"The time average performance from periodic reactor operation is sometimes superior to that obtained from steady state processing."

Effects of Pulsed Operations on Isothermal Reactions in a CSTR

by

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ABSTRACT

This paper shall look into the possible effects of deliberate unsteady state processing brought about by introducing sinusoidal fluctuations to stable plants. This practice is commonly referred to as PULSED operations. Effects of input disturbances such as sinusoidal variations in feed rate and/or feed composition are reflected on the time average value of the system output. It will be shown that the time average performance from periodic reactor operation is sometimes superior to that obtained from steady state processing.

The following cases are considered. (1) second order, irreversible reaction in an isothermal CSTR, $2A \rightarrow B$ and (2) results of work done by other authors on complex reactions using parallel reactions, $2A \rightarrow B$ and $A \rightarrow C$, and consecutive reactions $nA \rightarrow B \rightarrow C$.

INTRODUCTION

Most chemical processes are designed to operate at steady-state conditions. Some of the reactor inputs vary with time, but the steady-state design is based on the time average value of these fluctuating quantities. Physically, these input disturbances are removed or damped by installing surge tanks or control systems, so that the controlled plant is forced to have a relatively constant output close to the optimum steady state value. The aim of this paper is to show that the time average value of the outputs from periodic reactor operation due to forced oscillations results, in some cases, in a time average performance superior to steady-state design.

The case of introducing sinusoidal inputs to stable plants, commonly referred to as PULSED operations, is the simplest to handle mathematically. For a more general treatment of periodic processes, the reader is referred to work done by Horn and Lin (3). As a first case, a second order, irreversible reaction in an isothermal CSTR is considered. To estimate the potential advantages of this type of processing a perturbation analysis is used to approximate the periodic output of the process. Then, results of work done by Dorawala and Douglas (4) and Horn (3) are discussed for complex reaction mechanism.

Case I. Second order, irreversible reaction, $2A \rightarrow B$.

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Steady State Design

The conventional approach used in the design of a chemical reactor is first to determine the optimum steady-state design. For case I, the reaction rate is given by the expression

$$r = KA^2 \qquad (1)$$

We would like to produce G lbmoles/hr of product B using a CSTR having a cost C_v(₱/ft^3-hr), which includes all the operating costs and capital costs on a depreciated basis. The feed mixture is assumed to have an average composition A_{fs} (lbmoles/ft^3), and the cost of the feed stream may be taken as C_f (₱/lbmole A). If it is assumed that the cost required to separate A and B in the product stream is negligible and that A cannot be recycled, the calculation for optimum reactor design is as follows:

The total cost C_T, is given by the equation

$$C_T = C_v V_R + C_f q A_{fs} \qquad (2)$$

where V_R is the reactor volume (ft^3) and q is the feed rate (ft^3/hr). A steady state material balance on the reactor shows that

$$q (A_{fs} - A) = KV_R A^2 \qquad (3)$$

and the production rate may be written as

$$G = \frac{q (A_{fs} - A)}{2} \qquad (4)$$

If we let

$$x = \frac{A}{A_{fs}} \qquad (5)$$

then the above relationships provide sufficient information to determine the optimum conversion which satisfies $\frac{\partial C_T}{\partial x} = 0.$

The optimum conversion can be solved and the resulting equation is of the form:

$$x^2 = \frac{C_v}{KC_f A_{fs}^2} (1 - x) \qquad (6)$$

Thus, the optimum steady-state design procedure is straightforward.

Sinusoidal Variations in Feed Composition

(a) System Dynamics Negligible (low-frequency sinusoidal fluctuations)

Consider the case where the reactant material composition varies with time according to the equation

$$A_f = A_{fs} (1 + a \sin \omega t) \qquad (7)$$

Provided that the feed rate remains constant, (i.e, only the feed composition varies), the average cost of reactants is not affected.

To develop an expression for the time dependence of the fraction of unconverted material in the reactor effluent, the case where the frequency fluctuations in feed composition is very low will be considered. For this case, system dynamics is negligible; hence, the accumulation term in the material balance can be neglected. The mass balance equation is given by equation (3)

$$q\,(A_f - A) - KV_R A^2 = 0$$

By manipulation of the material balance equation and dividing through by A_{fs}:

$$\frac{A_f}{A_{fs}} - \frac{A}{A_{fs}} - \frac{KV_R A_{fs}}{q}\left(\frac{A}{A_{fs}}\right)^2 = 0 \qquad (8)$$

Let $x = \dfrac{A}{A_{fs}}$

$x_f = \dfrac{A_f}{A_{fs}}$ and $V = \dfrac{KV_R A_{fs}}{q}$

Equation (8) can be rewritten as:

$$x_f - x - Vx^2 = 0$$

Solving for x by the quadratic formula:

$$x = -\frac{1}{2V}\left[1 - (1 + 4\,Vx_f)^{1/2}\right] \qquad (9)$$

If the operation were to be at steady state, $A_f = A_{fs}$ and $x_f = 1.0$. Therefore,

$$x_s = -\frac{1}{2V}\left[1 - (1 + 4V)^{1/2}\right] \qquad (10)$$

where x_s is the steady state conversion.
Going back to equation (9) and expanding in a Taylor's series about $x_f = 1$,

$$x = x_s + \frac{\partial x}{\partial x_f}(x_f - 1) + \frac{1}{2}\frac{\partial^2 x}{\partial x_f^2}(x_f - 1)^2 + \ldots.$$

Carrying out the differentiation, we get

$$x = x_s + (1 + 4V)^{-1/2}(a \sin \omega t) - V\,(1 + 4V)^{-3/2}(a \sin \omega t)^2 + \ldots$$

The average value of x corresponding to

$$x_{av} = \frac{1}{T} \int_0^T xdt \text{ where T corresponds to one period is}$$

found to be

$$x_{av} = x_s - \frac{1}{2} a^2 V (1 + 4V)^{-3/2} \tag{11}$$

This final equation shows the time average effluent composition of reactant to be lower than the steady state value,therefore better conversion. This behavior is due to the presence of the non-linear reaction rate term, that is, more is gained when the feed composition is high than that which is lost when it is low. Therefore, the periodic process gives a higher time average conversion or that the same production rate can be achieved with a lower flow rate, thereby decreasing the raw material cost. This result is more explicit if we consider average production rate as follows:

$$G_{av} = \frac{q}{2T} \int_0^T (A_f - A)\, dt$$

Dividing by A_{fs} and using the definition for x:

$$G_{av} = \frac{q\, A_{fs}}{2} \left[1 - \frac{1}{T} \int_0^T xdt\right]$$

$$G_{av} = \frac{q\, A_{fs}}{2} \left[1 - x_s + \frac{1}{2} a^2 V (1 + 4V)^{-3/2}\right] \tag{12}$$

We observe from equation (12) that the production rate is higher than that predicted by the optimum steady state design, eqn. (4):

$$G_{av_s} = \frac{q\, A_{fs}}{2} (1 - x_s)$$

As in the case of the steady state design, we can use equation (12) back into the cost equation (eqn. (2)) to arrive at optimum conditions.

The approach used above should indicate the proper type of behavior of the systems under consideration unless it is possible to have resonance effects in the system.

(b) Dynamics of Nonlinear Reactor (high frequency sinusoidal fluctuations)

To determine the effect of high frequency fluctuations on the process it is necessary to include the accumulation term in the material balance equation.

$$V_R \frac{dA}{dt} = q (A_f - A) - KV_R A^2$$

$$\text{Let } \tau = \frac{qt}{V_R}, \quad \omega_o = \frac{V_R \omega}{q}, \quad x = \frac{A}{A_{fs}}, \quad V = \frac{KV_R A_{fs}}{q} \tag{13}$$

By using eqn. (13), we can reduce the material balance equation to the form

$$\frac{dx}{d\tau} + x + Vx^2 = x_f = \frac{A_f}{A_{fs}} = 1 + a \sin \omega_o \tau \tag{14}$$

The preceding nonlinear equation for the frequency response is a nonhomogeneous Ricatti equation. The frequency response of this nonlinear system will be approximated by considering a linearized system of equations and an approximate solution will be developed using perturbation techniques.

The solution is presented as follows:

$$\text{Let } x = x_s + y \qquad , \qquad \alpha = 2Vx_s \tag{15}$$

Substitute equation (15) into equation (14):

$$\frac{d(x_s + y)}{d\tau} = x_f - (x_s + y) - V(x_s + y)^2$$

$$\frac{dy}{d\tau} = (1 + a \sin \omega_o \tau) - x_s - y - V(x_s^2 + 2x_s y + y^2) \tag{16}$$

Note that for steady state conditions: $1 - x_s - Vx_s^2 = 0$

Then, equation (16) can be manipulated to the form

$$\frac{dy}{d\tau} + (1 + \alpha) y = a \sin \omega_o \tau - uV y^2 \tag{17}$$

We have inserted an artificial parameter u before the nonlinear term to keep track of the order of magnitude of various correction terms.

The perturbation solution is now developed by assuming a solution of the form

$$y = y_o + uy_1 + u^2 y_2 + \dots\dots \tag{18}$$

Substituting this back into equation (17), we obtain

$$\frac{d(y_o + uy_1 + u^2y_2 + \dots)}{d\tau} + (1 + \alpha)(y_o + uy_1 + u^2 y_2 + \dots) =$$

$$= a \sin \omega_o \tau - uV(y_o + uy_1 + u^2 y_2 + \dots)^2$$

Equating terms having like coefficients of power of u:

(a) $$\frac{dy_o}{d\tau} + y_o + \alpha y_o = a \sin \omega_o \tau$$

(b) $$\frac{dy_1}{d\tau} + y_1 + \alpha y_1 = - V y_o^2$$

(c) $$\frac{dy_2}{d\tau} + y_2 + \alpha y_2 = - 2 V y_o y_1$$

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The pseudo-steady state solution of equation (a) is obtained by taking the particular solution $y_{p_o} = A \sin \omega_o \tau + B \cos \omega_o \tau$.

By using the expression for y_{p_o} in equation (a) and comparing coefficients, we find that

$B = -A\omega_o/(1+\alpha)$

and $A = a(1+\alpha)/(\omega_o^2 + (1+\alpha)^2)$

Hence,

$$y_o = y_{p_o} = \frac{a}{\omega_o^2 + (1+\alpha)^2} \left\{ (1+\alpha) \sin \omega_o \tau - \omega_o \cos \omega_o \tau \right\} \tag{19}$$

Now that we have the expression for y_o, we can solve for y_1 by substituting y_o back into equation (b):

$$\frac{dy_1}{d\tau} + (1+\alpha) y_1 = -V \left\{ \frac{a^2}{[\omega_o^2 + (1+\alpha)^2]^2} \right\} \left\{ (1+\alpha) \sin \omega_o \tau - \omega_o \cos \omega_o \tau \right\}^2$$

$$= -V \left\{ \frac{a^2}{(\omega_o^2 + (1+\alpha)^2)^2} \right\} \left\{ (1+\alpha)^2 \sin^2 \omega_o \tau - 2(1+\alpha)(\omega_o \sin \omega_o \tau) (\cos \omega_o \tau) + \omega_o^2 \cos^2 \omega_o \tau \right\} \tag{20}$$

The following trigonometric identities were used:

$$2 \sin \omega_o \tau \cos \omega_o \tau = \sin (2\omega_o \tau)$$

$$\sin^2 \omega_o \tau = 1 - \cos^2 \omega_o \tau$$

$$\cos^2 \omega_o \tau = \frac{1}{2} + \frac{\cos 2\omega_o \tau}{2}$$

Manipulation of equation (20) and using the above trigonometric identities,

$$\frac{dy_1}{d\tau} + (1+\alpha) y_1 = \frac{-a^2 V}{[\omega_o^2 + (1+\alpha)^2]^2} \left\{ \frac{\omega_o^2 + (1+\alpha)^2}{2} + [\omega_o^2 - (1+\alpha)^2] \frac{\cos (2\omega_o \tau)}{2} - (1+\alpha)\omega_o \sin (2\omega_o \tau) \right\}$$

The particular solution of the above equation is then taken to be:

$$y_{p_1} = A + B \cos (2\omega_o \tau) + C \sin (2\omega_o \tau) \tag{21}$$

Substitute back equation (21) into the expression for y_1 and comparing coefficients as before, we find that:

$$A = \frac{-a^2 V}{2(1+\alpha)\,[\omega_o^2 + (1+\alpha)^2]}$$

$$B \quad \frac{-a^2 V}{[\omega_o^2 + (1+\alpha)^2]^2} \left\{ \frac{5\omega_o^2 - (1+\alpha)^2}{2} \right\} \left\{ \frac{1+\alpha}{4\omega_o^2 + (1+\alpha)^2} \right\}$$

$$C = \frac{a^2 V\omega_o}{[\omega_o^2 + (1+\alpha)^2]^2} \left\{ \frac{2(1+\alpha)^2 - \omega_o^2}{4\omega_o^2 + (1+\alpha)^2} \right\}$$

Therefore,

$$y_{p_1} = y_1 = \frac{-a^2 V}{2(1+\alpha)\,[\omega_o^2 + (1+\alpha)^2]} - \frac{a^2 V}{[\omega_o^2 + (1+\alpha)^2]^2}$$

$$\left\{ \frac{(1+\alpha)\,[5\omega_o^2 - (1+\alpha)^2]}{2\,[4\omega_o^2 + (1+\alpha)^2]} \right\} \cos(2\omega_o \tau) + \frac{a^2 V\omega_o}{[\omega_o^2 + (1+\alpha)^2]^2}$$

$$\left\{ \frac{2(1+\alpha)^2 - \omega_o^2}{4\omega_o^2 + (1+\alpha)^2} \right\} \sin(2\omega_o \tau)$$

Although it is possible to evaluate the second order correction function from the above equations, we will assume that the two terms are adequate for our purpose. Therefore, the complete solution with u = 1 is:

$$y = \left\{ \frac{a}{[\omega_o^2 + (1+\alpha)^2]} \right\} \left\{ (1+\alpha)\sin(\omega_o \tau) - \omega_o \cos(\omega_o \tau) \right\}$$

$$- \frac{a^2 V}{2(1+\alpha)\,[\omega_o^2 + (1+\alpha)^2]} + \frac{a^2 V}{[\omega_o^2 + (1+\alpha)^2]^2}$$

$$\left\{ \left[\frac{(1+\alpha)\,[(1+\alpha)^2 - 5\omega_o^2]}{2\,[4\omega_o^2 + (1+\alpha)^2]} \right] \cos(2\omega_o \tau) + \left[\frac{2(1+\alpha)^2 - \omega_o^2}{4\omega_o^2 + (1+\alpha)^2} \right] \omega_o \sin(2\omega_o \tau) \right\}$$

Hence, the frequency response of the nonlinear system can be written, approximately, as the linear frequency response, plus a d-c component, plus higher harmonics. The time average value of the output is therefore:

$$x_{av} = x_s - \frac{a^2 V}{2(1+\alpha)\,[(1+\alpha)^2 + \omega_o^2]} \qquad (22)$$

where α has previously been defined as $2Vx_s$.

Result from the steady-state calculation has

$$x_s = -\frac{1}{2V}\left\{1-(1+4V)^{1/2}\right\}$$

From x_s equation, $(1+\alpha) = (1+4V)^{1/2}$

Finally, going back to equation (22):

$$x_{av} = x_s - \frac{a^2 V}{2(1+4V)^{1/2}\,[(1+4V)+\omega_o^2]} \tag{23}$$

Observe from equation (23) that low-forcing frequencies ($\omega_o \approx o$), this equation becomes identical to the case where the system dynamics are negligible (see equation (11). At very high frequencies, the change in the average operating level approaches zero or that $x_{av} \approx x_s$. This is in complete accord with our intuition, for we expect that low frequency signals will not be damped as they pass through a first-order dynamic system but that high-frequency inputs will be almost completely damped.

Results of work done by Douglas and Rippin (1) on the effects of amplitude and frequency variations in the system are shown in Fig. 1 and 2. The values of the parameters used in this study are given in Table 1.

Sinusoidal Variations in Feed Rate

a) System Dynamics Negligible (low frequency fluctuations)

If we now allow the feed flow rate to vary sinusoidally as given by the equation

$$q = q_s + b\sin\omega t\,, \tag{24}$$

the material balance equation is then written as follows:

$$(q_s + b\sin\omega t)\,(A_f - A) - KVA^2 = 0$$

Using a similar procedure as before, we find that

$$x = \frac{1+\dfrac{b\sin\omega t}{q_s} - \left\{\left(1+\dfrac{b\sin\omega t}{q_s}\right)^2 + 4V\left(1+\dfrac{b\sin\omega t}{q_s}\right)\right\}^{1/2}}{-2V} \tag{25}$$

To get the deviation from steady-state operation, we have defined

$$y = x - x_s \qquad (15)$$

We then get the difference between equation (25) and equation (10).

$$(x_s - x) = \frac{1}{2V}\left\{\frac{b\sin\omega t}{q_s} - \left\{(1+\frac{b\sin\omega t}{q_s})^2 + 4V\right.\right.$$
$$\left.\left.(1+\frac{b\sin\omega t}{q_s})\right\}^{1/2} - (1+4V)^{1/2}\right\}$$

Taking the time average difference

$$(x_s - x)_{av} = -\frac{1}{2V}\left\{\frac{1}{T}\int_o^T \left[(1+\frac{b\sin\omega t}{q_s})^2 + 4V (1+\frac{b\sin\omega t}{q_s})\right]^{1/2} dt + (1+4V)^{1/2}\right\}$$

$$x_{av} = x_s + \frac{(1+4V)^{1/2}}{2V} + \frac{1}{2V}\ \frac{1}{T}\int_o^T \left[(1+\frac{b\sin\omega t}{q_s})^2 + 4V (1+\frac{b\sin\omega t}{q_s})\right]^{1/2} dt$$

The time average x will always be greater than x_s resulting in lower conversion.

(b) Effect of System Dynamics (high frequency fluctuations)

To evaluate the effect of higher frequency perturbation on the system, we take into account system dynamics. The equations used as follows:

$$V\ \frac{dA}{dt} = q\,(A_f - A) - KVA^2$$

where $q = q_s + b\sin\omega t$

A simulation of this type of process was undertaken by Douglas and Rippin (1) on an analog computer. Figure 3 shows the effects of amplitude on the system while Figure 4 shows the effects of frequency. The parameters used are given in Table 1. We note from these figures that the average conversion decreases due to the sinusoidal variations in feed rate.

SIMULTANEOUS FEED COMPOSITION AND FLOW RATE VARIATIONS

What happens when we simultaneously introduce sinusoidal variations in feed composition and flow rate? From various results, we might expect that the reduced performance caused by flow oscillations would just partially cancel out the improvements obtained with composition fluctuations.

For this case, we shall use both feed-composition and flow rate disturbances

$$A_f = A_{fs}\,(1 + a\sin\omega t)$$

$$q = q_s\,[1 + b\sin(\omega' t + \theta)]$$

where θ is the phase angle between the composition and flow fluctuations. This case has been considered in previous work done by Douglas (2). His results are presented here.

$$\text{Let } x = A/A_{fs}\,,\ Q = q_s A_{fs}/G\,,\ V = KV_R\ A_{fs}/q_s$$

$$\omega_1 = V_R\,\omega/q_s\,,\ \omega_2 = V_R\,\omega'/q_s\,,\ \tau = q_s t/V_R$$

Case 1. Effects of System Dynamics Negligible

For very low frequency disturbances,

$$x = -\frac{q}{q_s}\ \frac{1}{V}\ \left\{(1 - + 4V\frac{A_f}{A_{fs}}\ \frac{q_s}{q})^{1/2}\right\}$$

Expanding this equation in a Taylor's series about the steady-rate condition gives:

$$x = x_s + a\,(1 + 4V)^{-1/2} \sin \omega_1 \tau\ + b\,[1 + 2V - (1 + 4V)^{1/2}]$$

$$[2V\,(1+ 4V)^{1/2}]^{-1}\ \sin \omega_2\ \tau + \theta) - a^2V\,(1 + 4V)^{-3/2}\ \sin^2\omega_1 \tau$$

$$- b^2V\,(1 + 4V)^{-3/2}\ \sin^2\,(\omega_2\,\tau + \theta) + ab\,2V\,(1 + 4V)^{-3/2} \sin \omega_1 \tau \sin\,(\omega_2 \tau\ + \theta) + \ldots$$

Taking the average fraction of material unconverted, we get

$$x_{av} = x_s - \frac{1}{2V}\ (1 + 4V)^{-3/2}\,(a^2 + b^2 - 2ab \cos \theta) \tag{26}$$

where the term ab cos θ is present only if $\omega_1 = \omega_2$. We observe that maximum improvement in conversion is obtained when

(i) the amplitudes a and b, are large

(ii) $\omega_1 = \omega_2$

(iii) $\theta = 180^\circ$

Case 2. Effect of System Dynamics

The system of equations being considered for this case are the following:

$$V_R\ \frac{dA}{dt} = q\,(A_f - A) - KV_R A^2$$

$$A_f = A_{fs}\,(1 + a\sin\omega t)$$

$$x = x_s + y,\ \alpha = 2Vx_s$$

$$q = q_s\ [1 + b\sin\,(\omega t + \theta)]$$

Using the above equations, we come up with

$$\frac{dy}{d\tau} + (1 + \alpha)y = a \sin \omega_1 \tau + b\,(1 - x_s) \sin\,(\omega_2 \tau + \theta)$$

$$+\ \mu' ab\sin\,\omega_1 \tau \sin\,(\omega_2 \tau + \theta) - \mu' b \sin\,(\omega_2 \tau + \theta)\,y - \mu' Vy^2$$

where the arbitrary constant μ' has been introduced in front of the terms which make an analytical solution difficult.

We proceed with the same perturbation solution as before and end up with an expression for the average value of x as follows:

$$x_{av} = x_s + m_1 \sin \omega \tau + m_2 \cos \omega \tau + \frac{m_3}{1+\alpha} +$$

$$\frac{m_4 (1+\alpha) + 2 m_5 \omega}{(1+\alpha)^2 + 4\omega^2} \sin 2\omega\tau + \frac{m_5 (1+\alpha) - 2 m_4 \omega}{(1+\alpha)^2 + 4\omega^2} \cos 2\omega\tau$$

where $\omega_1 = \omega_2 = \omega$

$$m_1 = \frac{[a + b(1 + x_s)\cos\theta](1+\alpha) + b(1 - x_s)\sin\theta}{(1+\alpha)^2 + \omega^2}$$

$$m_2 = \frac{b(1 - x_s)\sin\theta\,(1+\alpha) - [a + b(1 - x_s)\cos\theta]}{(1+\alpha)^2 + w^2}$$

$$m_3 = \frac{1}{2}\,[ab\cos\theta - bm_1\cos\theta - bm_2\sin\theta - m_1^2 V - m_2^2 V]$$

$$m_4 = \frac{1}{2}\,[ab\cos\theta - bm_1\sin\theta - bm_2\cos\theta - m_1 m_2 V]$$

$$m_5 = \frac{1}{2}\,[-ab\cos\theta + bm_1\cos\theta - bm_2\sin\theta + m_1^2 V - m_2^2 V]$$

Result from work done by Douglas and Rippin (1) is shown in Figure 5. This plot shows that if both flow rate and flow composition vary with the same frequency, the outcome depends on the phase angle between the two signals. This seems to imply that to be able to get better conversion, we should introduce flow fluctuations such that it amplifies the effect of feed composition fluctuations rather than cancel it out, a contradiction of what is to be expected. In terms of physical considerations, however, this is quite reasonable since we decrease the flow rate when the feed composition is high and increase it when the feed composition is low, and because of the non-linear reaction rate, we gain more in the first case than we lose in the second.

EXTENSIONS TO COMPLEX REACTIONS

Dorawala and Douglas (4) used the perturbation technique analysis for complex kinetic mechanisms occurring in a CSTR. Their results for both isothermal and non-isothermal cases are presented here. The cases considered are given below:

Case 1. Consecutive reactions $nA \rightarrow B \rightarrow C$

$$V\frac{dA}{dt} = q(A_f - A) - K_1 V A^n$$

$$V\frac{dB}{dt} = q(B_f - B) + K_1 V A^n - K_2 V B$$

$$VC_p\,\rho\,\frac{dT}{dt} = q\,C_p\,(T_F - T) - \mu_a (T - T_c) + (-\Delta H_1) K_1 V A^n$$

$$+ (-\Delta H_2) K_2 V B$$

Case 2. Parallel reactions $2A \longrightarrow B$

$A \longrightarrow C$

$$V \frac{dA}{dt} = q(A_f - A) - K_1 VA^2 - K_2 VA$$

$$V \frac{dB}{dt} = q(B_f - B) + K_1 VA^2$$

$$VC_p \rho \frac{dT}{dt} = qC_p \rho (T_F - T) - \mu_a (T - T_c) + (-\Delta H_1) K_1 VA^2 + (-\Delta H_2) K_2 VA$$

For the parallel reaction case, Horn (3) found that the reactor temperature which maximized the yield of component B was finite only if $nE_2/E_1 > 1$, where n is the order of the first reaction ($n = 2$ in case 2). Horn also showed that there would be some periodic processes which had a time average yield in excess of the optimum steady-state value, provided that $E_2/E_1 < 1$.

ISOTHERMAL REACTORS

The results for the parallel reaction problem with flow rate variations and system parameters listed in Table II are given in Figure 6. From the graph, there is a qualitative agreement between the approximate analytical result and the numerical solution. This is accounted for by the fact that only the first order correction functions were included in the perturbation analysis. The linearized dynamic equations for this case have a pair of negative real roots so that the fact that the improvement goes through a maximum as the driving frequency increases seems surprising to the authors.

Figure 7 shows the dimensionless concentration of desired product B versus time. Only the linear frequency response and the constant terms of the analytical solution are plotted. Still, there seems to be a good agreement between the analytical and numerical results. This implies that the quadratic nonlinearity and the time variable coefficient do not produce much distortion for these 10 percent amplitude flow rate fluctuations, although the analytical solutions predict that the distortion increases with the square of the input amplitude.

For the consecutive reaction case, the parameters used are given in Table II and the results given in Figure 8. It is observed that both analytical and numerical solutions predict that the time average yield of the oscillating system is poorer than the optimum design at low frequencies, but that at some point the direction of the shift in average operating level changes sign so that an improved performance is obtained. This result demonstrates that any attempt to use the steady-state equations to evaluate the effect of oscillations on a system can be misleading. The maximum shift in the time average yield is very small, however, so that the linear frequency response provides an excellent description of the output oscillations.

NONISOTHERMAL REACTORS

Dorawala and Douglas expected much larger differences between the time average and optimum steady-state yields for this case since the system has an exponential nonlinearity in temperature and because the linearized system equations can have a pair of complex conjugate roots with a low damping coefficient, that is, the linearized equations can exhibit resonance. They also expected to obtain the greatest improvements when the forcing frequency is near the resonant value since the system amplifies the effects of fluctuating inputs in this region. Results for the parallel reaction case for several input amplitudes are shown in Figure 9. The approximate analytical solutions are in excellent agreement with numerical solutions, provided that the curves resemble trigonometric functions. However, when there is a very large distortion it becomes necessary to evaluate more correction terms in order to obtain a good agreement. This is unfortunate since the maximum improvement is obtained when the distortion is large. Hence, it is always necessary to use numerical solutions for the equations. The analytical results can only be used to obtain first estimates of the direction of the shift in the time average performance and to find the system parameters which have the greatest effect on that shift.

CONCLUSION

A perturbation analysis may be used to obtain an approximate analytical solution for the frequency response of nonlinear systems. The results show that the average value of the output for systems in periodic operation is different from the steady-state value, although this difference is small for mild nonlinearities; for highly non-linear systems or those which exhibit resonance, the deviations may be very significant.

The optimum steady-state design does not always correspond to maximum profit. Also, the results show that the standard control problem of designing a control system to compensate for input disturbances might not always be the best control strategy.

For systems which do not exhibit resonance, it is possible to estimate the difference between the steady-state behavior and the time average behavior using only the steady-state equations describing the system.

In some cases, the time average yield of a complex reaction in a periodically operated reactor is superior to the optimum steady-state design value. For complex reaction mechanisms, the perturbation analysis only provides a useful tool for obtaining first estimates and minimizing the amount of numerical computation.

The magnitude of improvement due to periods as seen from work done by Douglas and Rippin is really very small. Also, improvements on more complex mechanisms from work done by Dorawala and Douglas cannot be generalized for all types of systems.

From all of the above, we conclude that, much work, both theoretical and experimental, has yet to be done to finally establish the worth of periodic operation.

Table 1. Parameters for Isothermal Reactor

STEADY STATE
$V = 100,\ K = 1.2,\ q_s = 10,\ A_{fs} = 1.0$

Taken from J.M. Douglas and D.W.T. Rippin (1)

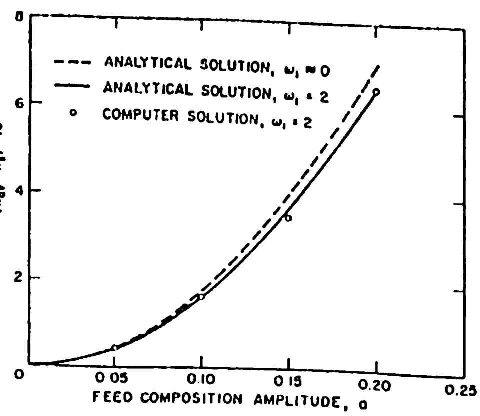

Figure 1. Effect of Feed Composition Perturbation Amplitude

Taken from J.M. Douglas (2).

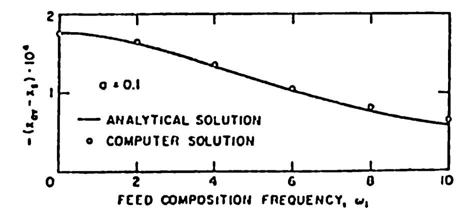

Figure 2. Effect of feed composition perturbation frequency

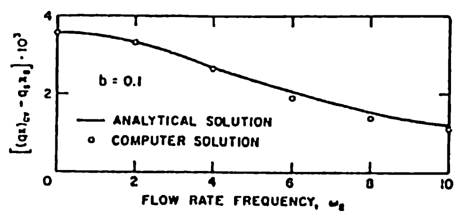

Figure 4. Effect of flow rate perturbation frequency

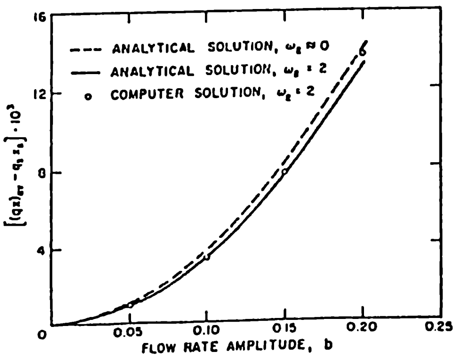

Figure 3. Effect of flow rate perturbation amplitude

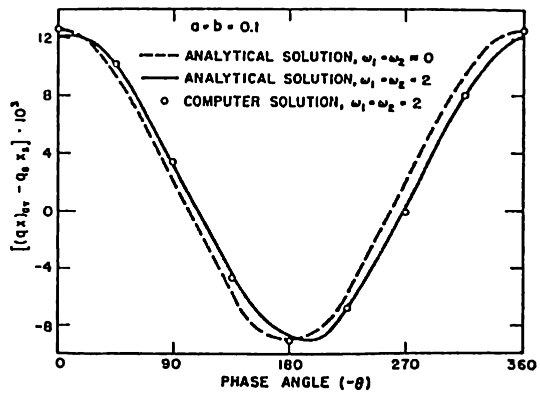

Figure 5. Simultaneous feed composition and flow rate disturbances

Taken from J.M. Douglas (2).

Table 2. System Parameters for Sinusoidal Inputs

Parameters	Parallel reactions			Consecutive reactions	
Reaction	$2A \rightarrow B, A \rightarrow C$	$2A \rightarrow B, A \rightarrow C$		$2A \rightarrow B \rightarrow C$	$A \rightarrow B \rightarrow C$
Energy	Isothermal	Nonisothermal		Isothermal	Nonisothermal
Fluctuation	q	q	T_f	q	q
A_f	0.01	0.01	0.01	1.0	0.0271
B_f	0	0	0	0	0
q_s	10	10	10	10	10
V	100	100	100	100	100
$C_p \rho$	1.0	1.0	1.0	1.0	1.0
k_{10}	1.0×10^{19}	1.0×10^{19}	1.0×10^{19}	1.0×10^{15}	3.337×10^{12}
k_{20}	9.49×10^{12}	9.49×10^{12}	9.49×10^{12}	7.14×10^{9}	1.721×10^{7}
E_1	28,000	28,000	28,000	29,500	22,800
E_2	21,000	21,000	21,000	22,100	14,820
$(-\Delta H_1)$		27,000	27,000		23,000
$(-\Delta H_2)$		20,000	20,000		1,366
$T_f = T_c$		319.1	319.1		365
U_a		88.5	88.5		327
K_c		1.2	0.5		1.498
A_s	0.00314	0.00314	0.00314	0.333	0.00651
B_s	0.00575	0.00575	0.00575	0.489	0.01302
T_s	333.4	333.4	333.4	400	380

Taken from T.G. Dorawala and J.M. Douglas (4).

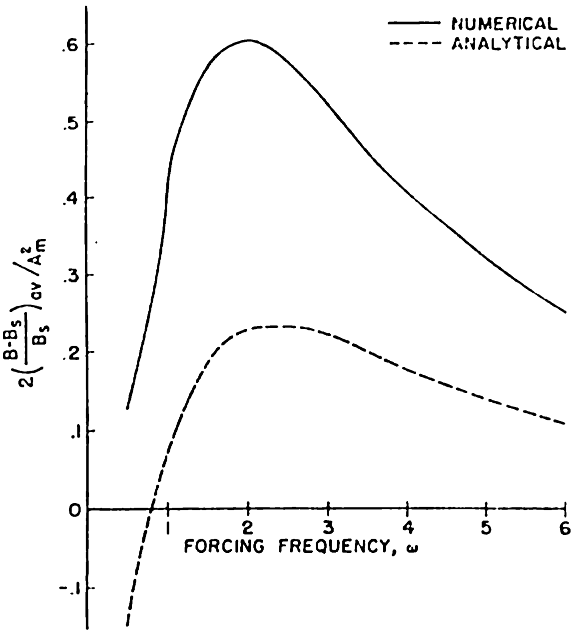

Figure 6. Effect of forcing frequency on the time average yield for parallel reactions.

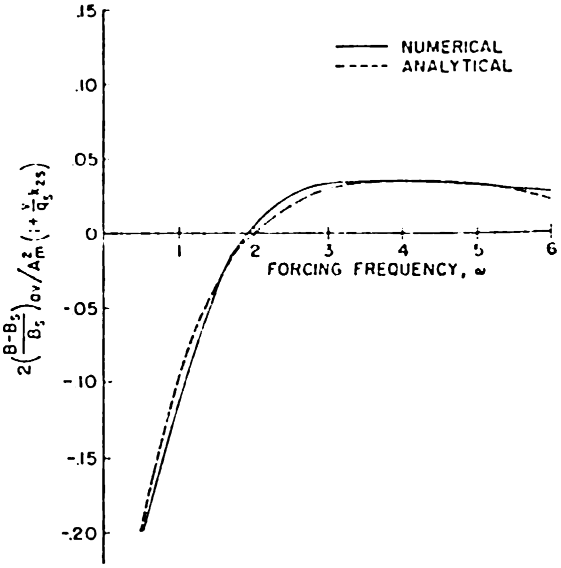

Figure 8. Effect of forcing frequency on the time average yield for consecutive reactions.

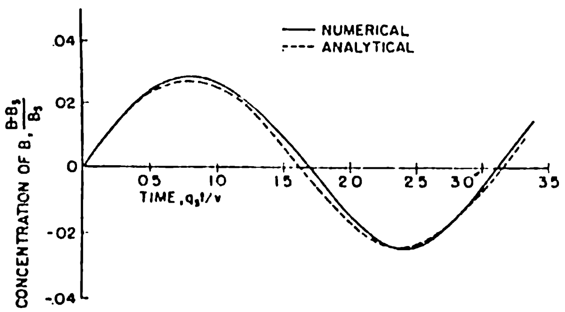

Figure 7. Time dependence of component B for parallel reactions.

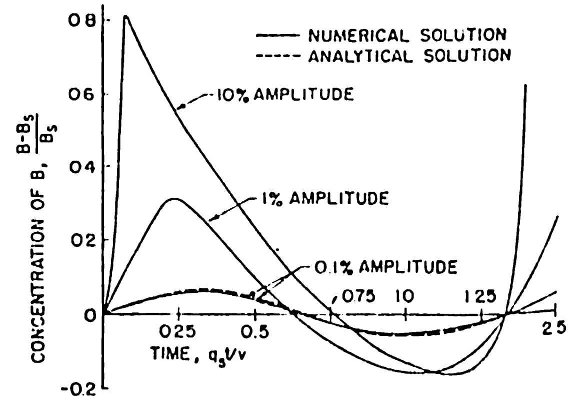

Figure 9. Time dependence of component B for parallel reactions.

Taken from T.G. Dorawala and J.M. Douglas (4).

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