Cyclic Operation of Reaction Systems: Effects of Heat and Mass Transfer Resistance

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Many examples have appeared in the recent literature which demonstrate the possible advantages of cyclic operation over steady state operation. In two different cases involving rather idealized models, it has been shown that very fast switching of process variables, such as temperature in a continuous flow stirred-tank reactor or reactant composition at a catalyst surface, results in better performance than that obtained at the optimum steady state (*3, 4*). In practice, of course, such fast switching is limited by heat and mass transfer resistance. This paper is concerned with the effects of these resistances on the optimum periodic operation of chemical reactors. For both of the examples discussed here it will be seen that there is an optimum period when transport resistance is included in the reactor model.

In the course of the following investigation, some general results on the theory of optimal periodic bang-bang control will be presented. Also, by employing different but related approaches—specifically attainable sets and optimal control theory—in the analysis of the examples, a comparison between these techniques can be made. Although the mathematical characterization of performance differs for these two methods, the same general form of system description will apply for both cases.

Many reaction systems can be characterized by a state vector x

$$x = (x^1, x^2, \ldots, x^b) \tag{1}$$

which is a continuous function of time and whose dynamic behavior is described by

$$\dot{x}(t) = f\{x(t), u(t)\} \quad \text{a.e.} \tag{2}$$

The control vector u

$$u = (u^1, u^2, \ldots, u^n) \tag{3}$$

is in most cases restricted to a set of admissible controls U due to physical limitations on possible control actions. This paper is concerned only with periodic processes where, if τ is the period, the conditions

$$x(t) = x(t + \tau) \tag{4a}$$

$$u(t) = u(t + \tau) \tag{4b}$$

must be satisfied for all t.

Steady state operation is, of course, a special case of a periodic process. For a constant admissible control $(u_* \epsilon U)$, the corresponding steady state x_* is computed from

$$f(x_*, u_*) = 0 \tag{5}$$

In previous publications (*2, 3*) two other special classes of cyclic operation which correspond to very large and very small periods have been treated in a general way. Here the terms large and small mean large or small with respect to the characteristic time for the dynamical system described by Equation (2) to reach steady state. Results obtained in this earlier work will be mentioned in the following development.

EXAMPLE I: PARALLEL REACTIONS IN A CONTINUOUS FLOW STIRRED-TANK REACTOR WITH HEAT FLUX CONTROL

Suppose that the parallel reactions

$$R \rightarrow P_1 \tag{6a}$$

$$R \rightarrow P_2 \tag{6b}$$

are carried out in a continuous flow stirred-tank reactor, where P_1 is the desired product and P_2 is a waste product. It is assumed that Reaction (*6a*) is of α^{th} order and Reaction (*6b*) is first order. The Arrhenius equation will be used to describe the temperature dependence of both reaction rates. The activation energies for (*6a*) and (*6b*) will be denoted as E_1 and E_2, respectively. Furthermore, the flow rate and composition of the feed material are taken as given, constant quantities.

This reaction scheme has already been investigated subject to the assumption that the temperaure in the tank can be controlled (*4*). It was shown that if

$$1 > E_2/E_1 > 1/\alpha \tag{7}$$

cycling of reactor temperature gives a higher output of P_1 than any steady state operation. The largest improvement was obtained, however, by very fast switching of the temperature between upper and lower limits. This policy is clearly impossible in practice, so the model employed in reference *4* will be extended here to include heat transfer resistance.

Instead of temperature, the control variable in the following problem is the heat flux through the reactor wall (see Figure 1). The reactor temperature then becomes a

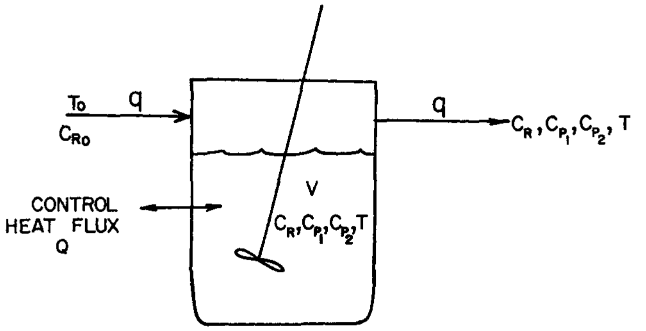

Fig. 1. Schematic diagram of continuous flow stirred-tank reactor with heat flux control. (example I).

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state variable. It is assumed that there is no heat of reaction nor heat of mixing and that the heat capacity per unit volume of reaction mixture is constant. Such a model is chosen to expedite the comparison with the direct temperature control case by minimizing the number of additional system parameters.

The dimensionless conservation equations for the continuous flow stirred-tank reactor with heat flux control can be written in the general form (2), where there are three state variables and the components of f are (see Appendix I)

$$f^1(x, u) = -a_1 e^{-1/x^3}(x^1)^\alpha - a_2 e^{-\delta/x^3}x^1 - x^1 + 1 \quad (8a)$$

$$f^2(x, u) = a_1 e^{-1/x^3}(x^1)^\alpha - x^2 \quad (8b)$$

$$f^3(x, u) = -x^3 + u \quad (8c)$$

Here x^1 is dimensionless R concentration, x^2 dimensionless P_1 concentration, x^3 dimensionless temperature, while the scalar control variable u is a dimensionless quantity directly related to heat flux. Conditions to be cited later apply to maximizing an objective function M of the general form

$$M = \frac{1}{\tau}\int_0^\tau m\{x(t)\}dt \quad (9)$$

Since maximization of P_1 output is desired for this example, here

$$m\{x(t)\} = x^2(t) \quad (10)$$

It can be shown that for any constant control u_*, there is a unique feasible ($x_*^i \geq 0$, $i = 1, 2, 3$) steady state for this system. Also, there is an optimal steady state operation for unrestricted u only if

$$\alpha\frac{E_2}{E_1} > 1 \quad (11)$$

Then the optimal steady control u_{**} is given by

$$u_{**} = \delta/\ln[a_2(\alpha\delta - 1)] \quad (12)$$

If Condition (11) is not satisfied, x_*^2 increases monotonically with u_*.

A sufficient condition for improvement of an optimum steady state process by cycling has appeared in the literature (*4*). For the present problem this condition fails to indicate whether or not improvement is possible. The published results (*4*) concern the case where the temperature and not the heat flux is the control variable. These results show that the faster the cycling of the temperature the higher is the yield of the desired product. Therefore one may conjecture that for the heat flux problem there is an optimum period τ corresponding to a maximum yield. This is suggested by the fact that the effect of fast cycling of the heat flux will be damped out by the system while slow cycling corresponds to slow variations in temperature. In both cases the system is approximately in the steady state most of the time. Therefore the yield of P_1 cannot be larger than at the optimum steady state.

OPTIMAL PERIODIC BANG-BANG CONTROLS

We shall consider a control which is switched periodically between the values $u_1, u_2, \ldots, u_h$. More specifically, the period τ is divided into h consecutive subintervals $t_1, t_2, \ldots, t_h$ such that

$$\sum_{i=1}^{h} t_i = \tau \quad (13a)$$

and for $0 \leq t < \tau$

$$u(t) = u_j \text{ for } \sum_{i=0}^{j-1} t_i \leq t < \sum_{i=0}^{j} t_i \quad (13b)$$

where $t_0 = 0$. These relationships plus the periodicity requirement (*4b*) determine the control for all time.

For fixed values of the switching levels u_j, the objective function becomes a function of the h switching intervals t_j. Necessary conditions for the optimum intervals are obtained by differentiating the objective function M with respect to the intervals t_j. The required derivatives, which may be derived using the calculus of variations (*5*), are

$$\frac{\partial M}{\partial t_j} = \frac{1}{\tau}[m\{x(t^*)\} + \lambda_i(t^*)f^i\{x(t^*), u_j\} - M]\,; \quad j = 1, 2, .., h \quad (14)$$

where t^* is any time in the subinterval of interest:

$$\sum_{i=0}^{j-1} t_i \leq t^* < \sum_{i=0}^{j} t_i \quad (15)$$

In Equation (14) and in the following, the summation convention is used. That is, occurrence of indices in pairs indicates summation over the range of these indices. The adjoint variables λ_i; $i = 1, 2, \ldots, b$, appearing in Equation (14) are continuous functions of time t and satisfy the equations

$$\frac{d\lambda_i(t)}{dt} = -\lambda_j(t)\frac{\partial f^j\{x(t), u(t)\}}{\partial x^i} - \frac{\partial m\{x(t)\}}{\partial x^i} \text{ a.e.}; \quad i = 1, 2, \ldots, b \quad (16)$$

and the periodicity conditions

$$\lambda_i(0) = \lambda_i(\tau), \quad i = 1, 2, \ldots, b \quad (17)$$

For unrestricted t_j, the derivative $\partial M/\partial t_j$ must vanish if the interval is of optimal length. Therefore for optimal periodic bang-bang control, the condition

$$m\{x(t)\} + \lambda_i(t)f^i\{x(t), u(t)\} = M \quad (18)$$

must hold for all t. If the control levels $u^1, u^2, \ldots, u^h$ are given, the optimum switching intervals, which result in satisfaction of Condition (19), can be determined by a hill-climbing method. After guessing a set of intervals $t_1, t_2, \ldots, t_h$, periodic solutions to the state Equation (2) and the adjoint equations (16) for the control (13) are calculated. Using these solutions, Equation (14) is used to evaluate the derivatives $\partial M/\partial t_j$; $j = 1, 2, \ldots, h$. Improved intervals then may be obtained from

$$t_j^+ = t_j + \epsilon\frac{\partial M}{\partial t_j}; \quad j = 1, 2, \ldots, h \quad (19)$$

where ϵ is a sufficiently small positive number. Next the t_j^+ intervals are improved by repeating these steps. This procedure continues until no further significant improvement of the objective function can be obtained. In the calculations which are discussed next, the following step length (ϵ) policy was adopted: ϵ is automatically halved if a step does not increase the objective function, and is tentatively doubled after the execution of three successful improvements.

Returning now to the heat flux control example, this theory will be applied. The control functions considered for this example is one with only two levels, the maximum and minimum values of the heat flux:

$$u_1 = u_{\max}, \text{ used when } 0 \leq t < t_1$$

$$u_2 = u_{\min}, \text{ used when } t_1 \leq t < t_1 + t_2 = \tau \quad (20)$$

The parameter values chosen for a sample calculation are the following:

$$\alpha = 2,\ \delta = 0.55,\ u_{\max} = 0.449,\ u_{\min} = 0.049,$$

$$a_1 = 10{,}0000,\ a_2 = 400.$$

The optimum steady state control and objective function for these parameters are

$$u_{oss} = 0.149,\ M_{oss} = 0.08462$$

The final hill-climbing results for control (20) are shown in Figure 2. Since the objective function for the optimum switching intervals is

$$M_{obb} = 0.09229$$

which is larger than the best steady state performance, cycling is superior to the optimal steady state operation. Also, there is an optimum period.

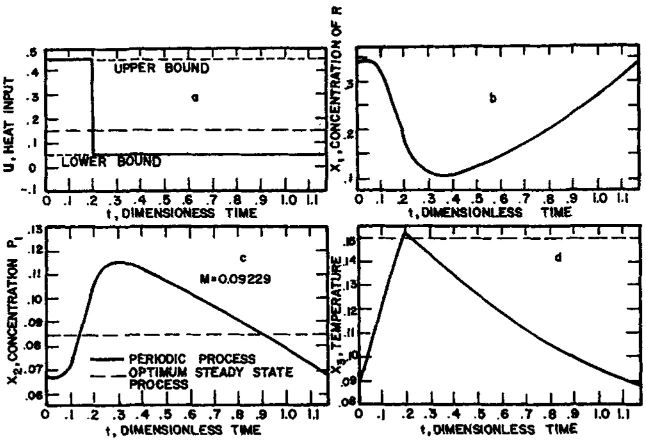

Fig. 2. Hill climbing results for heat flux control problem.

Pontryagin's maximum principle (*6*) can be used as a check on the hypothesis that Equation (20) gives the general form of the optimal heat flux control. This necessary condition for optimality requires that the Hamiltonian

$$H = \lambda_i f^i + m \tag{21}$$

be maximized with respect to u at every time t. Since in this example

$$\frac{\partial H}{\partial u} = \lambda_3 \tag{22}$$

it follows that for optimal control the conditions

$$u = u_{\max} \text{ for } \lambda_3 > 0 \tag{23a}$$

$$u = u_{\min} \text{ for } \lambda_3 < 0 \tag{23b}$$

must be satisfied. The adjoint variable λ_3 corresponding to the optimal control of the form (20) (see Figure 2*a*) is shown in Figure 3 along with this control. It is clear that the maximum principle [that is, Equation (23)] is satisfied.

It is interesting to notice that for this example the neglect of a constraint, that is, the energy balance, followed by analysis of fast switching, gave results which are qualitatively correct for the more exact model. Also, the analysis of the simplified temperature control case provided useful insight regarding a useful trial form of heat flux control. Analogous statements will be seen to apply to the following example in catalytic selectivity.

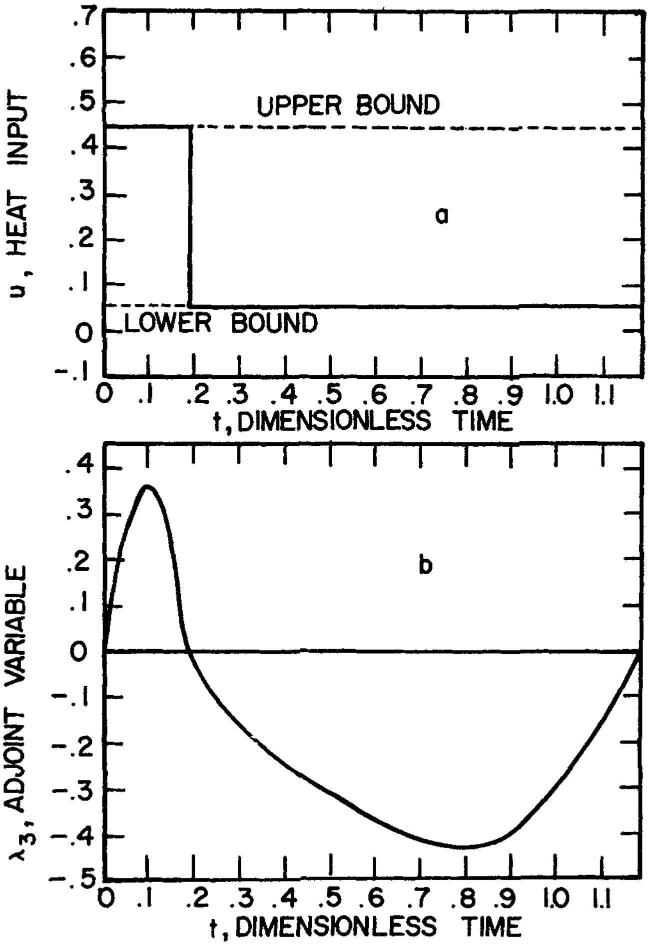

Fig. 3. Bang-bang control and corresponding adjoint variable for heat flux control problem.

EXAMPLE II: CATALYTIC SELECTIVITY FOR A LUMPED-PARAMETER MASS TRANSFER RESISTANCE MODEL

In this example it will be assumed that a single reactant R in the fluid phase reacts in the presence of the catalyst surface to form two fluid products, P_1 and P_2, by means of the reaction system

$$R \rightleftarrows A \tag{24a}$$

$$R + A \rightarrow 2P_1 \tag{24b}$$

$$R \rightarrow P_2 \tag{24c}$$

Here A is a chemisorbed species. In the following discussion the terms adsorption and chemisorption will be used interchangeably. Although heterogeneously catalyzed reactions always involve adsorbed phases such as A in the P_1 mechanism above, it is assumed that in this case the mechanism leading to P_2 is not important for the dynamical description of the system and that the overall rate of P_2 formation is second order. That this may be justified in cases of practical interest has already been discussed (*1*).

Generally, when reactions occur in a porous catalyst pellet, fluid composition within the catalyst varies with position and is different from the composition of the bulk fluid phase surrounding the catalyst. Although many workers have considered the resulting effects on selectivity for steady state operation, the problem of improving the selectivity of such a system by dynamic operation has not been treated before. For this reason, the simplest mass transport model will be used here.

Such a model may be obtained by lumping all mass transfer resistance into a boundary layer where no reaction occurs. That is, it is assumed that no concentration gradients exist within the catalyst and that there is a stagnant fluid boundary layer between the external catalyst surface and the bulk fluid phase. This situation is illustrated schematically in Figure 4. Mass transport of a component of the fluid phase, say reactant R, through this boundary layer is described by a relationship of the form

$$N_R = K_R[c_R - (c_R)_B] \tag{25}$$

The control variable for this example is the reactant concentration in the bulk fluid phase $(c_R)_B$. $(c_R)_B$ is restricted to nonnegative values and must be no larger than some maximum valued d. Therefore the appropriate set of admissible controls U is

$$U = [0, d] \tag{26}$$

The assumption is made here that product concentrations in the bulk fluid phase are zero and that the catalyst particle is isothermal.

By defining a set of dimensionless variables and parameters and performing a few simple manipulations (see Appendix II), the following mathematical description, which is valid for any periodic operation, may be obtained for this problem.

$$\dot{x}^1(t) = \frac{1}{\phi}[u(t) - x^1(t)] + \beta x^2(t) - x^1(t)[\mu + x^2(t) + \rho x^1(t)] \tag{27a}$$

$$\dot{x}^2(t) = \mu x^1(t) - [\beta + x^1(t)]x^2(t) \tag{27b}$$

$$\bar{r}^1 = \frac{1}{\tau}\int_0^\tau \frac{x^1(t)x^2(t)}{\mu}\,dt \tag{27c}$$

$$\bar{r}^2 = \frac{1}{\tau}\int_0^\tau [x^1(t)]^2\,dt \tag{27d}$$

$$\bar{r} = (\bar{r}^1, \bar{r}^2) \tag{27e}$$

Here x^1 and x^2 are the dimensionless concentration of R and A within the catalyst respectively, and u, which is the dimensionless bulk phase R concentration, is restricted by $u(t) \in [0, 1]$.

APPLICATION OF THE ATTAINABLE SET CONCEPT

Rather than optimization theory, the attainable set concept will be employed to compare periodic with steady state operation. Since this approach has been described elsewhere in some detail (*1*, *3*), only a brief summary will be given here. For each time invariant bulk phase reactant composition, there are corresponding time invariant values of reactant and adsorbed phase concentrations and hence corresponding rates of P_1 and P_2 formation. The steady state selectivity S_{ss} has been defined as the set of all rates of product formation $\bar{r}$ which can be attained by steady state operations (*3*). Since average rates in the convex hull of the steady state selectivity *co* S_{ss} are attainable by mixing steady state productions (*3*), we are interested here in determining whether or not time-average production rates outside of *co* S_{ss} can be obtained by cycling. If so, there is a definite potential for process improvement by periodic operation.

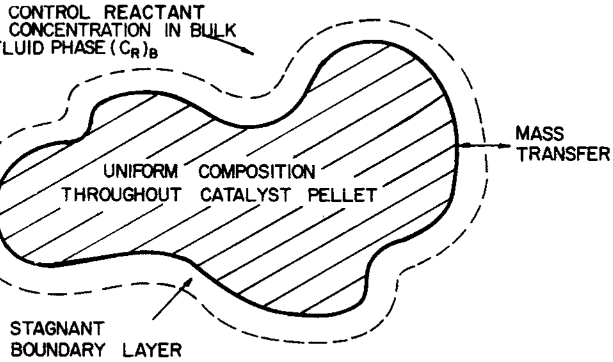

Fig. 4. Schematic diagram of lumped-parameter model of mass transfer resistance (example II).

In order to obtain the steady state selectivity S_{ss} for this example, steady state solutions to the state equations must be determined. From Equations (27*a*) and (27*b*), for steady state operation x^1 satisfies

$$\frac{2\phi\mu(x^1)^2}{x^1 + \beta} = u - x^1 - \rho\phi(x^1)^2 \tag{28}$$

and the corresponding x^2 is given by

$$x^2 = \frac{\mu x^1}{x^1 + \beta} \tag{29}$$

Using Equation (28) one can easily show that the steady state (x^1, x^2) corresponding to any given u is unique and that x^1 is an interior point of the closed interval $[0, u]$. Also, it can be demonstrated that x^1 is an increasing function of u. This means that S_{ss} is determined parametrically by

$$r = (r^1, r^2) = \left(\frac{w^2}{w + \beta}, w^2\right) \tag{30}$$

where the scalar w takes on all values between and including 0 and $\hat{x}^1$. $\hat{x}^1$ denotes the value of x^1 which satisfies Equation (28) for $u = 1$. Attention is now turned to the effects of mass transfer resistance on the dynamic behavior of the catalyst.

PERIODIC OPERATION OF THE CATALYST

The parameter ϕ appearing in Equations (27) is defined by

$$\phi = \frac{k_3 d V_p}{K_R \mathcal{A}_p} \tag{31}$$

ϕ may be considered the ratio of a characteristic reaction rate to a characteristic mass transfer rate. Therefore the magnitude of the influence of mass transfer resistance on the operation of the catalyst may be expected to vary directly with ϕ. In particular, for large ϕ, the term $[u(t) - x^1(t)]/\phi$ will always be small. This means that switching u will have only a small effect on the behavior of x^1. In turn, if x^1 changes very slowly, the steady state approximation will be valid for x^2. If this is the case, it can be shown that only rates in *co* S_{ss} are attainable. Therefore in the limit of very large ϕ, dynamic improvement of this system will not be possible.

If ϕ is very small, examination of Equation (27*a*) reveals $x^1(t) \cong u(t)$, so that the no-resistance case is approached. In the analysis of this case in a previous publication (*3*), it was shown that sufficiently rapid switching of the reactant concentration between its upper and lower limits results in average rates outside of *co* S_{ss}. Therefore it may be possible to obtain average rates not in *co* S_{ss} for the problem at hand, at least if ϕ is sufficiently small.

The class of controls considered here, as in the heat flux control problem discussed above, contains periodic bang-bang controls which switch between the control limits. More specifically, for $t \in [0, \tau)$

$$u(t) = \begin{cases} 1 & t\,\epsilon[0, \gamma\tau) \\ 0 & t\,\epsilon[\gamma\tau, \tau) \end{cases} \tag{32}$$

where $\gamma\epsilon(0, 1)$. Values of the control for all other times follow from the periodicity condition (*4b*). Following the concepts introduced in reference *1*, the set of average rates $\bar{r}$ attainable with controls of the general form (32) will be denoted S_{pbe}. The subscripts denote periodic bang-bang control with switching between extreme points of the admissible control set.

A direct calculation method will be used to determine S_{pbe}. For several different values of $\gamma\epsilon(0, 1)$, periodic states are computed for a set of periods τ. By plotting all rates calculated for a given γ, a curve, which will be denoted S_γ, is obtained in the space P spanned by $\bar{r}^1$ and $\bar{r}^2$. The end points of this curve are already known from S_{ss}, since for very large periods the rate $\gamma\bar{r}(1)$, where $\bar{r}(1)$ is the steady state rate for $u = 1$, is approached and for very small periods the steady state rate corresponding to $u = \gamma$ is approximated (*2*). Thus, as in the problem discussed in the first part of this paper, only a finite period can be optimal (in the sense of yielding average rates not in *co* S_{ss}). Here as before the term "finite" means that the period is neither very much smaller nor very much larger than the characteristic time for the system to reach steady state. Since

$$S_{pbe} = \bigcup_{\gamma\epsilon(0,1)} S_\gamma \tag{33}$$

S_{pbe} may be obtained graphically by constructing the envelope of several sets S_γ. This procedure is illustrated in Figure 5 for the parameter values

$$\phi = 0.5,\ \mu = 1,\ \beta = 0.3,\ \rho = 0.5 \tag{34}$$

The set S_γ for $\gamma = 0.4$ is the short, heavy line indicated in Figure 5. S_{pbe} is the entire region which encloses the family of short, heavy lines shown in the figure.

From Figure 5 it is obvious for the parameters given in (34) that *co* S_{ss} is a proper subset of S_{pbe}

$$co\ S_{ss} \subset S_{pbe} \tag{35}$$

so that a significant result of dynamic operation can be claimed. The physical explanation of the ability to obtain rates above *co* S_{ss} in this case follows immediately from Figure 6, in which the periodic state for the control parameters $\gamma = 0.2$ and $\tau = 10$ is shown. The trajectories $x^1(t)$ and $x^2(t)$ are somewhat out of phase. This results in a lower time average of the product $x^1(t)\ x^2(t)$ than would be obtained from in-phase behavior. On the other hand, the time average of $[x^1(t)]^2$ is independent of the phase relationship between $x^1(t)$ and $x^2(t)$. Therefore it is reasonable that in this case rates of production are attainable with larger values of $\bar{r}^2$ for given $\bar{r}^1$ than for any $\bar{r}\,\epsilon\, co\ S_{ss}$ with the same given $\bar{r}^1$.

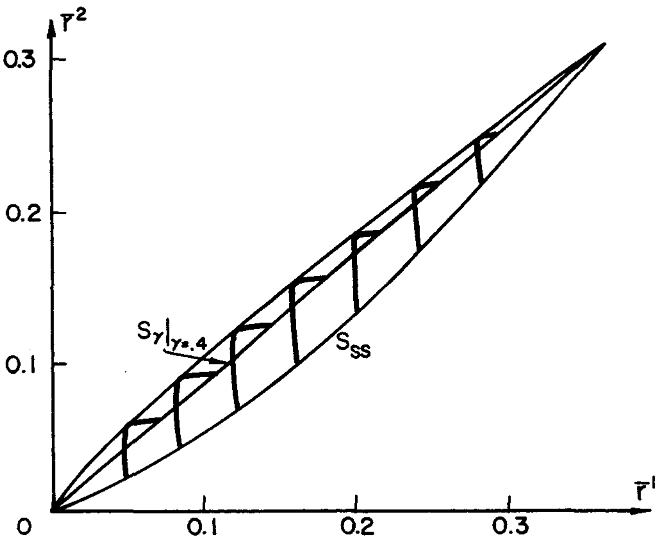

Fig. 5. Determination of S_{pbe} using the direct calculation method.

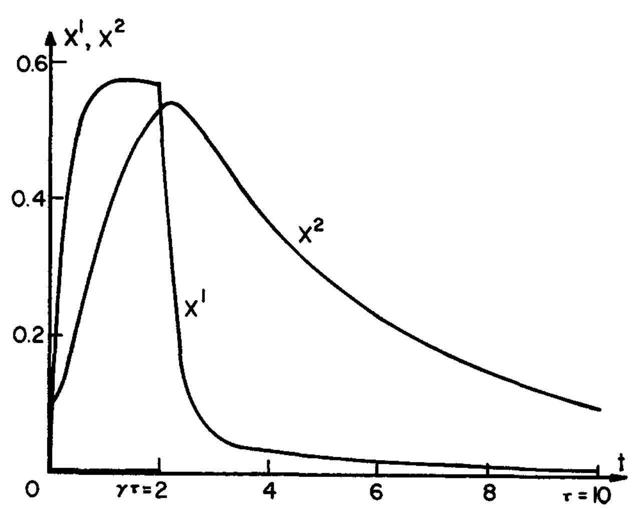

Fig. 6. A periodic state corresponding to a periodic bang-bang extreme point control.

It is interesting to note that the qualitative discussion concerning the effects of varying the parameter ϕ appears correct. In Figure 7 attainable sets S_{pbe} for different ϕ values with all else being equal are illustrated. The attainable set labeled *I* is S_{pbe} for the no-resistance case, which presumably will be approached as ϕ approaches zero. For the cases shown

$$S_{pbe}\big|_{\phi=\phi_1} \supset S_{pbe}\big|_{\phi=\phi_2} \tag{36}$$

if

$$\phi_1 < \phi_2 \tag{37}$$

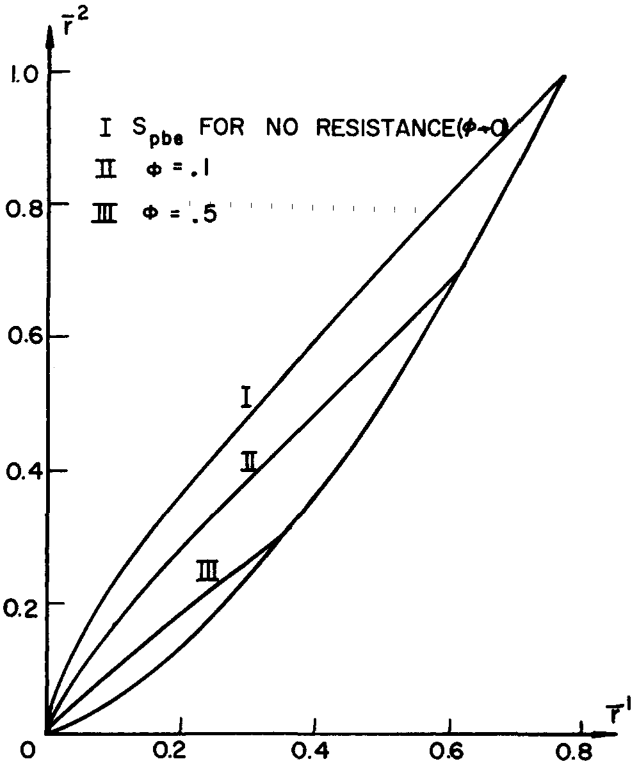

Fig. 7. Dependence of S_{pbe} on ϕ ($\beta = 0.3, \mu = 1, \rho = 0.5$).

Although it will not be proven, it seems plausible that this result will be valid over all ϕ for this example.

COMPARISON OF DIRECTIONS IN *P* SPACE

One indirect way of demonstrating the existence of average rates outside *co* S_{ss} involves comparing directions in the space *P* spanned by the average production rates. To this end we introduce the selectivity ratio defined by

$$s \equiv \frac{\bar{r}^2}{\bar{r}^1} \tag{38}$$

If by some means the existence of selectivity ratios which correspond to some dynamic periodic operation but to no steady state process can be demonstrated, then it follows that the average rate $\bar{r}$ corresponding to the periodic operation in question does not belong to *co* S_{ss}. This approach can be useful because in some cases (the present example included) it is easier to calculate directions in *P* space than points in *P* space. From Equations (27*c*), (27*d*) and (29), the selectivity ratio for any steady state process operation has the general form

$$s_{ss} = \frac{\bar{r}^2}{\bar{r}^1} = x^1 + \beta \tag{39}$$

From earlier remarks asserting the monotonicity of x^1 with u^1

$$(s_{ss})_{\max} = \hat{x}^1 + \beta \tag{40}$$

$$(s_{ss})_{\min} = \beta \tag{41}$$

where, as defined earlier, $\hat{x}^1$ is the first coordinate of the steady state x corresponding to $u = 1$.

Now turning to the class of periodic bang-bang extreme point controls, consider the case where the period τ is very long and the time $\gamma\tau$ during which the catalyst is exposed to reactant is very small. Since the time interval $[\gamma\tau, \tau]$ is very long, the state of the system at time τ will be approximately the steady state which corresponds to the control $u = 0$ $(x^1 = 0)$. On the other hand, it can be seen by considering difference approximations to Equations (27*a*) and (27*b*) that if the interval $[0, \gamma\tau]$ is sufficiently small, $x^2(\gamma\tau)$ and contributions to $\bar{r}^1$ and $\bar{r}_2$ during this interval will remain essentially zero while $x^1(\gamma\tau)$ is some small number ϵ. This means that both $x^1(t)$ and $x^2(t)$ will be on the order of ϵ or smaller during the interval of operation $[\gamma\tau, \tau]$. Therefore, when solving for trajectories over this interval, it is reasonable to neglect second-order terms in x^1 and x^2 in Equations (27*a*) and (27*b*). The end result of these heuristic remarks is that the limiting selectivity ratio s_o for very large τ and very small $\gamma\tau$ can be computed using the following equations:

$$x_p(0) = \{x_p^1(0), x_p^2(0)\} = (\epsilon, 0) \tag{42a}$$

$$x_p^1(t) = -\left(\frac{1}{\phi} + \mu\right) x_p^1(t) + \beta x_p^2(t) \tag{42b}$$

$$x_p^2(t) = \mu x_p^1(t) - \beta x_{p2}(t) \tag{42c}$$

and, finally

$$s_o = \frac{\mu \int_0^\infty [x_p^1(t)]^2 dt}{\int_0^\infty x_p^1(t) x_p^2(t) dt} \tag{43}$$

The linear initial value problem posed by Equations (42) is easy to solve using standard techniques. Substitution of the result into Equation (43), followed by some algebraic manipulations, gives the simple expression

$$s_o = \beta + \frac{1}{\phi} \tag{44}$$

Comparison of Equations (40) and (44) reveals that if

$$\phi \hat{x}^1 < 1 \tag{45}$$

then

$$s_o > (s_{ss})_{\max} \tag{46}$$

Therefore validity of Condition (45) guarantees that there exist average production rates $\bar{r}$ which can be obtained by cycling but not by steady state operation or mixing of steady state productions. The usefulness of this condition, which utilizes only the parameters of the system and steady state data, is illustrated in Figure 8 where $(s_{ss})_{\min}$, $(s_{ss})_{\max}$, and s_o are plotted as functions of ϕ for given values of μ, β, and ρ. It can be seen that Condition (46) is satisfied over a large range of ϕ values.

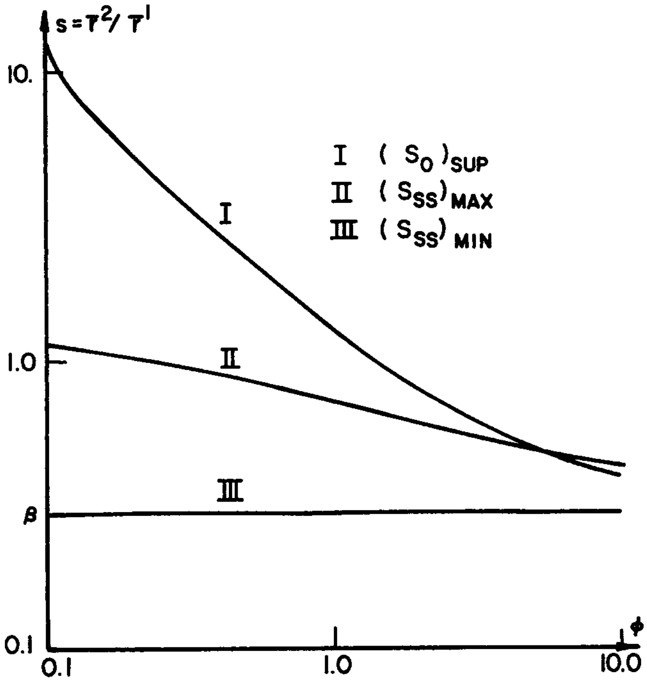

Fig. 8. Selectivity ratios versus ϕ ($\beta = 0.3$, $\mu = 1$, $\rho = 0.5$).

Several additional points are illustrated by the results shown in Figure 8. First, it can be seen that the expected effect of ϕ on the operation of the catalyst pellet again appears. The larger the value of ϕ, the larger the mass transfer limitation and therefore the smaller the difference between $(s_{ss})_{\max}$ and s_o. Also, for sufficiently large ϕ

$$(s_{ss})_{\max} > s_o \tag{47}$$

However, for certain parameter values for which Condition (47) holds, rates in S_{pbe} but not in *co* S_{ss} have been found by the direct calculation method. This serves as a reminder that analysis of directions in *P* space as applied here provides only sufficient conditions for the validity of Condition (35).

In particular, in this analysis a limiting direction at the origin has been determined for the case of $\gamma\tau$ approaching zero and τ approaching infinity. Since rates in the neighborhood of the origin are obtained by periodic bang-bang extreme point controls whenever γ (and not necessarily $\gamma\bar{r}$) is sufficiently small, there is no assurance that s_o is the supremum of the selectivity ratio for all rates in S_{pbe} in the neighborhood of the origin. In fact, it is easy to show that the supremum of s for rates in S_{pbe} must be greater than or equal to $(s_{ss})_{\max}$.

DISCUSSION

An important product of the above investigation is a verification of the usefulness of the analysis of relaxed steady state operation (fast switching) in connection with a simplified model. The earlier explorations cited provided valuable qualitative insights into the effects of cycling these reaction systems. Perhaps it would be useful to put the methodology employed in the examination of these systems into somewhat more general terms.

In many processes the control (for example, heat flux) indirectly affects certain state variables (for example, reactant concentration) by means of its more immediate influence on another state variable(s) (for example, reactor temperature). In this case the original system can be decomposed into two interacting subsystems, the first of which has the control as an input, and the other whose variables determine the performance of the system. This artificial decomposition, which is illustrated schematically in Figure 9, leads naturally to a simplified control problem. That is, for the purpose of preliminary investigation it is assumed that the state variable(s) most immediately associated with the control is itself a control variable, and the first subsystem mentioned above is temporarily ignored. The resulting simplified process model may be much more amenable to attack by standard techniques than the original problem.

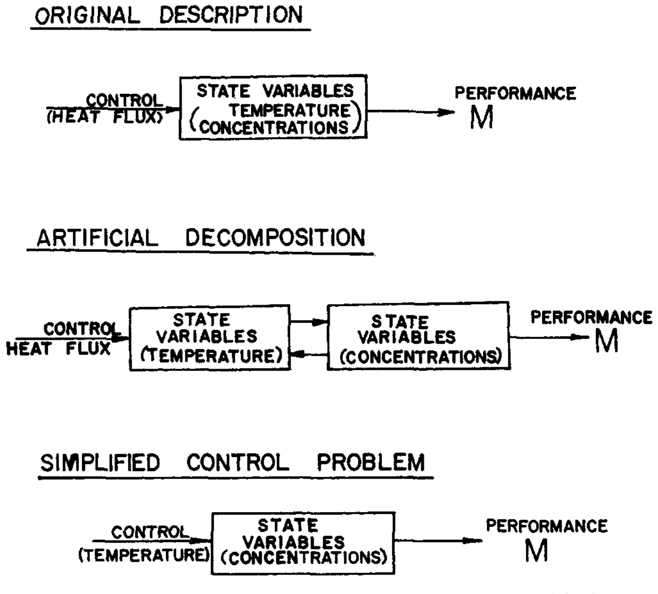

Fig. 9. Schematic illustration of decomposition to a simplified control model. *Each box represents a set of differential equations relating the rate of change of the state to the input.*

This approach is particularly well suited for the investigation of periodic processes, where the first objective is comparison of cyclic with steady state operation. Its success with the examples treated here has already been mentioned. However, a word of caution is due. There are cases which will be discussed in future publications where cycling improves the process for the original description but not for the simplified control problem. In such a situation, the unsteady state interactions between the subsystems mentioned above are of fundamental importance.

Although no general formulation is given here, the idea of comparing directions—particularly limiting directions as $\bar{r} \to 0$—rather than points in P space should have utility in other problems. The advantages and limitations of this approach are similar to those encountered in the more general test for comparing cyclic with steady state operation based on the maximum principle (3). Both have the advantage of requiring only steady state information, while both are somewhat weak in that only infinitesimal improvements over steady state operation can be guaranteed.

CONCLUSIONS

The effects of heat and mass transfer on two chemical reaction systems have been investigated. It has been shown that inclusion of these resistances results in differences in optimal periodic control and corresponding system behavior. A finite period is required, since high frequency oscillations are filtered out and low frequency cycling is equivalent to mixing steady state productions.

Alternate approaches in the analysis of periodic processes, namely, optimal control theory and attainable set comparison, were illustrated. Some new results and concepts were presented for each of these methods which should find application in other problems.

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NOTATON

A = chemisorbed species
$\mathfrak{A}_p$ = external surface area of the catalyst pellet
a_1, a_2 = dimensionless parameters. See Equation (49)
b = dimension of state vector
C_p = heat capacity per unit volume of reaction mixture
c_R = concentration of reactant R
c_{Ro} = feed concentration of R
d = maximum concentration of R in the bulk fluid phase
E_1, E_2 = activation energies
$f(x, u)$ = function equal to time rate of change of the state x
h = number of control levels in a periodic bang-bang control
H = Hamiltonian
h_1, h_2 = frequency factors for Arrhenius rate constants
k_1, k_2, k_3, k_4 = rate constants for catalytic selectivity problem
K_R = mass transfer coefficient of R
m = integrand in integral objective function
M = objective function
n = dimension of the control u
N_R = molar flux of R
P = space spanned by time-average rates of production
p_1, p_2 = concentrations of P_1 and P_2, respectively
P_1, P_2 = reaction products
q = volumetric flow rate through CSTR
Q = heat flux into CSTR
R = reactant
$\bar{r}$ = vector of average rates of production

$\bar{r}_1, \bar{r}_2$ = average production rates of P_1 and P_2, respectively
s = selectivity ratio. See Equation (38)
s_{ss} = selectivity ratio for steady state operation
s_o = limiting selectivity ratio for $\gamma \rightarrow 0, \gamma_T \rightarrow 0$
S_γ = attainable set of average rates. See text above Equation (33)
S_{pbe} = see text below Equation (32)
S_{ss} = steady state selectivity
T = temperature of reaction mixture in CSTR
$t_1, t_2, \ldots$ = intervals in periodic bang-bang control
u = control
U = set of admissible controls
V = volume of reaction mixture in CSTR
V_p = volume of catalyst pellet
w = scalar parameter
x = state
$x^1, x^2, \ldots$ = components of state vector
$\hat{x}^1$ = see text below Equation (30)
x_p = state vector for limiting selectivity ratio calculation

Greek Letters

α = order of Reaction (6*a*)
β = dimensionless kinetic parameter. See Equation (57)
γ = bang-bang control parameter. See Equation (32)
δ = ratio of activation energies
ϵ = step length for hill climbing
λ = adjoint vector
$\lambda_1, \lambda_2, \ldots$ = components of adjoint vector
μ = dimensionless kinetic parameter. See Equation (57)
ρ = dimensionless kinetic parameter. See Equation (57)
τ = period
ϕ = mass transfer reaction parameter. See Equation (57)

Subscripts and Superscripts

$*$ = steady state
$**$, oss = optimum steady state
obb = optimum bang-bang
B = evaluated in bulk fluid phase
$'$ = original variable with dimensions (for example t')

Mathematical Notation

a.e. = almost everywhere
co = convex hull
$\subset$ = is a proper subset of

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APPENDIX I: DERIVATION OF EQUATIONS FOR HEAT FLUX CONTROL OF CSTR

Material balances for components R and P_1 are given by

$$\frac{dc_R(t')}{dt'} = -h_1 e^{-E_1/RT(t')}[c_R(t')]^\alpha - h_2 e^{-E_2/RT(t')} c_R(t') + \frac{q}{V}[c_{Ro} - c_R(t')] \quad (48a)$$

$$\frac{dp_1(t')}{dt'} = h_1 e^{-E_1/RT(t')}[c_R(t')]^\alpha - \frac{q}{V} p_1(t') \quad (48b)$$

The energy balance is

$$C_p V \frac{dT(t')}{dt'} = qC_p[T^0 - T(t')] + Q(t') \text{ a.e.} \quad (48c)$$

Equation (8) follows from Equation (48) by introducing the dimensionless variables:

$$x^1 = c_R/c_{Ro} \quad x^2 = p_1/c_{Ro} \quad x^3 = RT/E_1 \quad t = t'q/V$$

$$\delta = E_2/E_1 \quad a_1 = \frac{Vh_1}{q} c_{Ro}{}^{\alpha-1} \quad a_2 = \frac{Vh_2}{q}$$

$$u = \frac{RT^0}{E_1} + \frac{QR}{qE_1C_p} \quad (49)$$

APPENDIX II: DERIVATION OF EQUATIONS FOR CATALYST PARTICLE WITH LUMPED MASS TRANSFER RESISTANCE

The original equations for this example are

$$\frac{dc_R(t')}{dt'} = \frac{\mathcal{A}_p K_R}{V_p}[(c_R(t'))_B - c_R(t')] - k_1 c_R(t') + k_2 a(t') - k_3 c_R(t') a(t') - k_4 [c_R(t')]^2 \text{ a.e.} \quad (50)$$

$$\frac{dp_1(t')}{dt'} = \frac{\mathcal{A}_p K_{p1}}{V_p}[-p_1(t')] + 2k_3 c_R(t') a(t') \quad (51)$$

$$\frac{dp_2(t')}{dt'} = \frac{\mathcal{A}_p K_{p2}}{V_p}[-p_2(t')] + k_4[c_R(t')]^2 \quad (52)$$

$$\frac{da(t')}{dt'} = k_1 c_R(t') - a(t')[k_2 + k_3 c_R(t')] \quad (53)$$

Average production rates for periodic operation are

$$(\bar{r}^i)' = \frac{1}{\tau' V_p} \int_0^{\tau'} \mathcal{A}_p K_{pi}\, p_i(t')\, dt'; \quad i = 1, 2 \quad (54)$$

However, by integrating Equations (51) and (52) over t' from $t' = 0$ to $t' = \tau'$ and making use of the periodicity condition

$$p_i(0) = p_i(\tau'); \quad i = 1, 2 \quad (55)$$

it follows from (54) that

$$(\bar{r}^1)' = \frac{2k_3}{\tau'} \int_0^{\tau'} c_R(t') a(t') dt' \quad (56a)$$

$$(\bar{r}^2)' = \frac{k_4}{\tau'} \int_0^{\tau'} [c_R(t')]^2\, dt \quad (56b)$$

Now Equations (27) may be obtained by substituting the dimensionless parameters defined below into these equations.

$$\left.\begin{array}{l} u = c_{R_B}/d \quad x^1 = c_R/d \quad x^2 = a/d \quad t = t'k_3d \\ \beta = k_2/k_3d \quad \mu = k_1/k_3d \quad \phi = \dfrac{k_3 d V_p}{K_R \mathcal{A}_p} \quad \rho = k_4/k_3 \\ \bar{r}^1 = \dfrac{(\bar{r}^1)'}{2k_1 d} \qquad \bar{r}^2 = \dfrac{(\bar{r}^2)'}{k_4 d^2} \end{array}\right\} \quad (57)$$

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