Periodic Forcing of the CSTR: an Application of the Generalized Π-Criterion

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Nonlinearities give the opportunity to influence the time average performance of a system by periodic forcing of external parameters. In this article, this concept is applied to the following reactions occurring in a continuous stirred tank reactor: $A \rightarrow B$, $A \rightarrow C$; $A \rightleftharpoons B$; $A \rightarrow B \rightarrow C$; and $A \rightarrow B$, $A + B \rightarrow C$. It is shown, using a generalized Π-criterion, that if the activation energies satisfy the constraint $E_1 > E_2$, then the yield of B is improved using high-frequency periodic perturbations in the temperature regardless of reaction order and operating conditions. Conversely, if $E_1 < E_2$, then high-frequency forcing always leads to a deterioration of the yield. There exist regions of parameter space where low-frequency forcing may lead to an improvement. Results valid for low and intermediate frequencies are developed and can be used to predict additional areas of parameter space of interest for periodic operation.

Introduction

Experiments and simulation studies verify that it is often advantageous to exploit the nonlinear behavior of chemical reactions and operate in a transient regime by periodic cycling of one or more control parameters. Dun and Gulari (1985), Wilson and Rinker (1982), and Lee et al., (1980) discuss a range of experimental results supporting this claim. One physical explanation for the phenomenon was given by Cutlip (1979), who periodically switched the feed in the isothermal oxidation of carbon monoxide. Since carbon monoxide is more readily adsorbed onto the surface of the catalyst than the oxygen, a periodic switching of the feed enabled the oxygen to cover a greater portion of the catalyst surface. Another experiment showing the same effect was performed by Jain et al. (1983). They used concentration cycling in the ammonia synthesis, and nitrogen was thought to react with the iron catalyst so that in the nitrogen-deficient portion of the cycle, nitrogen was available for reaction. This would lead to a more efficient utilization of the reactants. Lynch (1983) used Langmuir-Hinshelwood kinetics to model similar systems and by simulation showed that the optimum performance for a given steady state was achieved at intermediate frequencies and that accurate predictions could be made using simple models.

Some systematic studies have been made to elucidate the effects of choice of parameters on periodic operation. For example, Schadlich et al. (1983) considered the influence of sorption rate constants, reaction order, and ratio of the inlet concentrations on periodic performance. They studied both heterogeneous and homogeneous systems to maximize the conversion in single reactions and the selectivity in complex reactions. They found that for heterogeneous reactions of the form $A \rightarrow P$, if all the adsorption rate constants are equal and all the desorption rate constants are equal without any change in the number of moles, then an improvement results only for a reaction order greater than one. Under the same conditions, periodic operation is detrimental when we consider the reactions of the form $\nu_1 A_1 + \nu_2 A_2 \rightarrow P$. However, if the number of moles decreases, periodic operation at a very low frequency increases performance. Conversely, if the number of moles increases, then high-frequency periodic operation improves performance. For reactions of the form $\nu_1 A_1 \rightleftharpoons \nu_2 A_2$, variations of the sorption constants led to an improvement with periodic control for various reaction orders if the inert component was adsorbed on the surface. If the inert component was not adsorbed on the surface, then no generalizations could be made concerning how periodic control influence the steady-state performance. With a homogeneous reaction and constant total number of moles, an increase in conversion was observed. If the reaction order was greater than one, then a decrease in conversion occurred.

Another study by Renken (1972) investigated the importance

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of reaction rate constants and inlet concentrations on yield and selectivity performance for several reaction schemes. It was found that for simple second-order reactions, it was not advantageous to employ periodic control; however, for irreversible consecutive-competing reactions the yield would increase using periodic operation as long as k_1 was not much less than or greater than k_2 where k_1 and k_2 are the reaction rate constants for the two reactions. The selectivity increases, but the conversion decreases. From this rather brief discussion it is clear that a rather complex picture emerges.

Several attempts have been made to develop a theory for periodic control that can be used for predictive purposes. Horn and Lin (1967) used a perturbation approach. Horn and Bailey (1971) discussed comparisons between methods based on the maximum principle and an approach based on the use of relaxed controls. Fjeld (1974) developed this class of method further and showed that proper periodic controls exist when the generating vector fields are concave. This condition is checkable when the system has small dimension. Some examples provided illustrate the utility of this approach. A rigorous setting for these methods can be found in the work of Fillipov (1964).

This article uses an approach which was developed by Bryson and Ho (1975) and Bittanti et al. (1973). The essence of the result is that a frequency-dependent scalar $\Pi(\omega)$ provides sufficient and necessary conditions for the existence of periodic controls to improve the steady-state performance. A mixture of first-and second-order expansions are used to obtain this result and it has been applied quite successfully by Sincic and Bailey (1980), Schadlich et al. (1983), and more recently by Sterman and Ydstie (1990) to a range of simple reactions in a continuous stirred tank reactor (CSTR). Originally this theory was developed to study systems operating at the optimal steady state. A generalization, the details of which we give here, allows us to apply essentially the same method to a broader range of problems, and perturbations around arbitrary steady states can be analyzed. This problem turns out to be important since chemical processes rarely operate under optimum yield conditions since this may lead to large selectivity losses.

Theoretical Development

Following Horn and Lin's method (1967) we introduce the dimensionless state variables:

$$x_1=\frac{C_A}{C_{Ao}}, \qquad x_2=\frac{C_B}{C_{Ao}},$$

where x_2 is the yield of B, dimensionless temperature and time

$$u=\frac{V}{q}k_{10}C_{Ao}^{\alpha-1}\exp\frac{-E_1}{RT}, \qquad t=\frac{t'q}{V},$$

and system parameters

$$\gamma=\frac{V}{q}k_{20}C_{Ao}^{\beta-1}\left(\frac{V}{q}k_{10}C_{Ao}^{\alpha-1}\right)^{-\rho}, \qquad \rho=\frac{E_2}{E_1}.$$

The equations describing the transient behavior of the reaction systems can now be expressed in the form:

Table 1. Eigenvalues for the Reaction Schemes

Parallel Reaction Scheme	
$s = -1$	$s = -(\gamma\beta u^{\rho}x_1^{\beta-1}+\alpha u x_1^{\alpha-1}+1)$
Equilibrium Reaction Scheme	
$s = -(\gamma u^{\rho}\beta(1-x_1)^{\beta-1}+\alpha u x_1^{\alpha-1}+1)$	
Consecutive Reaction Scheme	
$s = -(\alpha u x_1^{\alpha-1}+1)$	$s = -(\gamma\beta u^{\rho}x_2^{\beta-1}+1)$
Parallel-Consecutive Reaction Scheme	
$s = [-m+\sqrt{(m^2-4n)}]/2$	$s = [-m-\sqrt{(m^2-4n)}]/2$
where	
$m = \gamma u^{\rho}x_1+\gamma u^{\rho}x_2+\alpha u x_1^{\alpha-1}+2$	
$n = \gamma u^{\rho}x_1+\gamma u^{\rho}x_2+\alpha u x_1^{\alpha-1}+2\alpha\gamma u^{\rho+1}x_1^{\alpha}+1$	

$$\dot{x}=f(x,u,\theta),$$

where $x=(x_1, x_2)^T$ is the state vector, $\theta=(\alpha, \beta, \gamma, \rho)^T$ is the vector of system parameters, and α and β are the reaction orders. The vector fields are defined below.

Parallel Reaction:

$$A^{\alpha}\rightarrow B,\ A^{\beta}\rightarrow C$$

$$\dot{x}_1=1-x_1-ux_1^{\alpha}-\gamma u^{\rho}x_1^{\beta}$$

$$\dot{x}_2=-x_2+ux_1^{\alpha}$$

Equilibrium Reaction:

$$A^{\alpha}\rightleftharpoons B^{\beta}$$

$$\dot{x}_1=1-x_1-ux_1^{\alpha}+\gamma u^{\rho}(1-x_1)^{\beta}$$

Consecutive Reaction:

$$A^{\alpha}\rightarrow B^{\beta}\rightarrow C$$

$$\dot{x}_1=1-x_1-ux_1^{\alpha}$$

$$\dot{x}_2=-x_2+ux_1^{\alpha}-\gamma u^{\rho}x_2^{\beta}$$

Parallel-Consecutive Reaction:

$$A^{\alpha}\rightarrow B,\ A+B\rightarrow C$$

$$\dot{x}_1=1-x_1-ux_1^{\alpha}-\gamma u^{\rho}x_1x_2$$

$$\dot{x}_2=-x_2+ux_1^{\alpha}-\gamma u^{\rho}x_1x_2.$$

The dimensionless temperature, $u \in S_{\omega}$, where S_{ω} is the space of τ-periodic functions, is considered to be a control variable, and γ, which depends on the residence time, is a fixed parameter, which may be optimized. We note that the vector fields are linear when $\alpha=\beta=\rho=1$, and there is then no incentive to apply periodic control. It follows that there are two parameters to consider: the ratio of the activation energies and the reaction orders.

Corollary. The reaction schemes described above have unique asymptotically stable equilibria.

Proof. For a fixed temperature $\bar{u}$, the steady state, $\bar{x}$, satisfies $f(\bar{x},\bar{u},\theta)=0$. The eigenvalues of $(\partial f/\partial x)|_{x=\bar{x},u=\bar{u}}$ are listed in Table 1. All physical parameters and state and control variables

are positive; and the reaction schemes have eigenvalues with strictly negative real parts. Consequently, the continuous family of fixed points $\{\bar{x}: f(\bar{x}, \bar{u}, \theta)=0\}$ is hyperbolic and stable, and has (Poincare) index $+1$. [For a definition of the index and the details of this development, see Guckenheimer and Homes (1983).] It is now quite straightforward to show that $x(t) \in \Gamma$, where Γ is compact (a rectangle it turns out) with boundary Ω; moreover, $\partial f/\partial n|_{\Omega}<0$. It follows that index $(\Gamma)=+1$. This then ensures the existence, uniqueness and stability of a single fixed point for every $\bar{u} \in R_+$ and $\theta \in R_+^4$.

This result was stated without proof for the parallel reaction in Horn and Lin (1967). In the case of the parallel consecutive reaction, the presence of a pair of complex conjugate eigenvalues when $m^2-4n<0$ implies that by judicious choice of frequency it may be possible to amplify the effect of applying periodic control at the resonance (Douglas, 1971). More importantly, the exponential stability of the system allows us to conclude that small perturbations do not interfere in a significant way and that we can apply linearization and first-order averaging to obtain results describing the behavior of the system. (Stability is not critical since the analysis in principle applies to small-amplitude perturbations around hyperbolic stationary points. In practice, however, an unstable system needs to be stabilized by feedback.)

The aim of the article is to study how the average of the yield of B changes as a function of the frequency of the input and system parameters. A performance measure Δ is defined so that

$$\Delta(\bar{u},\theta,a,\omega)=\lim_{t\to\infty}\frac{1}{\tau}\int_{t-\tau}^{t}\frac{x_2-\bar{x}_2}{\bar{x}_2}dt.$$

Here $\tau=2\pi/\omega$ is the period and ω is the forcing frequency. It follows that if $\Delta(\bar{u}, \theta, a, \omega)$ is positive for some $u \in S_\omega$, then periodic forcing for this set of parameter values leads to an increase in the yield. The main challenge consists of developing a theory that can be used to make predictions without having to integrate the equations explicitly or having to bring in the nonlinear analysis *holus bolus*.

As an introduction consider the following example.

Example. The second-order parallel reaction $A^2\to B$, $A\to C$ has the steady state

$$\bar{x}_2(\bar{u})=\frac{1}{4}\left[-(1+\gamma\bar{u}^{\rho})+\sqrt{(1+\gamma\bar{u}^{\rho})^2+4u}\right]^2$$

Using low-frequency symmetric square wave forcing with amplitude a centered on u, we may assume that transients are not significant due to stability and the system, for all practical purposes, is at rest at one of two steady states. By applying this "quasisteady-state" assumption, the change in the average steady-state yield, due to periodic forcing, can be expressed as:

$$\Delta(\bar{u},\theta,a,0)=\frac{\bar{x}_2(\bar{u}+0.5a)+\bar{x}_2(\bar{u}-0.5a)}{2\bar{x}}-1$$

A plot of this quantity as a function of u for $a=1$, and $\rho=2$ is shown in Figure 1. It appears that low-frequency forcing leads to an improvement, if $u>1.7$, and a deterioration otherwise. Later, it is shown that high-frequency forcing always

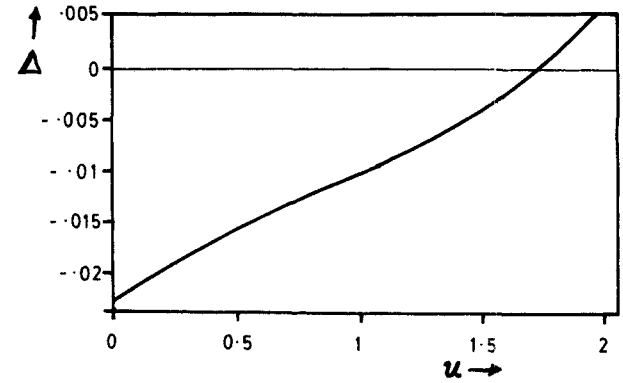

Figure 1. Quasi-steady-state approximation of the performance improvement.
$\Delta(\bar{u},\theta,a,0)$ with $\theta=(2,1,1,2)^T$, $a=1$ is shown vs, $\bar{u}$ for $\bar{u} \in [0,2]$. Note that only for $\bar{u} > \approx 1.7$ is $\Delta > 0$.

leads to a deterioration for this reaction system; and it is clear that intuition based on steady-state analysis does not suffice to completely explain the phenomenon of periodic control.

We rely on perturbation analysis and Fourier series expansion. Therefore, it is convenient to apply sinusoidal perturbations $\delta u(t)=a\sin(\pi\omega t)$ to given fixed points $\bar{u}$.

Lemma 1. Suppose $u(t)=\bar{u}+\delta u(t)$ where $\bar{u}$ is a fixed arbitrary temperature and $\delta u(t)=a\sin(\pi\omega t)$. First-order averaging leads to the approximation:

$$\Delta(\bar{u},\theta,a,\omega)=\frac{a^2}{4}\Pi(\omega)$$

where

$$\Pi(\omega)=\frac{A\omega^2+B}{C\omega^4+D\omega^2+E}+F$$

The parameters A,B,C,D,E, are defined in Tables 2-5.

Table 2. Parameters for Parallel Reaction Scheme

A	=	0
B	=	$a+2d(b+c+1)$
C	=	0
D	=	1
E	=	$(b+c+1)^2$
F	=	$-\gamma\lambda_1(\rho-1)\rho u^{\rho-2}x_1^{\beta}$
a	=	$[-\lambda_1(\gamma(\beta-1)\beta u^{\rho}x_1^{\beta-2}-(\alpha-1)\alpha u x_1^{\alpha-2}$ $+(\alpha-1)\alpha\lambda_2 u x_1^{\alpha-2}][-\gamma\rho u^{\rho-1}x_1^{\beta}-x_1^{\alpha}]^2$
b	=	$\gamma\beta u^{\rho}x_1^{\beta-1}$
c	=	$\alpha u x_1^{\alpha-1}$
d	=	$[\lambda_1(-\gamma\beta\rho u^{\rho-1}x_1^{\beta-1}-\alpha x_1^{\alpha-1})+\alpha x_1^{\alpha-1}]\times$ $(-\gamma\rho u^{\rho-1}x_1^{\beta}-x_1^{\alpha})$

Table 3. Parameters for Equilibrium Reaction Scheme

A	=	0
B	=	$a+2d(b+c+1)$
C	=	0
D	=	1
E	=	$(b+c+1)^2$
F	=	$\gamma\lambda_1(\rho-1)\rho u^{\rho-2}(1-x_1)^{\beta}$
a	=	$\lambda_1[\gamma(\beta-1)\beta u^{\rho}(1-x_1)^{\beta-2}-(\alpha-1)\alpha u x_1^{\alpha-2}]$ $[\gamma\rho u^{\rho-1}(1-x_1)^{\beta}-x_1^{\alpha}]^2$
b	=	$\gamma\beta u^{\rho}(1-x_1)^{\beta-1}$
c	=	$\alpha u x_1^{\alpha-1}$
d	=	$\lambda_1[-\alpha x_1^{\alpha-1}-\gamma\beta\rho u^{\rho-1}(1-x_1)^{\beta-1}][\gamma\rho u^{\rho-1}(1-x_1)^{\beta}-x_1^{\alpha}]$

Proof. We follow a line of reasoning similar to that outlined by Bryson and Ho (1975), and then use the averaging result offered by Tikhonov et al. (1980).

Define the Hamiltonian

$$H = x_2 + \lambda^T f$$

and a set of (Lagrange) multipliers

$$\dot{\lambda}_T = -\frac{\partial H}{\partial x}$$

so that from the definitions above

$$\Delta(\bar{u},\theta,a,\omega) = \frac{1}{\tau \bar{x}_2}\int_{t-\tau}^{t} (H - \lambda^T f)dt - 1.$$

Since $f = \dot{x}$, integration by parts and a second-order Taylor series expansion now yield:

$$\Delta(\bar{u},\theta,a,\omega) = \frac{1}{\tau \bar{x}_2}\left[\lambda^T \delta x|_{t-\tau} - \lambda^T \delta x|_t \right.$$

$$\left. + \int_{t-\tau}^{t} H_u \delta u + \frac{1}{2}(\delta x^T H_{xx}\delta x + \delta x^T H_{xu}\delta u + \delta u H_{ux}\delta x + H_{uu}\delta u^2)dt \right]$$

In the development of the Π-criterion, the key steps were to use linearization to motivate the periodicity in the state variable $[x(t) = x(t-\tau)]$ and recognize that for $u = u^o$, where u^o is the steady-state optimal control, we have $H_u = 0$. λ is then taken to be the constant multiplier associated with the optimal steady-state control. This approach does not work here since we are interested in perturbing around steady states $u \neq u^o$. Indeed, a feature of the CSTR problem is that a feasible optimal steady-state control may not exist.

To proceed, we make a recourse to averaging and introduce the function:

$$\bar{H}_x(\bar{\lambda}) = \frac{1}{\tau}\int_{t-\tau}^{t} H_x dt = \frac{1}{\tau}\int_{t-\tau}^{t} \left(\frac{\partial x_2}{\partial x}\right)^T + \bar{\lambda}^T \frac{\partial f}{\partial x} dt$$

Assuming now that we have

$$\frac{d\bar{H}}{d\bar{\lambda}} = \frac{1}{\tau}\int_{t-\tau}^{t} \frac{dH}{d\bar{\lambda}}$$

that is, the average of the derivative is equal to the mean value of the derivative, we can replace the equation for the multiplier with the averaged equation:

$$\dot{\bar{\lambda}} = -\bar{H}_x(\bar{\lambda})$$

which in principle should be much simpler to solve. In fact, since we are dealing with a τ-periodic signal, we have $d\bar{\lambda}/dt = 0$ so that we get the equation:

$$0 = \frac{1}{\tau}\int_{t-\tau}^{t} \left[\left(\frac{\partial x_2}{\partial x}\right)^T + \bar{\lambda}^T \frac{\partial f}{\partial x} \right] dt.$$

Table 4. Parameters for Consecutive Reaction Scheme

A	=	$-ab^2 - 2fc - 2fb(d+1) - 2h(e+1) + g$
B	=	$abe(2c-2b-be) - a(c-b)^2 + 2(d+1)(e+1)\times$ $[fc - fb(e+1) - h(d+1)] + g(d+1)^2$
C	=	1
D	=	$(d+1)^2 + (e+1)^2$
E	=	$(d+1)^2(e+1)^2$
F	=	$\gamma\lambda_2(1-\rho)\rho u^{\rho-2}x_2^{\beta}$
a	=	$\gamma(\beta-1)\beta\lambda_2 u^{\rho}x_2^{\beta-2}$
b	=	$x_1^{\alpha} - \gamma\rho u^{\rho-1}x_2^{\beta}$
c	=	$\alpha u x_1^{2\alpha-1}$
d	=	$\gamma\beta u^{\rho}x_2^{\beta-1}$
e	=	$\alpha u x_1^{\alpha-1}$
f	=	$\gamma\beta\lambda_2\rho u^{\rho-1}x_2^{\beta-1}$
g	=	$x_1^{2\alpha}(\alpha-1)\alpha u x_1^{\alpha-2}(\lambda_2-\lambda_1)$
h	=	$x_1^{2\alpha-1}\alpha(\lambda_2-\lambda_1)$

By using the assumption that the average of the derivative equals the derivative of the average:

$$\int_{t-\tau}^{t} \frac{\partial x_2}{\partial x} = \frac{\partial \bar{x}_2}{\partial x} \text{ and } \int_{t-\tau}^{t} \frac{\partial f}{\partial x} dt = \frac{\partial \bar{f}}{\partial x}$$

we get the expression for $\bar{\lambda}$

$$\bar{\lambda} = -\left(\frac{\partial \bar{f}}{\partial x}\right)^{-T} \frac{\partial \bar{x}_2}{\partial x}.$$

Thm 7.7 of Tikhonov et al. (1980) gives bounds and conditions for uniform convergence. These conditions are certainly satisfied (due to continuity and asymptotic stability), and we have uniform convergence of the quantity $\|\lambda - \bar{\lambda}\|$.

We now replace λ with its average value $\bar{\lambda}$ and use linearization to describe the response:

$$\delta x(t) = G(s)\delta u(t) \text{ with } G(s) = (sI - A)^{-1}B,$$

where $s = d/dt$ is the differential operator and

$$A = f_x(x_1, x_2, u, \theta), \quad B = f_u(x_1, x_2, u, \theta).$$

Table 5. Parameters for Parallel-Consecutive Reaction Scheme

A	=	$a(ai+2ef) + 2g[e(b+1) - ad] + 2h[a(c+1) + be]$
B	=	$bei[be - 2a(b+1)] + a^2i(b+1)^2 + 2f\{-be^2(c+1)$ $+ ae[-bd + (b+1)(c+1)] + a^2d(b+1)\}$ $+ 2g\{e[bd(c+1) + (c+cb)(c+2) + b + 1] + ad[bd$ $+ (b+1)(c+1)]\} + 2h\{be[-bd - (b+1)(c+1)]$ $+ abd(b+1) + a(b+1)^2(c+1)\}$
C	=	1
D	=	$-2bd + (b+1)^2 + (c+1)^2 - 1$
E	=	$bd[bd + (2b+2)(c+1)] + bc(b+2)(c+2)$ $+ (c+1)^2 + (b+1)^2 - 1$
F	=	$-\gamma(\rho-1)\rho u^{\rho-2}x_1x_2(\lambda_1+\lambda_2)$
a	=	$-\gamma\rho u^{\rho-1}x_1x_2 - x_1^{\alpha}$
b	=	$\gamma u^{\rho}x_1$
c	=	$\gamma u^{\rho}x_2 + \alpha u x_1^{\alpha-1}$
d	=	$\alpha u x_1^{\alpha-1} - \gamma u^{\rho}x_2$
e	=	$x_1^{\alpha} - \gamma\rho u^{\rho-1}x_1x_2$
f	=	$-\gamma u^{\rho}(\lambda_1+\lambda_2)$
g	=	$-\gamma\rho u^{\rho-1}x_1(\lambda_1+\lambda_2)$
h	=	$\lambda_2(\alpha x_1^{\alpha-1} - \gamma\rho u^{\rho-1}x_2) + \lambda_1(-\gamma\rho u^{\rho-1}x_2 - \alpha x_1^{\alpha-1})$
i	=	$(\alpha-1)\alpha u x_1^{\alpha-2}(\lambda_2-\lambda_1)$

By applying a Fourier transform and using the fact that $\delta u = a \sin(\pi\omega t)$ we then get

$$\Delta(\bar{u},\theta,a,\omega) = \frac{1}{2}[G(s)\delta u(t)]^T H_{xx} G(s)\delta u(t)$$

$$+ [G(s)\delta u(t)]^T H_{xu}\delta u + \delta u H_{ux} G(s)\delta u(t) + \delta u^T H_{uu}\delta u dt.$$

By applying a Fourier transform and using the fact that $\delta u = a\sin(\pi\omega t)$ we then get

$$\Delta\bar{u},\theta,a,\omega) = \frac{a^2}{4\bar{x}_2}\Pi(\omega)$$

where

$$\Pi(\omega) = G^T(-j\omega)H_{xx}G(j\omega) + H_{xu}^T G(j\omega) + G^T(-j\omega)H_{xu} + H_{uu}.$$

This expression corresponds to the one developed by Bittanti et al. (1974). The equations for the multipliers, however, are different, and $\bar{u}$ is prechosen rather than computed as the solution to an optimal control problem. Lemma 1 now follows by evaluating λ, f,G, etc. for each individual reaction scheme and computing $\Pi(\omega)$. These calculations are quite easy to carry out manually, since the matrix that needs to be inverted symbolically is triangular and we get the results shown in the tables, *qed.*

The expression in lemma 1 gives necessary and sufficient conditions for the existence of small-amplitude periodic perturbations that give improved yield. In particular, the yield for these types of reactions is improved whenever

$$\frac{A\omega^2 + B}{C\omega^4 + D\omega^2 + E} + F > 0. \tag{1}$$

The expression for $\Pi(\omega)$ can be evaluated for a given reaction and optimized with respect to free parameters. A plot of Δ (1, θ, 1, ω) with $\theta = (2, 1, 1, 2)'$ is shown in Figure 2. As expected, low-frequency perturbations yield positive values. However, for $\omega > 4$, the yield decreases. More examples are given by Sincic and Bailey (1980) and Sterman and Ydstie (1990).

By itself Π yields little insight into the problem. To proceed we consider limiting cases. First, for high frequencies we have the following astonishing result which is valid for all four reactions. (There are no particular technical problems associated with extending S_ω and taking the high-frequency limits to obtain the so-called "relaxed controls"; the integrals are well defined in a measure theoretic sense so that convergence of Π is guaranteed.)

Result 1. High-frequency periodic forcing of the temperature improves the yield of B when $E_2 < E_1$. When $E_2 = E_1$, there is no change; and when $E_2 > E_1$, the yield decreases.

Proof. The high-frequency limit yields

$$\lim_{\omega\to\infty} \frac{A\omega^2 + B}{C\omega^4 + D\omega^2 + E} = 0 \tag{2}$$

so that $\lim_{\omega\to\infty}\Pi(\omega) = F$. This implies that $\Pi > 0$ when $F > 0$, and the sign of F then determines whether high-frequency periodic operation improves the yield for operation around a given steady state. From physical arguments we know that the

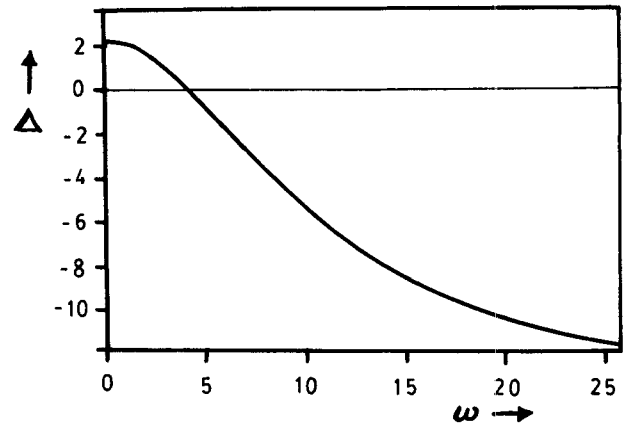

Figure 2. Estimated performance improvement $\Delta(\bar{u},\theta a,0)$ as a function of frequency using the Π-criterion.

Same example as in Figure 1 with $\theta = (2,1,1,2)^T$, $a = 1$ and $\bar{u} = 2$. Note that while low-frequency forcing leads to an improvement (as predicted by the quasi-steady-state result), higher-frequency forcing ($\omega > \approx 4$) gives a deterioration.

state variables (x_1, x_2), the input variable (u) and the system parameters (γ, ρ, α, β) are positive. The expressions in Tables 2-5 explain that the sign of F are determined by ρ and the sign of the Lagrange multipliers. The expressions for the Lagrange multipliers are obtained directly from the definition of the Hamiltonian.

For the parallel reaction scheme we then get after some algebra:

$$F = -\gamma\lambda_1(\rho - 1)\rho u^{\rho-2}x_1^\beta$$

with

$$\lambda_1 = \frac{\alpha u x_1^{\alpha-1}}{1 + u\alpha x_1^{\alpha-1} + \gamma u^\rho \beta x_1^{\beta-1}} > 0, \quad \lambda_2 = 1.$$

For the equilibrium reaction there is only one state variable (x_1), and the yield (x_2) is replaced with $1 - x_1$ in the definition of the Hamiltonian. This gives

$$F = -\gamma\lambda_1(\rho - 1)\rho u^{\rho-2}(1 - x_1)^\beta$$

with

$$\lambda_1 = \frac{-1}{1 + u\alpha x_1^{\alpha-1} + \gamma u^\rho \beta (1 - x_1)^{\beta-1}} < 0$$

For the consecutive reaction we have

$$F = -\gamma\lambda_2(\rho - 1)\rho u^{\rho-2}x_2^\beta$$

with

$$\lambda_2 = \frac{1}{1 + \gamma u^\rho \beta x_2^{\beta-1}} > 0$$

and finally for the parallel-consecutive reaction scheme:

$$F = -\gamma(\rho-1)\rho u^{\rho-2}x_1x_2(\lambda_1+\lambda_2)$$

In this case, the Hamiltonian satisfies

$$H = x_2 + \lambda_1(1 - x_1 - ux_1^q - au^\rho x_1x_2) + \lambda_2(-x_2 + ux_1^\alpha - au^\rho x_1x_2)$$

so that for a given steady state:

$$\frac{\partial H}{\partial x_1} = 0 = \lambda_1(-1 - \alpha u x_1^{\alpha-1} - au^\rho x_2) + \lambda_2(\alpha u x_1^{\alpha-1} - au^\rho x_2)$$

$$\frac{\partial H}{\partial x_2} = 0 = 1 + \lambda_1(-au^\rho x_1) + \lambda_2(-1 - au^\rho x_1)$$

hence

$$\lambda_1 = \frac{1 - \lambda_2(1 + au^\rho x_1)}{au^\rho x_1}$$

and

$$\lambda_2 = \frac{\lambda_1(1 + \alpha u x_1^{\alpha-1} + au^\rho x_2)}{\alpha u x_1^{\alpha-1} - au^\rho x_2}$$

By rearranging this, we get

$$\lambda_1 + \lambda_2 = \frac{1 + 2\alpha u x_1^{\alpha-1}}{2a\alpha u^{\rho+1}x_1^\alpha + 1 + \alpha u x_1^{\alpha-1} + au^\rho(x_1+x_2)} > 0.$$

From the above, we see that in all cases

$$H_{uu} = F > 0 \text{ provided } \rho < 1 \qquad (3)$$

(refer to Table 5). If $\rho = 0$, then $F = 0$; and finally if $\rho > 1$, then F is negative and the result follows, *qed*.

This result is limited to the extent that only the high frequency or "relaxed regime" is properly investigated. However, it is quite easy to see that

$$\lim_{\omega\to\infty} \frac{\partial \Pi(\omega)}{\partial \omega} = 0$$

and due to smoothness of Π, we can continue to lower frequencies. Improvements can in some cases be experienced at quite low frequencies. This point will be elaborated in the next section. For now we have the following result.

Result 2. Low-frequency periodic forcing of the temperature improves yield whenever

$$B + EF > 0.$$

Proof. ($\omega \to 0$) so that

$$\Pi(0) = \lim_{\omega\to 0} \frac{A\omega^2 + B}{\omega^4 + D\omega^2 + E} + F = \frac{B}{E} + F.$$

qed.

It is difficult to translate this into conditions that can be interpreted in a physical manner. Thus, one significant shortcoming of the methods based on the Π-criterion shows up: the algebra gets to be too tedious to carry out! As we shall see below, some progress can be made in the case of first- and some second-order reactions.

The limits discussed above are known, respectively, as the relaxed steady-state operation ($\omega \to \infty$), which was the subject of the key article by Horn and Lin (1967) and the low-frequency periodic operation ($\omega \to 0$) where the quasisteady-state assumption applies.

First- and Second-Order Reactions

Specializing to first- ($\alpha = \beta = 1$) and a few second- ($\alpha = 2$, $\beta = 1$) order reactions, we obtain a few more insights and results of practical interest. Towards the end of the section we also discuss the effect of including a heat balance.

Corollary. For first- and second-order parallel and equilibrium reactions, the yield is a monotonic function of frequency with maximum at $\omega = \infty$ provided $E_2 < E_1$.

Proof. In the case of the parallel and the equilibrium reactions

$$\Pi(\omega) = \frac{B}{\omega^2 + E} + F$$

and it follows that the optimal frequency can be found by solving for ω:

$$\frac{\partial \Pi}{\partial \omega} = 0 = \frac{-2B\omega}{(\omega^2 + E)^2}.$$

Thus, the maximum is obtained at $\omega = \infty$ provided $B < 0$. In the case of first-order reactions,

$$B = 2(1 + \gamma\rho u^{\rho-1})(\gamma\rho u^\rho - 1 - \gamma u^\rho)$$

Now, when $\rho < 1$ we have $B \le -2(1 + \gamma\rho u^{\rho-1}) < 0$. For the second-order parallel reaction,

$$B = 2[u + \gamma u^{\rho+1}][-\gamma\rho u^{\rho-1}x_1 - x_1^2]^2 + 4[x_1 + \gamma x_1 u^\rho(1-\rho)][-\gamma\rho u^{\rho-1}x_1 - x_2^2]$$

Since $\rho < 1$, we have

$$2[u + \gamma u^{\rho+1}][-\gamma\rho u^{\rho-1}x_1 - x_1^2] < 4[x_1 + \gamma x_1 u^\rho(1-\rho)]$$

it follows that $B < 0$ also in this case, and the result is established, *qed.*

This result was anticipated for the second-order parallel reaction by Horn and Lin (1967).

In the case of the consecutive and parallel consecutive reactions,

$$\Pi(\omega) = \frac{A\omega^2 + B}{C\omega^4 + D\omega^2 + E} + F$$

A similar approach to the one described above can be applied to find the optimal frequency, but the expressions are unwieldy. From examples it appears that there may be intermediate solutions.

Thus far, all of the results have concerned the case $E_2 < E_1$. This regime can quite conveniently be analyzed using the high-frequency limiting results. In the case $E_2 > E_1$, high-frequency periodic forcing leads to a deterioration, while intermediate and low-frequency perturbations may yield improvements.

A periodic control is said to be (locally) proper if there exists $a > 0$ and $\omega \epsilon (0, \infty)$ so that

$$\Delta(\bar{u}_o, \theta, a, \omega) > \Delta(\bar{u}_o, \theta, 0, 0)$$

where $\bar{u}_o$ is the optimal steady-state control. That is, proper periodic perturbations lead to an improvement over and beyond that achievable at the optimal steady state. The existence of such controls can be linked to a concavity property of the state space.

First, we have a negative result.

Result 3. When $E_2 > E_1$ the optimal steady-state control for the first-order parallel and equilibrium reaction is:

$$u_o = \left[\frac{1}{\gamma(\rho - 1)}\right]^{\frac{1}{\rho}}$$

The optimal yield is $x_2^o = u^o/(1 - u^o + \gamma u^\rho)$, and it is *not* possible to improve upon this using periodic control. That is, there exists no proper periodic control for this problem.

Proof. To solve the steady-state problem, define the Hamiltonian:

$$H = x_2 + \lambda_1(f_1 - \dot{x}_1) + \lambda_2(f_2 - \dot{x}_2)$$

At steady state, $\dot{x}_1 = \dot{x}_2 = 0$, and at the optimum,

$$\frac{\partial H}{\partial u} = 0$$

Solving this problem yields first:

$$x_1 = \frac{1}{1 + u + \gamma u^\rho}, \quad x_2 = u x_1$$

$$\lambda_1 = \frac{u}{1 + u + \gamma u^\rho}, \lambda_2 = 1.$$

and then

$$u_o = \left[\frac{1}{\gamma(\rho - 1)}\right]^{\frac{1}{\rho}}$$

Thus, to obtain a feasible optimal control ($u^o > 0$), we need $\rho > 1$. From Table 2,

$$d = \frac{1 + \gamma u^\rho (1 - \rho)(-1 - \gamma \rho u^{\rho - 1})}{(1 + u + \gamma \rho u^\rho)^2}.$$

By using the expression for the optimal control, this gives $d = 0$ and hence $\Pi(\omega) = F$ which is independent of frequency. Since $\rho > 1$ is equivalent to $E_2 > E_1$, $F < 0$ is implied, which proves that periodic control does not improve performance.

The same analysis and results apply to the equilibrium reaction scheme. The only difference is that now the steady-state variable and Lagrange multiplier are:

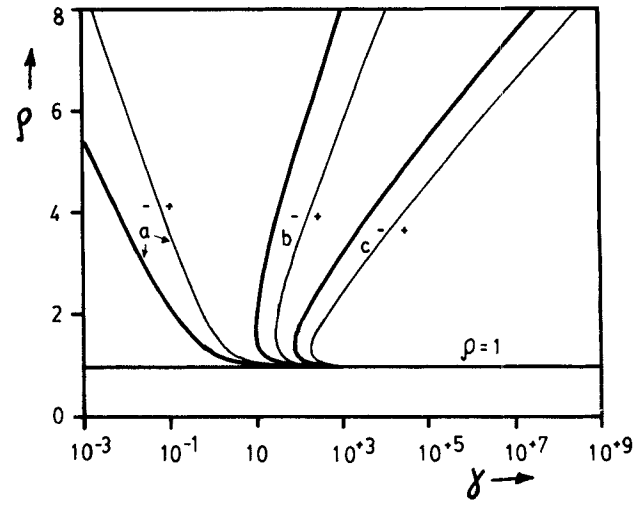

Figure 3. First-order parallel and equilibrium reactions: (a) $u = 2,6$; (b) $u = 0.33$; and (c) $u = 0.09$.

The locus of points satisfying the equality $B + EF = 0$ (thin lines) divides the plane into regions indicated with: + signs low-frequency forcing leading to an improvement; − signs giving a deterioration. High-frequency forcing is a little different. Here, improvements result if, and only if, $\rho < 1$. The solutions to the optimal steady-state control problem are indicated by bold lines. Note that these are found to be in the "negative" regions and above the line $\rho = 1$.

$$x_1 = \frac{1 + \gamma u^\rho}{1 + u + \gamma u^\rho}, \quad \lambda_1 = \frac{-1}{1 + u + \gamma u^\rho}.$$

qed.

From a practical point of view, this implies that there is no incentive to use periodic control for first-order parallel and equilibrium reactions operating close to the optimum yield. Nevertheless, industrial reactions do not often operate at optimum yield, and there may be a significant incentive to apply periodic control as will become clear below.

The results of first-order parallel and equilibrium reactions are summarized in Figure 3. The line $\rho = 1$ divides the plane into two regions. In the upper region high-frequency periodic control decreases the yield, and in the lower region high-frequency periodic control improves the yield. This follows from result 1 and is independent of reaction order. The solution curves ($B + EF = 0$) and fixed u further divide the $\gamma - \rho$ plane. In the region to the left, indicated by $-ve$ sign, periodic control is detrimental to the system. In the region to the right, indicated by $+ve$ sign, the yield is improved. As the temperature (u) increases, the size of the region where periodic operation gives improved yield increases. For all the values of u, the solution curve asymptotes to $\rho = 1$. The figure also includes the curves that represent the solution to the optimal control problem, result 3. They show the optimal value of γ $\{\gamma^o = 1/[u^\rho(\rho - 1)]\}$ as a function of ρ for the three different values of u. These curves all lie in the region indicated by negative signs and they asymptote to one, indicating that if the reaction operates under optimal yield conditions, any periodic perturbation causes the average yield to decrease. The reason why a feasible optimal control does not exist when $E_2 < E_1$ is that an unconstrained optimization leads to the use of negative u. The problem is clearly prevented if we include a constraint. The optimum will then be at this constraint. If this is a "hard" constraint, then

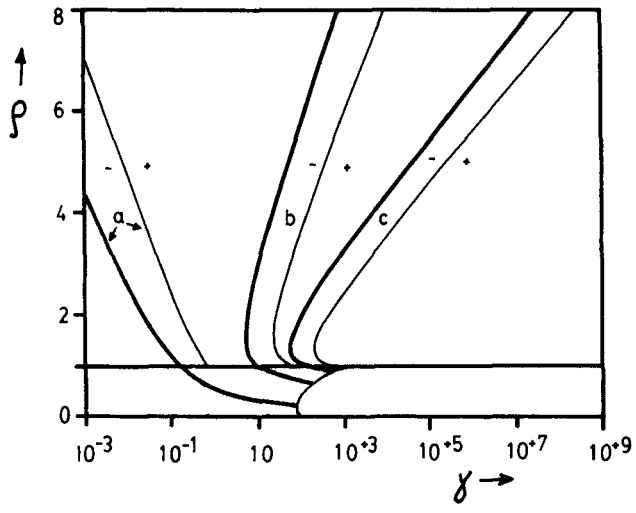

Figure 4. Consecutive reaction: (a)$u=2.6$; (b)$u=0.33$; and (c)$u=0.09$.

For legend, see Figure 3. The locus of points corresponding to steady-state optimal policies now extend well below the line $\rho = 1$, and it is possible to improve the optimal steady-state performance by using high-frequency forcing.

any periodic perturbation leads to a deterioration of the performance. If it is a "soft" constraint, then periodic control may lead to an improvement, since we then may tolerate periodic but not continual constraint violation. This may, for example, be the case when there are downstream equipment capacity constraints.

In the case of higher-order reaction schemes, there may be an incentive to apply periodic control to improve the yield even under optimal steady-state yield conditions.

Result 4. The optimal steady-state control for the second-order parallel reaction ($\alpha=2$, $\beta=1$ is) :

$$u^o=\left[\frac{1}{\gamma(2\rho-1)}\right]^{\frac{1}{\rho}}$$

The optimal yield is:

$$x_2^o=\frac{1}{2}\left[-(1+\gamma u^\rho)+\sqrt{(1+\gamma u^\rho)^2+4u^o}\right]$$

High-frequency periodic control improves on this, when $0.5<E_2/E_1<1$: i.e., proper periodic controls exist.

Proof. The solutions to the optimal control problem yields

$$x_2^o=\frac{1}{2u^o}\left[-(1+\gamma u^\rho)+\sqrt{(1+\gamma u^\rho)^2+4u^o}\right]$$

and

$$\lambda_1=\frac{2ux_1}{1+2ux_1+\gamma u^\rho},\ \lambda_2=1$$

It follows that a feasible control can be computed provided $0.5<\rho<1.0$, *qed.*

The latter result is supported by simulation studies and discussed further by Horn and Lin (1967), Fjeld (1974), and Sterman and Ydstie (1990). In the latter study, the parameters were chosen so that $\gamma=1$, and $\rho=0.75$, and the optimal control then becomes $u_o=2.51984$. Periodic control improved upon this for all the frequencies $\omega>\omega_c=6.14$ min $^{-1}$.

For the consecutive reaction scheme, periodic controls exist that improve the optimal steady-state yield.

Result 5. In the consecutive reaction, the optimal steady-state control is:

$$u^o=\left[\frac{1}{\gamma[\rho(1+u^o)-1]}\right]^{\frac{1}{\rho}}$$

The optimal yield is:

$$x_2^o=\frac{u^o}{(1+\gamma u^o)(1+u^o)}$$

High-frequency proper periodic controls exist.

Proof. The steady-state solution for the optimal control problem gives:

$$x_1=\frac{1}{1+u},\qquad x_2=\frac{u}{(1+\gamma u^\rho)(1+u)},$$

$$\lambda_1=\frac{u}{(1+\gamma u^\rho)(1+u)},\qquad \lambda_2=\frac{1}{1+\gamma u^\rho}. \tag{4}$$

A feasible solution to the optimal control problem exists if

$$u^o>\frac{1}{\rho}-1$$

The high-frequency result applies when $\rho<1$, and it is clear that certain choices of parameter values will give $\Pi(\infty)>0$ and an improvement, *qed.*

The result for the consecutive reaction is summarized in Figure 4. Like in the previous example, high-frequency periodic control improves yield for $\rho<1$. For $\rho>1$, low-frequency periodic control improves the yield in the regions indicated by $+ve$ signs, and the solution to the optimal steady-state problem lies outside this. As before, the region where periodic control increases, the yield increases in size with u. With this reaction scheme, however, the solution curves do not asymptote to $\rho=1$. This difference indicates, as stated in result 5, that there exists a feasible optimal control in the region where high-frequency forcing improves yield (result 1). This ensures the existence of *proper periodic controls*, i.e., perturbations that lead to states not achievable by the use of any constant control. Figure 5 shows this result and the region of parameter space where high-frequency periodic control improves yield relative to that achievable with optimal steady-state controls.

It turns out that the expressions describing the steady-state controls for the parallel consecutive reaction scheme are too complicated to yield any obvious insights.

Having established regions of parameter space where periodic control may be used to improve yield, it is of interest to evaluate which parameter values give the most significant improvement. We focus on the system parameters

$$\gamma=\frac{V}{q}k_{20}\left(\frac{V}{q}k_{10}\right)^{-\rho}\ \text{and}\ \rho=\frac{E_2}{E_1}.$$

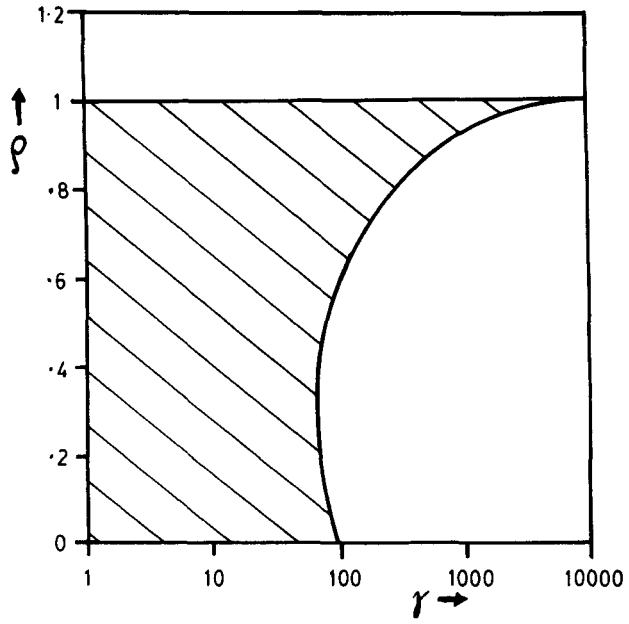

Figure 5. High-frequency periodic forcing.
It improves (unconstrained) steady-state optimal policies if, and only if, the parameters are chosen to lie in the shaded region. Above the line $\rho = 1$, high-frequency periodic forcing always deteriorates the performance; and to the right of the shaded region below the line $\rho = 1$, the optimal policy is at a constraint.

The control variable is a function of the residence time, the frequency factors, the activation energy, and the system temperature. By assuming that the residence time is fixed, changes in the control variable are due to temperature variations.

At the relaxed steady state, $\Pi(\omega) = F$ and the optimal values for γ and ρ are obtained by solving the equations

$$\frac{\partial F}{\partial \gamma} = 0 \text{ and } \frac{\partial F}{\partial \rho} = 0$$

In the case of the parallel and equilibrium reactions

$$\gamma^o = \frac{1+u}{u^\rho}$$

which upon substitution into F yields:

$$F = \frac{(1-\rho)\rho}{4u(1+u)}.$$

Optimizing with respect to ρ yields $\rho = 0.5$ and we have

Corollary. The maximum improvement using high-frequency perturbations in the case of parallel and equilibrium reactions is given by:

$$\Delta(\bar{u}, \theta, a, \infty) = \frac{0.25a^2}{16u(1+u)}$$

and it is obtained for the case $E_2 = 0.5E_1$ and $\gamma = (1+u)/\sqrt{u}$. In the case of the first-order consecutive reaction and $\rho < 1$, we have

Table 6. Optimum Set of Parameters

	u	ρ^o	γ^o	π	x_2	%
	Parallel and Equilibrium Reaction Scheme					
$\rho<1$:						
	0.090	0.5	3.63	0.637	0.0413	385.8
	0.328	0.5	2.32	0.144	0.123	29.0
	2.600	0.5	2.23	0.00668	0.3611	0.46
$\rho>1$:						
	0.090	7.05	1×10^{8}	37.741	0.017	55,500
	0.328	8.00	1×10^{5}	8.515	0.022	9,676
	2.600	8.00	1×10^{-2}	0.541	0.106	128
	Consecutive Reaction Scheme					
$\rho<1$:						
	0.090	0.5	3.33	0.63700	0.083	191.9
	0.328	0.5	1.75	0.14400	0.123	29.3
	2.600	0.5	0.62	0.00668	0.722	0.23
$\rho>1$:						
	0.090	7.1	1×10^{8}	39.093	0.017	57,489
	0.328	8.0	1×10^{5}	7.533	0.017	11,008
	2.600	8.0	1×10^{-3}	0.597	0.234	64

$$\gamma_0 = \frac{1}{u^\rho} \text{ and } F = \frac{(1-\rho)\rho}{4u(1+u)}.$$

so that the optimum becomes $\rho = 0.5$ and $\gamma = \sqrt{u}/u$.

The low-frequency limit is difficult to evaluate, and an optimal expression for γ has not been obtained. Numerical evaluation using γ and ρ in intervals

$$1\times10^{-3} < \gamma < 1\times10^{8} \text{ and } 1 < \rho < 8.0 \qquad (5)$$

yield the results listed in Table 6. The percentage improvement ($\Delta \times 100\%$) in yield is listed in the last column of Table 7.

We note that when $E_1 > E_2$ the effect of applying periodic control is most dramatic for $E_2 \approx 0.5E_1$ and $\gamma \in [0.5,4]$. When $E_1 < E_2$, low-frequency periodic control leads to the most improvement when $E_2 \approx 7.5E_1$; however, there is a great variation in the optimal choice of γ.

We finish the discussion with a note on the inclusion of a heat balance. Consider the parallel reaction $A^\alpha \rightarrow B$, $A \rightarrow C$ with the state equations:

$$\begin{aligned}
\dot{x}_1 &= 1 - x_1 - ux_1^\alpha - \gamma u^\rho x_1 \\
\dot{x}_2 &= -x_2 + ux_1^\alpha \\
\dot{x}_3 &= x_3(z - \ln x_3)[uv(z - \ln x_3) - 1 + b(v(z - \ln x_3) \\
&\quad - 1 + (z - \ln x_3)(mx_3x_1^\alpha + mn\gamma x_3^\rho x_1^\alpha))]
\end{aligned}$$

Table 7. Parameters for First-Order Parallel Reaction with Heat Balance

$$\begin{aligned}
A &= ab^2 \\
B &= c^2b^2a - 2b^2cde \\
C &= c^2 + g^2 + 2fd \\
D &= (cg - df)^2
\end{aligned}$$

$$\begin{aligned}
a &= \lambda_1[-\gamma\rho x_1(\rho-1)x_3^{\rho-2}] \\
b &= x_3v(z - \ln x_3)^2 \\
c &= -1x_3^{\rho-\gamma} \\
d &= x_1 - \gamma x_1\rho x_3^{\rho-1} \\
e &= \lambda_1(-1 - \gamma\rho x_3^{\rho-1}) + \lambda_2 \\
f &= x_3(z - \ln x_3)^2(mx_3 + mn\gamma x_3^\rho \\
g &= (z - \ln x_3)[v(u+b)(z - \ln x_3 - 2)] + 2mx_1x_3(z - \ln x_3 - 1) \\
&\quad + mn\gamma x_1x_3^\rho[(z - \ln x_3)(1+\rho) - 2)] + (1+b)(1 - z + \ln x_3)
\end{aligned}$$

where we now have the dimensionless control variable,

$$u=\frac{T_f}{T_c},$$

the dimensionless state variable,

$$x_3=\frac{V}{q}k_{10}\exp(-E_1/RT)C_{A0}^{\alpha-1},$$

and the parameters

$$b=\frac{Ua}{C_p\rho q},\qquad m=\frac{R(-\Delta H_1)c_{A0}}{E_1C_p\rho},\qquad n=\frac{-\Delta H_2}{-\Delta H_1},$$

$$v=\frac{T_cR}{E_1},\qquad z=\ln\left(\frac{V}{q}k_{10}\right)$$

This system of equations may have multiple equlibria, including stable and unstable hyperbolic so some care has to be taken when applying the averaging analysis.

The Hamiltonian becomes

$$H=x_2+\lambda_1(f_1-\dot{x}_1)+\lambda_2(f_1-\dot{x}_2)+\lambda_3(f_1-\dot{x}_3).$$

Since the controlled variable appears only in the heat balance equation, this implies

$$\frac{\partial H}{\partial u}=\lambda_3 x_3(z-\ln x_3)^2 v \text{ and } \frac{\partial^2 H}{\partial u^2}=0$$

It follows that $\lambda_3=0$ so that we get

$$\Pi=\frac{A\omega^2+B}{\omega^4+C\omega^2+D}$$

where the expressions for parameters are given in Table 7. Since $\lim_{\omega\to\infty}\Pi(\omega)=0$ it follows that high-frequency periodic forcing has no effect on the yield.

The low-frequency limit is harder to analyze in the general case, since

$$\Pi(0)=\frac{B}{D}$$

and B is a fairly complicated function of the system parameters. In the case of perturbations around the optimum steady-state yield

$$\lambda_1=\frac{\alpha x_1^{\alpha-1}x_3}{1+\alpha x_1^{\alpha-1}x_3+\gamma x_3^{\rho}},\lambda_2=1 \text{ and } \lambda_3=0$$

Restricting the analysis to first-order reactions we have result 6.

Result 6. Low-frequency periodic perturbation of the feed temperature T_c always leads to a decrease of the yield relative to the optimum steady state for first-order parallel reactions.

Proof. The state variables become

$$x_1=\frac{1}{1+x_3+\gamma x 1_3^{\rho}},\quad x_1=x_1x_3,\quad x_3=\left[\frac{1}{\gamma(\rho-1)}\right]^{\frac{1}{\rho}}$$

Substitution into the expression for Π gives

$$\Pi=\frac{c^2b^2a}{(cg-df)^2}$$

thus,

$$a=\frac{-\rho x_1}{x_3(1+x_3+\gamma x_3^{\rho})}<0$$

qed.

For higher-order systems, B has to be evaluated in each individual case. It is certainly possible for periodic control to improve upon the optimal yield for higher-order reactions when a heat balance is included. An example involving second-order reactions and a heat balance is given by Douglas (1978).

Conclusions

We have analyzed the feasibility of using periodic perturbation in the temperature to improve yield in a few simple reactions occurring in CSTR's. The main conclusion of this work is that if the activation energy of the desired reaction is larger than that of the undesired, then there is an incentive to apply periodic control. The effect is maximized using high frequency for first- and second-order parallel and equilibrium reactions. This obviously has consequences for the design and control of such systems.

If the activation energy of the desired reaction is greater than that of the undesired, then high-frequency periodic perturbations leads to a deterioration of the performance. However, there exists windows in parameter space where low-frequency periodic control can be used to improve yield. The size of these windows increases with temperature. Low-frequency periodic perturbations may lead to an improvement provided that the reactor in not operating at the optimal steady-state yield condition, but at some elevated temperature or residence time. We show that proper periodic controls do not exist in the case of first-order parallel and equilibrium reactions. In the case of second-order parallel reactions and first-order consecutive reactions, proper periodic controls exist.

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Notation

a = amplitude of periodic forcing
A,B,C,P = chemical species
C_A,C_{A0} C_B,C_{B0} = compositions
C_p = molar heat capacity
E_1,E_2 = activation energies
H = Hamiltonian
q = liquid volumetric flow rate
R = gas constant
t,t' = dimensionless and real time
T = temperature

T_c = coolant temperature
T_f = feed temperature
u = dimensionless temperature
$\bar{u}$ = average value for u
u^o = optimal steady-state value for u
Ua = heat flux
V = reactor volume
k_{10}, k_{20} = frequency factors
x_2 = yield
$\bar{x}_2$ = average value of x_2
x_2^o = optimal steady state for x_2

Greek letters

α, β = reaction order
γ = dimensionless parameter related to the residence time
Δ = change in steady-state yield (function of $\bar{u}, \theta, a, \omega$)
ΔH = heat of reaction
θ = vector of system parameters ($\alpha, \beta, \gamma, \rho$)
λ = vector of Lagrange multipliers
ρ = ratio of activation energies (E_2/E_1)
ω = frequency of periodic forcing

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