucleation effects. Low-order cycling is more representative of industrial operations, but high-order cycling should be easier to study in a laboratory. Moreover, an experimental demonstration of high-order cycling should provide additional verification of the simple theoretical models used to describe crystallizers, as well as providing some justification for using the theory of nonlinear oscillations to study the periodic operation of crystallizers as discussed in Part I.

In order to design a laboratory crystallizer that will oscillate even when the inputs are maintained constant, it is necessary to obtain values of the stability parameter b/g greater than about 12 for a Class I system (where high