The Effect of Lewis Number on the Stability of a Catalytic Reaction

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An extensive numerical study was carried out to determine the effect of Lewis number on the stability of a chemical reaction occurring inside a porous catalyst pellet. It is found that when the Lewis number is different from 1, the coupling between the concentration and temperature causes several pathological effects during the transient periods. One of the most interesting phenomenon is the occurrence of a unique unstable steady state with a periodic appearance of a very hot spot.

When an exothermic chemical reaction occurs inside a porous catalytic pellet, multiple steady state solutions may exist (*16*). The stability problems associated with this case have been discussed by several investigators (*1, 2, 4, 7, 11, 13, 14*). Luss and Amundson (*11*) have shown that if the Lewis number $\left(N_{Le} = \dfrac{D\rho C_p}{k} \right)^*$ is unity, topological considerations enable the determination of the asymptotic stability of the various steady states. Moreover, it was shown that if $2n + 1$ steady state solutions exist, $n + 1$ are asymptotically stable, and the others are unstable. Another recent work has shown (*13*) that for the case of $N_{Le} = 1$, finite regions of stability can be obtained by the use of the maximum principle for parabolic differential equations.

If the Lewis number is different from 1, the determination of asymptotic or global stability is much more complex. Gavalas (*4*) has given a very elegant proof that if a steady state is unstable for $N_{Le} = 1$, it will be unstable also for any other values of the Lewis number. However, there is as yet no analytical method to predict the qualitative effect of the Lewis number on the stability of those steady states which are stable if $N_{Le} = 1$.
Kirby and Schmitz (*6*) have demonstrated that the Lewis number affects the stability of a laminar diffusion flame. Wei (*15*) has shown that if the Lewis number is smaller than 1, the transient temperature may exceed by a large amount the maximum possible temperature rise under steady state conditions. This has been clearly demonstrated in the recent work of Hlavacek and Marek (*5*).

In this work we report the results of a detailed numerical study on the effect of the Lewis number on the asymptotic and global stability of various unique and nonunique steady states. The computations revealed several very interesting pathological phenomena, such as the occurrence of a unique unstable steady state with a periodic appearance of a hot spot (Figures 4 and 5).

DETERMINATION OF ASYMPTOTIC STABILITY

The dimensionless transient equations describing a single chemical reaction occurring in a catalyst pellet of volume $\mathbf{\Omega}$ and boundary $\mathbf{\Sigma}$ are

$$\frac{\partial z}{\partial \tau} = \nabla^2 z - r(z, y) \qquad \mathbf{x} \in \mathbf{\Omega} \qquad (1)$$

$$N_{Le}\frac{\partial y}{\partial \tau} = \nabla^2 y + \beta r(z, y) \qquad \mathbf{x} \in \mathbf{\Omega} \qquad (2)$$

subject to the boundary conditions

$$y = 1 \qquad \mathbf{x} \in \mathbf{\Sigma} \qquad (3)$$

$$z = 1 \qquad \mathbf{x} \in \mathbf{\Sigma} \qquad (4)$$

$$y(\mathbf{x}, 0) = y_0(\mathbf{x}) \qquad \tau = 0 \qquad (5)$$

$$z(\mathbf{x}, 0) = z_0(\mathbf{x}) \qquad \tau = 0 \qquad (6)$$

where

$$y = \frac{T}{T_a} \qquad z = \frac{c}{c_a} \qquad (7)$$

$$N_{Le} = \frac{D\rho c_p}{k} \qquad r(z, y) = L^2 r(zc_a, yT_a)/c_a D$$

The steady state equations are obtained by eliminating the time derivatives in Equations (1) and (2). The conditions under which a unique steady state solution exists have been described (*3, 4, 10, 11*).

To determine asymptotic stability, we have to examine the following linearized equations

$$\frac{\partial \hat{\xi}}{\partial \tau} = \nabla^2 \hat{\xi} - \left(\frac{\partial r}{\partial z}\right)_{ss} \hat{\xi} - \left(\frac{\partial r}{\partial y}\right)_{ss} \hat{\eta} \qquad (8)$$

$$N_{Le}\frac{\partial \hat{\eta}}{\partial \tau} = \nabla^2 \hat{\eta} + \beta\left(\frac{\partial r}{\partial z}\right)_{ss} \hat{\xi} + \beta\left(\frac{\partial r}{\partial y}\right)_{ss} \hat{\eta} \qquad (9)$$

subject to the boundary conditions

$$\hat{\eta} = \hat{\xi} = 0 \qquad \mathbf{x} \in \mathbf{\Sigma} \qquad (10)$$

where

$$\hat{\xi} = z(\mathbf{x}, \tau) - z(\mathbf{x})_{ss} \qquad (11)$$

$$\hat{\eta} = y(\mathbf{x}, \tau) - y(\mathbf{x})_{ss} \qquad (12)$$

We will assume

$$\hat{\xi}(\mathbf{x}, \tau) = \xi(\mathbf{x})\, e^{-\lambda\tau} \qquad (13)$$

$$\hat{\eta}(\mathbf{x}, \tau) = \eta(\mathbf{x})\, e^{-\lambda\tau} \qquad (14)$$

Substitution of (13) and (14) into Equations (8) and (9) yields

$$\nabla^2 \xi + \left[\lambda - \left(\frac{\partial r}{\partial z}\right)_{ss}\right] \xi - \left(\frac{\partial r}{\partial y}\right)_{ss} \eta = 0 \qquad (15)$$

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* The Lewis number is often defined as the reciprocal of the quantity.

$$\nabla^2\eta + \beta\left(\frac{\partial r}{\partial z}\right)_{ss}\xi + \left[\beta\left(\frac{\partial r}{\partial y}\right)_{ss} + \lambda N_{Le}\right]\eta = 0 \quad (16)$$

$$\xi = \eta = 0 \qquad x \in \Sigma \quad (17)$$

Thus, the system will be asymptotically stable if and only if the real parts of all the eigenvalues of Equations (15) and (16) are positive.

In this work the eigenvalues of Equations (15) and (16) were obtained by the Galerkin method. This method has been described in detail by Kuo and Amundson (*7*); therefore it will be sketched only briefly here. Since we have used spherical pellets in all the examples, the following trial solutions were chosen:

$$\xi(x) = \sum_{m=1}^{N} a_n \frac{\sin m\pi x}{x} \quad (18)$$

$$\eta(x) = \sum_{m=1}^{N} b_n \frac{\sin m\pi x}{x} \quad (19)$$

These values were substituted back into Equations (15) and (16), and each equation was multiplied by $x \sin m\pi x$ and integrated over the interval $0 \leq x \leq 1$, for $m = 1, 2, \ldots, N$. This gave a set of homogenous linear algebric equations. Thus, the eigenvalues could be found as the eigenvalues of the coefficient matrix of this set of linear equations. The coefficient matrix was then expanded into its characteristic polynomial equation by Leverrier-Faddeev method, and the eigenvalues were solved by Newton-Raphson iteration technique. The details of the numerical scheme can be found elsewhere (*8*).

It was found that seven terms of approximation in Equations (18) and (19) were required in order to obtain sufficient accuracy in computing the eigenvalues. A hundred points grid was used to represent the profiles. A grid of two hundred points yielded identical results. For the small Lewis number cases, large numerical errors could occur unless very high precision was used in the computations. Therefore, we have carried out all the eigenvalue computations in a C.D.C.-6600 computer using double precision.

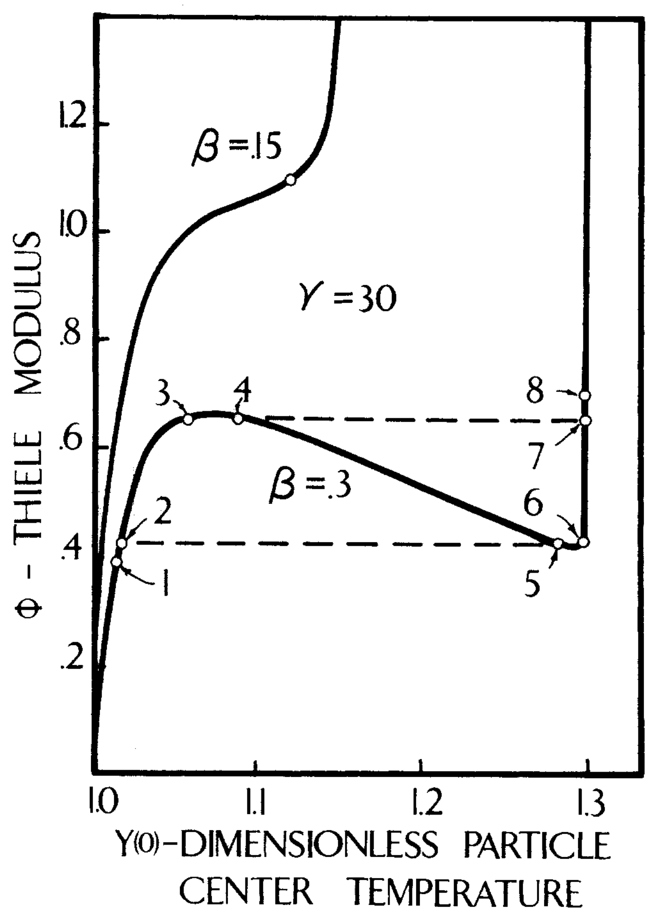

Fig. 1. Dimensionless particle center temperature as a function of β and ϕ for an irreversible first-order reaction in a spherical particle. The circles are the steady states used for the numerical examples.

TABLE 1. DISTRIBUTION OF FOURTEEN EIGENVALUES FOR THE CASE OF A UNIQUE STEADY STATE, $\beta = 0.15$, $\gamma = 30$, $\phi = 1.1$

N_{Le}	Real eigenvalues +	Real eigenvalues −	Complex eigenvalues + Real part	− Real part
2.0	12		2	
1.8	12		2	
1.6	12		2	
1.5	10		4	
1.4	10		4	
1.2	14		0	
1.0	14		0	
0.9	2		12	
0.8	4		10	
0.6	6		8	
0.5	8		6	
0.4	8		6	
0.2	10		2	2
0.1	12	2		

NUMERICAL EXAMPLES

The stability of a spherical catalyst pellet in which a first-order irreversible reaction occurs was investigated. The steady state equation is (*16*)

$$\frac{1}{x^2}\frac{d}{dx}\left(x^2\frac{dy}{dx}\right) + \phi^2(1+\beta-y)e^{\gamma\left(1-\frac{1}{y}\right)} = 0 \quad (20)$$

It has been shown (*10*) that for this kinetic expression, uniqueness is assured if

$$\beta\gamma < 4(1+\beta) \quad (21)$$

Figure 1 shows the value of the dimensionless temperature at the center of the pellet for various values of ϕ for $\gamma = 30$. The circles on the curve indicate the various steady states whose stability was investigated. In the case of $\beta = 0.15$, a unique steady state exists for all values of the

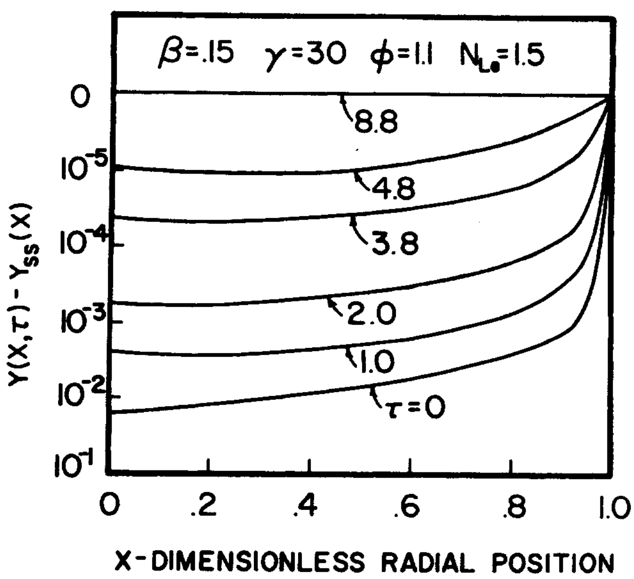

Fig. 2. Temperature response to a disturbance of a unique steady state.

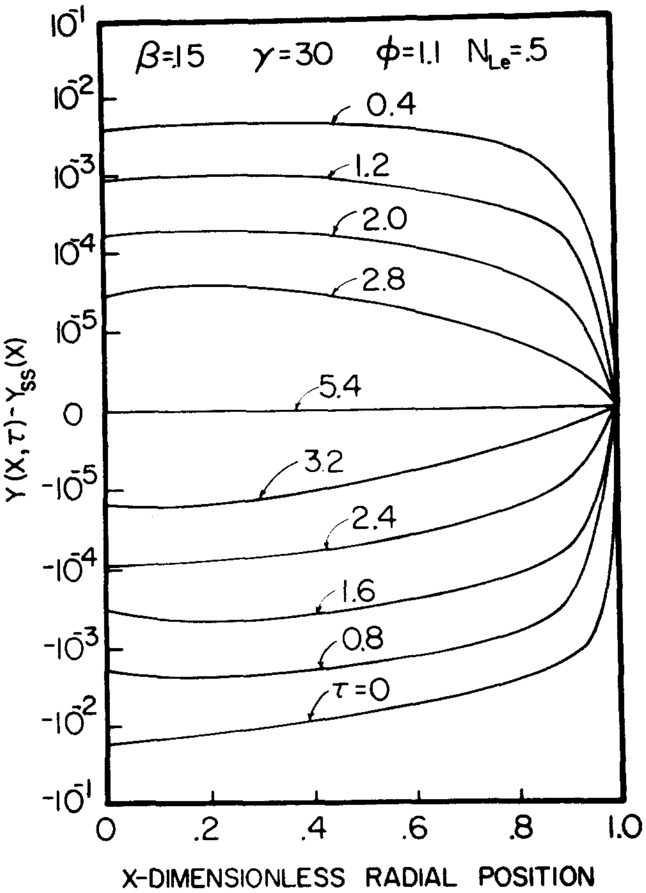

Fig. 3. Temperature response to a disturbance. Same initial conditions as in Figure 2.

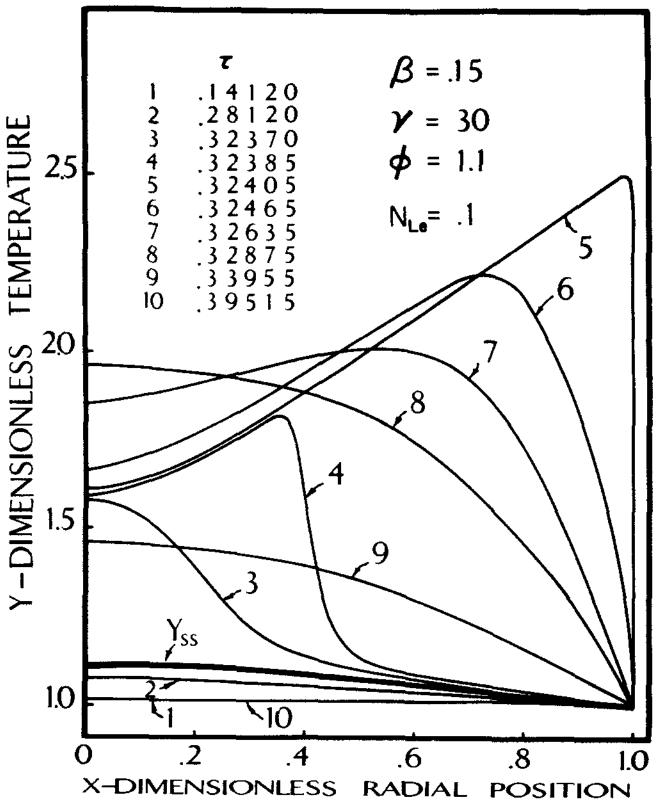

Fig. 4. One cycle of dimensionless temperature oscillations for a unique unstable steady state.

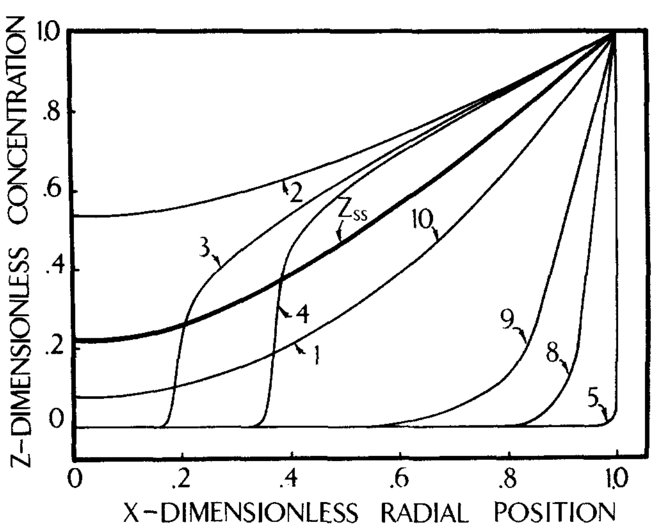

Fig. 5. One cycle of dimensionless concentration oscillations for a unique unstable steady state. The time corresponding to each profile can be read from Figure 4.

Thiele modulus, while for $\beta = 0.3$, multiple steady state solutions exist for $0.41 < \phi < 0.66$.

ASYMPTOTIC STABILITY

Table 1 reports the distribution of the fourteen eigenvalues for $\beta = 0.15$, $\gamma = 30$, $\phi = 1.1$. The results indicate that for all Lewis numbers larger or equal to 1, the system is asymptotically stable. For large Lewis numbers, some of the eigenvalues become complex. When the Lewis number is smaller than 1, a rather large number of complex eigenvalues are obtained. For example, for $N_{Le} = 0.9$, twelve out of fourteen eigenvalues are complex. For the cases of $N_{Le} > 1$, the imaginary part was at least one order of magnitude smaller than the real part. However, for $N_{Le} < 1$, the imaginary part of the eigenvalues was of the same order as that of real part.

If $N_{Le} \leq 0.2$, the system becomes unstable. For $N_{Le} = 0.2$, there exist two complex eigenvalues with a negative real part, and for $N_{Le} = 0.1$, there exist two real negative eigenvalues.

The trends shown in Table 1 are similar to those obtained for several different cases which are not reported here. For all cases it was noted that the system remained asymptotically stable for $N_{Le} \geq 1$, and it became unstable for small values of the Lewis numbers.

Table 2 reports the distribution of the fourteen eigenvalues for a kinetic expression for which nonunique steady state solutions exist for certain values of the Thiele modulus. Figure 1 shows the position of the various cases on the three branches of solutions. Cases 2, 5, and 6 correspond to $\phi = 0.42$, while cases 3, 4, and 7 correspond to $\phi = 0.655$. Cases 1 and 8 correspond to $\phi = 0.39$ and 0.69, respectively. According to the proof by Luss and Amundson (*12*), if $N_{Le} = 1$, all the steady states on the intermediate branch, that is, cases 4 and 5, will be unstable, while all the other cases will be asymptotically stable.

The eigenvalues were computed for various values of Lewis numbers up to 0.08, and more detailed results are reported elsewhere (*8*). It was found that for very small Lewis numbers $N_{Le} << 0.08$ the numerical error prevented the accurate computation of the eigenvalues by the Galerkin method.

Gavalas (*4*) has proven that all the steady states which are unstable for $N_{Le} = 1$, that is, cases 4 and 5, should be unstable for all Lewis numbers. The computations reported

Table 2. Distribution of Fourteen Eigenvalues for Three Different Lewis Numbers, $\beta = 0.3, \gamma = 30$

Case	$N_{Le} = 1.5$ Real +	$N_{Le} = 1.5$ Real −	$N_{Le} = 1.5$ Complex + Real part	$N_{Le} = 0.5$ Real +	$N_{Le} = 0.5$ Real −	$N_{Le} = 0.5$ Complex + Real part	$N_{Le} = 0.5$ Complex − Real part	$N_{Le} = 0.1$ Real +	$N_{Le} = 0.1$ Real −	$N_{Le} = 0.1$ Complex + Real part
1	14			14				14		
2	14			14				14		
3	12		2	10		4		12		2
4	13	1		11	1	2		11	1	2
5	11	1	2	3	1	10		11	1	2
6	6		8	2		10	2	8	2	4
7	14			4		10		10	2	2
8	14			6		8		10	2	2

in Table 2 confirmed this point. It can be seen that a real negative eigenvalue was always obtained for cases 4 and 5 for all the Lewis numbers. For Lewis numbers different from 1, some of the eigenvalues for cases 4 and 5 became complex, and the real part of the complex eigenvalues was always positive for any Lewis number in the range $0.08 \leq N_{Le} \leq 2$.

Other computations have shown that all the cases which were asymptotically stable for $N_{Le} = 1$ remained stable for Lewis numbers larger than 1. These results can be seen from Table 2 for $N_{Le} = 1.5$. The results of many other cases are reported in reference 8. For several of the cases, complex eigenvalues occur for $N_{Le} > 1$. However, the complex parts are always much smaller than the real parts. When Lewis numbers are smaller than 1, the steady states on the high temperature branch, that is, cases 6, 7 and 8, became unstable for certain small Lewis numbers. As can be seen from Table 2, all these three steady states are unstable for $N_{Le} = 0.1$. Case 6 is already unstable for $N_{Le} = 0.5$.

All the steady states on the low temperature branch, that is, cases 1, 2, and 3, remained asymptotically stable for all Lewis numbers from 2.0 to 0.08. However, it should be mentioned that these steady states might become unstable for very small Lewis numbers. This is an interesting subject for further research.

RESPONSE TO LARGE DISTURBANCES

Transient computations were performed to determine the exact response of the system to finite disturbances. The numerical method described by Liu (9) was used in all the computations. For all the transients, except those described in Figures 4 and 5, a grid of one hundred points was used. The case described in Figures 4 and 5 required a grid of 1,000 points.

We will first describe the transients for the unique steady state for which the linearized eigenvalues are reported in Table 1. Figure 2 describes the response of the system to a rather small disturbance. The disturbance was chosen such that the initial residual enthalpy $E(x, 0) = y(x, 0) - 1 + \beta\,[z(x, 0) - 1]$ was equal to 0. Thus, if the Lewis number were equal to 1, both the temperature and concentration profiles would have converged uniformly and without any oscillations to the steady state profiles (13). It is seen from Figure 2 that this was also the case for Lewis numbers equal to 1.5. However, it can be seen from Figure 3 that when the Lewis number was changed to 0.5, oscillations occurred as the system converged to the steady state. Note that according to Table 1 for both cases, the linearized stability analysis predicts the existence of complex eigenvalues. However, for the case of $N_{Le} = 1.5$, the imaginary part of these eigenvalues is much smaller than in the case of $N_{Le} = 0.5$. Another typical trend, which can be detected from these figures, is that the response of the system becomes faster for smaller Lewis numbers.

When the Lewis number for the system was decreased to 0.1, the unique steady state becomes unstable as predicted by the linearized analysis reported in Table 1. Numerical computations have shown that after a short initial period, periodic oscillations in the temperature and concentration profiles were obtained. Figures 4 and 5 show these oscillations. For the sake of clarity, only one cycle in

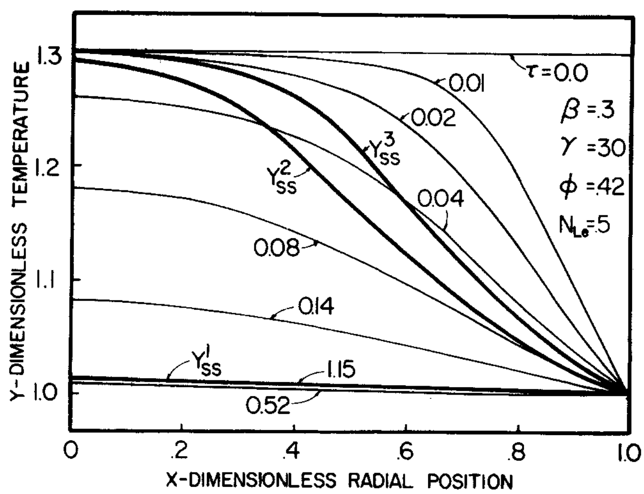

Fig. 6. Temperature response to a large disturbance of the high temperature steady state.

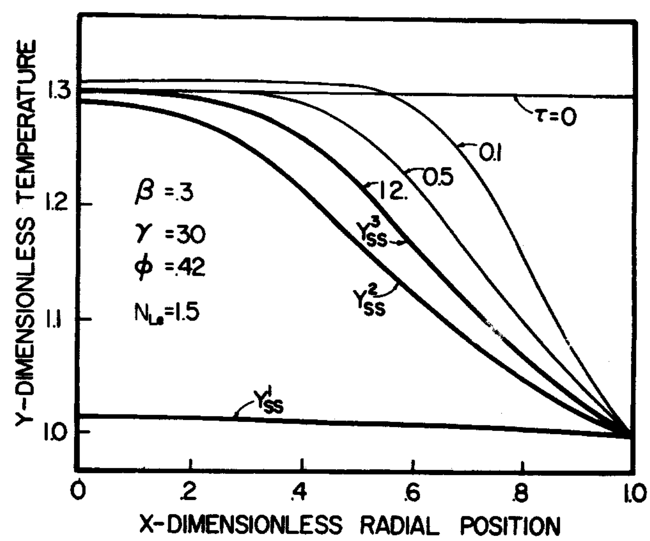

Fig. 7. Temperature response to a large disturbance of the high temperature steady state.

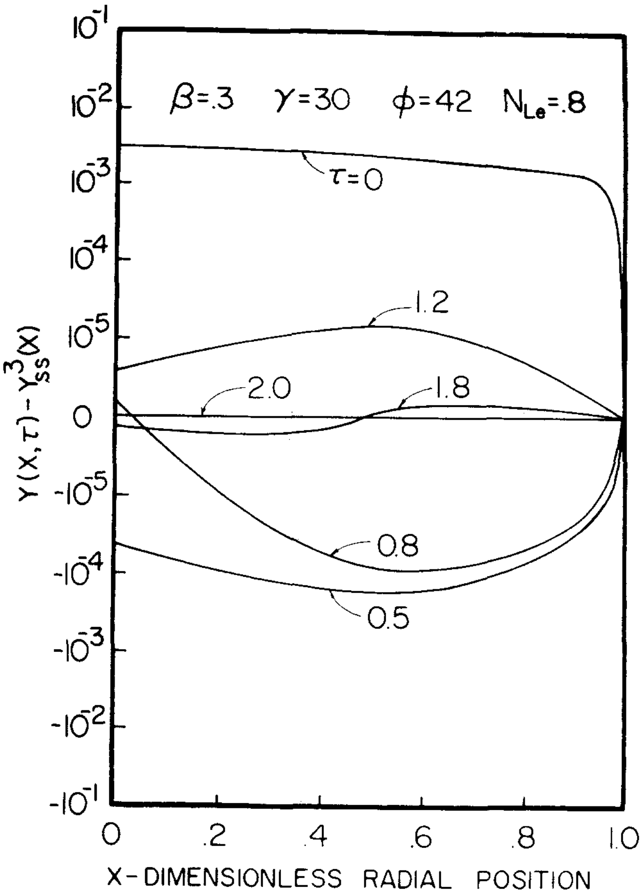

Fig. 8. Temperature oscillations around the high temperature steady state.

the profiles is presented.

One can notice that during the transient cycle a very hot spot develops very near to the surface of the catalyst. After the reactant is almost completely depleted, the temperature decreases below the steady state value. Then the concentration in the pellet starts to increase, and a new cycle occurs. One should notice the very fast response compared with that shown in the previous figures. It should be mentioned that Hlavacek and Marek (*5*) have also observed the occurrence of hot spots as well as the

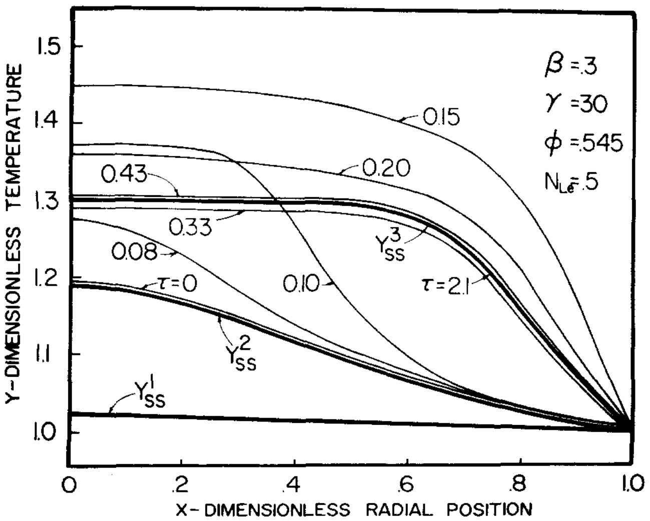

Fig. 9. Temperature response to a slight perturbation of the intermediate steady state.

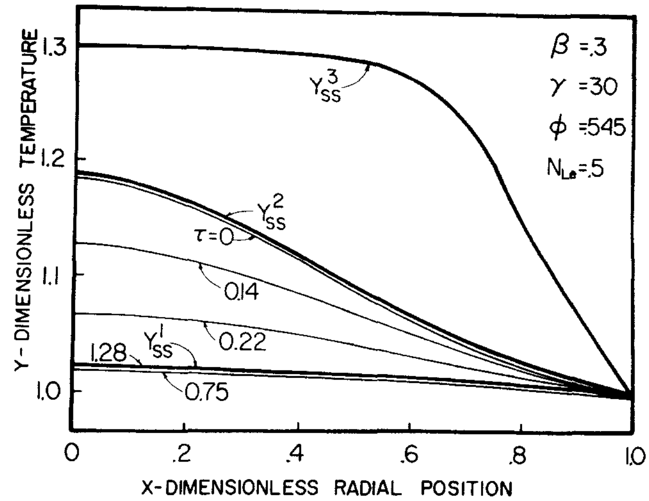

Fig. 10. Temperature response to a slight perturbation of the intermediate steady state.

existence of continuous oscillations in the average temperature and concentration within a catalyst pellet for a unique steady state.

Severe numerical problems were encountered in solving this problem owing to the very fast response and very large temperature and concentration gradients. A grid of 1,000 points was used to simulate the radial profile, and a very small time increment was used to assure numerical stability. The machine time required for the computation of one cycle in these profiles was 40 hr. on a Sigma 7 computer. In order to be able to study in detail the transient behavior for low Lewis numbers, it is important to find a different stable numerical method, which would enable use of larger time increments and corresponding saving in machine time.

Figure 6 describes a transient response for a case that three steady state solutions exist (cases 2, 5, and 6 in Figure 1). According to the results reported in Table 2, only the low temperature steady state is asymptotically stable. It is seen that the temperature profiles converge to this steady state with a slight overshoot. However, the concentration profile converged with no oscillations to the steady state profile.

Figure 7 describes the response of the same system to the same disturbance but with a Lewis number of 1.5. For this case, both the high and the low temperature steady states are asymptotically stable. It is seen that the system converged to the high temperature steady state without overshoot. It should be noted that at $\tau = 0.1$, the temperature exceeded the maximum possible temperature under steady state conditions, even though the initial residual enthalpy was 0.

Figure 8 describes temperature oscillations around the high temperature steady state for the same system and $N_{Le} = 0.8$. It is seen that the oscillations decay with time. In this case, twelve out of the fourteen eigenvalues are complex.

Figure 9 describes the response of an intermediate unstable steady state to a positive perturbation in the temperature profile. The value of the Lewis number is 0.5. It is seen that the system moved towards the high temperature steady state with a considerable overshoot. It has been proven (*13*) that if the Lewis number were equal to 1, no overshoot could occur for the disturbance shown in Figure 9. The transient behavior of this system for $N_{Le} = 1$ has been described in Figure 4 of (*13*).

The response of the same system to a negative temperature disturbance is shown in Figure 10. Again, one notices a slight overshoot in the temperature profile which would not occur for $N_{Le} = 1$.

The transient described in Figures 2 to 10 were typical of the many cases we have investigated and clearly indicate the pathological effects which may occur when $N_{Le} \neq 1$. A detailed report of other cases can be found elsewhere (*8*).

In all the cases it was found that the smaller the Lewis number, the faster was the response of the system and the smaller was the time increment required for stable numerical integration.

CONCLUSIONS AND REMARKS

It was demonstrated in this work that the Lewis number has an important effect on the stability of a catalyst pellet in which a chemical reaction occurs. When $N_{Le} = 1$, the asymptotic stability is assured if the index of the steady state solution is +1. However, in this work it was shown that when $N_{Le} < 1$, the steady states, for which the index is equal to 1 and which are stable if $N_{Le} = 1$, may become unstable. Gavalas (*4*) has shown that a steady state solution with an index of −1 implies instability for any Lewis number. Thus, we have to conclude that if the Lewis number is different from 1, the condition that the index of the steady state solution is equal to 1 is only necessary but not sufficient for asymptotic stability. This situation is similar to the case of a continuously stirred tank reactor for which the slope condition is necessary but not sufficient to guarantee asymptotic stability.

When $N_{Le} = 1$ and the residual enthalpy is equal to 0, there is no coupling effect between the two transient equations for the concentration and temperature. In fact, these two variables are linearly related for this case (*14*). However, if the Lewis number is different from 1, the transient values of the concentration and temperature are no more linearly related, and there is a strong coupling effect between the two transient differential equations. This coupling is responsible for the various pathological effects during the transient period and for the changes in the stability of the various steady states for small Lewis numbers.

For the case of Lewis number equal to 1, topological arguments can be used to determine asymptotic stability without having to know even the steady state profiles. It would be very desirable to obtain some qualitative results on the effect of the Lewis number which will enable the a priori prediction of the effects observed in this work. The basic difficulty is that the mathematical tools required to obtain such results directly from the structure of the governing differential equations are not yet well developed. Berger and Lapidus (*2*) suggested determining asymptotic stability via a Liapunov functional. However, the criteria presented in their work are very conservative and require the knowledge of the steady state profile.

It should be pointed out that internal temperature gradients are important only for catalytic pellets with low thermal conductivity and for which the Lewis number is much larger than 1. Thus, the pathological behavior demonstrated by the systems with a low Lewis number is mainly of academic interest.

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NOTATION

a_n = coefficients in the orthogonal expansion described by Equation (18)
b_n = coefficients in the orthogonal expansion described by Equation (19)
C = concentration
D = diffusion coefficient
E = dimensionless residual enthalpy
ΔE = activation energy
ΔH = heat of reaction
k = thermal conductivity
$\hat{k}$ = reaction rate constant
L = characteristic length of catalytic pellet
N_{Le} = Lewis number, $(\rho C_p D)/(k)$
r = consumption rate of reactant
R = radius of pellet, gas constant
T = temperature
x = dimensionless radial position
$\mathbf{x}$ = position vector
y = dimensionless temperature
z = dimensionless concentration

Greek Letters

β = $\dfrac{(-\Delta H)DCa}{kTa}$
γ = $(\Delta E)/(RTa)$
λ = eigenvalue
ρ = density
τ = dimensionless time
ϕ = Thiele modulus $R \quad \dfrac{\hat{k}}{D}$
$\boldsymbol{\Sigma}$ = external surface of the pellet
$\boldsymbol{\Omega}$ = interior of catalyst pellet
$\hat{\xi}$ = concentration disturbance
ξ = concentration disturbance defined in Equation (13)
$\hat{\eta}$ = temperature disturbance
η = temperature disturbance defined in Equation (14)

Subscripts

a = ambient conditions
0 = initial conditions
ss = steady state conditions

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