Stability and Uniqueness of A Catalyst Particle Problem: Parameter Optimization in Liapunov Functions

In the analysis of stability and uniqueness of steady state through the Liapunov functional technique, the Liapunov functional is not unique and different forms can lead to significantly different results. A method is proposed in which the state vector and/or the parameters in the weighting matrix $S(x)$ are optimized to obtain less conservative results than those reported previously. For the problem of stability and uniqueness of the steady state of a chemical reaction occurring in a catalyst particle with slab geometry, several sufficient conditions for stability have been developed for both cases of unity and nonunity Lewis numbers in terms of the system parameters and steady state profiles, the system parameters and the catalyst center temperature, and the system parameters alone. These conditions are shown to be stronger than the previously reported results (Murphy and Crandall, 1970). Sufficient conditions for uniqueness have also been developed. For unity Lewis number our uniqueness condition is stronger than the previously reported result (Luss and Amundson, 1967), and for non-unity Lewis number our uniqueness result is new.

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SCOPE

Under certain conditions multiple steady states are possible for a chemical reaction occurring in a catalyst particle with slab geometry (Weisz and Hicks, 1962; Amundson and Raymond, 1965). When this occurs at least one of the steady states is shown to be unstable (Gavalas, 1968). Since many industrially important reactors are packed with catalysts, the study of the stability and uniqueness plays an important role in chemical reactor design and operation.

The desirable results are criteria in terms of design and operating parameters, which will predict a single stable steady state and also predict which one of steady states is stable when multiple steady states are possible.

This problem has been studied by Wei (1965), Berger and Lapidus (1968), and Murphy and Crandall (1970) who modeled the catalyst particle as a slab and applied the Liapunov functional technique. This problem has also been considered by Kuo and Amundson (1967) using the comparison theorem and Sturm's oscillation theorem for the case of equal mass and heat diffusion (unity Lewis number). Lee and Luss (1968) used Galerkin's method to determine the local stability character of the steady states of spherical catalyst particles. Conditions for existence of a single steady state, that is, uniqueness conditions, have been developed by Gavalas (1966), Luss and Amundson (1967), and Luss (1968) by using topological methods.

One advantage of the Liapunov functional approach is that the Liapunov functional is not unique, and different forms can lead to significantly less conservative results than those currently available. In this paper this is accomplished for the problem of the catalyst particle with slab geometry by a judicious choice of state variables and optimizing the parameters in the Liapunov function.

CONCLUSIONS AND SIGNIFICANCE

The Liapunov stability technique has been applied to a class of distributed parameter systems. In particular, the catalyst particle with slab geometry for both unity and nonunity Lewis number. The stability criteria are presented in terms of steady state profiles and system parameters, the steady state catalyst center temperature and system parameters, and system parameters only. These last criteria are also criteria for the uniqueness of the steady state. For the special case of Lewis number equal to unity, the uniqueness criterion developed here, Condition (34) is less conservative than criterion developed previously by Luss and Amundson (1967), that is, Condition (37). The uniqueness criterion presented here for the more general case of the nonunity Lewis number, Condition (35), is a new result previously not available in the literature. Also, the stability criterion for nonunity Lewis number presented here, Condition (26), is less conservative than the stability criterion previously developed by Murphy and Crandall (1970), that is, Condition (25).

The relationship between the degree of conservatism of the sufficient conditions for stability and the number of

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adjustable parameters in the Liapunov functional has been examined and the results are given in Table 1. As expected, the conditions become less conservative as the number of parameters increases. The number of adjustable parameters can be changed by increasing the parameters in the weighting matrix and/or by changing the state variables. It can also be expected that different, and conceivably stronger, results can be obtained if other functional forms are chosen for the elements of the weighting matrix.

LIAPUNOV STABILITY ANALYSIS

The technical literature gives very little guidance on what type of Liapunov functional to choose. Zubov (1966) has suggested that for a system of parabolic partial differential equations the following Liapunov functional be used:

$$V = \frac{1}{2} \int_\Omega u^T(x, t)\, u(x, t)\, dx$$

For a linear system of ordinary differential equations the Liapunov function is a quadratic form. The above equation is the distributed analog of this quadratic form with the weighting matrix S equal to the identity matrix; in other words, the L_2 norm has been used. However, the L_2 norm is restricted as it allows none of the freedom usually associated with a Liapunov function for lumped-parameter systems. In this paper we shall consider as a candidate for a Liapunov functional the general norm.

$$V = ||u(x, t)||_S^2 = \int_\Omega u^T(x, t)\, S(x)\, u(x, t)\, dx \quad (1)$$

Obviously, if $S(x)$ is positive definite then V is also positive definite.

Using this Liapunov functional and considering the distributed parameter system

$$\frac{\partial u}{\partial t} = A_2 \frac{\partial^2 u}{\partial x^2} + A_0\, u \quad (2)$$

with boundary conditions

$$u_x(t, 0) = u(t, 1) = 0 \quad (3)$$

the following theorem can be proved.

Theorem 1

The distributed system (2) to (3) is stable in the sense of Liapunov if there exist the following properties

(i) $SA_2 \geqq 0$ (4)

(ii) $S_x(0)\, A_2 \leqq 0$, and (5)

(iii) $S_{xx}A_2 + S\, A_0 + A_0^T\, S \stackrel{\Delta}{=} Q_2 = Q_2^T < 0$ (6)

The proof is given in Appendix A*. A limited version in which A_2 is a diagonal positive definite matrix was presented by Murphy and Crandall (1970). The difficulty in the application of this theorem is usually found in the search for the weighting matrix $S(x)$. Since $S(x)$ is not unique, more conclusive results might possibly be obtained with different forms of $S(x)$. This is illustrated in the latter sections.

APPLICATION TO CATALYST PARTICLE SYSTEM

Using the theorem obtained from the previous section, we can investigate the stability characteristics of a catalyst particle with slab geometry. In stability analysis of the catalyst particle system, two separate cases are investigated. In case I, the Lewis number is restricted to unity in order that the unsteady state heat and mass balance equations can be uncoupled. In case II, no restriction is placed on the Lewis number.

SYSTEM DYNAMICS

Consider a catalyst particle modeled as a slab in which a single irreversible first-order reaction occurs. The dimensionless heat and mass balances are (Murphy and Crandall, 1970)

$$Le \frac{\partial n}{\partial t} = \frac{\partial^2 n}{\partial x^2} + \beta f \quad (7)$$

$$\frac{\partial y}{\partial t} = \frac{\partial^2 y}{\partial x^2} - f \quad (8)$$

where

$f = \phi^2 y \exp[q(n-1)/n]$
$Le = \rho C_p E_a/\lambda$; Lewis number
$\beta = (-\Delta H) E_a C_0/\lambda\, T_0$
$\phi^2 = L^2 k(T_0)/E_a$, Thiele modulus
$q = E/RT_0$

and the boundary conditions are

$$\frac{\partial n(t, 0)}{\partial x} = \frac{\partial y(t, 0)}{\partial x} = 0 \quad (9)$$

$$n(t, 1) = y(t, 1) = 1 \quad (10)$$

By linearizing Equations (7) through (10) about the steady states, we obtain

$$Le \frac{\partial u_1}{\partial t} = \frac{\partial^2 u_1}{\partial x^2} + \beta f_n u_1 + \beta f_y u_2 \quad (11)$$

$$\frac{\partial u_2}{\partial t} = \frac{\partial^2 u_2}{\partial x^2} - f_n u_1 - f_y u_2 \quad (12)$$

with boundary conditions

$$\frac{\partial u_1(t, 0)}{\partial x} = \frac{\partial u_2(t, 0)}{\partial x} = 0 \quad (13)$$

$$u_1(t, 1) = u_2(t, 1) = 0 \quad (14)$$

where $u_1 = n - n_{ss}$ and $u_2 = y - y_{ss}$

Liapunov Functional

The objective is to pick the elements $s_{ij}(x)$ in the weighting matrix $S(x)$ such that Inequalities (4) through (6) are satisfied. Any number of $s_{ij}(x)$ can be chosen which can meet the above inequalities, and therefore, a judicious choice can lead to a significantly better result. For a second-order system, $S(x)$ is a 2×2 matrix and the Liapunov function of Equation (2) takes the form

$$V(x) = \int_\Omega (u_1 s_{11} u_1 + 2 u_1 s_{12} u_2 + u_2 s_{22} u_2)\, dx$$

Since the objective is to demonstrate the concept of optimizing the parameters in S(x) we will restrict our-

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* Appendices A, B, and C have been deposited as Document No. 01995 with the National Auxiliary Publications Service (NAPS), c/o Microfiche Publications, 305 East 46th Street, New York 10017 and may be obtained for $0.00 for microfiche and $0.00 for photocopies.

selves to a simple Liapunov function of the form

$$V(x) = \int_0^1 \cos k_1 x \, (u_1^2 + a_1 u_1 u_2 + a_2 u_2^2) dx \qquad (15)$$

in which we allow the maximum number of parameters to be three. Admittedly this is a simple form; nevertheless, it is sufficient to demonstrate the concept involved and that it leads to stronger results than those previously available. In sequel we will show how to optimize these parameters so as to obtain the least conservative result with the given number of parameters by analyzing the results with one optimum parameters, two optimum parameters, and three optimum parameters. We also demonstrate that the Liapunov function can be altered by changing the state variables, which is equivalent to changing s_{ij}.

STABILITY CONDITIONS FOR CATALYST PARTICLE SYSTEM $Le = 1$

Case I. Two parameters (k_1 and a_2); k_1 *optimized*

Let

$$S(x) = \begin{pmatrix} \cos k_1 x & 0 \\ 0 & \cos k_1 x \end{pmatrix}$$

where

$$0 < k_1 < \frac{\pi}{2}$$

This case is equivalent to setting $a_1 = 0$ and $a_2 = 1$ in Equation (15). With this $S(x)$ the first two requirements of Theorem 1 are automatically fulfilled. Applying (iii) of Theorem 1, we have

$$-k_1^2 + 2\beta f_n < 0 \qquad (16)$$

and

$$(k_1^2 - 2\beta f_n)(k_1^2 + 2f_y) - (\beta f_y - f_n)^2 > 0$$

or

$$(\beta f_n - f_y) + \sqrt{(\beta f_n - f_y)^2 + (f_n + \beta f_y)^2} < k_1^2 \qquad (17)$$

Note that Condition (17) implies Condition (16), and the least restrictive condition for Condition (17) is $k_1 \to \pi/2$, therefore, the optimal value of k_1 is $\pi/2$ and the sufficient condition for stability is

$$f' + \sqrt{f'^2 + (f_n + \beta f_y)^2} < \frac{\pi^2}{4} \qquad (18)$$

where

$$f' = \beta f_n - f_y \qquad (19)$$

Case II. Three parameters (k_1, a_1 *and* a_2); k_1 *optimized*

In this case we retain the same $S(x)$ as in Case I but define a new state variable $u_3 = u_1 + \beta u_2$ in order to introduce an additional parameter a_1 and at the same time to simplify the computation involved.

Then

$$\frac{\partial u}{\partial t} = \frac{\partial^2 u}{\partial x^2} + \begin{pmatrix} f' & f_y \\ 0 & 0 \end{pmatrix} u \qquad (20)$$

with boundary conditions

$$\frac{\partial u}{\partial x}(t, 0) = 0, \quad u(t, 1) = 0 \qquad (21)$$

where $u = \text{col}\,(u_1, u_3)$

Note that Equations (20) and (21) are the same form as Equations (2) and (3). Therefore, Theorem 1 can be applied and the sufficient conditions for stability are (A_2 is identity matrix in this case)

a) $s_{11x}(0) \leq 0$ and $s_{22x}(0) \leq 0$

b) Q_2 is a negative definite matrix, where

$$Q_2 = \begin{pmatrix} s_{11xx} + 2s_{11}f' & S_{11}f_y \\ s_{11}f_y & s_{22xx} \end{pmatrix}$$

Now, as in Case I of the following $S(x)$ is chosen to satisfy

$$S(x) = \begin{pmatrix} \cos k_1 x & 0 \\ 0 & \cos k_1 x \end{pmatrix}$$

where $0 < k_1 < \pi/2$ Then, the sufficient condition for stability is obtained by following the same procedure given in Case I and is given by

$$\sqrt{f'^2 + f_y^2} + f' < \frac{\pi^2}{4} \qquad (22)$$

It is noted that Condition (22) is a sufficient condition for stability for a steady state of the system, Equations (20) and (21). But the stability of u_1 and u_3 implies the stability of u_1 and u_2 because u_3 is a linear combination of u_1 and u_2. Therefore it is also a sufficient condition for stability for the system, Equations (7) through (10). Note also that this choice of state vector (u_1, u_3) is

TABLE 1. STABILITY CRITERIA

(A) $Le = 1$

State variables		$S(x)$	Stability condition*	Type of Liapunov functional (V)
Case I	u_1, u_2	$\begin{pmatrix} \cos k_1 x & 0 \\ 0 & \cos k_1 x \end{pmatrix}$	$f' + \sqrt{f'^2 + (f_n + \beta f_y)^2} < \frac{\pi^2}{4}$	$V = \int_0^1 \cos k_1 x (u_1^2 + u_2^2) dx$
Case II	u_1, u_3**	$\begin{pmatrix} \cos k_1 x & 0 \\ 0 & \cos k_1 x \end{pmatrix}$	$f' + \sqrt{f'^2 + f_y^2} < \frac{\pi^2}{4}$	$V = 2 \int_0^1 \cos k_1 x \left(u_1^2 + \beta u_1 u_2 + \frac{1}{2} \beta^2 u_2^2 \right) dx$
Case III	u_1, u_3	$\begin{pmatrix} \cos k_1 x & 0 \\ 0 & k_2 \cos k_1 x \end{pmatrix}$	$f' < \frac{\pi^2}{8}$	$V = (1 + k_2) \int_0^1 \cos k_1 x \left(u_1^2 + \frac{2\beta k_2}{1 + k_2} u_1 u_2 + \frac{\beta^2 k_2}{1 + k_2} u_2^2 \right) dx$
Case IV	u_1, u_2	$\begin{pmatrix} \cos k_1 x & k_3 \cos k_1 x \\ k_3 \cos k_1 x & k_2 \cos k_1 x \end{pmatrix}$	$f' < \frac{\pi^2}{8}$	$V = \int_0^1 \cos k_1 x (u_1^2 + 2k_3 u_1 u_2 + k_2 u_2^2) dx$

* Luss and Amundson obtained the uniqueness condition: $f' < 0$.
** $u_3 = u_1 + \beta u_2$.

(B) $Le \neq 1$

State variables	$S(x)$	Stability condition
u_1, u_2	$\begin{pmatrix} \cos k_1 x & 0 \\ 0 & \cos k_1 x \end{pmatrix}$	$\left(\frac{\pi}{2}\right)^4 + \left(\frac{\pi}{2}\right)^2 (2f_y - 2\beta f_n) - \left(\frac{\beta f_y}{Le} + f_n\right)^2 Le \geq 0$***
u_1, u_2	$\begin{pmatrix} \cos k_1 x & 0 \\ 0 & k_2 \cos k_1 x \end{pmatrix}$	$f_n < \frac{\pi^2}{8\beta}$

*** Obtained by Murphy and Crandall (1970).

equivalent to choosing $a_1 = \beta$ and $a_2 = 1/2\ \beta^2$ in Equation (15).

Case III. Three parameters (k_1, a_1 *and* a_2); *two optimized* (k_1 and a_1, or k_1 and a_2)

In this case the state vector is the same as Case II but an additional parameter in $S(x)$ (a_1 or a_2) is optimized Let

$$S(x) = \begin{pmatrix} \cos k_1 x & 0 \\ 0 & k_2 \cos k_1 x \end{pmatrix}$$

with $u = (u_1, u_3)^T$. This is equivalent to choosing $a_1 = 2\beta k_2/(1 + k_2)$ and $a_2 = k_2\beta^2/(1 + k_2)$. Then, the sufficient condition can be derived by following the same procedure given in Case I,

$$f'(x) < \frac{\pi^2}{8} \tag{23}$$

Case IV. Three parameters (k_1, a_1 and a_2); *all optimized.*

With the original state vector (u_1, u_2) and the following $S(x)$

$$S(x) = \cos k_1 x \begin{pmatrix} 1 & k_3 \\ k_3 & k_2 \end{pmatrix}$$

this case is equivalent to choosing $a_1 = 2k_3$ and $a_2 = k_2$ and optimizing all three parameters a_1, a_2 and k_1 in Equation (15). The sufficient condition for stability as derived in Appendix B* is

$$f'(x) < \frac{\pi^2}{8} \tag{24}$$

Discussions on Cases I through IV

An examination of the results summarized in Table 1 reveals that Case II is less conservative than Case I, Case III is less conservative than Case II and Cases III and IV are equivalent. The reduction of conservatism from Case I to Case II is due to the introduction of the parameter a_1 which adds the cross product term, $u_1 u_2$, to the integrand of the Liapunov functional. The reduction of conservatism going from Case II to Case III is caused by the optimization of an additional parameter, k_2. In Case IV all three parameters were optimized, and it turned out that the optimal values of a_1 and a_2 are related by β, the parameter used in the new state variable u_3. The net result is that this is equivalent to Case III in which a new state variable u_3 was used and two parameters were optimized, that is, the same Liapunov function is obtained when the parameters are set to their optimal values.

Stability Conditions for Catalyst Particle Systems, $Le \neq 1$

This problem has been treated by Murphy and Crandall by using the functional norm matrix

$$S(x) = \begin{pmatrix} \cos k_1 x & 0 \\ 0 & \cos k_1 x \end{pmatrix}$$

and the stability condition was given by

$$\left(\frac{\pi}{2}\right)^4 + \left(\frac{\pi}{2}\right)^2 (2f_y - 2\beta f_n) - \left(\frac{\beta f_y}{Le} + f_n\right)^2 Le \geq 0 \tag{25}$$

As in the case of $Le = 1$ it is possible to obtain less conservative results than that given by Murphy and Crandall (1970) by following the same approach given above. We shall demonstrate this simply by introducing

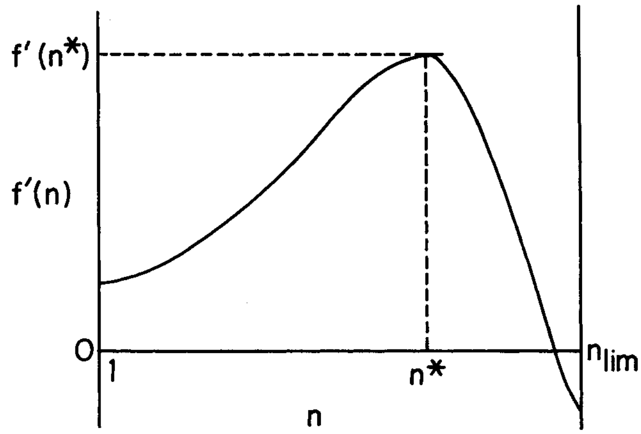

Fig. 1. A plot of $f'(n)$ vs. n.

an additional parameter k_2 in $S(x)$. Let $S(x)$ be given by

$$S(x) = \begin{pmatrix} \cos k_1 x & 0 \\ 0 & k_2 \cos k_1 x \end{pmatrix}$$

and then we have the stability condition (see Appendix C*)

$$f_n(x) < \frac{\pi^2}{8\beta} \text{ for } x \in [0, 1] \tag{26}$$

Condition (26) is shown in Appendix D to be less conservative than Condition (25), the result of Murphy and Crandall (1970). This is due to the introduction and optimization of k_2 to obtain the least conservative result. The optimal value of k_2 changes with changes in system parameters. Note also that Condition (26) is more conservative than that for the corresponding case of $Le = 1$, Condition (24). This is also shown in Appendix D.

The stability criteria presented above are summarized in Table 1. Each of these criteria involves the system parameters ϕ, β, and q and requires knowledge of steady state data, that is, we must compute for the entire interval $x \in [0, 1]$. However, we can estimate the supremum from the steady state equations and then examine the inequality which is discussed in the next section. In this way the criteria need not be evaluated at every point.

Sufficient Conditions for Stability in Terms of Center Temperature

In this section we limit the treatment to those cases of the previous sections which lead to the least conservative results, that is,

$$f'(x) < \frac{\pi^2}{8} \text{ for } Le = 1$$

and

$$f_n(x) < \frac{\pi^2}{8\beta} \text{ for } Le \neq 1$$

Case I: Le = 1

The stability criterion can be written as

$$\sup_{0 \leq x \leq 1} f'(x) < \frac{\pi^2}{8} \tag{27}$$

We can evaluate the supremum of $f'(x)$ with the aid of the steady state equations. At steady state, we have (Raymond and Amundson, 1964)

$$y = (n_{\lim} - n)/\beta$$

* See footnote on page 322.

* See footnote on page 322.

and

$$f'(x) = \phi^2 \left[\frac{q(n_{\text{lim}} - n)}{n^2} - 1 \right]$$

$$\exp\left[\frac{q(n-1)}{n} \right] = f'(n)$$

Condition (27) is equivalent to the following condition

$$\sup_{n(1) \leq n \leq n(0)} f'(n) = \sup_{1 \leq n \leq n(0)} f'(n) < \frac{\pi^2}{8}$$

Also $f'(n)$ has the following properties

(i) The local maximum occurs at $n = n^*$, where

$$n^* = q n_{\text{lim}}/(q + 2\, n_{\text{lim}})$$

and

(ii) $\left. \dfrac{d f'(n)}{d n} \right|_{n=1} > 0$

Figure 1 shows the relations between $f'(n)$ and n, therefore, the supremum of $f'(n)$ is given by

$$\sup_{1 \leq n \leq n(0)} f'(n) = \begin{cases} f'(n^*) & \text{if } n^* \leq n(0) \\ f'(n(0)) & \text{if } n^* > n(0) \end{cases}$$

Therefore Condition (24), in terms of steady state profiles and system parameters, can be reduced to

$$f'(\bar{n}) < \pi^2/8 \tag{28}$$

where

$$\bar{n} = \begin{cases} n^* & \text{if } n^* \leq n(0) \\ n(0) & \text{if } n^* > n(0) \end{cases}$$

This is the stability criterion which is, in terms of the center temperature, $n(0)$, and system parameters only.

Case II: Le $\neq 1$

The sufficient condition for stability is

$$\sup_{0 \leq x \leq 1} f_n(x) < \frac{\pi^2}{8\beta} \tag{29}$$

where

$$f_n = \phi^2 \frac{q(n_{\text{lim}} - n)}{\beta n^2} \exp\left[q(n-1)/n\right]$$

Condition (29) can be written as

$$\sup_{1 \leq n \leq n(0)} f_n(n) < \frac{\pi^2}{8\beta}$$

Figure 2 shows the relationship between $f_n(n)$ and n,

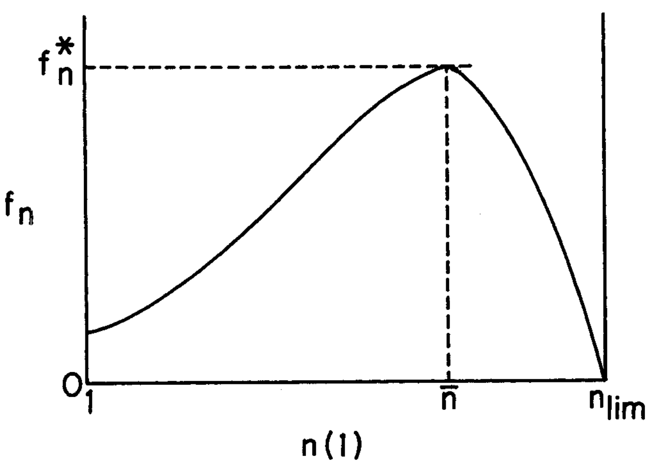

Fig. 2. A plot of f_n vs. $n(1)$.

and the supremum occurs at

$$n = \begin{cases} n^* & \text{if } n^* \leq n(0) \\ n(0) & \text{if } n^* > n(0) \\ 1 & \text{if } n^* \leq 1 \end{cases} \tag{30}$$

where

$$n^* = \left(\frac{q}{2} + n_{\text{lim}} \right) - \left[\left(\frac{q}{2} \right)^2 + n_{\text{lim}}{}^2 \right]^{1/2} \tag{31}$$

Therefore, the sufficient condition for stability in terms of center temperature and system parameters only, is

$$\frac{n_{\text{lim}} - n}{n^2} \exp\left[q(n-1)/n\right] < \frac{\pi^2}{8 q \phi^2} \tag{32}$$

where n is given by Equation (30).

It is noted that the conditions obtained here, Conditions (28) and (32) are the same conditions as Condition (24) and (26) since Conditions (28) and (32) are the supremum of Conditions (24) and (26) respectively. Now the criteria are in terms of the center dimensionless temperature and system parameters only. Although the steady state information is still required, only the values of $n(0)$ are necessary for the calculation of the supremum value of $f'(x)$ or $f_n(x)$. Criteria (28) and (32) are more easily varified than Criteria (24) and (26) because a minimum amount of computation is required, that is, only a single point and not the entire profile.

Sufficient Conditions for Stability in Terms of System Parameters, (Sufficient Conditions for Uniqueness)

Sufficient conditions for stability, Conditions (24) and (26), are extended to determine the unique stable steady state solution. The sufficient conditions are now developed in terms of system parameters only.

Case I: Le $= 1$

Since

$$n(0) \leq n_{\text{lim}}$$

therefore

$$\sup_{1 \leq n \leq n(0)} f'(n) \leq \sup_{1 \leq n \leq n_{\text{lim}}} f'(n)$$

If the following condition

$$\sup_{1 \leq n \leq n_{\text{lim}}} f'(n) < \frac{\pi^2}{8} \tag{33}$$

is satisfied then Condition (27) is satisfied, and then Condition (33) is also a sufficient condition for stability. As shown in Figure 1, the supremum of $f'(n)$ occurs at $n = n^*$ only and the sufficient condition is given by

$$f'(n^*) < \frac{\pi^2}{8} \tag{34}$$

where $n^* = q\, n_{\text{lim}}/(q + 2\, n_{\text{lim}})$.

Case II: Le $\neq 1$

Since $f_n(n)$ has a maximum value when $n = n^*$ for all n (Figure 2), Condition (32) is satisfied if the following condition is satisfied:

$$\frac{n_{\text{lim}} - n^*}{n^{*2}} \exp\left[q(n^* - 1)/n^*\right] < \frac{\pi^2}{8 q \phi^2} \tag{35}$$

where n^* is given by Equation (31).

It is noted that Conditions (34) and (35) are in terms of system parameters only. They are rather restrictive conditions since $n(0)$ was given its maximum value, n_{lim}, and therefore Conditions (34) and (35) may be more conservative than Conditions (28) and (32), respectively. However, these results, Conditions (34) and (35), are interesting since they represent criteria for stability which show the interrelation among all of the system parameters and do not require steady state solution. They are therefore useful for practical application.

Since Conditions (34) and (35) are independent of steady state profiles and at least one of the multiple steady states is shown to be unstable (Gavalas, 1968) the solution of the steady state equations for a system which has been proved stable must be unique. Thus Conditions (34) and (35) are also sufficient conditions for uniqueness.

At this point it is interesting to consider the earlier work by Luss and Amundson (1967) for unity Lewis number. They obtained the following

$$\sup_{T_a \le T \le T_{ad}} f'(T) \le 0 \tag{36}$$

as a sufficient condition for the existence of the unique steady state using the Sturm-Liouville Comparison Theorem. In terms of our notation, Condition (36) is equivalent to

$$\sup_{1 \le n \le n_{lim}} f'(n) = f'(n^*) \le 0 \tag{37}$$

which is more conservative than our result, Condition (34).

NOTATION

A_0, A_2 = terms defined in Equation (2)
C = concentration of reactant
C_p = heat capacity of fluid
E = activation energy
E_a = effective mass diffusivity
f = dimensionless reaction rate
f' = term defined by $f' = \beta f_n - f_y$
ΔH = heat of reaction
k = reaction rate, $k = k_0 e^{-E/RT}$
k_0 = frequency in Arrhenius reaction rate law
k_1, k_2, k_3 = constants used in Liapunov function
L = reactor length
Le = Lewis number
n = dimensionless temperature, $n = T/T_0$
n_{lim} = dimensionless limiting temperature for reactor
Q_2 = term defined in Equation (6)
q = dimensionless activation energy, $q = E/RT_0$
R = gas constant
S = Liapunov function general norm matrix
T = temperature of fluid
t = dimensionless time
u = state vector in function space
V = Liapunov function
x = dimensionless spatial variable
y = dimensionless concentration, $y = C/C_0$

Greek Letters

ρ = density of fluid
λ = effective thermal conductivity
β = parameter defined by $\beta = (-\Delta H) E_a C_0 / \lambda T_0$
ϕ^2 = parameter defined by $\phi^2 = L^2 k / E_a$
Ω = spatial region

Subscripts and Superscripts

$*$ = referred to optimal quantities
T = transpose
0 = inlet condition
n, x, y = differentiation with respect to n, x, and y respectively

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APPENDIX D. COMPARISON OF DIFFERENT CRITERIA

Comparison of Conditions (24) and (26)

Condition (24) is equivalent to

$$\beta f_n - f_y < \frac{\pi^2}{8}$$

or

$$f_n < \frac{\pi^2}{8\beta} + \frac{1}{\beta} f_y \text{ for all } x \tag{D1}$$

Condition (D1) can be written as

$$\sup_{0 \le x \le 1} f_n < \frac{\pi^2}{8\beta} + \frac{1}{\beta} \min_{0 \le x \le 1} f_y \tag{D2}$$

and Condition (26) is given by

$$\sup_{0 \le x \le 1} f_n < \frac{\pi^2}{8\beta} \tag{D3}$$

Since

$$\min_{0 \le x \le 1} f_y = \phi^2 \exp\left[q(n(0) - 1)/n(0)\right] > 0$$

Therefore, Condition (D3) is more conservative then Condition (D2), that is, Condition (26) is more conservative than Condition (24).

Comparison of Our Result, Condition (26), with That of Murphy and Crandall

Our Condition (25), Condition (40) of Murphy and Crandall (1970), is given by

$$\left(\frac{\pi}{2}\right)^4 + \left(\frac{\pi}{2}\right)^2 (2f_y - 2\beta f_n) - \left(\frac{\beta f_y}{Le} + f_n\right)^2 Le \ge 0 \tag{D4}$$

Rearranging Condition (D4) yields

$$(\beta f_n - f_y) + \left\{ Le\left(\frac{\beta f_y}{Le} + f_n\right)^2 + (f_y - \beta f_n)^2 \right\}^{1/2} \leq \frac{\pi^2}{4}$$

or

$$\beta f_n - f_y + \left\{ Le\left(\frac{\beta f_y}{Le} - f_n\right)^2 + (\beta f_n + f_y)^2 \right\}^{1/2} \leq \frac{\pi^2}{4} \quad (D5)$$

Define

$$S_1 = \beta f_n - f_y + \left\{ Le\left(\frac{\beta f_y}{Le} - f_n\right)^2 + (\beta f_n + f_y)^2 \right\}^{1/2}$$

Then

$$S_1 \geq \beta f_n - f_y + \{(\beta f_n + f_y)^2\}^{1/2} = 2\beta f_n \quad (D6)$$

Condition (26) can be written as

$$\sup_{0 \leq x \leq 1} (2\beta f_n) < \frac{\pi^2}{4} \quad (D7)$$

and Condition (D5) is equivalent to

$$\sup_{0 \leq x \leq 1} S_1 \leq \frac{\pi^2}{4} \quad (D8)$$

From Conditions (D6), (D7), and (D8) it can be concluded that the Condition (D7) is less conservative than Condition (D8), that is, our result, Condition (26), is less conservative than the result obtained by Murphy and Crandall (1970).

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Approximation in Control of Nonlinear Dynamic Systems

The type of system approximation in which the system state space x is mapped into a scalar domain V by a quadratic transformation

$$V = \frac{1}{2} \mathbf{x}'\mathbf{Q}\mathbf{x}$$

where Q is appropriately determined, is used to develop a suboptimal control procedure for unconstrained lumped parameter dynamic systems via the application of Pontryagin's Maximum Principle. The optimization problem in the scalar domain becomes an initial value problem when the scalar adjoint variable is held constant throughout the course of control. The resulting computational scheme includes an effective and simple way to construct the transformation matrix Q and a straightforward minimum seeking approach to locate the best constant overall average scalar adjoint parameter. For the class of problems with quadratic performance index, system equation approximation further reduces the determination of Q to the solution of a matrix Riccati equation.

The application of the proposed suboptimal control procedure to four chemical engineering systems shows that the procedure is simple, direct, and efficient and works particularly well for problems where the final time is large.

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SCOPE

In establishing optimal control for nonlinear complex chemical engineering systems one usually turns to the Pontryagin's Maximum Principle. Recently, considerable effort has been directed towards developing means of solving the two point boundary value problem (TPBVP) resulting from the use of the maximum principle. In addition to the difficulty of solving the TPBVP, there are the difficulties of determining the initial control policy and of instability of the adjoint equations.

Suboptimal procedures have been therefore introduced recently to simplify the computational procedure. These are useful only if the resulting control policy is reasonably close to the optimal. The approximations frequently used in the suboptimal procedures include system equation approximation (such as linearization) and/or adjoint equation approximation.

Very promising results have been obtained by transforming the n-dimensional state space to a scalar domain by a quadratic transformation $V = \frac{1}{2}\mathbf{x}' \mathbf{Q} \mathbf{x}$, thereby describing the state in terms of the scalar V. This simplifies the problem considerably, since now the adjoint equation becomes a scalar differential equation.

In this paper we employ system linearization and state transformation. Furthermore, we use an average adjoint