Complex Reactions in Oscillating Reactors

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Previous work has shown that perturbation methods are useful for estimating the difference between the time average conversion obtained from an oscillating reactor and the optimum steady state value. The present study extends this approach to complex kinetic mechanisms. Both forced and self-generated oscillations are studied, and in the latter case both positive and negative feedback control systems are used to alter the shape of the oscillations. The results indicate that large improvements in yields sometimes can be observed for parallel reactions but that only small improvements are possible for consecutive reactions, in the range of system parameters considered.

There have been numerous studies in the last few years which indicate that periodic operation of chemical processes sometimes is superior to a conventional steady state design. Perturbation techniques have been found to be useful for estimating the potential advantages of periodic processing for single reactions in stirred tank reactors. The present study uses these methods to determine the effect of both forced and self-generated oscillations on complex kinetic mechanisms.

The great advantage of a perturbation analysis is that it provides an approximate analytical solution for the periodic outputs of the plant. Hence, it is possible to develop expressions for the difference between the time average and steady state performance in terms of the system parameters. These relationships are often useful for the design of periodic processes. However, it should be recognized that a perturbation approach will not normally lead to the optimal periodic system. As Horn (*6*) demonstrated, a determination of the optimal periodic operating conditions requires a complete solution of the nonlinear optimization equations obtained using a modification of Pontigagin's maximum principle. It is our hope that the perturbation solutions will provide a simple way of establishing the incentive for more detailed studies of periodic processing.

SYSTEM EQUATIONS

The systems chosen for the main part of the investigation were an elementary set of consecutive reactions, $nA \longrightarrow B \longrightarrow C$, and a set of parallel reactions, $2A \longrightarrow B$ and $A \longrightarrow C$, in a continuous stirred-tank reactor. In the first case the dynamic equations are

$$V\frac{dA}{dt} = q(A_f - A) - k_1 VA^n \tag{1}$$

$$V\frac{dB}{dt} = q(B_f - B) + k_1 VA^n - k_2 VB \tag{2}$$

$$VC_p\rho\frac{dT}{dt} = qC_p(T_f - T) - U_a(T - T_c) + (-\Delta H_1)k_1 VA^n + (-\Delta H_2)k_2 VB \tag{3}$$

where n is the order of the first reaction and

$$k_1 = k_{10}e^{-E_1/RT}, \quad k_2 = k_{20}e^{-E_2/RT}$$
$$U_a = \frac{U_c A_c K q_c}{1 + Kq_c}, \quad K = \frac{2C_{pc}\rho_c}{U_c A_c} \tag{4}$$

The corresponding expressions for the parallel reaction scheme are

$$V\frac{dA}{dt} = q(A_f - A) - k_1 VA^2 - k_2 VA \tag{5}$$

$$V\frac{dB}{dt} = q(B_f - B) + k_1 VA^2 \tag{6}$$

$$VC_p\rho\frac{dT}{dt} = qC_p\rho(T_f - T) - U_a(T - T_c) + (-\Delta H_1)k_1 VA^2 + (-\Delta H_2)k_2 VA \tag{7}$$

At steady state conditions each of the accumulation terms must be equal to zero. Then, the reactor outputs can be calculated by solving the first material balance equation in either set for A in terms of T. This result can be used to eliminate A from the second material balance, which can then be solved for B in terms of T. Finally, these two relationships can be used to eliminate the composition variables from the energy equation, so that a single expression for the reactor temperature is obtained. Because of the transcendental nature of this equation, it must be solved either graphically or numerically. Bilous and Amundson (*1*) showed that between one and five solutions are possible, depending upon the system parameters.

While the procedure above can be used to find the steady state operating points under any set of conditions, we are primarily interested in determining the optimum reactor design so that we can compare the periodic operation with the best steady state performance. However, a rigorous evaluation of the optimum design would require a detailed treatment of the process economics and a simultaneous consideration of all the plant units, as well as process and equipment alternatives. Hence, in order to keep the analysis as simple as possible we restricted our attention to the elementary problem where an attempt is made to find the reactor temperature, or the coolant flow rate, which maximizes the yield of one of the intermediate components for a fixed set of other design parameters. This type of optimization problem normally is simple to solve by implicit differentiation, the introduction of Lagrange multipliers, or the elimination of all but one of the dependent variables followed by differentiation. The solution not only provides useful information for a more detailed economic evaluation, but also can be used to establish the optimum steady state control policy for the reactor.

Horn (*6*) has published a general solution of this problem using the implicit differentiation technique. For the parallel reaction problem described above he found that the re-

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actor 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 ($n = 2$ for our example). In addition, he was able to show that there would be some periodic process which had a time average yield in excess of the optimum steady state value, providing that $E_2/E_1 < 1$. Horn's solution for the optimal yield and the general criterion he developed for determining whether or not periodic operation might be superior to the optimum steady state design can also be applied to the consecutive reaction scheme. The results are not as simple as for parallel reactions, and the transcendental nature of the equations causes temperature to appear in the inequality conditions.

In all of the examples discussed below, we selected the parameters so that there was a single steady state solution which corresponded to the optimum yield of component B. However, Horn's criterion indicated that the yield could be improved by periodic changes in the reactor temperature or coolant flow rate. We explored the effect of feed rate and feed temperature fluctuations on stable reactors and studied the oscillations generated by unstable nonisothermal reactors. A comparison between the time average and optimum steady state yield actually is valid only in the last case, since the feed rate and feed temperature were considered to be fixed quantities in the optimum steady state design problem. Of course, it would be possible to find the optimum values of these quantities using an economic analysis. Nevertheless, the difference between the periodic and steady state performance of a stable reactor with these input fluctuations should provide some additional insight into the effect of dynamic operation on complex reactions.

FORCED OSCILLATIONS

The optimum design of most reactors will be stable. This can be verified by linearizing the system equations and calculating the characteristic roots (*1*). However,for this type of system we can force the outputs of the stable reactor to oscillate by manipulating the inputs periodically. For the sake of simplicity we will consider only sinusoidal variations, even though it is unlikely that these will be the optimal periodic inputs. Then, if the results show that there is sufficient justification for a more detailed analysis of periodic processing, Horn's method (*6*) can be used to solve the optimization problem.

With this approach, what we are actually studying is the frequency response of nonlinear reactor systems. Ritter and Douglas (*3*, *8*) demonstrated that classical perturbation methods (*7*) could be used to obtain approximate analytical solutions for the response with single reactions. Their results showed that the effect of the nonlinearities was to introduce higher harmonics and a shift in the time average conversion. It is possible to extend the analysis to complex kinetic mechanisms, and in this way to obtain predictions of the effect of sinusoidal input fluctuations on the time average yield for both isothermal and nonisothermal reactors.

Isothermal Reactors

The results for the parallel reaction problem, see Equations (5) and (6), with flow rate variations and the system parameters listed in Table 1 are given in Figure 1. It is apparent from the graph that the agreement between the approximate analytical result and a numerical solution of the equations is qualitatively correct. A better agreement could be obtained by including more than the first-order correction functions in the perturbation analysis. The fact that the improvement goes through a maximum as the driving frequency increases is somewhat surprising since the linearized dynamic equations have a pair of negative real roots.

A plot of the dimensionless concentration of the desired product B versus time is given in Figure 2. Only the linear frequency response and constant terms of the analytical solution are plotted, that is, the second- and higher-harmonic terms have been neglected, and it is obvious that these provide an adequate description of the nonlinear system. This implies that the quadratic nonlinearity and the time variable coefficient do not produce much distortion for these 10% amplitude flow rate fluctuations, although the analytical solutions predict that the distortion increases with the square of the input amplitude.

The maximum improvement observed was only 0.3%, whereas Horn's results for this same problem show that about a 20% improvement is possible with temperature fluctuations (*6*). This large variation in operating characteristics may be attributed to the fact that the temperature oscillations introduce an exponential nonlinearity into the equations. The importance of this type of term will become more apparent later, when the energy balance is included in the dynamic model.

Table 1. 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

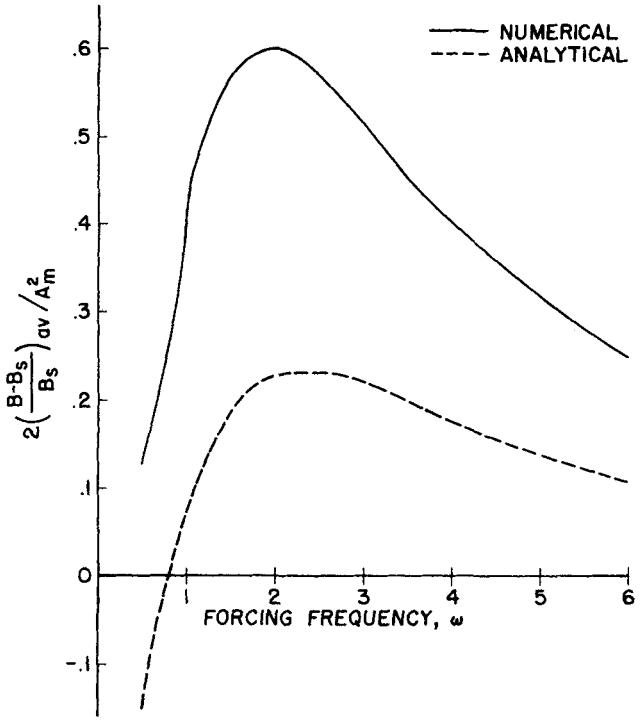

Fig. 1. Effect of forcing frequency on the time average yield for parallel reactions.

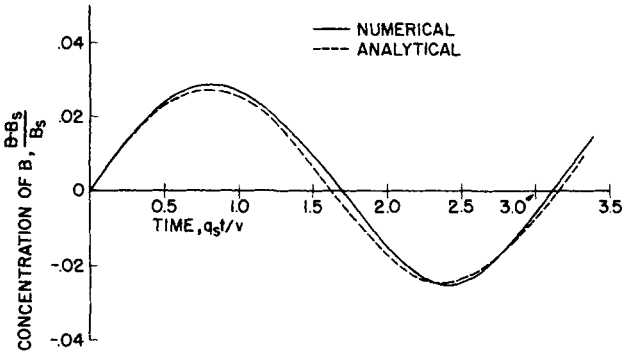

Fig. 2. Time dependence of component B for parallel reactions.

A similar study was made for consecutive reactions. The parameters are given in Table 1 and the results are shown in Figure 3. For this case, there is excellent agreement between the analytical and numerical solutions. Both predict that the time average yield of the oscillating system is poorer than the optimum design at low frequencies, but 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 (a low frequency analysis) can be misleading. The maximum shift in the time average yield is very small, however, that is, about 0.02% for a 10% input amplitude, so that the linear frequency response provides an excellent description of the output oscillations. The curves for this case resemble those given in Figure 2.

Nonisothermal Reactors

It should be possible to observe much larger differences between the time average and optimum steady state yields for a nonisothermal reactor both because the system has an exponential nonlinearity in temperature and because the

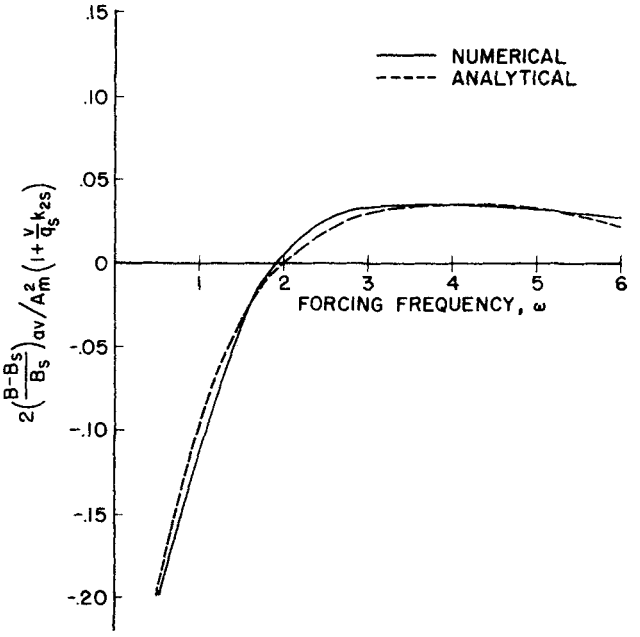

Fig. 3. Effect of forcing frequency on the time average yield for consecutive reactions.

linearized system equations can have a pair of complex conjugate roots with a low damping coefficient, that is, the linearized equations can exhibit resonance. It seems plausible to expect 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. In addition, it is a simple matter to lower the natural damping coefficient of the reactor, which increases the height of the resonant peak, by installing a conventional control system.

The parameters for the study of parallel reactions are essentially the same as those used previously (see Table 1). The maximum improvement for sinusoidal changes in flow rate (10% amplitude) was almost 2% and this was observed near resonance. However, if the oscillations are introduced in feed temperature (again with a 10% amplitude) the improvement is slightly higher than 15%. A plot of the numerical solutions for the effluent composition of component B for several input amplitudes is given in Figure 4. The approximate analytical solutions provide excellent descriptions of the outputs, providing

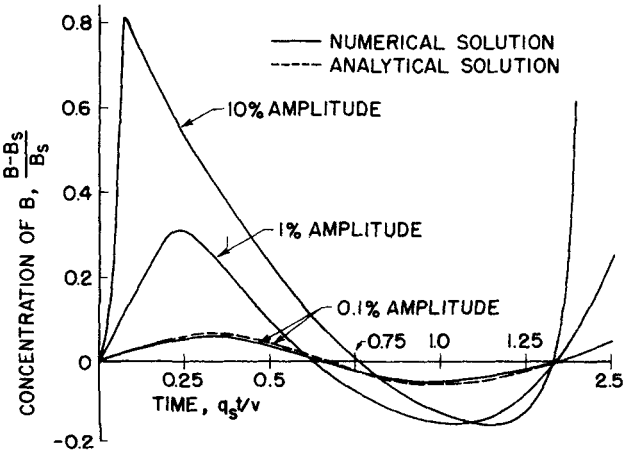

Fig. 4. Time dependence of component B for parallel reactions.

that the curves resemble trigonometric functions (see Figure 4). However, when there is a very large distortion it becomes necessary to evaluate an excessive number of 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 compute numerical solutions of the equations, but the analytical results can 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.

The results for the nonisothermal, consecutive reaction problem are similar to those discussed above. Sinusoidal flow rate variations with a 10% amplitude give about a 0.1% improvement in yield. The analytical solutions provide a better description of the effluent oscillations for this case because there is less distortion.

CHEMICAL OSCILLATORS

The simplest technique for ensuring that a reactor will generate oscillations is to select the parameters in such a way that there is only a single steady state solution which is unstable (*4*, *5*). With this restriction the system can never operate at steady state conditions. Also, since it is a fairly simple matter to show that the system is bounded and is unstable on the boundary we normally expect that the reactor will generate periodic outputs, that is, all trajectories will approach a single closed curve in the three-dimensional phase space. However, this condition is not sufficient since the system might have multiple limit cycles or approach and fill a limiting surface in an aperiodic manner. Similarly, if there are multiple solutions of the steady state equations, sometimes it is possible to obtain limit cycles but the analysis is much more complex. Despite these potential difficulties, we assume that periodic outputs will be observed whenever there is a single unstable equilibrium point, and eventually we will check this assumption by integrating the system equations numerically.

In order to make it possible to alter the number of singular points and their stability characteristics, we will consider a simple feedback control system where the coolant flow rate is changed proportional to the difference between the actual reactor temperature and the optimum steady state value, that is, the heat transfer coefficient in Equation (4) can be written as

$$U_a = U_{as} + K_c(T - T_s) \tag{8}$$

For a convential negative feedback controller, the value of K_c in Equation (8) will be positive. With this arrangement the heat transfer coefficient will increase whenever the reactor temperature exceeds the design value so that the temperature will tend to decrease. However, if we install the controller so that K_c is negative then the heat transfer coefficient decreases when the actual temperature is higher than T_s, so that the reactor temperature continues to increase. The second configuration is called positive feedback control, and it is apparent that it will tend to make stable systems become unstable. In this way sometimes we can change a stable reactor into an oscillator (*5*).

Qualitative Description of Oscillator Performance

Before undertaking a quantitative analysis of the behavior of an oscillator, it is helpful to attempt to make qualitative predictions of the system performance from a direct inspection of the system equations. In the case of parallel reactions, for example, it is clear that if we choose the system parameters so that the optimum steady state design equations are satisfied and the linearized forms of Equations (5) and (7) when considered together have a pair of complex conjugate roots with positive real parts, then we expect the system to oscillate. From our knowledge of second-order systems (*4*, *5*), the shift in the time average value of either A or T will be positive and the other will be negative. Now if we consider the term k_1VA^2 in Equation (6) as a periodic forcing function with a DC component, it is obvious that the time average value of B will be greater than its initial value (the optimum design condition) if the DC component of the forcing function is positive. Thus, for this case it should be a fairly simple matter to find system parameters such that the oscillator performance is better than the optimum steady state value.

Similar limiting arguments can be presented for the case of consecutive reactions. If the term k_1VA^n in Equations (2) and (3) is approximately constant, we could select the parameters in these equations so that the roots of the linear system would be complex conjugate with positive real parts. Hence, the system would oscillate, and if the parameters are such that the optimum steady state design equation is satisfied and if the shift in the average operating level of B is positive, then we will have accomplished our objective. Another possibility for this reaction scheme is to consider a case where the term $(-\Delta H_2)k_2VB$ in Equation (3) is very small. Then, if we select the parameters so that Equations (1) and (3) correspond to a second-order oscillator, we need only consider the behavior of Equation (2) as a linear system with a periodic coefficient (because of the presence of the k_2VB term) and a periodic forcing function k_1VA^n. We see immediately that we might be better off with an A^2 in this term since the shifts in the time average values of A and T, or k, are expected to have opposite signs. However, even the first-order case will introduce a shift and the periodic coefficient in the equation has the same effect. Thus, a careful balancing of system parameters might lead to an improvement.

Of course, in the general case the equations cannot be uncoupled in this manner and the terms in all three equations affect the characteristic roots. Hence, it is necessary to develop an approximate analytical solution which can be used to estimate whether or not an improved performance might be expected. This can be accomplished in a straightforward manner by extending the work of Poincare or Krylov and Bogoliubov (*4*, *5*, *7*), although the algebra involved is quite tedious. The solutions are given in reference *2*, but are not repeated here because they are too lengthy.

Oscillator Performance for Parallel Reactions

Sets of system parameters were selected so that the optimum steady state design equations were satisfied and so that the approximate analytical solution predicted that the oscillator performance would be superior to the optimum steady state system. For parallel reactions with the parameters given as case I in Table 2, approxomately a 20% improvement was obtained. The numerical solutions for this case are presented in Figure 5, and the time average values obtained from both the analytical and numerical so-

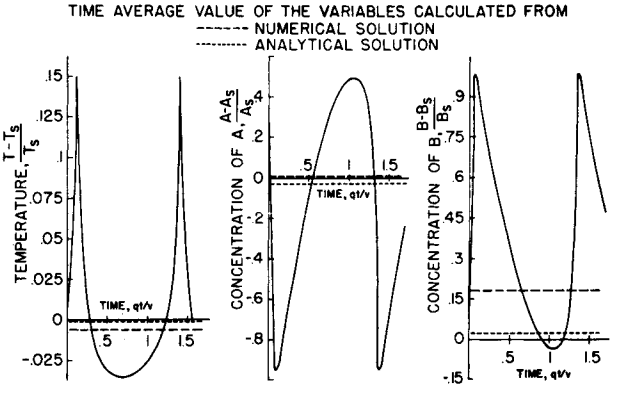

Fig. 5. Fluctuating outputs from a chemical oscillator for parallel reactions.

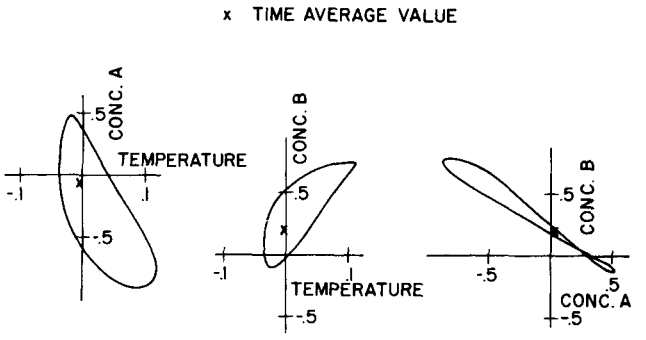

Fig. 6. Projections of limit cycle.

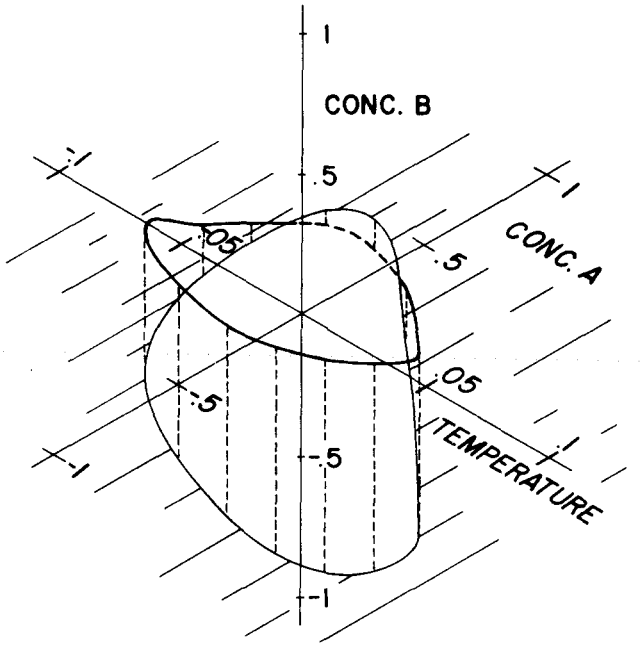

Fig. 7. Limit cycle.

lutions are shown on the graph. Figure 6 shows the projections of the limit cycle on the coordinate axes and Figure 7 is a three-dimensional sketch of the limit cycle.

The effect of the controller gain on the size and shape of the limit cycle for the parameters given as case II in Table 2 is shown in Figure 8. Curve C represents the case with no control, curves A and B are with positive feedback control, and curves D and E have negative feed-

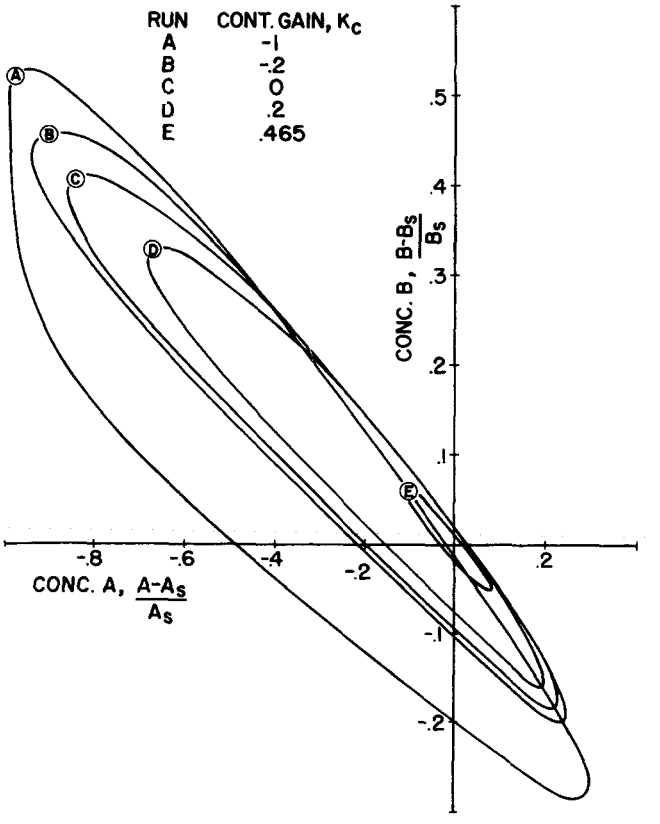

Fig. 8. Effect of controller gain on limit cycle.

TABLE 2. SYSTEM PARAMETERS FOR OSCILLATORS

	Parallel reaction, $2A \longrightarrow B$ and $A \longrightarrow C$		Consecutive reaction	
Parameters	Case I	Case II	$A \longrightarrow B \longrightarrow C$	$A \longrightarrow B \longrightarrow C \longrightarrow D$
A_f	0.01	0.01	0.0271	0.01
B_f	0	0	0	0
C_f	0	0	0	0
q_s	10	10	10	10
V	100	100	100	100
$C_p \rho$	1.0	1.0	1.0	1.0
k_{10}	1.0×10^{19}	1.0×10^{19}	3.387×10^{12}	2.14×10^{12}
k_{20}	3.98×10^{12}	9.49×10^{12}	1.721×10^{7}	0.606
k_{30}	0	0	0	39.5
E_1	28,000	28,000	22,800	24,000
E_2	19,600	21,000	14,820	1,440
E_3	0	0	0	4,896
$(-\Delta H_1)$	29,000	27,000	23,000	65,640
$(-\Delta H_2)$	20,000	20,000	1,366	−51,800
$(-\Delta H_3)$	0	0	0	203,000
$T_f = T_c$	300	319.1	365	389.25
U_{as}	54.6	88.5	327	236.5
K_c	1.24	−1 to 0.465	0	0
A_s	0.00283	0.00314	0.00651	0.00333
B_s	0.0001102	0.00575	0.01302	0.00386
C_s	0.00695	0.00561	0.00757	0.000197
T_s	322.4	333.4	380	400

back control. The time dependence of the desired product, predicted by both the analytical and numerical solutions, is shown in Figure 9 for cases A, C, and E. It is apparent from the graph that the approximate solutions are only qualitatively correct, and that the discrepancy increases as the distortion increases. The shift in the time average yield of B, obtained from the numerical and analytical solutions, is plotted against controller gain in Figure 10. It is interesting to note that the analytical solution provides a good estimate of the range of positive and negative feedback controller gains where an improvement is possible, despite the fact that the magnitude of the predicted shift is only approximate.

The relatively poor agreement between the analytical and numerical solutions, even for the case of small limit cycles, is due to the nature of the Taylor series approximation used in the analysis. That is, in the development of the perturbation solution the right-hand sides of the system equations, Equations (1) through (3) or (5) through (7), are expanded in a Taylor series around the steady state design condition and all terms up to third-order in the expansion are retained. Unfortunately, however, it can be shown that these third-order polynomial approximations sometimes have multiple singular points even though the original nonlinear functions on the right-hand sides of the equations only had one singular point. In other words, unless precautions are taken a Taylor series approximation may introduce spurious singular points into the solution and these can completely change the

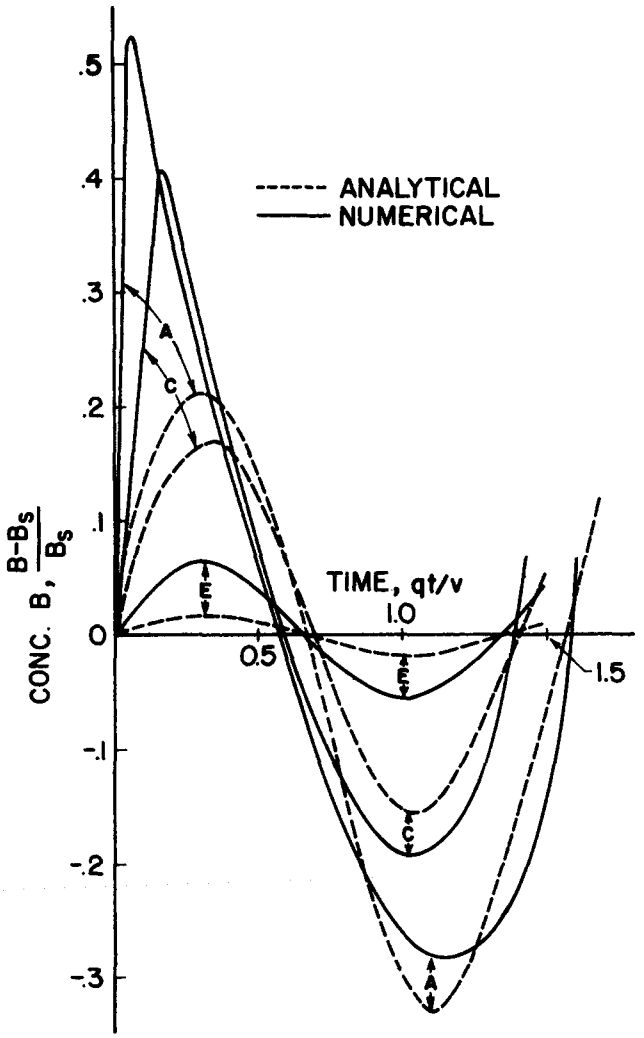

Fig. 9. Effect of controller gain on the fluctuations of component B.

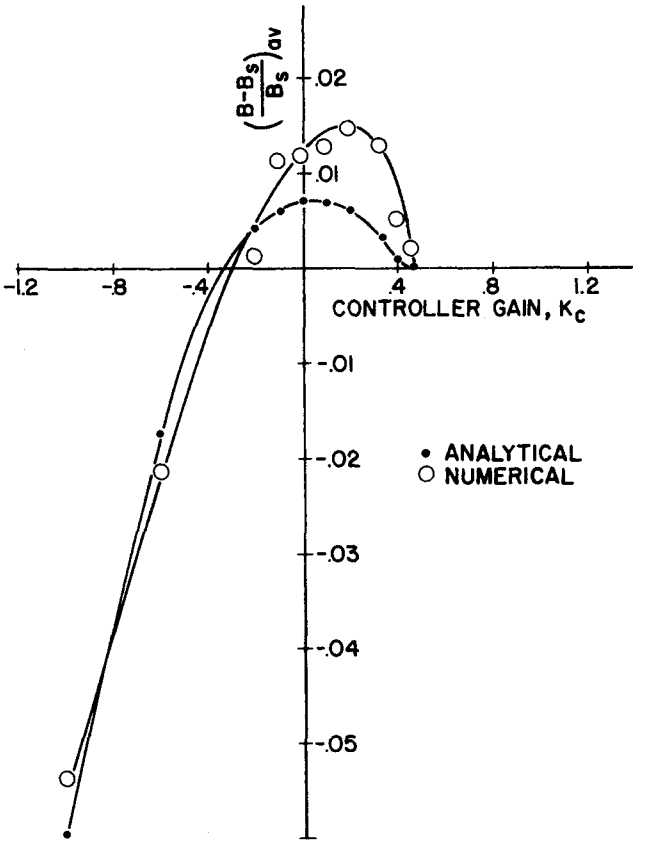

Fig. 10. Effect of controller gain on the time average yield.

topology of the system. This kind of a discrepancy normally can be avoided by eliminating the third derivative in temperature term from the expansion. Although this modification is somewhat arbitrary and reduces the accuracy of the analytical solutions, it does seem to lead to predictions which are valid in a qualitative sense.

Another limitation of the approximate analytical results is that the greatest improvements of periodic operation over the optimum steady state design conditions occur when there is large distortion. However, as the distortion increases, the assumptions used in the analysis start to break down, so that the solution actually is not valid in the region of greatest interest. It would seem that part of this difficulty could be resolved by including additional higher-order correction functions in the solution, but the algebraic complexity of the analysis seriously limits this approach. Thus we must recognize that even though the theory is useful for predicting the direction of the shift in the time average performance from steady state operation, it will only give conservative estimates of the magnitude of this shift.

Oscillator Performance for Consecutive Reactions

A number of studies were made for the simple consecutive mechanism in chemical oscillators. The qualitative techniques described previously were used to select the system parameters. With these parameters the analytical solution predicted that very small improvements should be obtained, but numerical integration of the nonlinear equations showed that the time average yield of B always decreased. In other words, the analytical results resemble those in Figure 10, where the curve is positive for a certain range of controller gains, but the numerical results approach the axis asymptotically. A plot of the projections of the limit cycles for the parameters listed in Table 2 is given in Figure 11. We believe that the discrepancy between the analytical and nu-

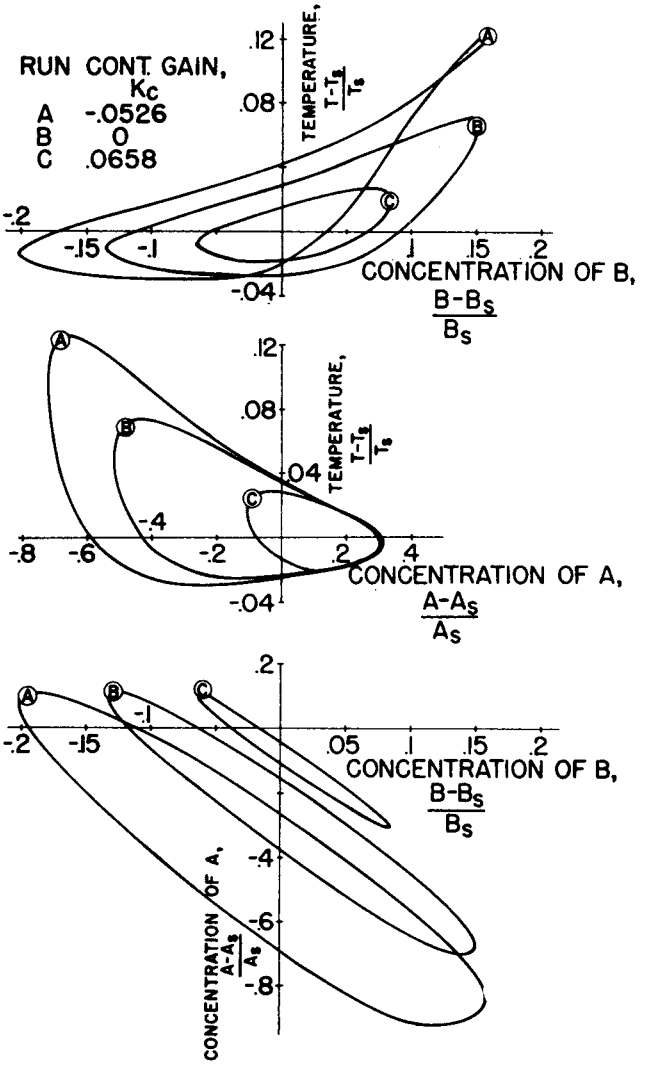

Fig. 11. Projections of limit cycle for consecutive reactions with different controller gains.

merical solutions is again due to the nature of the Taylor series approximation.

Higher-Order Chemical Oscillators

The analytical techniques for chemical oscillators described above can be applied to higher-order systems, providing that there is only a single pair of complex conjugate roots having positive real parts. However, the approach must be modified if this is not the case. In order to illustrate the behavior of coupled oscillators, we considered the consecutive reaction mechanism $A \longrightarrow B \longrightarrow C \longrightarrow D$ with the system equations

$$V\frac{dA}{dt} = q(A_f - A) - k_1VA \tag{1}$$

$$V\frac{dB}{dt} = q(B_f - B) + k_1VA - k_2VB \tag{2}$$

$$V\frac{dC}{dt} = q(C_f - C) + k_2VB - k_3VC \tag{9}$$

$$VC_p\rho\frac{dT}{dt} = qC_p\rho(T_f - T) - U_a(T - T_c) + (-\Delta H_1)k_1VA + (-\Delta H_2)k_2VB + (-\Delta H_3)k_3VC \tag{10}$$

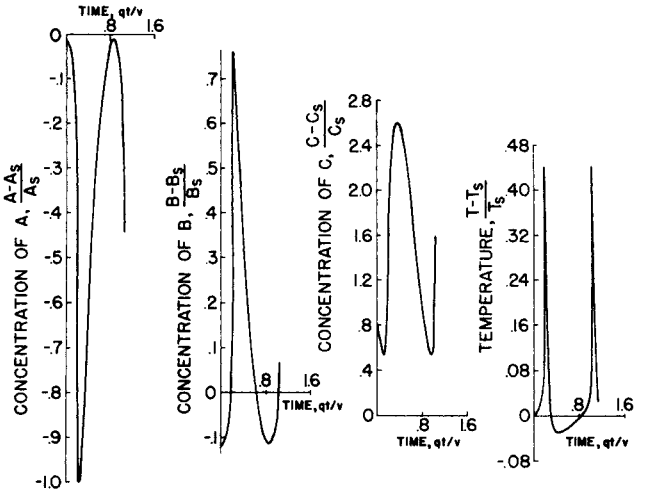

Fig. 12. Fluctuating outputs from a chemical oscillator for consecutive reactions.

We made no attempt to satisfy the optimum steady state design equations or Horn's criterion, but picked the parameters so that there were two pairs of complex conjugate roots each having positive real parts (see Table 2). A simple limit cycle in the four-dimensional space was obtained. The numerical solutions for the reactor oscillations are shown in Figure 12, and the computed improvement in B is about 11% while that in C is 160%. It is interesting to note that the oscillator frequency is significantly different from the imaginary part of both pairs of roots.

CONCLUSION

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. The well-known methods of nonlinear mechanics often can be used to estimate this difference both for cases of forced and self-generated oscillations. The approach is not always successful because a Taylor series expansion is used to approximate the reaction rate. Nevertheless, it provides a useful tool for obtaining first estimates and minimizing the amount of numerical computation.

It is difficult to draw conclusions about the potential advantages of periodic operation since a wide range of system parameters and reaction mechanisms was not considered. However, the 15 to 20% improvements which have been obtained make it appear as if additional work is warranted.

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NOTATION

A = composition of component A
A_c = heat transfer area of cooling coil
A_m = forcing amplitude, fraction of the forced parameter
B = composition of component B
C = composition of component C
$C_p\rho$ = heat capacity times density
E_i = activation energy of i^{th} reaction
$-\Delta H_i$ = heat of the i^{th} reaction
k_i = reaction rate constant for the i^{th} reaction
K = constant as defined by Equation (4)

K_c = controller gain; see Equation (8)
n = reaction order
q = flow rate
R = gas constant
T = temperature
t = time
U_a = overall heat transfer coefficient
U_c = heat transfer coefficient
V = reactor volume

Subscripts

av = average
c = coolant
f = feed
s = steady state

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Langmuir-Hinshelwood Kinetics of the Dehydration of Methanol Catalyzed by Cation Exchange Resin

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Rates of the dehydration of methanol to dimethyl ether catalyzed by cation exchange resin (polystyrenesulfonic acid) were measured with a differential flow reactor and gas chromatographic analysis. Reaction temperature was 119°C., pressure was 1 atm., and feeds were methanol and mixtures of methanol with argon, dimethyl ether, and water.

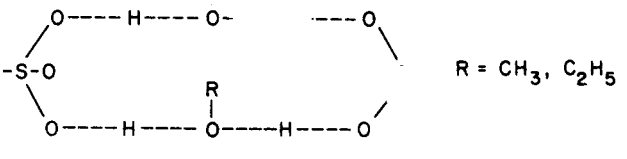
Rate data for the methanol reaction as well as the previously investigated ethanol dehydration reaction are well represented by Langmuir-Hinshelwood kinetics with adsorption parameters in the rate equations approximately equal to corresponding values of Langmuir adsorption equilibrium constants estimated from or available in the literature. The reaction model is consistent with previous conclusions regarding mechanism. Its pertinence suggests that at reaction conditions the ion exchange resin offers a nearly homogeneous array of catalytic sites.

Sulfonic acid ion exchange resins are active catalysts for the dehydration of alcohols to ethers and olefins. At sufficiently low temperatures ether formation from ethanol occurs without side reaction to olefin, as shown by Kabel and Johanson (*1*). In the following report the kinetic investigation of Kabel and Johanson is extended to the similar methanol dehydration.

$$2\,CH_3OH = H_2O + CH_3—O—CH_3$$

The alcohol dehydrations have a characteristic of general interest in catalytic kinetics, inhibition by a reaction product (water). The polymer catalyst is well suited to experimental investigation as it has a well-defined structure and is stable and of reproducible activity. The resin differs from typical solid catalysts in lacking rigid pores and true internal surface.

The methanol and ethanol dehydration reactions have been investigated with the resin catalyst in various ionic forms (*2*). Catalytic activity for reaction of each pure alcohol increased with catalyst sulfonic acid group concentration, and salt forms lacked activity. It was postulated that a hydrogen-bonded intermediate is formed involving reactant alcohol and catalyst sulfonic acid groups:



Similar bonds are formed between adjacent sulfonic acid groups alone (*3*) and also when water is bridged between sulfonic acid groups (*4*).

The kinetic data for ethanol dehydration have been examined by investigators concerned with statistical methods of parameter estimation and discrimination among reaction models (*5* to *7*). These analyses essentially confirm the

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