Plantwide Operation of Processes with Crystallization

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Simple analytical expressions are developed to model the steady-state operation of a chemical plant with a continuous crystallizer. The equations show analytically how uncontrolled variables change with the changing production rate depending on the values of key kinetic parameters and the choice of controlled variables. Because the results are derived, their validity and limitations are more apparent than heuristics that are suggested based on case studies. Furthermore, because the equations are simple and analytic, it is possible to develop insight and understanding about the behavior of the process. Finally, these results can be readily taught to process engineers and used to rapidly screen alternative control structures for operability problems. Results are illustrated with a case study process to produce adipic acid. © 2007 American Institute of Chemical Engineers *AIChE J,* 53: 2885–2896, 2007
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Introduction

Plantwide control is the field within process systems engineering that is concerned with the design of plantwide control structures, that is, the selection and pairing of controlled and manipulated variables in the plantwide context. Research in this field is important because even if each individual controller is well designed and each process unit is well controlled in isolation, this does not guarantee that the units will work well together, or that the complete process will be stable, robust, efficient, and economical. Over the past 30 years, the field of plantwide process control has matured considerably, with hundreds of papers and several books[1,2] having been written on the topic. Several authors have proposed systematic, hierarchical methods for plantwide control.[1,3,4] Mathematical programming methods have also been applied to the problem of plantwide control design.[5,6]

Among other things, researchers have recognized that the specification of the plantwide control structure will also determine the steady-state operating policy of the plant through the specification of the controlled variables. For a given disturbance or production rate change, the new steady state where the process settles down will depend on which process variables are controlled to a constant value. Control structures that implement infeasible or uneconomical operating policies can be screened out in advance without the need to test their dynamic behavior. To this end, Luyben[7] has identified what he terms the “snowball effect,” a steady-state operability problem caused by some control structures. Skogestad[8] has advocated a steady-state economic analysis to identify-controlled variables and develop so-termed “self-optimizing” control structures. In spite of this considerable progress, the vast majority of the applications of plantwide control published in the literature have dealt with vapor-liquid systems consisting of a reactor followed by one or more distillation columns and recycle.

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Automatic control of continuous crystallizers as stand-alone units has also received considerable attention in the literature. Tavare[9] summarizes 40 articles on this topic published before 1990. A more recent and very readable review covering many aspects of crystallizer control is given by Larsen et al.[10] The vast majority of publications in this field deal with the monitoring, control, and optimization of the crystal size distribution (CSD). In spite of the large number of publications dealing with crystallizer control, we are not aware of any that deal with the control of crystallizers in the plantwide context.

The purpose of this work is to begin to explore the problem of plantwide control of processes with crystallization. Taking the lead from previous results, we begin by addressing the problem of steady-state plantwide operation of processes with crystallization. To this end, we derive a simple analytical expression for the dimensionless holdup of a mixed-suspension, mixed-product removal (MSMPR) crystallizer in the plantwide context in terms of dimensionless plantwide variables, and we use the result to express the steady-state gain between uncontrolled process variables and the production rate. Effectively, we show analytically how the plantwide process operates when the production rate is changed for various choices of controlled variables.

That the expressions are analytical and the results are derived (rather than inferred from case studies) is advantageous for two reasons. One is that the limitations of the analysis are easy to see; whereas the applicability of heuristics determined from case studies is often unclear. More importantly, because the results are analytical, we can develop insight and understanding into why the gain is what it is, and why the process behaves as it does. Understanding the behavior of the process helps the engineer to make more intelligent decisions in designing the control structure. Finally, because the expressions are simple, they can be readily taught to process engineers and rapidly applied to quickly screen alternative control structures. Results are illustrated with a case study of a process to produce adipic acid.

Review of MSMPR Design Equations

The MSMPR is an idealized model of a continuous crystallizer originally due to Randolph[11] and discussed in detail in the book by Randolph and Larson.[12] Like the well-known CSTR reactor model, it employs a number of assumptions to produce a simple analytical model of the process. The assumptions inherent in the MSMPR model, which are discussed below, are assumed throughout this work with the understanding that some amount of accuracy has been sacrificed for the sake of simplicity and the ability to obtain an analytical solution. At the end of this work, the predictions that are developed based on the MSMPR model are compared with the results based on a more realistic crystallizer model that is solved numerically.

Analysis with dimensional variables

In this section, the design equations for a MSMPR crystallizer are derived and nondimensionalized. The idea of deriving analytical expressions for crystallizer design by combining population balance equations, a material balance and the kinetic expressions for nucleation and growth is not new. Similar results can be found, for example, in the book by Jancic and Grootscholten,[13] and the dissertation by Seymor.[14] However, the results are not widely discussed in the literature. Therefore, the derivation is briefly summarized here to lay the foundation for subsequent analysis.

The general statement of the population balance for a crystallization system is

$$\frac{\partial f(L,t)}{\partial t} + \frac{\partial (G(L,t)f(L,t))}{\partial L} = \sum_i \dot{f}_i \tag{1}$$

where f is the CSD function, G is the linear growth rate, L is the length coordinate, and the terms $\dot{f}_i$ account for rate of generation and loss of particles by various mechanisms including attrition, breakage, fines dissolution, and flow into and out of the control volume. A number of assumptions are applied to simplify Eq. 1:

- Growth rate is independent of particle size.
- The only mechanism by which particles may appear in the system is by secondary nucleation, and such particles have essentially zero size upon formation.
- The only way that particles can be removed from the system is to exit through the unclassified product stream.
- There is no fines dissolution, attrition, agglomeration, breakage, etc.
- The change of volume on crystallization is negligible.

With these assumptions, at steady state, Eq. 1 reduces to:

$$G\frac{df}{dL} = -\frac{q}{V_c}f \tag{2}$$

subject to the boundary condition:

$$f(L=0) = f_0 = B/G \tag{3}$$

where q is the volumetric flow rate into and out of the crystallizer, V_C is the crystallizer volume, and G and B are the growth and nucleation rates. For these rates, we assume the common empirical expressions:

$$G = k_g(\Delta C)^g \tag{4}$$

$$B = k_b G^i M_T^j \tag{5}$$

where M_T is the magma density in kilograms per cubic meter, that is, the mass of solid crystals per unit volume of solution in the crystallizer and in the product stream. ΔC may have different units depending on how the kinetic parameters are regressed for the particular system under study. For the case study, presented in this work, ΔC has units of kg (solute)/kg (solvent). The parameters k_b, k_g, g, i, and j are empirical kinetic parameters. In almost all cases, $g > 1$, $i > 1$, and $0 \leq j \leq 1$.

Equation 2 can be solved analytically. Define

$$\xi = \frac{V_c G}{q} \tag{6}$$

ξ has units of length, and the particle size distribution in the crystallizer is

$$f(L) = f_0 \exp(-L/\xi) \tag{7}$$

The particle size distribution is a simple decaying exponential. A useful way of summarizing the properties of the

CSD is to calculate the moments of the distribution. The moments are defined as

$$\mu_i = \int_o^\infty L^i f(L) dL \tag{8}$$

And these can also be determined analytically:

$$\begin{aligned} \mu_0 &= f_0 \xi \\ \mu_1 &= f_0 \xi^2 \\ \mu_2 &= 2 f_0 \xi^3 \\ \mu_3 &= 6 f_0 \xi^4 \\ \mu_4 &= 24 f_0 \xi^5 \end{aligned} \tag{9}$$

Note that the magma density M_{T} is related to the third moment:

$$M_{\mathrm{T}} = k_{\mathrm{v}} \rho_{\mathrm{c}} \mu_3 \tag{10}$$

Also, the production rate of solids is given by

$$P = q M_{\mathrm{T}} = q k_v \rho_{\mathrm{c}} \mu_3 \tag{11}$$

With these preliminary matters established, we develop explicit, analytical expressions for the magma density M_{T} and the crystallizer volume V_{C} in terms of the design degrees of freedom G, q, and P.

First, we solve for the third moment of the CSD in terms of G and ξ by substituting the definition of f_0 (Eq. 3) and the expression for the nucleation rate (Eq. 5) into the expression for the third moment of the CSD (Eq. 9).

$$\begin{aligned} \mu_3 = 6 f_0 \xi^4 = 6(B/G)\xi^4 &= 6(k_{\mathrm{b}} G^i (k_{\mathrm{v}} \rho_c \mu_3)^j / G)\xi^4 \\ &= 6 k_{\mathrm{b}} G^{i-1} (k_{\mathrm{v}} \rho_{\mathrm{c}} \mu_3)^j \xi^4 \end{aligned} \tag{12}$$

$$\mu_3^{1-j} = 6 k_{\mathrm{b}} G^{i-1} (k_{\mathrm{v}} \rho_c)^j \xi^4 \tag{13}$$

$$\mu_3 = (6 k_{\mathrm{b}} G^{i-1} (k_{\mathrm{v}} \rho_c)^j \xi^4)^{\frac{1}{1-j}} \tag{14}$$

Next, this result is substituted into Eq. 10 and the definition of ξ (Eq. 6) is applied to eliminate G:

$$\begin{aligned} M_{\mathrm{T}} = k_{\mathrm{v}} \rho_{\mathrm{c}} \mu_3 &= k_{\mathrm{v}} \rho_{\mathrm{c}} \left(6 k_{\mathrm{b}} G^{i-1} (k_{\mathrm{v}} \rho_{\mathrm{c}})^j \xi^4 \right)^{\frac{1}{1-j}} \\ &= (6 k_{\mathrm{b}} k_{\mathrm{v}} \rho_{\mathrm{c}} G^{i-1} \xi^4)^{\frac{1}{1-j}} \end{aligned} \tag{15}$$

$$\begin{aligned} M_{\mathrm{T}} = k_{\mathrm{v}} \rho_{\mathrm{c}} \mu_3 &= \left(6 k_{\mathrm{b}} k_{\mathrm{v}} \rho_{\mathrm{c}} \left(\frac{\xi q}{V_{\mathrm{C}}} \right)^{i-1} \xi^4 \right)^{\frac{1}{1-j}} \\ &= (6 k_{\mathrm{b}} k_{\mathrm{v}} \rho_{\mathrm{c}} q^{i-1} {V_{\mathrm{C}}}^{1-i} \xi^{3+i})^{\frac{1}{1-j}} \end{aligned} \tag{16}$$

Finally, Eq. 11 is applied to give:

$$\frac{P}{q} = (6 k_{\mathrm{b}} k_{\mathrm{v}} \rho_{\mathrm{c}} q^{i-1} {V_{\mathrm{C}}}^{1-i} \xi^{3+i})^{\frac{1}{1-j}} \tag{17}$$

$$V_{\mathrm{C}}^{\frac{i-1}{1-j}} = P^{-1} q^{\frac{i-j}{1-j}} \xi^{\frac{3+i}{1-j}} (6 k_{\mathrm{b}} k_{\mathrm{v}} \rho_{\mathrm{c}})^{\frac{1}{1-j}} \tag{18}$$

$$V_{\mathrm{C}} = (6 k_{\mathrm{b}} k_{\mathrm{v}} \rho_{\mathrm{c}} P^{j-1} q^{i-j} \xi^{3+i})^{\frac{1}{i-1}} \tag{19}$$

Equation 19 is the first of two key design and operation equations used throughout this article in dimensional form. It is worthwhile to verify that Eq. 19 is dimensionally correct, that is, the right side of Eq. 19 has units of volume. This result is shown in the Appendix.

It is also possible to solve for the crystal growth rate G as a function of P, q, and ξ. Application of Eq. 6 gives

$$\frac{\xi q}{G} = (6 k_{\mathrm{b}} k_{\mathrm{v}} \rho_{\mathrm{c}} P^{j-1} q^{i-j} \xi^{3+i})^{\frac{1}{i-1}} \tag{20}$$

$$G = (6 k_{\mathrm{b}} k_{\mathrm{v}} \rho_{\mathrm{c}} P^{j-1} q^{1-j} \xi^4)^{\frac{-1}{i-1}} \tag{21}$$

Equation 21 is the second of two key design and operation equations used throughout this article in dimensional form. Equations 19 and 21 are applicable for both process design and steady-state process operation. It is worthwhile to consider the available degrees of freedom. There are two equations and five variables (V_{C}, P, q, ξ, and G). Therefore, for either design or steady-state operation, it is possible to specify three of these variables and calculate the other two using these equations. Also, the growth rate G can be considered to be a surrogate for the supersaturation, because growth rate is directly related to the supersaturation according to Eq. 4. If the growth rate is specified (explicitly or implicitly through the specification of other variables), the supersaturation is determined as well. The magma density M_{T} is given by the ratio P/q according to Eq. 11.

No specification has been made regarding the mechanism by which supersaturation is achieved. The results are valid regardless of whether evaporation, cooling, antisolvent addition, or some other mechanism is employed. Furthermore, no specification has been made on the crystallizer temperature or rate of evaporation, antisolvent addition, etc. This may seem counter-intuitive because the growth rate (and thus the supersaturation) is specified, and one generally thinks of manipulating the crystallizer temperature (or rate of evaporation, etc.) to control the supersaturation. However, it is not necessary to do so: the supersaturation will "find its own level" if other process variables are suitably controlled. In the remainder of this article, for simplicity, we assume that the crystallizer is a cooling crystallizer and that the crystallizer operating temperature is constant.

Nondimensionalization of MSMPR design equations

To nondimensionalize Eqs. 19 and 21, we introduce the nominal production rate $\bar{P}$ and the nominal average crystal size $\bar{\xi}$. Then

$$P' = P/\bar{P} \tag{22}$$

$$\xi' = \xi/\bar{\xi} \tag{23}$$

$$q' = \frac{q\rho}{\bar{P}} \tag{24}$$

and

$$V_{\mathrm{C}} = (P'\bar{P})^{\frac{j-1}{i-1}} \left(\frac{q'\bar{P}}{\rho} \right)^{\frac{i-j}{i-1}} (\xi'\bar{\xi})^{\frac{3+i}{i-1}} (6 k_{\mathrm{b}} k_{\mathrm{v}} \rho_{\mathrm{c}})^{\frac{1}{i-1}} \tag{25}$$

$$V_{\mathrm{C}} = (6 k_{\mathrm{b}} k_v \bar{\xi}^{3+i} \bar{P}^{i-1} \rho^{j-i+1})^{\frac{1}{i-1}} P'^{\frac{j-1}{i-1}} q'^{\frac{i-j}{i-1}} \xi'^{\frac{3+i}{i-1}} \tag{26}$$

Therefore, we define:

$$V'_{\mathrm{C}} = V_{\mathrm{C}}(6k_{\mathrm{b}}k_{\mathrm{v}}\bar{\xi}^{3+i}\bar{P}^{i-1}\rho^{j-i+1})^{\frac{-1}{i-1}} \tag{27}$$

so that:

$$V'_{\mathrm{C}} = P'^{\frac{j-1}{i-1}}q'^{\frac{i-j}{i-1}}\xi'^{\frac{3+i}{i-1}} \tag{28}$$

Equation 28 is the dimensionless form of the first key design and operation equation, analogous to Eq. 19. Likewise,

$$G = (P'\bar{P})^{\frac{1-j}{i-1}}\left(\frac{q'\bar{P}}{\rho}\right)^{\frac{j-1}{i-1}}(\xi'\bar{\xi})^{\frac{-4}{i-1}}(6k_{\mathrm{b}}k_{\mathrm{v}}\rho_{\mathrm{c}})^{\frac{1}{i-1}} \tag{29}$$

$$G = (6k_{\mathrm{b}}k_{\mathrm{v}}\rho_{\mathrm{c}}^{2-j}\bar{\xi}^{-4})^{\frac{1}{i-1}}P'^{\frac{1-j}{i-1}}q'^{\frac{j-1}{i-1}}\xi'^{\frac{-4}{i-1}} \tag{30}$$

So, we define

$$G' = G(6k_{\mathrm{b}}k_{\mathrm{v}}\rho_{\mathrm{c}}^{2-j}\bar{\xi}^{-4})^{\frac{-1}{i-1}} \tag{31}$$

so that:

$$G' = P'^{\frac{1-j}{i-1}}q'^{\frac{j-1}{i-1}}\xi'^{\frac{-4}{i-1}} \tag{32}$$

Equation 32 is the dimensionless form of the second key design and operation equation, analogous to Eq. 21. Note that

$$\xi' = \frac{V'_{\mathrm{C}}G'}{q'} \tag{33}$$

Insight from MSMPR design equations

It is worthwhile at this point to take a step back from the derivations and consider the insight that can be obtained from the design equations. Equations 28 and 32 are the dimensionless analogues of Eqs. 19 and 21 and the same degrees of freedom analysis applies: from the set $\{V'_{\mathrm{C}}, G', P', q', \xi'\}$ three variables can be specified and the other two can be determined from the equations. Also, recall that in the usual case, $i > 1$, and $0 \leq j \leq 1$.

Consider first the case where the production rate is increased while maintaining both the crystallizer feed flow rate and the average crystal size constant. Equation 28 shows that if q' and ξ' are maintained constant, then $V'_{\mathrm{C}} \sim P'^{\frac{j-1}{i-1}}$, that is, V'_{C} decreases with the increasing P' and the magnitude of the decrease is greatest when i and j are small, and least when i and j are large. Furthermore, from Eq. 32, $G' \sim P'^{\frac{1-j}{i-1}}$: G' increases with increasing P' and the magnitude of the increase is greatest when i and j are small, and least when i and j are large.

This simple result can be understood intuitively as well. Because the average crystal size remains constant, intuition suggests that to increase the production rate, more crystals must be produced per unit time, that is, the overall nucleation rate, which is the product of the specific nucleation rate multiplied by the crystallizer holdup ($V_{\mathrm{C}}B$) must increase at a rate directly proportional to the production rate. Furthermore, if the crystallizer feed and effluent flow rate are maintained constant, the magma density M_{T} must also increase proportionally with the production rate. From Eq. 5, if $j = 1$, then the nucleation rate increases proportionally with the magma density with constant G. From Eq. 6, if G is constant as well as q and ξ, then V_{C} must be maintained constant as well. The production rate increase is accomplished simply by increasing the magma density, and thus the nucleation rate.

However, if $j < 1$, then it is necessary to increase G as well to achieve a proportional increase in B. The amount by which it is necessary to increase G will depend on i as well as j. Finally, from Eq. 6, it is clear that if G is increased while q and ξ are maintained constant, it is necessary to *decrease* the crystallizer holdup V_{C}. Unfortunately, decreasing V_{C} will tend to reduce the overall nucleation rate ($V_{\mathrm{C}}B$) because less volume is available for nucleation, and this will necessitate a further increase in G. Fortunately, i is always greater than one, so that the nucleation rate will increase faster than the required crystallizer holdup will decrease. However, if i is small (i.e., close to one) then the sensitivity of the nucleation rate to changes in the growth rate is weak, and large changes in the growth rate will be required to achieve the desired result. The system will be difficult to control under these circumstances.

Now consider the case wherein the crystallizer feed/effluent flow rate q is increased, while the production rate and the average crystal size are maintained constant. From Eq. 28, if the production rate and the average crystal size are maintained constant, then $V'_{\mathrm{C}} \sim P'^{\frac{i-j}{i-1}}$. If $j = 1$, then V'_{C} increases linearly with q'. Otherwise, V'_{C} increases with the increasing q', and the rate of increase is greatest if i is small. From Eq. 32, $G' \sim P'^{\frac{j-1}{i-1}}$. If j is equal to one, G' will not change with q'. Otherwise, G' will decrease with the increasing q', and the rate of increase will be greatest if i and j are small.

This can also be understood intuitively. In this scenario, the overall nucleation rate $V_{\mathrm{C}}B$ must remain constant. Because neither the production rate nor the average crystal size has changed, the objective is to produce crystals of the same size at the same rate. However, the magma density M_{T} must decrease because the crystallizer effluent flow rate has increased. Furthermore, from Eq. 6, if q is increased while ξ is maintained constant, then the quantity ($V_{\mathrm{C}}G$) must also increase. First, consider the case where $j = 0$. If $j = 0$, then from Eq. 5, $B \sim G^i$ or $V_{\mathrm{C}}B \sim V_{\mathrm{C}}G^i$. Thus, it is desired to increase the quantity $V_{\mathrm{C}}G$ in such a manner that the quantity $V_{\mathrm{C}}G^i$ remains constant. Since $i > 1$, this can be accomplished by increasing V_{C} while simultaneously decreasing G. The percentage increase in V_{C} will be greater than the percentage decrease in G.

If $j > 0$, then the same trend is observed except that the decrease in G is less dramatic because the effect of the changing magma density of the nucleation rate (Eq. 5). If $j = 1$, then the growth rate G remains constant. The specific nucleation rate B increases proportionally with the change in q, and the crystallizer holdup V_{C} decreases linearly with the production rate, so that the overall nucleation rate ($V_{\mathrm{C}}B$) and the averages crystal size ξ remain constant. When G changes, the magnitude of the change depends on the kinetic exponent i as well as j. When i is large, the system is sensitive to changes in G and smaller changes in G are required to produce the required effect.

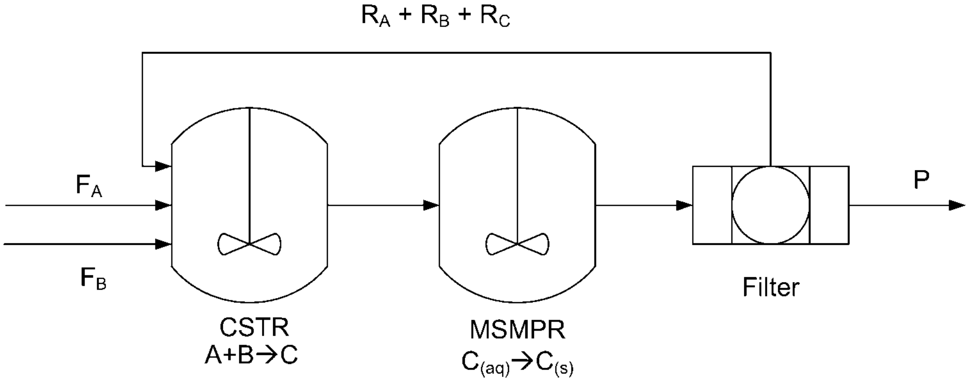

Figure 1. Process flow diagram for generic plantwide crystallization process.

Finally, consider the case wherein the average crystal size ξ is to be increased while maintaining the crystallizer feed/effluent flow rate q and the production rate P constant. Equation 28 shows that for constant P and q, $V'_C \sim \xi^{\frac{3+i}{i-1}}$. The crystallizer holdup increases with the increasing ξ, and the rate of increase is independent of j and decreases with increasing i. Equation 32 shows that for constant P and q, $G' \sim \xi^{\frac{-4}{i-1}}$. Thus, in this case, the growth rate is decreasing with the increasing average crystal size, and the magnitude of the gain decreases with the increasing i and is independent of j.

Because the production rate and the feed/effluent flow rate are maintained constant, the magma density must also be maintained constant. Because the exponent j determines the effect of the magma density on the nucleation kinetics, it is expected that this parameter will not enter into the analysis for this case because the magma density must be maintained constant. Because the average crystal size is larger, the overall nucleation rate V_CB must decrease. Fewer crystals are required per unit time since the average crystal size is larger. However, at the same time, from Eq. 6, if the average crystal size ξ is to be increased while q is maintained constant, then the quantity (V_CG) must also increase. As discussed earlier, from Eq. 5, $V_CB \sim V_CG^i$ for constant M_T. Therefore, the goal is to increase the quantity (V_CG) while at the same time decreasing the quantity (V_CG^i). Because $i > 1$, this can be accomplished by decreasing G while at the same time increasing V_C. As mentioned earlier, a large value of i will make the system more sensitive to changes in G and necessitate a smaller change.

If more than one variable from the set $\{P, q, \xi\}$ is changed at the same time, then the impact on the crystallizer holdup will be some combination of the phenomena described earlier.

The results developed in this section are valid either for a crystallizer operating as a stand-alone unit, or for a crystallizer in the plantwide context. In the following section, we consider a simple plantwide flowsheet with a reactor and crystallizer wherein material is recycled back from the crystallizer to the reactor.

Plantwide Design and Operation Equations

Consider the generic process shown in Figure 1 to produce product C at a rate of P kg/s from reactant species A and B. A and B are liquids at room temperature, and C is a low molecular weight crystalline solid, which is moderately soluble in B, the solubility being a strong function of temperature. Thus, in addition to being a reactant, species B serves as a solvent for the crystallization of C. Therefore, it is present in stoichiometric excess within the process, and species A is the limiting reactant. For simplicity, it is assumed that all species (including both the liquid and solid phase of species C) have the same mass density ρ. The crystallizer is assumed to be a cooling crystallizer, and the operating temperature of the crystallizer is assumed to be constant.

Fresh feed of species A and B flow into a reactor wherein the irreversible reaction A + B → C takes place. The reaction rate is expressed on a mass concentration basis. For simplicity, the kinetics are assumed to be first order with respect to species A and zero order with respect to species B:

$$r = k[\mathrm{A}] \tag{34}$$

where r is the specific reaction rate, equivalent to the rate of production of species C, in kg/(m^{3}s), [A] and has units of kg/m^3, and k has units of s^{-1}. This assumption is reasonable because species B is present in large excess. The analysis could be repeated for different kinetic expressions; however, the emphasis of this work is the control of crystallization in the plantwide context, therefore a relatively simple kinetic expression, which captures the essential behavior of the process, is employed for the reactor.

An overall material balance shows that

$$P = k[\mathrm{A}]V_R \tag{35}$$

where the reactor volume V_R has units of m^3. At the process design stage, recycle flow rates are used as degrees of freedom, therefore we define the reactor effluent volumetric flow rate q:

$$q = (R_A + R_B + R_C + P)/\rho \tag{36}$$

Then

$$P = k\frac{R_A}{q}V_R \tag{37}$$

Equation 37 is nondimensionalized using the nominal production rate $\bar{P}$:

$$P' = \frac{P}{\bar{P}} \tag{38}$$

$$R'_{\mathrm{A}} = \frac{R_{\mathrm{A}}}{\bar{P}} \tag{39}$$

$$q' = \frac{q\rho}{\bar{P}} \tag{40}$$

$$V'_{\mathrm{R}} = V_{\mathrm{R}} \frac{k\rho}{\bar{P}} \tag{41}$$

whence

$$P' = \frac{R'_{\mathrm{A}}}{q'} V'_{\mathrm{R}} \tag{42}$$

$$V'_{\mathrm{R}} = \frac{P'q'}{R'_{\mathrm{A}}} \tag{43}$$

and

$$q' = R'_{\mathrm{A}} + R'_{\mathrm{B}} + R'_{\mathrm{C}} + 1 \tag{44}$$

In this work, it is assumed that the operating temperature of the crystallizer will not change, therefore the saturation concentration in the crystallizer will be constant, and the concentration of species C relative to species B in the crystallizer will be approximately constant:

$$\frac{R'_{\mathrm{C}}}{R'_{\mathrm{B}}} \approx C_{\mathrm{sat}} \tag{45}$$

The relationship is not an exact equality because in fact the concentration of species C exceeds the saturation concentration by an amount equal to the supersaturation. However, in normal process operation, the supersaturation is small compared to the saturation concentration, and so it can be neglected in this equation. Assuming that the relationship of Eq. 45 is an exact equality, substitution of this result into Eq. 44 gives

$$q' = R'_{\mathrm{A}} + R'_{\mathrm{B}}(1 + C_{\mathrm{sat}}) + 1 \tag{46}$$

and further substitution into Eq. 43 gives

$$V'_{\mathrm{R}} = P' \frac{R'_{\mathrm{A}} + R'_{\mathrm{B}}(1 + C_{\mathrm{sat}}) + 1}{R'_{\mathrm{A}}} \tag{47}$$

It is worthwhile again to consider operational degrees of freedom. In Eqs. 43 and 46, there are a total of five variables: $\{V'_{\mathrm{R}}, P', q', R'_{\mathrm{A}}, R'_{\mathrm{B}}\}$. Therefore, the reactor also has three degrees of freedom, and the operating policy for the reactor can be established by fixing any three from that set, with the caveat that q', R'_{A}, and R'_{B} cannot all be set independently. Among the five variables, two (q' and P') also appear in the crystallizer design/operation equations. If these two variables are set as part of the plantwide or crystallizer-operating policy, then only one degree of freedom remains for the reactor. It is possible to specify the reactor holdup V'_{R} or some property of the reactor concentration or recycle flows, such as R'_{A} and R'_{A}/q'.

Process Operation

Policies with constant reactor effluent flow rate

In the first instance, we consider control structures that control the reactor effluent flow rate to be a constant value. This is generally recommended by Luyben to avoid the so-called "snowball effect."[1,7]

Consider the case wherein both the reactor effluent flow rate q' and the average crystal size ξ' are controlled to a constant value. This is possible if the crystallizer holdup V'_{C} is allowed to vary. In this case, Eq. 28 shows the steady-state gain between the production rate P' and the uncontrolled variable V'_{C}:

$$V'_{\mathrm{C}} \sim P'^{\frac{j-1}{i-1}} \tag{48}$$

In the general case, the gain is nonlinear. The engineer may wish to have an expression available for the local linear approximation of the steady-state gain between the production rate P' and the crystallizer holdup V'_{C}. Therefore, we consider Eq. 28 to be an expression for P' as a function of V'_{C} and linearize the expression around the nominal operating point using a first-order Taylor series expansion:

$$V'_{\mathrm{C}}(P') \approx \bar{V}'_{\mathrm{C}} + (P' - \bar{P}')\frac{dV'_{\mathrm{C}}}{dP'} \tag{49}$$

It is straightforward to evaluate the derivative:

$$\frac{dV'_{\mathrm{C}}}{dP'} = \left(\frac{j-1}{i-1}\right) P'^{\frac{j-1}{i-1}-1} q'^{\frac{i-j}{i-1}} \xi'^{\frac{3+i}{i-1}} \tag{50}$$

whence:

$$\Delta V'_{\mathrm{C}} \approx \left(\frac{j-1}{i-1}\right) P'^{\frac{j-1}{i-1}-1} q'^{\frac{i-j}{i-1}} \xi'^{\frac{3+i}{i-1}} \Delta P' \tag{51}$$

For ease of interpretation, we wish to express the gain on a relative basis, that is, to find an expression for $\Delta V'_{\mathrm{C}}/V'_{\mathrm{C}}$ as a function of $\Delta P'/P'$. This is accomplished by dividing both sides of Eq. 51 by V'_{C} and multiplying the right side of Eq. 51 by P' / P' to give

$$\frac{\Delta V'_{\mathrm{C}}}{V'_{\mathrm{C}}} \approx \left(\frac{j-1}{i-1}\right) \frac{1}{V'_{\mathrm{C}}} P'^{\frac{j-1}{i-1}-1} q'^{\frac{i-j}{i-1}} \xi'^{\frac{3+i}{i-1}} \frac{\Delta P'}{P'} \tag{52}$$

However, in comparison with the original equation for V'_{C} (Eq. 28) shows that

$$\frac{\Delta V'_{\mathrm{C}}}{V'_{\mathrm{C}}} \approx \left(\frac{j-1}{i-1}\right) \frac{\Delta P'}{P'} \tag{53}$$

That is, the steady-state relative linear gain between the crystallizer holdup and the production rate is just the exponent of the production rate in the design Eq. 28. This result is both simple and useful. It allows the process engineer to make a very quick estimate of the gain between the production rate and the crystallizer holdup for this particular operating policy. For example, in the adipic acid case study, the

Table 1. Values of the Sensitivity Parameter k for Various Operating Policies and Uncontrolled Variables

		Uncontrolled Variables				
Policy No.	Controlled Variables	V'_C	G'	q'	ξ'	Figure(s)
1	q', ξ'	$\frac{j-1}{i-1}(< 0)$	$\frac{1-j}{i-1}(> 0)$	–	–	3,5
2	q', V'_C	–	$\frac{1-j}{3+i}(> 0)$	–	$\frac{1-j}{3+i}(> 0)$	4
3	q', G'	$\frac{1-j}{4}(> 0)$	–	–	$\frac{1-j}{4}(> 0)$	3,4
4	$(q'/P'), \xi'$	1	0	–	–	
5	$(q'/P'), V'_\mathrm{C}$	–	$\frac{4}{3+i}(> 0)$	–	$\frac{1-i}{3+i}(< 0)$	4
6	$(q'/P'), G'$	1	–	–	0	
7	ξ', V'_C	–	$\frac{1-j}{i-j}(> 0)$	$\frac{1-j}{i-j}(> 0)$	–	5
8	ξ', G'	1	–	1	–	3
9	V'_C, G'	–	–	$\frac{j-1}{j+3}(< 0)$	$\frac{1-j}{j+3}(> 0)$	4,5

crystallization kinetic parameters are $i = 3.5$ and $j = 0.4$. Therefore, the term in parenthesis in Eq. 53 is -0.24. Thus, a 10% increase in the production rate will result in a decrease in the crystallizer holdup of ~2.4%

The results given in Eqs. 48 and 53 are representative of the general case: for any crystallizer operating policy, the relationship between an uncontrolled variable Z' and the production rate P' is given by

$$Z' \sim (P')^k \tag{54}$$

and the linear approximation to the gain at the nominal operating point is given by

$$\frac{\Delta Z'}{Z'} \approx k\frac{\Delta P'}{P'} \tag{55}$$

where k is the exponent on the production rate in the equation, which gives the value of the uncontrolled variable Z as a function of the production rate and the controlled variables. k is hereafter referred to as the "gain parameter." The gain parameter k is unique for each operating policy and each uncontrolled variable and depends only on the values of i and j. For example, for the operating policy discussed earlier of constant q' and ξ' for the gain between the crystallizer holdup and production rate, $k = (j - 1) / (i - 1)$. Because in the usual case $i > 1$, and $0 \leq j \leq 1$, k is also expected to be less than zero in this case, meaning that V'_C decreases with increasing P' and the slope of the linear approximation is negative. If k is zero, then Z' does not change with the changing P'. Table 1 lists the value of k for each uncontrolled variable for each operating policy considered in this article.

It may at first seem counterintuitive that the crystallizer holdup must decrease when the production rate is increased. This is a result of the particular control structure employed. To increase the production rate while keeping the crystallizer feed flow rate and average crystal size constant, it is necessary to increase the growth rate (supersaturation) in the crystallizer, and this can only be accomplished by reducing the crystallizer holdup (from Eq. 33). Indeed, the steady-state linear gain between the crystal growth rate and the production rate can be calculated in an analogous manner using Eq. 32:

$$\frac{\Delta G'}{G'} \approx \left(\frac{1-j}{i-1}\right)\frac{\Delta P'}{P'} \tag{56}$$

As mentioned earlier, the linear approximation of the steady-state percentage gain between the production rate and the uncontrolled variable is simply the exponent on the production rate in the nonlinear gain expression (Eq. 32). In the remainder of this section, different equations analogous to Eqs. 28 and 32 for different combinations of controlled variables are derived. For subsequent results, the linear gain results, which are analogous to Eqs. 53 and 56, are not reported. However, the reader should appreciate that in all cases the linear percentage gain between the uncontrolled variable and the production rate is simply the exponent on the production rate in the relevant non-linear gain expression. This exponent, the gain parameter k, is recorded in Table 1 for each uncontrolled variable and for each operating policy.

Instead of controlling the average crystal size ξ', it may be desirable instead to control the crystallizer holdup to a constant value, allowing the average crystal size to vary when the production rate is changed. In this case, the linear steady-state gain between the average crystal size and the production rate can be calculated by first modifying Eq. 28 to express the average crystal size ξ' as a function of the other variables:

$$\xi' = P'^{\frac{1-j}{3+i}} q'^{\frac{j-i}{3+i}} V_\mathrm{C}'^{\frac{i-1}{3+i}} \tag{57}$$

From this equation, it is seen that for this operating policy and for the uncontrolled variable ξ', $k = (1 - j) / (3 + i)$. In an analogous manner, the steady-state linear gain between the crystal growth rate and the production rate for this control configuration can be determined. Combining Eqs. 32 and 33 gives

$$G' = P'^{\frac{1-j}{i+3}} q'^{\frac{j+3}{i+3}} V_\mathrm{C}'^{\frac{-4}{i+3}} \tag{58}$$

From this equation it is seen that in this case k has the same value for both uncontrolled variables: $k = (1 - j) / (3 + i)$.

For this operating policy, both the crystal growth rate and the average crystal size increase with the increasing production rate by the same magnitude on a percentage basis.

Finally, instead of controlling either the average crystal size or the crystallizer holdup, it may be desirable to control the crystal growth rate (supersaturation) to a constant value. In this case, the steady-state gain between the production rate and the crystallizer holdup and average crystal size can also be calculated. Equation 32 can also be modified to express the average crystal size:

$$\xi' = P'^{\frac{1-j}{4}} q'^{\frac{j-1}{4}} G'^{\frac{1-i}{4}} \tag{59}$$

Also, substitution of Eq. 33 into Eq. 59 gives

$$V'_{\mathrm{C}} = P'^{\frac{1-j}{4}} q'^{\frac{j+3}{4}} G'^{\frac{-3-i}{4}} \tag{60}$$

Thus, for this operating policy, $k = (1 - j) / (3 + i)$ for both ξ' and V'_{C}.

Policies with constant reactor effluent flow rate/production rate ratio

Yu and coworkers[15,16] have advocated so-termed balanced control structures, in which the reactor effluent flow rate is scaled linearly with the production rate. They showed that for vapor-liquid processes with recycle, this helps to spread the burden associated with a production rate change more evenly amongst the process units, avoiding placing an undue burden on any one process unit. The gains between uncontrolled variables and the production rate can also be calculated for this case with a different modification of Eq. 28. Equation 28 can be written as

$$V'_{\mathrm{C}} = P'^{\frac{i-1}{i-1}} (q'/P')^{\frac{i-j}{i-1}} \xi'^{\frac{3+i}{i-1}} = P'(q'/P')^{\frac{i-j}{i-1}} \xi'^{\frac{3+i}{i-1}} \tag{61}$$

Using this equation, an analysis analogous to that performed in the previous section can be completed to determine the gain between the production rate and the uncontrolled variables for the case of constant crystallizer holdup (V'_{C}) as well as constant average crystal size (ξ') and constant supersaturation or crystal growth rate (G').

Also, an analogous modification of Eq. 32 gives

$$G' = (P'/q')^{\frac{1-j}{i-1}} \xi'^{\frac{-4}{i-1}} \tag{62}$$

From which it is seen that the crystal growth rate is invariant when the production rate is increased while maintaining a constant ratio of production rate to reactor effluent flow rate ($k = 0$). In a similar manner, the gain parameter can also be calculated for the case that the crystallizer holdup is maintained constant. Modification of Eq. 57 gives

$$\xi' = P'^{\frac{1-i}{3+i}} (q'/P')^{\frac{j-i}{3+i}} V'^{\frac{i-1}{3+i}}_{\mathrm{C}} \tag{63}$$

And modification of Eq. 58 gives

$$G' = P'^{\frac{4}{i+3}} (q'/P')^{\frac{j+3}{i+3}} V'^{\frac{-4}{i+3}}_{\mathrm{C}} \tag{64}$$

Finally, in the case, wherein the growth rate G' is kept constant, modification of Eq. 59 gives

$$\xi' = (q'/P')^{\frac{j-1}{4}} G'^{\frac{1-i}{4}} \tag{65}$$

and modification of Eq. 60 gives

$$V'_{\mathrm{C}} = P'(q'/P')^{\frac{j+3}{4}} G'^{\frac{-3-i}{4}} \tag{66}$$

Policies that use reactor effluent flow rate to control a crystallizer property

Finally, it may be desirable to use the reactor effluent flow rate to control a property of the crystallizer. In this case, it is possible to control any two variables from the set $\{V'_{\mathrm{C}}, \xi', G'\}$ and to calculate the gain between the production rate and the uncontrolled variable, as well as the gain between the production rate and the reactor effluent flow rate. These results are also summarized in Table 1.

For the case that V'_{C} and ξ' are maintained constant, further modification of Eq. 28 gives

$$q' = P'^{\frac{1-j}{i-j}} V'^{\frac{i-1}{i-j}}_{\mathrm{C}} \xi'^{\frac{-3-i}{i-j}} \tag{67}$$

and substitution of Eq. 33 gives

$$G' = P'^{\frac{1-j}{i-j}} V'^{\frac{j-1}{i-j}}_{\mathrm{C}} \xi'^{\frac{-3-j}{i-j}} \tag{68}$$

Likewise, if G' and V'_{C} are controlled, modification of Eq. 58 gives

$$q' = P'^{\frac{j-1}{j+3}} G'^{\frac{i+3}{j+3}} V'^{\frac{4}{j+3}}_{\mathrm{C}} \tag{69}$$

and substitution of Eq. 33 gives

$$\xi' = P'^{\frac{1-j}{j+3}} G'^{\frac{j-i}{j+3}} V'^{\frac{j-1}{j+3}}_{\mathrm{C}} \tag{70}$$

Finally, if G' and ξ' are controlled, modification of Eq. 59 gives

$$q' = P' \xi'^{\frac{4}{j-1}} G'^{\frac{i-1}{j-1}} \tag{71}$$

and substitution of Eq. 33 gives

$$V'_{\mathrm{C}} = P' \xi'^{\frac{3+j}{j-1}} G'^{\frac{i-j}{j-1}} \tag{72}$$

Effect of operating policies on reactor holdup and concentration

So far, we have not discussed the impact of the crystallizer operating policy on the reactor, nor have we considered the possibility of using the reactor effluent/crystallizer feed flow rate q' to control a reactor property.

Conventional wisdom from vapor-liquid process case studies suggests that there is a tradeoff at both the design and operation stages between the recycle flow rate of reactants and reactor holdup. Specifically, as the recycle flow rate of reactants increases, the required per-pass conversion decreases, the concentration of reactants in the reactor increases (while the concentration of products decreases), and the required reactor holdup decreases.

Consider the case that the production rate P' increases while the reactor holdup V'_R remains constant. From Eq. 43, the ratio $R'_A/q' \gg R'_A/(R'_A + R'_B + R'_C + 1)$ must also increase. If the concentration of species A in the reactor is already large, that is, $R'_A = R'_B + R'_C + 1$, then this is difficult to accomplish. The ratio approaches a limiting value of unity as the recycle flow rate of species A approaches infinity. If the production rate change is large, it is possible that the desired production rate cannot be accomplished, even with an infinite recycle flow rate. This is the "snowball effect" of Luyben. By contrast, if $R'_A \ll R'_B + R'_C + 1$, then a change in the production rate is relatively easy to accomplish. A small change in the recycle flow rate will have a substantial impact on the value of the ratio. This is the case that is assumed in this work, that is, we have assumed that the per-pass conversion of species A is high and species B is present in substantial excess to prevent thermal runaway and because species B also serves as the solvent for the crystallization of the product C.

If q' is held constant (or manipulated by the crystallizer control structure) and the production rate is increased, we consider two possible operating policies. The first is to keep the reactor holdup constant. In this case, from Eq. 43:

$$R'_A = P' \frac{q'(P')}{V'_R} \tag{73}$$

where $q'(P')$ is constant if the control structure maintains q' constant or is given by the relevant expression in Table 1 if q' is manipulated to control some property of the crystallizer. If q' is maintained constant, then the recycle flow rate of species A scales linearly with the production rate. Substitution of Eq. 73 into Eq. 46 gives

$$R'_B = \frac{q'(P') - 1}{(1 + C_{\text{sat}})} - P' \frac{q'(P')}{V'_R(1 + C_{\text{sat}})} \tag{74}$$

If q' is constant, then R'_B also scales linearly with P'.

An alternative policy is to keep the concentration of species A in the reactor x'_A constant, where

$$x'_A = R'_A/q' \tag{75}$$

The control of intensive variables such as composition is a hallmark of so-termed balanced control structures.[15,16] Substitution of Eq. 75 into Eq. 43 shows

$$V'_R = \frac{P'}{x'_A} \tag{76}$$

Therefore, for this operating policy, the reactor holdup scales linearly with the production rate regardless of how the reactor effluent flow rate is manipulated. Substitution of Eq. 75 into Eq. 46 gives

$$R'_B = \frac{q'(P')(1 - x'_A) - 1}{(1 + C_{\text{sat}})}. \tag{77}$$

Insight for plantwide operation and control

The entries in Table 1 show how the process will operate for a given set of kinetic parameters and a given operating policy, and it can be used to select an operating strategy that can achieve the desired production goals without violating process constraints. For example, if q' or V'_C is maintained constant, then the gain between the production rate and uncontrolled parameters will decrease with the increasing j, becoming zero when $j = 1$. Otherwise, the gains are independent of j. Likewise, the gain increases with increasing i for many control structures. The situation is most severe in the case that q' and ξ' are controlled to be constant. If the kinetic parameter i is close to one, then with this control structure, a change in the production rate may result in a very large change in the crystallizer holdup and supersaturation. Therefore, this choice of controlled variables is not recommended in this scenario.

Three operating policies are seen to be equivalent. If ξ' and G' are held constant, then both V'_C and q' will scale linearly with the production rate. This operating policy is most analogous to the so-termed balanced control structures of Yu and coworkers.[15,16]

If ξ' is allowed to vary, then, in general, the gain exponent is less than unity for reasonable values of the kinetic parameters. This means that a 10% change in the production rate will result in a change of less than 10% in the uncontrolled variables.

Case Study: Adipic Acid Production

This section presents results from a plantwide case study of a process to produce adipic acid. More details regarding the case study can be found in the web-published supplement to this manuscript.

Process description

Figure 2 shows the process flow diagram for the adipic acid process. Fresh cyclohexanol and nitric aid are fed to a CSTR, wherein the following reaction takes place at 80°C at 1 atm:

cyclohexanol + nitric acid
→ adipic acid + nitrous oxide + water

$$C_6H_{12}O + 2HNO_3 \rightarrow C_6H_{10}O_4 + N_2O + 2H_2O$$

A kinetic model for this reaction is adapted from the work of van Asslet and van Krevelen[17] as described in the web-published supplement. The nitrous oxide has a much higher vapor pressure than the other species and it is assumed that all of the nitrous oxide is collected through a vapor vent in the reactor. The per-pass conversion of cyclohexanol is kept high to prevent thermal runaway. Nitric acid/water solution is present in excess and serves as the solvent for crystallization.

The reactor effluent is fed to a concentrating still wherein excess water (which is fed into the process with the nitric acid and also produced by the reaction) is removed. The concentration of nitric acid in the waste-water stream is kept

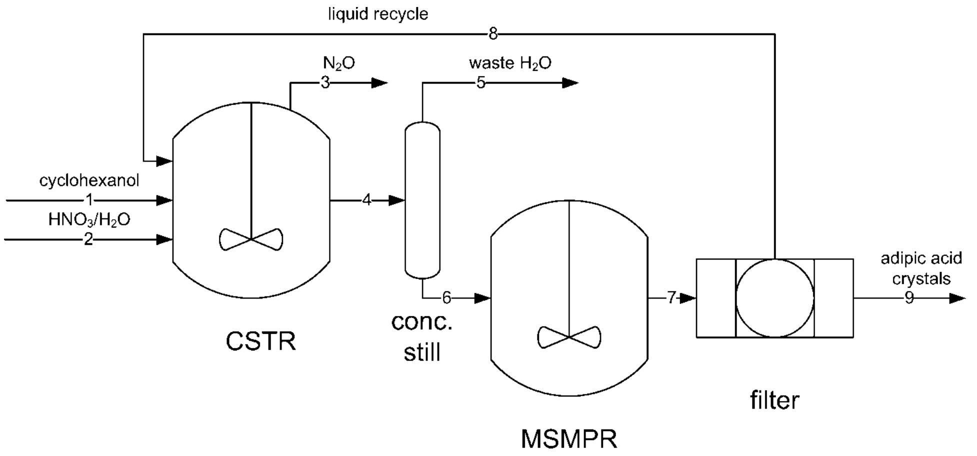

Figure 2. Process flow diagram for plantwide adipic acid manufacturing process.

low to minimize the cost of waste treatment and to avoid unnecessary loss of the valuable raw material. The bottoms product from the concentrating still is fed to a cooling crystallizer, which is operated at 60°C. Physical properties and kinetic parameters for the crystallization of adipic acid are taken from Wibowo et al.[18]

The effluent from the crystallizer is fed through a filter, which separates the adipic acid crystals from the solution. The remaining liquid, which includes unreacted cyclohexanol and uncrystallized adipic acid as well as nitric acid and water, is fed back to the reactor. The nominal production rate is 10,000 kg/h (2.78 kg/s), and the nominal characteristic crystal size is 50 μm (5×10^{-5} m). Downstream units, which purify the product by dissolving and recrystallizing the adipic acid, are not modeled in this case study because they are outside of the recycle loop.

Results of plantwide operating policies

Figure 3 shows how the crystallizer holdup changes with changing production rate for various operating policies. Policy 1 maintains the average crystal size and the crystallizer volumetric flow rate constant. From Table 1, for this policy, the crystallizer holdup is predicted to decrease with the increasing production rate. The slope of the linear approximation of the function about the nominal operating point $(\bar{P}, \bar{V}_C)$ is predicted to be $((j-1)/(i-1))(\bar{V}_C/\bar{P})$. This approximation is depicted in the figure as a dashed line. The agreement between the predicted linear approximation and the observed process behavior is quite good.

Similarly, for policy 3 (constant crystallizer feed volumetric flow rate and crystal growth rate), the crystallizer holdup is predicted to increase with increasing production rate, and again the actual trend closely matches the linear prediction. Finally, for policy 8, the required crystallizer holdup is predicted to rise with the production rate more rapidly than for policy 3, and this is also borne out by the case study results.

Figure 4 shows how the average crystal size changes with the changing production rate for various operating policies. As mentioned earlier, the predicted linear approximations for each policy are shown with dashed lines. In all cases, the observed nonlinear relationship and the predicted linear approximation are very similar. As expected, for policies 2, 3, and 9, the average crystal size increases with the increasing production rate, whereas for policy 5 the average crystal size decreases with increasing production rate.

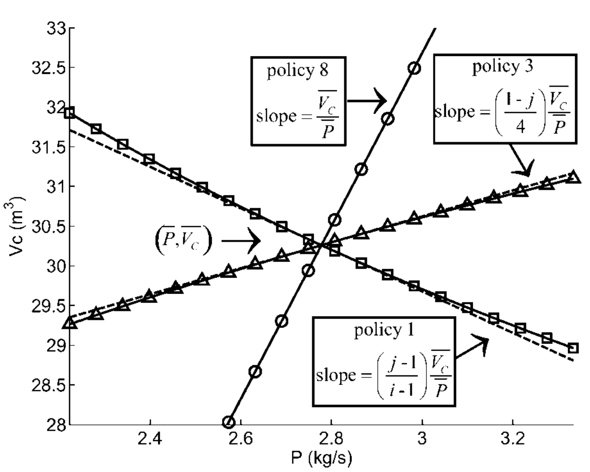

Figure 3. VC vs. *P* for different operating policies (□ policy 1; Δ policy 3; ○ policy 8).

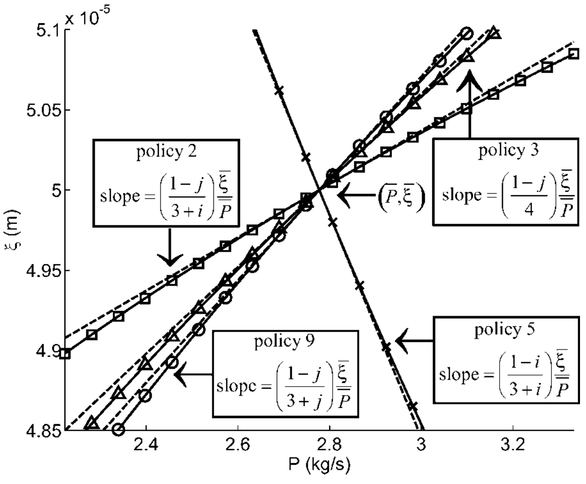

Figure 4. ζ vs. P for different operating policies (□ policy 2; Δ policy 3; X policy 5; ○ policy 9).

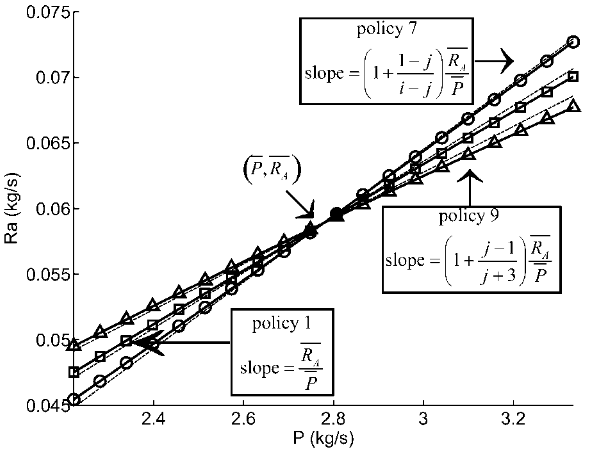

Figure 5. R_A vs. P for different operating policies (□ policy 1; ○ policy 7; △ policy 9).

Figure 5 shows the behavior of the recycle flow rate of cyclohexanol, R_A, which varies with the production rate for various operating polices with constant reactor holdup V_R. In all cases, the recycle flow rate of cyclohexanol increases with the increasing production rate; however, the rate of increase depends on the operating policy as predicted by the analysis presented in the previous section: Plantwide Design and Operation Equations.

Extension to the R-z crystallizer model

The most restrictive assumption in this work is that the crystallizer is described by the MSMPR model. The advantage of the MSMPR model is that it allows for the development of analytical expressions for the gain between the production rate and various other process variables for various operating policies. These gains turn out to be very simple expressions dependent only on the kinetic parameters *i* and *j*. The analytical expressions, in turn, allow for the development of insight as to why the process behaves as it does. However, the MSMPR model does not provide a very realistic description of the way that industrial crystallizers actually operate. In reality, there is usually some classification of the product crystals, either deliberately to improve the CSD, or inadvertently as a result of incomplete mixing around the crystallizer outlet. Furthermore, fines dissolution is also often incorporated into the crystallizer design and operation to improve the CSD.

To account for these effects, Randolph and Larson[12] have proposed what they term the *R-z* crystallizer model, which they claim gives a reasonably accurate description of the behavior of actual industrial crystallizers. In this model, it is assumed that fines and product crystals are removed at a rate *R* and *z* times the nominal (MSMPR) rate, where fines are crystals smaller than L_F (the fines cutoff length) and product crystals are crystals larger then L_P (the product cutoff length).

As described in the web-published supplement, a second adipic acid process was designed for the case that the crystallizer is described by the *R-z* crystallizer model with $R = z = 1.5$, $L_F = 2 \times 10^{-5}$ m, $L_P = 5 \times 10^{-5}$ m and the same specification on the production rate and average crystal size is applied. For the *R-z* crystallizer, the average crystal size is defined based on the volume average size of the crystals in the product stream:

$$\xi = \frac{\mu_{p,4}}{4\mu_{p,3}} \tag{78}$$

Because the *R-z* crystallizer model is more complicated than the MSMPR model, it is not possible to develop equations analogous to Eqs. 19 and 21; therefore the model was solved numerically.

Figure 6 shows how the crystallizer holdup changes with changing production rate for various operating policies using the redesigned process. It is analogous to Figure 3. Notice that the process design is considerably different. When compared with the MSMPR case, the crystallizer in the *R-z* process has a larger residence time, a smaller volumetric effluent flow rate, and a smaller holdup, as discussed in the web-published supplement. Nevertheless, the trends in the behavior of process variables as the production rate changes are very close to the predictions developed in this work based on a linearization of the MSMPR model equations. Although the figures are not shown in this article because of space constraints, the average crystal size ξ and other properties of the process with the *R-z* crystallizer also closely match the predictions developed in this article.

Conclusions

This article presents simple analytical expressions for the steady-state plantwide behavior of processes with crystallization for various operating policies. For a given operating policy, it is shown analytically how uncontrolled variables change with the changing production rate. The process behavior is shown to be a simple function of the kinetic parameters *i* and *j*. These results can be used by the process engineer to gain insight into the behavior of processes with crystallization. They are also useful for plantwide control structure design, because they permit the engineer to estimate the steady-state feasibility of a given control structure, so that infeasible control structures can be eliminated from consideration without the need to test their dynamic behavior.

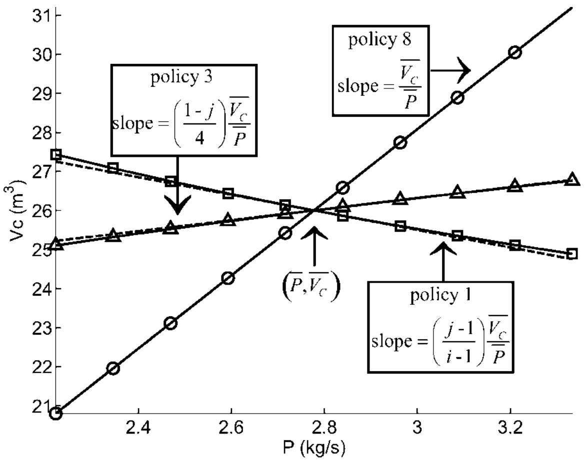

Figure 6. VC vs. P for different operating policies (□ policy 1; △ policy 3; ○ policy 8) using the alternative process design with an *R-z* crystallizer.

A number of assumptions have been employed to develop these results; perhaps the most restrictive is the assumption that the behavior of the crystallizer can be described by the MSMPR model. This assumption is necessary to develop the simple analytical results that are presented in this paper. The analytical results were compared with the numerical calculations based on the *R-z* crystallizer model and found to be in good agreement. However, crystallization processes are notoriously complex and difficult to model. There are many phenomena, including, for example, size-dependant growth, agglomeration, and incomplete mixing in the bulk that are not accounted for even by the *R-z* model. It would be impossible to test the model in every conceivable circumstance. Therefore, engineers should use caution in applying these results to predict the behavior of real-world systems.

Space constraints do not permit us to fully develop and explain the intuition behind the behavior of the process under all possible operating policies. However, because all of the results are derived, the reader can return to the equations and follow them to develop insight as to why the process behaves as it does for a given operating policy.

In this work, we have limited the analysis to a single-dependent variable: the production rate P. We have shown how uncontrolled variables change with production rate for various operating policies. It is also possible to repeat the analysis for other independent variables. For example, in some circumstances, it is necessary to control the average crystal size explicitly, and the required average crystal size may be different at different times for different products. It would be possible to repeat the analysis to show how uncontrolled variables change as the average crystal size is adjusted.

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Notation

B = nucleation rate (1/(m^3 s))
f = crystal size distribution function (1/m^3 m)
G = crystal growth rate (m/s)
g = growth parameter (dimensionless)
i = nucleation parameter (dimensionless)
j = nucleation parameter (dimensionless)
k = gain parameter (dimensionless)
k_b = nucleation parameter $(1/(\mathrm{m}^3\ \mathrm{s})(\mathrm{m/s})^{-g}\ (\mathrm{kg/kg})^{-j}$
k_g = growth parameter $(\mathrm{m/s})(\mathrm{kg/m}^3)^i$
k_v = volumetric shape factor (dimensionless)
M_T = magma density (kg/m^3)
P = production rate of solid product (kg/s)
q = crystallizer volumetric feed flow rate (m^3/s)
V = crystallizer volume (m^3)
ΔC = supersaturation (kg/kg)
μ_i = ith moment of the crystal size distribution (m^i/m^3)
ξ = characteristic length (m)
ρ_c = crystal density (kg/m^3)
ρ_s = solution density (kg/m^3)

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Appendix

This Appendix verifies that the dimensionality of Eq. 19 is correct. The reader is referred to the nomenclature for the meaning and units of each variable. Using SI units, from Eq. 19:

$$\mathrm{m}^3 = \left(\frac{1}{\mathrm{m}^3\mathrm{s}}\left(\frac{\mathrm{m}}{\mathrm{s}}\right)^{-i}\left(\frac{\mathrm{kg}}{\mathrm{m}^3}\right)^{-j}\left(\frac{\mathrm{kg}}{\mathrm{m}^3}\right)\left(\frac{\mathrm{kg}}{\mathrm{s}}\right)^{j-1}\left(\frac{\mathrm{m}^3}{\mathrm{s}}\right)^{i-j}\mathrm{m}^{3+i}\right)^{\frac{1}{i-1}} \tag{A1}$$

$$\mathrm{m}^3 = \left(\mathrm{m}^{-3}\mathrm{s}^{-1}\mathrm{m}^{-i}\mathrm{s}^{i}\mathrm{kg}^{1-j}\mathrm{m}^{-3(1-j)}\mathrm{kg}^{j-1}\mathrm{s}^{1-j}\mathrm{m}^{3(i-j)}\mathrm{s}^{j-i}\mathrm{m}^{3+i}\right)^{\frac{1}{i-1}} \tag{A2}$$

$$\mathrm{m}^3 = \left(\mathrm{m}^{-3+3i}\right)^{\frac{1}{i-1}} \tag{A3}$$

$$\mathrm{m}^3 = \mathrm{m}^3 \tag{A4}$$

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