

The Use of Positive Feedback Control Systems to Improve Reactor Performance

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Positive feedback control systems sometimes can be used to make stable chemical reactors generate periodic outputs. For one set of system parameters the time average conversion obtained from the oscillating reactor was approximately 20% higher than the economic optimum steady state value; for another case the time average operating cost was approximately 5% lower than that corresponding to the optimum steady state design. A general method for predicting when an improvement can be obtained is presented.

Previous work has shown that in some cases the conversion obtained from a chemical oscillator, that is, a reactor designed to generate periodic outputs even when the inputs are maintained constant, is higher than the corresponding steady state value (3, 4). The importance of this observation has been questioned, however, since normally it is possible to increase the conversion simply by raising the reactor temperature or increasing the volume and with either of these latter techniques the problems associated with unsteady state operation can be avoided. In order to demonstrate that the performance of an oscillator actually can exceed the optimum steady state operation it is necessary to consider the process economics. While a complete determination of the optimum economic plant design requires a detailed description of every unit in the plant, and therefore is a profoundly difficult task, it is possible to define a somewhat oversimplified design problem which has the correct structure and which can be used to make comparisons between steady state and periodic reactor operation.

In a previous investigation it was noted that it might be possible to use positive feedback control systems to make stable reactors generate oscillations (4). Since it has never been demonstrated, even theoretically, that this kind of a very unconventional control system will operate in a satisfactory manner, a study was made to see if a positive feedback controller could be used to obtain an improved production rate from a stable reactor, and in particular from a reactor designed to have an economic optimum steady state performance.

Obviously, it is helpful to have a criterion which will predict whether or not the oscillator operation might be superior to the steady state case. At present, the only procedure available for this purpose is limited to first-order chemical reactions (4). Hence, a more general method has been developed and tested in this investigation.

OPTIMUM STEADY STATE DESIGN

In order to provide a basis of comparison for oscillating reactors, we must first determine the optimum steady state design conditions. If we limit our attention to a very simple reactor design problem where we attempt to produce G lb. mole/hr. of a product B by the first-order chemical reaction, $A \rightarrow B$, then we know from elementary reactor design considerations (2) that the highest conversion per unit volume is obtained with a plug flow reactor operated isothermally. However, isothermal operation is seldom economical on an industrial scale because of the

large costs required to heat the reactants to the appropriate reaction temperature and the additional cost to remove (or supply) the heat of reaction along the reactor length. If adiabatic operation is employed and the reaction is exothermic, then a continuous stirred tank reactor gives a higher conversion per unit volume, at least at conversions below those corresponding to the maximum reaction rate. Hence we will consider the design of a continuous stirred tank reactor, and include the possibility of operating in excess of the adiabatic temperature by inserting a heating coil in the vessel. For the sake of simplicity, we assume that the cost required to separate A and B in the effluent stream is negligible and that reactant material cannot be recycled.

The rate at which the system produces profit may be written as

$$P_r = C_B G - C_T \quad (1)$$

but since the production rate is constant, it is clear that the system design which minimizes the total cost is the same as that which maximizes the profit. An expression for the total cost is

$$C_T = C_V V + C_f q X_f + C_H q_H + C_A A_H \quad (2)$$

where the first two terms refer to the operating cost and the capital cost on a depreciated basis of the reactor and the last two terms are the corresponding costs of the heating coil. The relationship between the production rate and the system variables is

$$G = q(x_f - x) \quad (3)$$

The material and energy balances for the reactor are

$$q(x_f - x) - k V x = 0 \quad (4)$$

$$q C_{PP}(T_f - T) + (-\Delta H)k V x + Q_H = 0 \quad (5)$$

where

$$k = k_0 e^{-E/RT} \quad (6)$$

and the heat duty supplied by the heating coil can be determined from the energy loss of the heating fluid

$$Q_H = q_H C_{PH} \rho_H (T_H - T_o) \quad (7)$$

or the heat transfer between the coil and the reactor

$$Q_H = U A_H \left[\frac{T_H - T_o}{\ln \frac{T_H - T}{T_o - T}} \right] \quad (8)$$

We can simplify the algebra of the problem somewhat if we assume that the log-mean driving force can be approximated by an arithmetic mean

$$Q_H = UA_H \left[\frac{1}{2} (T_H + T_o) - T \right] \quad (9)$$

Equations (3) through (7) and either Equation (8) or (9) provide six relationships between the nine design variables, q , x , T , k , Q_H , q_H , T_o , A_H , and V , and the other specified quantities. Hence, any three of the design variables may be chosen arbitrarily but, obviously, we want to select the set of values which leads to the minimum cost for the system, Equation (2). A number of approaches can be used for this purpose. For example, we can use the expressions above to eliminate six of the variables from the problem and obtain a cost equation which only depends upon three independent variables

$$C_T = \frac{C_V G}{kx} + \frac{C_f G x_f}{x_f - x} - \left[(-\Delta H) G + \frac{GC_{PP}(T_f - T)}{x_f - x} \right] \cdot \left[\frac{2C_A}{U(T_H + T_o - 2T)} + \frac{C_H}{C_{PH}\rho_H(T_H - T_o)} \right] \quad (10)$$

Then we can take the partial derivatives of this relationship with respect to T , T_o , and x , set them equal to zero, solve the three algebraic equations we obtain for the optimum values and finally use system equations to find the remaining design variables. Alternately, we could use a three dimensional direct search procedure or a hill climbing routine (10) to find the minimum of Equation (10).

It should be noted however, that a solution of this problem does not always exist. In fact, by examining the ex-

pressions for the partial derivatives, it is possible to show that there will not be a solution unless

$$1 > \frac{(-\Delta H)(x_f - x)}{C_{PP}(T_H - T_f)} + \left(\frac{E}{RT^2} \right) \left(\frac{x}{x_f - x} \right) \frac{(T - T_f)(T_H - T)}{(T_H - T_f)} \quad (11)$$

Similarly, it can be shown that a stirred tank reactor with a cooling coil can never correspond to an optimum design. This result might explain why Westbrook and Aris (9) found that the optimum conditions for a somewhat similar reactor design problem were obtained with adiabatic operation, that is, no cooling.

The optimum steady state designs for four sets of system parameters are given in Table 1. In each case there was only a single steady state solution. Plots of the total cost vs. the design variables in the neighborhood of the optimum were used to show that the total cost was a minimum, for example, see Figures 1 and 2. The graphs make it apparent that the optimum design is quite sensitive with respect to certain design variables, Figure 1, but is relatively insensitive to others, Figure 2. These results for a stirred tank reactor can be compared with the optimum designs for other types of reactor in order to find the system which has the most profitable performance.

POSITIVE FEEDBACK CONTROL

If we assume that the dynamics of the heating coil are negligible and that our previous approximation for the log-mean driving force for the heat transfer from the coil remains valid during unsteady state operation, then the dynamic equations can be written as

TABLE 1. OPTIMUM STEADY STATE DESIGN

Cost data	Case I	Case II	Case III	Case IV
C_A (\$)/(hr.)(sq. cm.)	0.0353	0.0979	0.0705	0.0910
C_f (\$)/(g. mole)	0.0579	0.0236	0.0903	0.0400
C_H (\$)/(g.)	0.00001	0.00002	0.00002	0.00002
C_V (\$)/(hr.)(liter)	0.0571	0.0148	0.0222	0.0576
System constants				
$C_P \rho$ (cal.)/(cc.)(°K.)	1.0	1.0	1.0	1.0
$C_{PH} \rho_H$ (cal.)/(cc.)(°K.)	1.0	1.0	1.0	1.0
E (cal.)/(g. mole)	72,000	59,800	96,000	68,000
$(-\Delta H)$ (cal.)/(g. mole)	28,000	12,900	26,250	8,889
k_o (sec.) ⁻¹	5.65×10^{21}	3.01×10^{30}	5.46×10^{29}	8.20×10^{32}
Design data and system inputs				
G (g. mole)/(hr.)	2,550	1,285	1,280	4,050
T_f (°K.)	306	300	289	325
T_H (°K.)	606	373	606	404
U (cal.)/(sq. cm.)(sec.)(°K.)	1.0	1.0	1.0	1.0
x_f (g. mole)/(cc.)	0.01	0.005	0.01	0.0075
Optimum design variables				
A_H (sq. cm.)	2,661	920	1,768	1,860
k (hr.) ⁻¹	0.180	0.072	0.036	0.360
Q_H (cal.)/(sec.)	9,325	2,310	6,165	5,032
q (cc.)/(sec.)	100	100	50	200
q_H (cc.)/(sec.)	1,865	770	1,234	1,480
T (°K.)	600	369	600	400
T_o (°K.)	601	370	601	401
V (liters)	5,000	12,500	12,500	6,000
x (g. mole)/(cc.)	0.00285	0.00143	0.00285	0.00188
Optimum costs				
$C_V V$ (\$)/(hr.)	285	185	278	346
$C_f q A_f$ (\$)/(hr.)	208	42	162	216
$C_A A_H$ (\$)/(hr.)	94	91	125	169
$C_H q_H$ (\$)/(hr.)	67	55	88	107
C_T (\$)/(hr.)	654	373	653	838

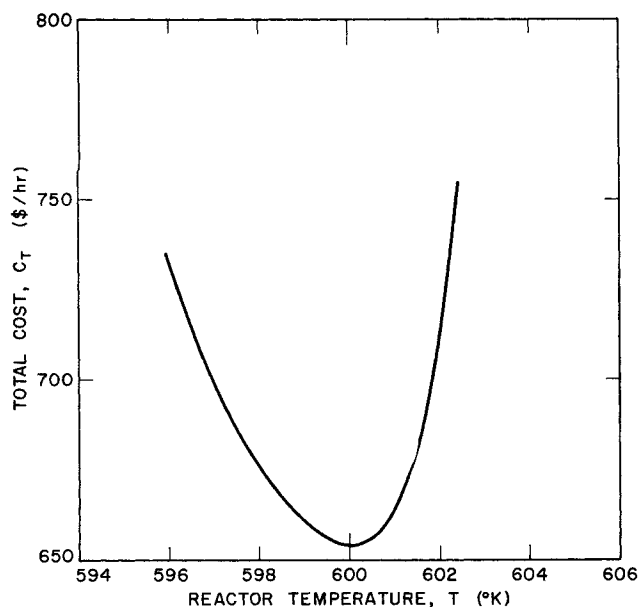


Fig. 1. Total cost vs. reactor temperature.

$$V \frac{dx}{dt} = q(x_f - x) - kVx \quad (12)$$

$$VC_{P\rho} \frac{dT}{dt} = qC_{P\rho}(T_f - T) + U_a(T_H - T) + (-\Delta H)kVx \quad (13)$$

where

$$k = k_0 e^{-E/RT}, \quad U_a = \frac{2C_{P\rho}Hq_H}{\left(1 + \frac{2C_{P\rho}Hq_H}{UA_H}\right)} \quad (14)$$

These are the equations normally used to describe the dynamic behavior of a stirred tank reactor, and their stability characteristics are well known (1). Thus, it is a simple matter to show that the optimum steady state designs given in Table 1 correspond to stable equilibrium points.

However, since we are interested in comparing the operation of an oscillating reactor with the optimum steady state performance, we need to make the equilibrium point unstable. One way this can be accomplished is to reverse the normal connections of a proportional feedback controller so that it supplies a positive feedback. In other words, we attach the controller in such a way that if the reactor temperature exceeds the design value we increase the flow rate of heating material through the coil, which increases the heat transfer to the reactor and tends to make the temperature continue to increase. Similarly, if the reactor temperature falls below the design value, we decrease the flow of heating material.

The range of controller gains corresponding to unstable operation of the optimum design can be established by determining the characteristic roots of the linearized system equations (1, 5). Assuming that the effect of heating flow rate on the overall heat transfer coefficient is approximately linear and that we make the change in this flow rate proportional to the difference between the actual reactor temperature and the steady state value, we find that

$$U_a = U_{as} + K(T - T_s) \quad (15)$$

where K includes the controller gain. If we let

$$x_1 = -\frac{x - x_s}{x_s}, \quad x_2 = -\frac{T - T_s}{T_s}, \quad \tau = \frac{qt}{V},$$

$$\begin{aligned} \beta_1 &= \frac{V}{q} k_0 e^{-E/RT_s}, \quad \beta_3 = \frac{E}{RT_s}, \quad \beta_4 = 1 + \frac{U_{as}}{qC_{P\rho}}, \\ \beta_5 &= \frac{(-\Delta H)Vk_0 x_s e^{-E/RT_s}}{qC_{P\rho}T_s}, \quad \beta_6 = \frac{KT_s}{qC_{P\rho}}, \\ \beta_7 &= 1 - \frac{T_H}{T_s} \end{aligned} \quad (16)$$

and substitute these expressions into the nonlinear system equations, Equations (12) and (13), we obtain

$$\frac{dx_1}{d\tau} = -x_1 - \beta_1 \left[1 - (1 - x_1) \exp\left(\frac{\beta_3 x_2}{x_2 - 1}\right) \right] \quad (17)$$

$$\begin{aligned} \frac{dx_2}{d\tau} &= -\beta_4 x_2 + \beta_5 \left[1 - (1 - x_1) \exp\left(\frac{\beta_3 x_2}{x_2 - 1}\right) \right] \\ &\quad - \beta_6 x_2 (\beta_7 - x_2) \end{aligned} \quad (18)$$

Then linearizing these equations, determining the characteristic roots in terms of the system parameters, and requiring that the roots correspond to either an unstable focus or node (3 to 5), we find that the criteria for oscillatory operation is (4, 6)

$$\beta_1 (\beta_4 + \beta_6 \beta_7) > \beta_3 \beta_5 + \beta_6 \beta_7 > 1 + \beta_1 \quad (19)$$

It is a simple matter to find the values of the controller gain, or β_6 , which satisfy this relationship since all of the other parameters are known from the optimum steady state design calculations. Also, since β_7 is a negative quantity for our problem, $T_H > T_s$, the range of allowable values of β_6 will be limited.

Of course, the simple stability analysis above only guarantees that the steady state operating condition will be unstable. However, for most system parameters it is possible to show that the system must remain within a certain region and that the boundary of the region is unstable, that is $0 < x < x_f$ is a strict inequality according to Equation (12). Then, the existence of a single unstable equilibrium point and an unstable boundary implies that the system trajectories must approach a stable limit cycle (3, 4, 8).

In physical terms, we can describe the oscillatory behavior as follows. If the uncontrolled reactor is initially

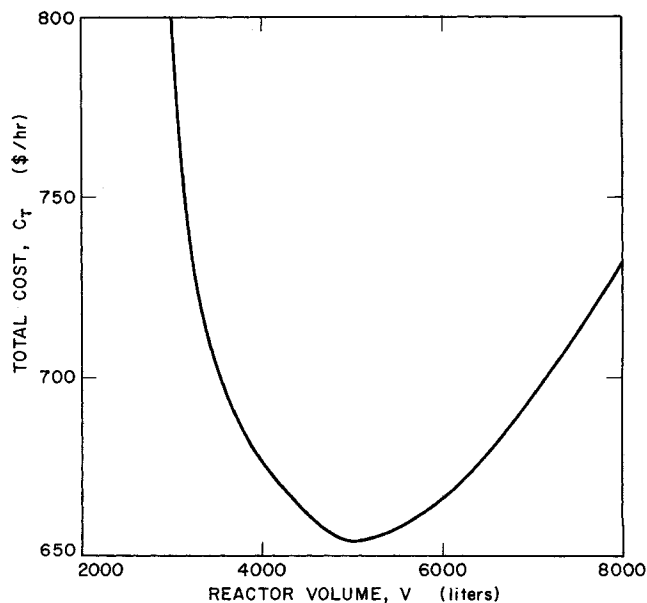


Fig. 2. Total cost vs. reactor volume.

operating at steady state and then the feedback loop of the positive feedback control system is closed, the original steady state operating condition will become unstable and any small disturbance will make the reactor move away from this operating point. Supposing that a disturbance initially causes a slight increase in the reactor temperature, then the control system will automatically increase the flow rate of the heating material which will cause the reactor temperature to continue to increase. At the same time, the increase in temperature will increase the rate of the chemical reaction, and therefore the heat generated by the reaction, so that an additional temperature rise will be encountered. However, at some point the reactant concentration in the vessel will drop to such a small value that the reaction rate, and correspondingly the heat generated by the reaction, will become very small; in fact much smaller than at the original steady state operating condition. As the heat generation starts to decrease the amount of heat supplied by the controller will decrease, and providing that the system parameters are in a certain range, at some point the convective heat loss will cause the reactor temperature to decrease. The decreasing temperature then makes the control system continue to cut down on the flow rate of heating fluid so that as the temperature drops the amount of heat added through the coil becomes smaller and smaller. Also, additional heat will be removed from the system by the convective flow through the reactor. During this cooling period, the reactant concentration will gradually build up and at some point the reaction rate term, and the rate of heat generated by the reaction, will become appreciable and the temperature will start to increase. After this initial increase, the control system will start supplying additional heat to the system and the autocatalytic nature of the reaction rate will again cause the temperature to increase. Hence, the system will continue to generate periodic out-

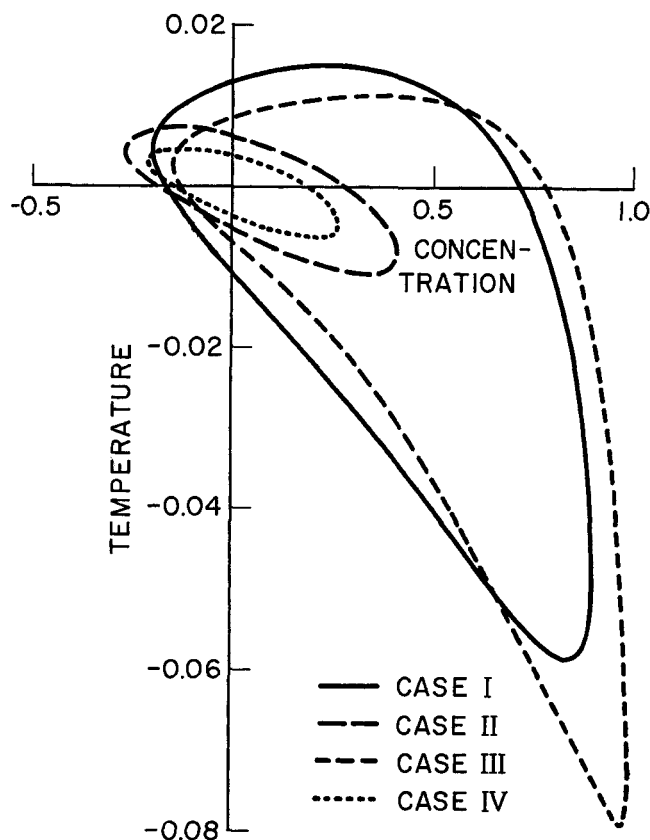


Fig. 4. Composition-temperature phase plane.

puts, even though the reactor inputs remain constant at their original steady state values.

ESTIMATION OF THE TIME AVERAGE SYSTEM PERFORMANCE

It is apparent that the linearized dynamic equations will not give an adequate description of the oscillatory behavior of the reactor because they do not include the bounded nature of the system equations. Also it is possible that the time average performance of the oscillator might be different from the steady state design conditions, that is, the system nonlinearities might be such that more is gained when the system goes to high temperatures than is lost at low temperatures. Hence, it is necessary to develop a method which provides at least an approximate description of the oscillator output in order to assess the potential advantages of periodic operation.

Two simple procedures which can be used for this purpose were published by Douglas and Gaitonde (4). However, they are limited to the case of a first-order chemical reaction. Another method published by Luus and Lapidus (7) can be used to estimate the size of the limit cycle, but does not consider the shift in the time average performance of the system. Hence, a more general method which is applicable to any system of two first-order nonlinear differential equations is presented in the Appendix. This solution is more complicated than those published previously, because it is more general. Although a perturbation method (8) was used to develop the approximate solution and a small parameter μ is included in the analysis, the existence of a small parameter in the nonlinear system equations is not actually necessary since it is only used to keep track of terms having different orders of magnitude.

As shown by the example in the Appendix, the expression for the time average value of the reactant effluent composition is

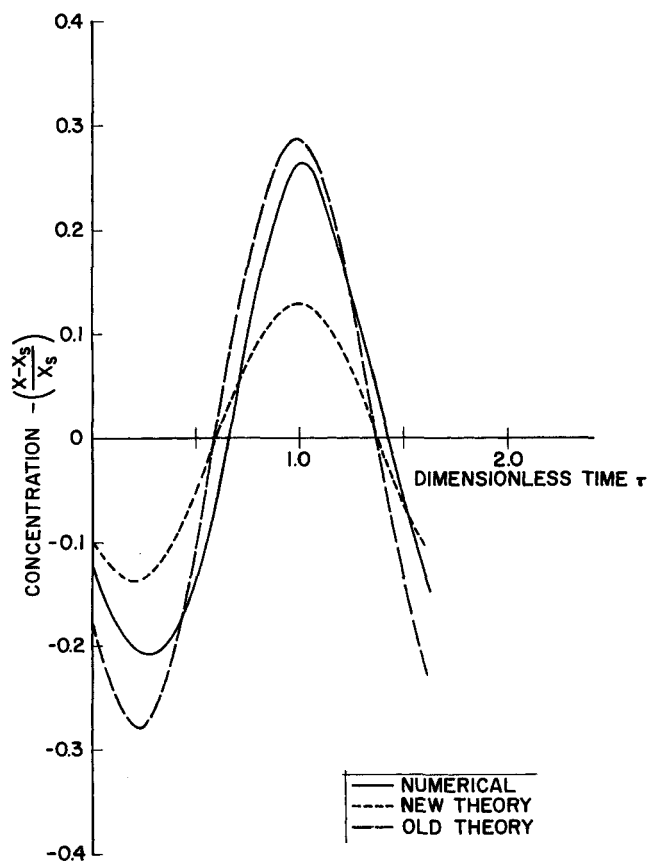


Fig. 3. Oscillating reactor composition.

TABLE 2. TIME AVERAGE OSCILLATOR OUTPUTS

Time Average Output	Case I	Case II	Case III	Case IV
$x_{1\text{avg}}$, theoretical	0.00272	0.00142	0.00270	0.00187
$x_{1\text{avg}}$, numerical	0.00230	0.00135	0.00224	0.00183
% improvement in x_1 , theoretical	3.97	0.68	4.97	0.27
% improvement in x_1 , numerical	18.72	4.71	21.42	2.03
% decrease in temperature, theoretical	0.0284	0.0030	0.0300	0.0010
% decrease in temperature, numerical	0.0440	0.0072	0.0400	0.0008
Optimum steady state operating cost	275.5	97.8	251.0	323.0
Operating cost of oscillator, theoretical	272.8	97.7	247.9	322.7
Operating cost of oscillator, numerical	261.4	96.7	238.1	320.7

$$x_{1\text{avg}} = \{[2(1 + \beta_1) - d_{ec}] (K_7 + K_8) + \omega_0 K_9\} \frac{A_0^2}{\omega} \quad (20)$$

where the parameters are defined in the Appendix. A large number of assumptions were used in the derivation of this result, and therefore we do not expect it to give a very accurate prediction of the difference between the time average performance of the system and the steady state output. The most important feature of the analysis is that it does predict periodic outputs and it does indicate the direction of the shift in the mean value. Once this kind of an estimate has been obtained and the most promising range of parameters pinpointed, then an accurate description of the oscillating output can be determined by numerical integration of the equations.

The approximate analytical solution shows that a positive feedback control system will lead to an improvement of the time average performance of the reactor for all four cases listed in Table 1, and therefore numerical solutions of the nonlinear equations were generated on a digital computer. The theoretical and numerical estimates of the shift in the average operating levels are compared in Table 2. Although the maximum improvement listed in Table 2 is 20%, cases corresponding to 40% differences can be obtained.

A graphical comparison between the effluent compositions for case 4 is given in Figure 3. It is apparent from the graph that the new approximate analytical solution is only qualitatively correct for this set of system parameters. In fact, this new solution does not fit as well as our original solution (4), which is probably due to the fact that more complicated expressions were used to approximate the nonlinear functions. The accuracy of the solution is expected to degenerate as the output signal becomes less like a sine wave, or as the limit cycle deviates from an ellipse. Hence, the approximate solution is expected to give a poor prediction for cases 1 and 3 (see the numerical solutions plotted in Figures 4 and 5) although the direction of the shift is correct.

The numerical results indicate that the oscillating reactor produces a higher time average conversion, and therefore a higher production rate, than the optimum steady state system. If there is no demand for this additional production, then it is possible to maintain the initial specified value with a smaller amount of feed material, and a corresponding decrease in the raw material cost. A crude estimate of the savings in operating costs for the four cases under consideration is given in Table 2, and in the best case the improvement is approximately 5.0%. A more accurate evaluation could be obtained by numerically solving the nonlinear equations for several values of the feed rate and then determining the actual value which gives the same time average production rate by interpolation. The time average value of the flow rate of heating material also will be different from the optimal steady state value.

However, we know from the control law that the difference must be proportional to the mean value of the effluent temperature, and therefore it can be estimated theoretically or obtained numerically. The economic effect of this variation is included in the calculation given in Table 2.

CONCLUSIONS

It has been shown that positive feedback control systems sometimes can be used to force normally stable reactors to generate oscillations. The results of a crude economic analysis for the proportional control system considered in the study indicate that in some cases the time average performance of these oscillating reactors is better, that is, a 5% lower operating cost, than the optimum steady state design. Rough initial estimates of the difference between these two cases can be obtained by using the approximate analytical solutions given in the Appendix. It might be possible to obtain additional improvements by adding derivative and integral modes to the control system or by using other measurement and control variables. However, these cases were not investigated.

Of course, the oscillating reactors described above do not necessarily correspond to the optimum periodic process. Thus, for a complete analysis it would be necessary to determine the optimum periodic inputs using Horn's (6) approach, estimate the cost of producing these inputs, and then compare this result to the profit obtained from the chemical oscillator minus the cost of the positive feedback control system. Also, for realistic problems, the separation costs of the product and product quality specifications would have to be considered, as well as the optimum de-

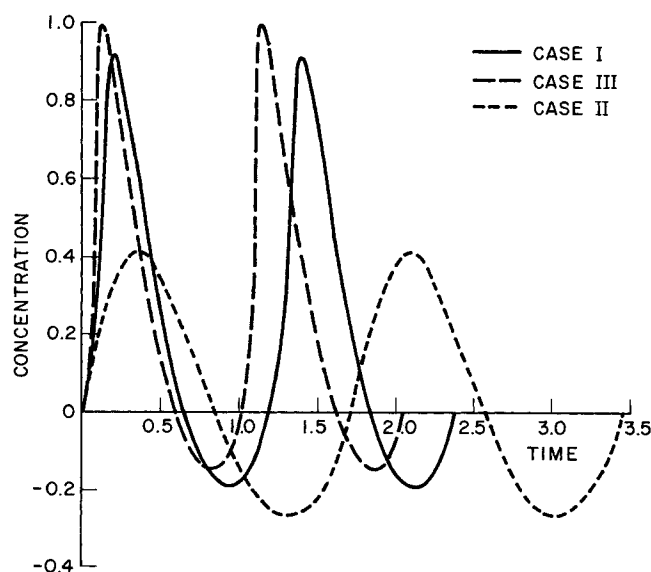


Fig. 5. Oscillating reactor composition.

signs for other types of reactors. However, the use of positive feedback control systems might provide a simple way of increasing the capacity of some existing operating units even in cases where they do not give the optimal periodic operation.

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NOTATION

A = Jacobian matrix, see Equation (24)
 A_0 = amplitude of limit cycle
 A_H = heat exchanger area
 $a_{11}, a_{12}, a_{13}, a_{14}$ = elements of A , see Equation (24)
 C_A = cost of heating coil, $(\$)/(\text{area})(\text{time})$
 C_B = value of product, $(\$/\text{amount of } B)$
 C_f = cost of reactant material, $(\$/\text{amount of } A)$
 C_H = cost of heating material, $(\$/\text{amount})$
 C_p, C_{PH} = heat capacity of reactant and heating fluid, respectively
 C_T = total cost of reactor and heat exchanger, $(\$/\text{time})$
 C_V = cost of reactor, $(\$)/(\text{volume})(\text{time})$
 d_{ec}, d_{fc} = constants defined by Equation (52)
 E = activation energy
 f = nonlinear vector function
 f_1, f_2 = nonlinear functions, see Equation (21)
 G = specified production rate
 g = nonlinear vector function
 $(-\Delta H)$ = heat of reaction
 I = identity matrix
 K = constant proportional to controller gain, see Equation (15)
 K_1, K_2, K_3 = constants defined by Equations (54)
 K_4, K_5, K_6 = constants defined by Equations (56)
 K_7, K_8, K_9 = constants defined by Equations (58)
 k = reaction rate constant
 k_c = controller gain
 k_o = frequency factor
 $m(t)$ = vector function of time, see Equations (39) and (40)
 m_1 to m_7 = terms in m , see Equation (40)
 m_{12}, m_{22} = components of m_2
 m_{13}, m_{23} = components of m_3
 P = transformation matrix
 P_r = profit rate
 $p_{11}, p_{12}, p_{21}, p_{22}$ = elements of P
 Q_H = heat duty of coil
 q = feed rate of reactant
 q_H = flow rate of heating material
 R = gas constant
 r = radius of limit cycle
 T = reactor temperature
 T_f = feed temperature
 T_H = inlet temperature of heating fluid
 $T_{H\text{avg.}}$ = average temperature of heating fluid
 T_o = outlet temperature of heat coil
 t = time
 U = overall heat transfer coefficient
 U_a = see Equation (14)
 V = reactor volume
 x = state vector
 x_f, x = reactant composition in feed and effluent streams, respectively
 x_1, x_2 = dimensionless composition and temperature
 y = canonical state vector

y_0, y_1 = generating solution and first order correction functions, respectively

y_{10}, y_{20} = components of y_0

Greek Letters

α = real part of characteristic root
 $\beta_1, \beta_3, \beta_4, \beta_5, \beta_6, \beta_7$ = constants defined by Equations (16)
 Λ = matrix defined by Equation (28)
 Λ_ω = matrix defined by Equations (29) and (30)
 μ = small parameter
 ρ, ρ_H = density of reactants and heating fluid, respectively
 τ = dimensionless time, see Equation (16)
 ω = frequency of nonlinear oscillator, see Equation (34)
 ω_0 = imaginary part of characteristic root
 ω_1, ω_2 = correction terms for oscillator frequency, see Equation (34)

Subscripts

avg. = average
 f = feed
 H = heating fluid
 s = steady state

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APPENDIX

Approximate Solution for Chemical Oscillators

We consider any system described by two first-order nonlinear differential equations

$$\dot{x}_1 = f_1(x_1, x_2), \quad \dot{x}_2 = f_2(x_1, x_2) \quad (21)$$

Once the steady state solution of interest has been obtained by setting the accumulation terms equal to zero and finding the roots of the algebraic equations, it is possible to translate the coordinate system so that this point is at the origin. This transformation will not change the form of the equations above, and therefore we will now consider that the state variables represent deviations from the origin. If we write the equations in matrix notation we obtain

$$\dot{x} = f(x_1, x_2) \quad (22)$$

We can avoid dealing with very complex functions on the right hand sides of the equations by expanding them in a Taylor series about the origin, and we will keep all terms up to the third-order. Then, we can write

$$\dot{x} = A x + g(x) \quad (23)$$

where \mathbf{A} is the Jacobian matrix

$$\mathbf{A} = \begin{pmatrix} \frac{\partial f_1}{\partial x_1} & \frac{\partial f_1}{\partial x_2} \\ \frac{\partial f_2}{\partial x_1} & \frac{\partial f_2}{\partial x_2} \end{pmatrix} = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \quad (24)$$

and $\mathbf{g}(\mathbf{x})$ is a vector containing all of the second and third order terms. The partial derivatives in both \mathbf{A} and $\mathbf{g}(\mathbf{x})$ should be evaluated at the origin, and therefore are known constants.

The simplest case for obtaining self-generated oscillations occurs when the \mathbf{A} matrix has a pair of complex conjugate characteristic roots with positive real parts. For this case, it is somewhat simpler to follow the analysis if we make a canonical transformation

$$\mathbf{x} = \mathbf{P} \mathbf{y} \quad (25)$$

By choosing the columns in this transformation matrix \mathbf{P} to be the right-hand eigenvectors of the Jacobian \mathbf{A} , the state equations for \mathbf{y} will have a diagonal form. However, since the characteristic roots are complex conjugates, the state variables \mathbf{y} would have to be complex variables. In order to avoid this complication we choose \mathbf{P} as

$$\mathbf{P} = \begin{pmatrix} 2(\alpha - a_{11}) & 2\omega_0 \\ -2a_{21} & 0 \end{pmatrix} \quad (26)$$

where α is the real part of the characteristic roots and ω_0 the imaginary part. With this transformation, our new state equations become

$$\dot{\mathbf{y}} = \mathbf{\Lambda} \mathbf{y} + \mathbf{P}^{-1} \mathbf{g}(\mathbf{P} \mathbf{y}) \quad (27)$$

where

$$\mathbf{\Lambda} = \mathbf{P}^{-1} \mathbf{A} \mathbf{P} = \begin{pmatrix} \alpha & -\omega_0 \\ \omega_0 & \alpha \end{pmatrix} \quad (28)$$

Now, if we partition the $\mathbf{\Lambda}$ matrix, we can write

$$\mathbf{\Lambda} = \omega_0 \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} + \alpha \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad (29)$$

or

$$\mathbf{\Lambda} = \omega_0 \mathbf{\Lambda}_\omega + \alpha \mathbf{I} \quad (30)$$

where $\mathbf{\Lambda}_\omega$ can be determined by inspection. Substituting this result into the state equations gives

$$\dot{\mathbf{y}} = \omega_0 \mathbf{\Lambda}_\omega \mathbf{y} + \alpha \mathbf{I} \mathbf{y} + \mathbf{P}^{-1} \mathbf{g}(\mathbf{P} \mathbf{y}) \quad (31)$$

It's apparent that this set of equations would have periodic solutions if the last two terms on the right hand side were missing. Hence we multiply these terms by a small parameter μ

$$\mathbf{y} = \omega_0 \mathbf{\Lambda}_\omega \mathbf{y} + \mu [\alpha \mathbf{I} \mathbf{y} + \mathbf{P}^{-1} \mathbf{g}(\mathbf{P} \mathbf{y})] \quad (32)$$

and assume that we can find a solution having the form (4, 11)

$$\mathbf{y} = \mathbf{y}_0 + \mu \mathbf{y}_1 + \mu^2 \mathbf{y}_2 + \dots \quad (33)$$

$$\omega = \omega_0 + \mu \omega_1 + \mu^2 \omega_2 + \dots \quad (34)$$

where $\mathbf{y}_0, \mathbf{y}_1, \dots$, are a number of functions to be determined, ω will be the actual frequency of the nonlinear oscillator, and $\omega_1, \omega_2, \dots$, are a number of frequency correction terms. Substituting this assumed solution into the state equations and equating terms having like coefficients of μ (4, 8), we obtain the set of equations

$$\dot{\mathbf{y}}_0 = \omega \mathbf{\Lambda}_\omega \mathbf{y}_0 \quad (35)$$

$$\mathbf{y}_1 = \omega \mathbf{\Lambda}_\omega \mathbf{y}_1 - \omega_1 \mathbf{\Lambda}_\omega \mathbf{y}_0 + \alpha \mathbf{I} \mathbf{y}_0 + \mathbf{P}^{-1} \mathbf{g}(\mathbf{P} \mathbf{y}_0) \quad (36)$$

where we have only included the equations for the generating solution \mathbf{y}_0 and the first order correction functions \mathbf{y}_1 .

The first equation in this set describes a simple harmonic oscillator. If we choose the boundary conditions as $\mathbf{y}_{10} = \mathbf{A}_0$, $\mathbf{y}_{20} = 0$ at $t = 0$, where the first subscript of a state variable refers to the row in the state vector and the second refers to the generating solution, first order correction function, etc., and \mathbf{A}_0 is the unknown amplitude of the oscillation, then the generating solution becomes

$$\mathbf{y}_{10} = \mathbf{A}_0 \cos \omega \tau, \quad \mathbf{y}_{20} = \mathbf{A}_0 \sin \omega \tau \quad (37)$$

This result can now be used to eliminate the generating solution \mathbf{y}_0 from the equation for the first correction function \mathbf{y}_1 , Equation (36). If the third order polynomial function $\mathbf{g}(\mathbf{P} \mathbf{y}_0)$ is written explicitly in terms of the generating solution, trigonometric identities used to replace powers of trigonometric terms by higher order harmonics, and the resulting expressions added to the second and third terms on the right hand side of Equation (36) we obtain

$$\dot{\mathbf{y}}_1 = \omega \mathbf{\Lambda}_\omega \mathbf{y}_1 + \mathbf{m}(\tau) \quad (38)$$

where

$$\mathbf{m}(\tau) = -\omega_1 \mathbf{\Lambda}_\omega \mathbf{y}_0 + \alpha \mathbf{I} \mathbf{y}_0 + \mathbf{P}^{-1} \mathbf{g}(\mathbf{P} \mathbf{y}_0) \quad (39)$$

and has the form

$$\mathbf{m}(\tau) = \mathbf{m}_1 + \mathbf{m}_2 \cos \omega \tau + \mathbf{m}_3 \sin \omega \tau + \mathbf{m}_4 \cos 2 \omega \tau + \mathbf{m}_5 \sin 2 \omega \tau + \mathbf{m}_6 \cos 3 \omega \tau + \mathbf{m}_7 \sin 3 \omega \tau \quad (40)$$

The complimentary solution of Equation (38) will be a linear combination of $\sin \omega \tau$ and $\cos \omega \tau$ terms. Since these terms also appear in the nonhomogeneous portion of the equations, $\mathbf{m}(\tau)$, the particular integral must include terms having the form $\tau \sin \omega \tau$ and $\tau \cos \omega \tau$. However, these terms would make the solution for the correction function \mathbf{y}_1 unbounded as τ increases, and since we are looking for a stable periodic output we will remove the secular terms by setting their coefficients equal to zero.

$$m_{22} - m_{13} = 0, \quad m_{23} + m_{12} = 0 \quad (41)$$

These equations provide two relationships which can be used to evaluate \mathbf{A}_0 , the unknown amplitude of the oscillation, and ω_1 , the first-order frequency correction. It is also apparent that the particular integral will include a constant term since the nonhomogeneous function $\mathbf{m}(\tau)$ includes a constant vector \mathbf{m}_1 . The boundary conditions for the correction function \mathbf{y}_1 are taken as $\mathbf{y}_1(0) = 0$, since the initial conditions for the state variable \mathbf{y} have been included in the generating solution \mathbf{y}_0 . Once the solution for \mathbf{y}_1 has been determined, the approximate solution in terms of the canonical variables becomes

$$\mathbf{y} = \mathbf{y}_0 + \mu \mathbf{y}_1 + \dots \quad (33)$$

or, since $\mu = 1$, see Equations (31) and (32),

$$\mathbf{y} = \mathbf{y}_0 + \mathbf{y}_1 + \dots \quad (42)$$

Our small parameter arguments will be valid even for the case where $\mu = 1$ providing that \mathbf{y}_1 is small compared with \mathbf{y}_0 (4).

The solution in terms of the original state variables is obtained by making the linear transformation given by Equation (25). Hence, the approximate solutions for the outputs are

$$x_1 = x_{1av} + p_{11} \mathbf{A}_0 \cos \omega \tau + p_{12} \mathbf{A}_0 \sin \omega \tau + \dots \quad (43)$$

$$x_2 = x_{2av} + p_{21} \mathbf{A}_0 \cos \omega \tau + p_{22} \mathbf{A}_0 \sin \omega \tau + \dots \quad (44)$$

where

$$\mathbf{P} = \begin{pmatrix} p_{11} & p_{12} \\ p_{21} & p_{22} \end{pmatrix} = \begin{Bmatrix} -3 \left(\frac{\partial f_1}{\partial x_1} + \frac{\partial f_2}{\partial x_2} \right) \left[\frac{1}{4} \left(\frac{\partial f_1}{\partial x_1} - \frac{\partial f_2}{\partial x_2} \right)^2 + \left(\frac{\partial f_1}{\partial x_2} \right) \left(\frac{\partial f_2}{\partial x_1} \right) \right]^{1/2} \\ -2 \frac{\partial f_2}{\partial x_1} \\ 0 \end{Bmatrix} \quad (45)$$

$$A_0^2 = -16 |P| \left(\frac{\partial f_1}{\partial x_1} + \frac{\partial f_2}{\partial x_2} \right) \left\{ \begin{pmatrix} p_{22} \\ -p_{12} \end{pmatrix}^T \begin{pmatrix} \frac{\partial^3 f_1}{\partial x_1^3} & \frac{\partial^3 f_1}{\partial x_1^2 \partial x_2} & \frac{\partial^3 f_1}{\partial x_1 \partial x_2^2} & \frac{\partial^3 f_1}{\partial x_2^3} \\ \frac{\partial^3 f_2}{\partial x_1^3} & \frac{\partial^3 f_2}{\partial x_1^2 \partial x_2} & \frac{\partial^3 f_2}{\partial x_1 \partial x_2^2} & \frac{\partial^3 f_2}{\partial x_2^3} \end{pmatrix} \cdot \begin{pmatrix} 3 p_{11}^3 + 3 p_{11} p_{12}^2 \\ 3 p_{11}^2 p_{21} + p_{12}^2 p_{21} \\ 3 p_{21}^3 \end{pmatrix} \right. \\ \left. + \begin{pmatrix} -p_{21} \\ p_{11} \end{pmatrix}^T \begin{pmatrix} \frac{\partial^3 f_1}{\partial x_1^3} & \frac{\partial^3 f_1}{\partial x_1^2 \partial x_2} & \frac{\partial^3 f_1}{\partial x_1 \partial x_2^2} & \frac{\partial^3 f_1}{\partial x_2^3} \\ \frac{\partial^3 f_2}{\partial x_1^3} & \frac{\partial^3 f_2}{\partial x_1^2 \partial x_2} & \frac{\partial^3 f_2}{\partial x_1 \partial x_2^2} & \frac{\partial^3 f_2}{\partial x_2^3} \end{pmatrix} \cdot \begin{pmatrix} 3 p_{12}^3 + 3 p_{11}^2 p_{12} \\ p_{12} p_{21}^2 \\ 2 p_{11} p_{12} p_{21} \\ 0 \end{pmatrix} \right\}^{-1} \quad (46)$$

where $|P|$ is the determinant of P , a superscript T represents the transpose of the vector and a superscript -1 represents the reciprocal of the number. Also,

$$\omega = \omega_0 + \omega_1 \quad (47)$$

where,

$$\omega_1 = \frac{A_0^2}{16 |P|} \begin{pmatrix} -p_{21} \\ p_{11} \end{pmatrix}^T \begin{pmatrix} \frac{\partial^3 f_1}{\partial x_1^3} & \frac{\partial^3 f_1}{\partial x_1^2 \partial x_2} & \frac{\partial^3 f_1}{\partial x_1 \partial x_2^2} & \frac{\partial^3 f_1}{\partial x_2^3} \\ \frac{\partial^3 f_2}{\partial x_1^3} & \frac{\partial^3 f_2}{\partial x_1^2 \partial x_2} & \frac{\partial^3 f_2}{\partial x_1 \partial x_2^2} & \frac{\partial^3 f_2}{\partial x_2^3} \end{pmatrix} \begin{pmatrix} 3 p_{11}^3 + 3 p_{11} p_{12}^2 \\ 3 p_{11}^2 p_{21} + p_{12}^2 p_{21} \\ 3 p_{21}^3 \end{pmatrix} \\ + \begin{pmatrix} p_{22} \\ -p_{12} \end{pmatrix}^T \begin{pmatrix} \frac{\partial^3 f_1}{\partial x_1^3} & \frac{\partial^3 f_1}{\partial x_1^2 \partial x_2} & \frac{\partial^3 f_1}{\partial x_1 \partial x_2^2} & \frac{\partial^3 f_1}{\partial x_2^3} \\ \frac{\partial^3 f_2}{\partial x_1^3} & \frac{\partial^3 f_2}{\partial x_1^2 \partial x_2} & \frac{\partial^3 f_2}{\partial x_1 \partial x_2^2} & \frac{\partial^3 f_2}{\partial x_2^3} \end{pmatrix} \begin{pmatrix} 3 p_{12}^3 + 3 p_{11}^2 p_{12} \\ p_{12} p_{21}^2 \\ 2 p_{11} p_{12} p_{21} \\ 0 \end{pmatrix} \quad (48)$$

and

$$\begin{pmatrix} x_{1 \text{ avg}} \\ x_{2 \text{ avg}} \end{pmatrix} = \frac{-A_0^2}{2\omega |P|} \begin{pmatrix} p_{11} & p_{12} \\ p_{21} & p_{22} \end{pmatrix} \begin{pmatrix} -p_{21} & p_{11} \\ -p_{22} & p_{12} \end{pmatrix} \begin{pmatrix} \frac{1}{2} \frac{\partial^2 f_1}{\partial x_1^2} & \frac{\partial^2 f_1}{\partial x_1 \partial x_2} & \frac{1}{2} \frac{\partial^2 f_1}{\partial x_2^2} \\ \frac{1}{2} \frac{\partial^2 f_2}{\partial x_1^2} & \frac{\partial^2 f_2}{\partial x_1 \partial x_2} & \frac{1}{2} \frac{\partial^2 f_2}{\partial x_2^2} \end{pmatrix} \cdot \begin{pmatrix} p_{11}^2 + p_{12}^2 \\ p_{11} p_{12} \\ p_{21}^2 \end{pmatrix} \quad (49)$$

Example

For the continuous stirred tank reactor system described by Equations (17) and (18), we find that

$$P = \begin{pmatrix} p_{11} & p_{12} \\ p_{21} & p_{22} \end{pmatrix} = \begin{pmatrix} 2(1 + \beta_1) - d_{ec} & 2\omega_0 \\ -2\beta_5 & 0 \end{pmatrix} \quad (50)$$

where

$$\omega_0 = \sqrt{d_{fc} - \frac{1}{4} d_{ec}^2} \quad (51)$$

and

$$d_{ec} = 1 + \beta_1 + \beta_4 - \beta_3\beta_5 + \beta_6\beta_7,$$

$$d_{fc} = (1 + \beta_1)(\beta_4 + \beta_6\beta_7) - \beta_3\beta_5 \quad (52)$$

The amplitude of the oscillation is

$$A_0^2 = \frac{-2d_{ec}}{K_1 + K_2 + K_3} \quad (53)$$

where

$$K_1 = 3\beta_5^2\beta_3(\beta_3 - 2) \left(1 + \beta_1 - \frac{d_{ec}}{2} \right),$$

$$K_2 = \beta_1\beta_3\beta_5^2(\beta_3 - 2),$$

$$K_3 = -\beta_3\beta_5^2(\beta_3 - 2) \left(1 + \beta_1 - \frac{d_{ec}}{2} \right) \quad (54)$$

and the frequency correction term is

$$\omega_1 = \frac{A_0^2}{4} (K_4 + K_5 + K_6) \quad (55)$$

where

$$K_4 = \beta_3\beta_5^2(\beta_3 - 2)\omega_0,$$

$$K_5 = -3\beta_1\beta_3\beta_5^2(\beta_3 - 2) \cdot \left(1 + \beta_1 - \frac{d_{ec}}{2} \right) / \omega_0,$$

$$K_6 = 3\beta_3\beta_5^2(\beta_3 - 2) \left(1 + \beta_1 - \frac{d_{ec}}{2} \right)^2 / \omega_0 \quad (56)$$

Also, the time average outlet composition is

$$x_{1 \text{ avg}} = \{ [2(1 + \beta_1) - d_{ec}] (K_7 + K_8) + \omega_0 K_9 \} \frac{A_0^2}{\omega} \quad (57)$$

where

$$\omega = \omega_0 + \omega_1,$$

$$K_7 = \frac{\beta_1\beta_3\beta_5}{2\omega_0} \left[2 \left(1 + \beta_1 - \frac{d_{ec}}{2} \right) - \beta_5(\beta_3 - 2) \right]$$

$$K_8 = \frac{\beta_5 \left(1 + \beta_1 - \frac{d_{ec}}{2} \right)}{\omega_0} \left[\frac{\beta_3\beta_5}{2} (\beta_3 - 2) - \beta_6 - \beta_3 \left(1 + \beta_1 - \frac{d_{ec}}{2} \right) \right]$$

$$K_9 = \frac{\beta_3\beta_5^2}{2} (\beta_3 - 2) - \beta_5\beta_6 - \beta_3\beta_5 \left(1 + \beta_1 - \frac{d_{ec}}{2} \right) \quad (58)$$

The terms containing $\partial^3 f_1 / \partial x_2^3$ and $\partial^3 f_2 / \partial x_2^3$ have been neglected in the analysis above since they lead to spurious solutions. Thus, when the nonlinear steady state equations are approximated by the complete Taylor series expansion up to third order terms, more than one steady state solution is obtained. Since the original nonlinear functions only lead to one solution, as do the third-order polynomials without these two additional terms, they must be dropped from the analysis. Otherwise, the topology of the system is altered, and our approximate solution predicts that the reactor will not generate oscillations, that is, A_0^2 is found to be a negative number.

Perhaps it should be mentioned that the method of Luus and Lapidus (7) suffers from the same difficulty. Thus, if a third-order polynomial is used to approximate the Arrhenius equation, their Equation (56) becomes

$$\exp \frac{25 T}{T + 2} = \exp (12.5 T) = 1 + 12.5 T + 78 T^2 + 325 T^3 \quad (59)$$

If this function is carried through the analysis, their Equation (50) becomes

$$\frac{dr}{dt} = r (1.125 - 0.125 k_c - 9.75 r^2 + 60.94 r^2) \quad (60)$$

so that as time approaches infinity the solution for the radius of the limit cycle, their Equation (62) is

$$r^2 = \frac{1.125 - 0.125 k_c}{-51.19} \quad (61)$$

This result indicates that a limit cycle will not be obtained if $k_c < 9$, but will exist if $k_c > 9$, which is exactly the opposite of their conclusions. Since their results do agree with the numerical solutions of the nonlinear equations, it's apparent that including the third derivative term in the approximation changes the topology of the system.

Thermal Instability of a Horizontal Layer of Liquid with Maximum Density

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An investigation is carried out to determine the onset of convection of a horizontal layer of liquid subject to temperatures of T_1 and T_2 at lower and upper surfaces, respectively. The liquid is assumed to possess a maximum density value at T_{\max} with T_{\max} between T_1 and T_2 . The temperature-density relationship within the temperature range $|T_1 - T_2|$ can be expressed as $\rho = \rho_{\max} [1 - \gamma_1 (T - T_{\max})^2 - \gamma_2 (T - T_{\max})^3]$.

Both rigid-rigid and rigid-free surface conditions were considered. The critical Rayleigh number defined in Equations (20) and (24) is found to be dependent upon two parameters. Experimental observations on the onset of convection were made and compared with the theoretical results. The experimental work consists of the measurement of the melting rate of a block of ice with melting from both below and above. In all cases, excellent agreement between experimental and theoretical results were obtained.

When a layer of liquid whose density decreases monotonically with the increase of temperature is subject to an adverse temperature gradient, (that is $T_1 > T_2$ where the subscripts 1 and 2 refer to the lower and upper surfaces, respectively) the system is potentially unstable because of its top-heavy situation. The onset of convection is indicated if the Rayleigh number exceeds its critical value. For a liquid with constant thermal expansion coefficient, Rayleigh number is defined as

$$N_{Ra} = \frac{\rho g (T_1 - T_2) d^3}{\nu \kappa} \quad (1)$$

A somewhat complicated situation arises if the liquid possesses a maximum density over the temperature range $T_2 - T_1$. The liquid density increases upward from the lower surface until it reaches maximum and decreases afterward. Only part of the liquid layer is potentially unstable. Furthermore, the onset of convection is possible with both heating from below and above. For a liquid whose temperature-density relationship can be expressed as

$$\rho = \rho_{\max} [1 - \gamma (T - T_{\max})^2] \quad (2a)$$

and with a definition of Rayleigh number as

$$N_{Ra} = \frac{2\gamma (T_1 - T_{\max}) g (T_1 - T_2) d^3}{\nu \kappa} \quad (2b)$$

it was found (2, 5, 7) that the critical Rayleigh number which is the criterion for the onset of convection, is dependent upon the temperature difference ratio $(T_1 - T_{\max}) / (T_1 - T_2)$.

A major limitation of these earlier works is that the particular temperature-density relationship used [that is Equation (2a)] has only a limited range of applicability. For example, in the case of water, the representation of temperature-density data by a parabolic expression is only valid for the temperature of $0 \sim 8^\circ\text{C}$. Furthermore, these investigations were restricted to the special case of two rigid boundary surfaces.

The object of the present work is to present a more complete analysis on the effect of liquid maximum density on the thermal instability of a horizontal layer of liquid using a density-temperature relationship with a wider range of applicability. Two types of hydrodynamic boundary conditions, both rigid-rigid and rigid-free surfaces, are considered because of their equal importance. In addition, experimental observations on the onset of convection were also carried out in order to verify the validity of the theoretical results.

ANALYSIS

The pertinent equations of continuity, motion, and energy can be written as:

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