Stability of High Dimensional Nonlinear Systems using Krasovskii's Theorem

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Liapunov's direct method is used to establish a finite region of asymptotic stability for nonlinear systems with an arbitrary number of state variables. The procedure is a geometric one in multidimensional space which uses the Fletcher-Powell minimization technique to find the maximum time derivative of the Liapunov function on the closed Liapunov hypersurface. Three detailed examples are presented, the first being the classical 2-variable CSTR with heat transfer and the third being a 32-variable 16-stage model of an adiabatic tubular reactor with axial diffusion.

The need to determine a finite region of asymptotic stability (RAS) for nonlinear systems arises, for example, in the case of an exothermic reaction taking place within a CSTR. In the usual situation this physical system has three steady states and the intermediate state is unstable since any infinitesimal perturbation in either the system's temperature or concentration will cause the system to go to the upper or lower steady state. By contrast, the upper and lower steady states are stable to infinitesimal perturbations in the state variables. However, in addition to this information it is important to establish the stability limits of a region around each stable point such that one may predict the result of finite perturbations.

One way to approach this problem is to consider the direct solution or integration of the nonlinear system equations. However, this becomes more and more difficult as the number of variables increases; such an increase could result from dealing with more than one CSTR and/or more than one reactant. In these cases the space of the state or dependent variables is of dimensionality greater than two and it is necessary to consider families of trajectories in high dimensional space.

An alternate procedure would be one which does not integrate the system equations but merely relies on certain properties of the system equations to establish a finite RAS. One such method is due to Liapunov and uses a Liapunov function of the form suggested by Krasovskii.

In this paper we shall present a computational method for determining a finite RAS from a Krasovskii type Liapunov function. The method applies to an n-dimensional system of nonlinear ordinary differential equations where n is finite and generally greater than two. The stability problem is shown to be equivalent to the minimization of a nonlinear function (the derivative of the Liapunov function) subject to an equality constraint. As such it is possible to evolve an iterative technique based upon a penalty function which solves for the largest RAS without actually integrating the system differential equations. Three numerical examples of varied degrees of complexity are given to show the results of the method.

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LIAPUNOV'S DIRECT METHOD AND KRASOVSKII'S THEOREM

Liapunov's direct method is extensively discussed in the applied mathematical literature (*9, 10, 12, 13*). Briefly stated this method defines a positive definite function, the Liapunov function, and it is the sign definiteness of the total time derivative of the Liapunov function which determines the stability of a system. The Liapunov function is analogous in some respects to the energy of a mechanical system (*10*). If the time derivative of the energy of a mechanical system can be shown to be negative for all configurations except the equilibrium point then any perturbation in the mechanical system will decay to the equilibrium point and the system is asymptotically stable in the large. If instead of the scalar energy of the system a scalar positive definite Liapunov function is defined, and the total time derivative of the Liapunov function is negative definite for all possible configurations, except at the equilibrium point, then the system is asymptotically stable in the large.

However, while the energy of a mechanical system is unique the Liapunov function is not. In addition, Liapunov's direct method only supplies a sufficient and not a necessary condition for stability. Thus the main difficulty in employing Liapunov's direct method is the determination of that Liapunov function which yields the largest RAS. Very little guidance can be obtained from the literature for the determination of the form of such a function for high dimensional nonlinear systems, although, a satis-

factory form is suggested by Krasovskii's theorem. Recently, Berger and Perlmutter (*2* to *4*), and Luecke and McGuire (*15*, *16*) discussed the application of a Krasovskii type Liapunov function to the determination of a finite RAS. These authors succeeded in applying Krasovskii's theorem to a single CSTR where a graphical method of solution can be used. Berger and Perlmutter (*4*) suggest that Krasovskii's theorem can be extended to a large number of state variables, but it has been shown that their approach is in some doubt (*1*).

The basic features of Krasovskii's theorem can be outlined in a simple fashion. Consider that the state or system equations are of the stationary vector form

$$\dot{\mathbf{x}}(t) = \mathbf{f}(\mathbf{x}) \tag{1}$$

where $\mathbf{f}(\mathbf{0}) = \mathbf{0}$. The Krasovskii method proposes a Liapunov function which describes closed surfaces (*13*) in the n-dimensional space of the state variables. The proposed Liapunov function is of the following form (*9*):

$$V(\mathbf{x}) = \mathbf{f}^T \mathbf{A}\, \mathbf{f} \tag{2}$$

where $\mathbf{A}$ is a constant positive definite symmetric matrix. Thus $V(\mathbf{x})$ is a positive definite quadratic form in the derivatives of the state variables. Assuming that $\mathbf{f}$ has continuous first derivatives and its Jacobian matrix, $\mathbf{J} = \{\partial f_i/\partial x_j\}$, satisfies the condition that $(\mathbf{A}\,\mathbf{J} + \mathbf{J}^T\mathbf{A})$ is negative definite then one can show [see (*10*)] that the equilibrium state $\mathbf{x}_e = \mathbf{0}$ is asymptotically stable in the large and Equation (2) is one of its Liapunov functions. This follows directly from

$$\dot{V}(\mathbf{x}) = \mathbf{f}^T\mathbf{A}\dot{\mathbf{f}} + \dot{\mathbf{f}}^T\mathbf{A}\mathbf{f} \tag{3}$$

which, with Equation (1), yields

$$\dot{V}(\mathbf{x}) = \mathbf{f}^T(\mathbf{A}\mathbf{J} + \mathbf{J}^T\mathbf{A})\mathbf{f} \tag{4}$$

There are several important features concerning the above form of Liapunov function. First, in usual chemical reactor stability studies where multiple equilibrium states occur the RAS is bounded and not global. The Liapunov function, (2), permits determination of the bounded RAS because within the bounded region $\dot{V}(\mathbf{x})$ must be negative definite and outside this region $\dot{V}(\mathbf{x})$ may be positive definite. The bounded region is defined by the surface $V(\mathbf{x})$ equal to a constant and these surfaces, $V(\mathbf{x}) = K$, are closed in n-space. Another fortunate feature is that the closed surfaces, $V(\mathbf{x}) = K$, are nested surfaces, and as the constant, K, of the surface increases, the distance of the surface from the origin uniformly increases.

The second aspect of the Krasovskii function is that there are two ways of examining the sign definiteness of $\dot{V}(\mathbf{x})$ in a region. The easiest method is to examine $\dot{V}(\mathbf{x})$ directly as it is defined by Equation (3). The other method, which supplies only a sufficient condition that $\dot{V}(\mathbf{x})$ will be negative, consists of using the sign definiteness condition of $[\mathbf{A}\mathbf{J} + \mathbf{J}^T\mathbf{A}]$. This second approach to determine the sign of $\dot{V}(\mathbf{x})$, is satisfactory, but since only a sufficient condition is determined, the RAS defined by the principle minor method will probably be smaller than that predicted by the actual $\dot{V}(\mathbf{x}) = 0$ surface. In a practical situation Luecke and McQuire (*15*) investigated the stability of a single CSTR and showed that the RAS was greatly enlarged by considering the $\dot{V}(\mathbf{x}) = 0$ surface and not the surfaces defined by the sign of the principle minors as Berger and Perlmutter had previously done (*2*).

The final feature of this form of Liapunov function concerns the determination of the elements of the positive definite symmetric $\mathbf{A}$ matrix. The RAS does change with changes in the values of the elements a_{ij}. A method to determine the largest RAS, by systematically varying the elements of $\mathbf{A}$, was proposed in another article by Luecke and McGuire (*16*). The use of their method is presently restricted to a two state variable situation where a graphical procedure is satisfactory. Obviously, setting $\mathbf{A}$ equal to the identity matrix $\mathbf{I}$ will produce a conservative RAS; nevertheless in the present work we shall do just this since the systematic varying of the elements of $\mathbf{A}$ would merely increase the complexity of the computations and detract from detailing the features of the present method.

COMPUTER ALGORITHM

As yet a method for applying Krasovskii's theorem for determining a bounded RAS has not been developed for systems which have more than two state variables. In the standard example in the literature (*2*, *3*, *15*, *16*) the stability region of a single CSTR is determined. Since this system has only one concentration and one temperature variable a 2-dimensional graphical solution can be used to determine the RAS. A communication by Berger and Perlmutter (*4*) and a paper by Warden, Aris, and Amundson (*21*) have pointed out the extreme difficulty of extending the previous methods to three or more variables. It will be shown that the method proposed in the present paper can be used for high dimensional systems and the difficulties mentioned by these authors are not encountered.

First consider how the RAS is determined for the two variable CSTR case where a graphical solution is possible. The curve $\dot{V}(\mathbf{x}) = 0$ is determined and placed on a plot of temperature vs. concentration. Then beginning at very small values of the Liapunov constant K the closed curves of $V(\mathbf{x}) = K$ are also put on the plot. The constant K is increased until the closed Liapunov curve just touches the curve $V(\mathbf{x}) = 0$, thus determining the RAS. Within the closed curve, $V(\mathbf{x}) = K$, (except at the steady state point $\dot{V}(\mathbf{x})$ is less than zero. On this closed curve $\dot{V}(\mathbf{x})$ will equal zero at only one point, and it will be less than zero at all other points on the closed curve.

If the closed Liapunov surface has not intersected $\dot{V}(\mathbf{x}) = 0$ then everywhere upon the closed surface $V(\mathbf{x}) = K$, $\dot{V}(\mathbf{x})$ will be less than zero and in fact $\dot{V}(\mathbf{x})$ will have both a maximum and a minimum upon $V(\mathbf{x}) = K$. The basic procedure involves searching the $V(\mathbf{x}) = K$ surface for the minimum of $-\dot{V}(\mathbf{x})$ and then increasing K by a small amount and recomputing the minimum of $-\dot{V}(\mathbf{x})$ on this larger closed surface. The largest RAS is determined by that K for which the minimum of $-\dot{V}(\mathbf{x})$ is just zero. The search procedure is started at values of K for which the minimum of $-\dot{V}(\mathbf{x})$ is positive or in other words where $\dot{V}(\mathbf{x})$ is negative.

In attempting to extend these ideas based upon the 2-dimensional problem to the n-dimensional problem, two problems immediately arise. The first is how to keep the resulting minimum value of $-\dot{V}(\mathbf{x})$ on the $V(\mathbf{x}) = K$ surface. The second is what procedure to use in order to minimize $-\dot{V}(\mathbf{x})$ on this surface. But if we think further we see that what we are trying to do is minimize a nonlinear function $[-\dot{V}(\mathbf{x})]$ subject to an equality constraint $[V(\mathbf{x}) = K]$.

Obviously we now can cast the problem into one already considered extensively in the literature. In fact we shall solve the problem via the penalty function approach, which uses an unconstrained version of the original constrained problem. In this approach a new function is minimized rather than the original one; this new function is formed by augmenting the original function with a

weighted square of the constraint. Thus, the new function to be minimized is

$$F = \left\{ -\dot{V}(\mathbf{x}) + \frac{C'}{2} [V(\mathbf{x}) - K]^2 \right\} \tag{5}$$

where C' is a weighting positive constant. As shown by such workers as Fiacco and McCormick (*7*), Rothenberger and Lapidus (*19*), Okamuna (*17*), Russell (*20*), Denn and Aris (*6*), and Kelley (*11*) in a wide variety of applications with the use of the penalty function, as the weighting constant becomes sufficiently large the minimum of the new unconstrained function will approach the minimum of the original function while satisfying the constraint.

In order to accomplish the minimimization of (5) a general iterative computer technique is required. Recently, Fletcher and Powell (*8*) have reported great success in minimization of arbitrary functions using a technique which they have made computationally feasible. The reader is referred to their paper for a full discussion, but briefly stated the method is second-order and approximates the function by a Taylor series expansion about a point in the state space. Only exact first derivatives of the function need be computed and the method determines an approximation to the second derivative Hessian matrix. This approximation becomes equal to the true Hessian matrix at the minimum of the function.

As previously mentioned the A matrix of the Liapunov function (2) will be chosen as the identity matrix. Therefore

$$V(\mathbf{x}) = \mathbf{f}^T\mathbf{f} = \sum_{i=1}^{n} f_i^2 \tag{6}$$

and

$$\frac{\dot{V}(\mathbf{x})}{2} = \sum_{i=1}^{n} f_i \dot{f}_i = \sum_{i=1}^{n} f_i \sum_{j=1}^{n} \frac{\partial f_i}{\partial x_j} f_j \tag{7}$$

where n is the total number of state variables. The augumented function to be minimized is then

$$F = \left\{ -\frac{\dot{V}(\mathbf{x})}{2} + \frac{C'}{2} [V(\mathbf{x}) - K]^2 \right\} \tag{8}$$

or

$$F = \left\{ -\sum_{i=1}^{n} f_i \sum_{j=1}^{n} \frac{\partial f_i}{\partial x_j} f_j + \frac{C'}{2} \left(\sum_{i=1}^{n} f_i^2 - K \right)^2 \right\} \tag{9}$$

Since the Fletcher and Powell minimization involves an iterative search it is necessary to choose initial values of the state variables and also an initial K value. The steady state point is a point of inflection for the function to be minimized because at that point $\mathbf{f}(\mathbf{0}) = \mathbf{0}$. It is thus best to choose a point in the state space which is slightly displaced from the steady state point.

NUMERICAL EXAMPLES

In order to illustrate the present method of determining a finite RAS for a high dimensional nonlinear system three examples will be presented. In all the examples the CSTR is used as a basic reactor element; a first-order exothermic irreversible chemical reaction is always involved.

The first example will be the classical single CSTR with heat transfer. The second example will be a three stage CSTR system with heat transfer. The final example will be a 16 stage model of an adiabatic tubular reactor operating at low conversion. The RAS of the 16 stage model gives an estimate of the RAS of a distributed parameter adiabatic reactor. In each case only a single value of C' in Equation (9) will be given, this value being the result of some preliminary work on a choice for C' which allowed for a smooth minimization of F.

Single CSTR

The system is nonadiabatic, and heat transfer takes place at the walls of the vessel. This hypothetical system is the same as that originally proposed by Berger and Perlmutter (*2*). Heat and mass balances for the system are given by

$$\rho V c_p \frac{dT}{dt} = \Delta H V r - U A_r (T - T_A) - \rho q c_p (T - T_o) \tag{10}$$

$$V \frac{dC}{dt} = -Vr - q(C - C_o) \tag{11}$$

where

$$r = A \exp [-Q'/T] C \tag{12}$$

In order to normalize and collect terms we first define

$$\eta = \frac{\rho c_p T}{\Delta H C_o} \qquad y = \frac{C}{C_o} \qquad a = \rho V c_p$$

$$b = U A_r + \rho q c_p \qquad \tau = \frac{V}{q} \qquad \tau_o = \frac{\rho V c_p}{U A_r} \tag{13}$$

and then specify the perturbations from the steady state point

$$x_1 = \eta - \eta_{ss}$$

$$x_2 = y - y_{ss} \tag{14}$$

These changes convert Equations (10) and (11) into

$$\frac{dx_1}{dt} = \frac{r}{C_o} - \frac{r_{ss}}{C_o} - \frac{b}{a}(x_1 - x_{1ss}) = f_1(x_1, x_2) \tag{15}$$

$$\frac{dx_2}{dt} = -\frac{r}{C_o} + \frac{r_{ss}}{C_o} - \frac{1}{\tau}(x_2 - x_{2ss}) = f_2(x_1, x_2) \tag{16}$$

where

$$\frac{r}{C_o} = A x_2 \exp(-Q/x_1) \quad \text{and} \quad Q = \frac{Q' \rho c_p}{\Delta H C_o} \tag{17}$$

Equations (15) and (16) are in the proper form to use Krasovskii's approach since $\mathbf{f}(0,0) = \mathbf{0}$ and $\mathbf{f}$ has continuous first derivatives. The Liapunov function is explicitly defined as

$$V(\mathbf{x}) = \mathbf{f}^T\mathbf{f} = f_1^2 + f_2^2 = K \tag{18}$$

The graphical solution for the RAS of this problem, using the parameter values given in (*2*), is shown in Figure 1. This figure shows that the closed Liapunov function described by a K value of 0.38 just intersects the $\dot{V}(\mathbf{x}) = 0$ surface. This graphical result was first obtained by Luecke and McGuire (*15*) and is the largest RAS for the given Liapunov function.

Even though this RAS can be determined graphically we now desire to apply the minimization technique of the present paper. This will show, at least for this case, that the technique works and the correct minimum of F is attained. The computation was started with an initial value of $K = 0.07$ and of the state variables x_i as $x_i = 1.01\, x_{iss}$. The results are shown in Figure 2 which is a plot of $-\dot{V}(\mathbf{x})/2$ vs. K for $C' = 10^3$. A value of $K = 0.38$ is the approximate point of intersection of the closed Liapunov curve with $\dot{V}(\mathbf{x}) = 0$. This is the same result found by the graphical technique. For the minimization with 35 different K values and one value of C' the total computation time was approximately 1.5 min. on an IBM 7094 computer.

Thus in the first example, where the answer can be

checked by alternate means, the method works well and with a small amount of computation. If the answer were obtained by a direct integration of the system equations to establish the stability bounds the computation time would be at least as much as for the present method.

Three CSTR System

In order to test the minimization method more fully a hypothetical example of a nonadiabatic three stage system was formulated. The objective in this example is to allow for the possibility of multiple steady states for each of the three stages. For each stage there are two state variables, a temperature and a composition, making a total of six variables for the overall system. The parameters of the system will be taken as constant for all of the stages. Within each stage a single first-order irreversible exothermic chemical reaction is taking place.

The perturbation equations for each stage are equivalent to those previously presented, Equations (15) and (16), taking into account the series nature of the setup. Thus for stage 2 the equations, as an illustration, are

$$\frac{dx_3}{dt} = \frac{r_2}{C_o} - \frac{r_{2ss}}{C_o} - \frac{b}{a}(x_3 - x_{3ss}) + \frac{1}{\tau}(x_1 - x_{1ss}) \tag{19}$$

$$\frac{dx_4}{dt} = -\frac{r_2}{C_o} + \frac{r_{2ss}}{C_o} - \frac{1}{\tau}(x_4 - x_{4ss} - x_2 + x_{2ss}) \tag{20}$$

with

$$\frac{r_i}{C_o} = Ax_{2i}\exp(-Q/x_{2i-1}) \tag{21}$$

For this three stage example the following system parameters were chosen for each stage:

$A = 10^8$ hr.$^{-1}$	$\rho = 40$ lb./cu.ft.
$Q' = 1.2 \times 10^4$ °R.	$T_o = T_A = 530$°R.
$U = 5$ B.t.u./hr. sq.ft. °F.	$\Delta H = 4 \times 10^4$ B.t.u./lb.mole
$A_r = 50$ sq.ft.	$q = 25$ cu.ft./hr.
$V = 25$ cu.ft.	$C_o = 0.2000$ lb.mole/cu.ft.
$c_p = 0.5$ B.t.u./lb. °F.	

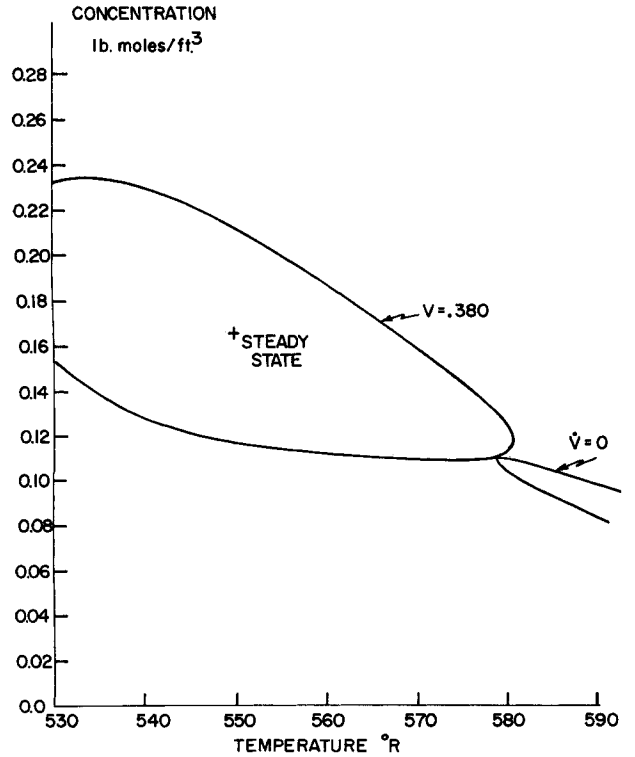

Fig. 1. Single CSTR result of the graphical method.

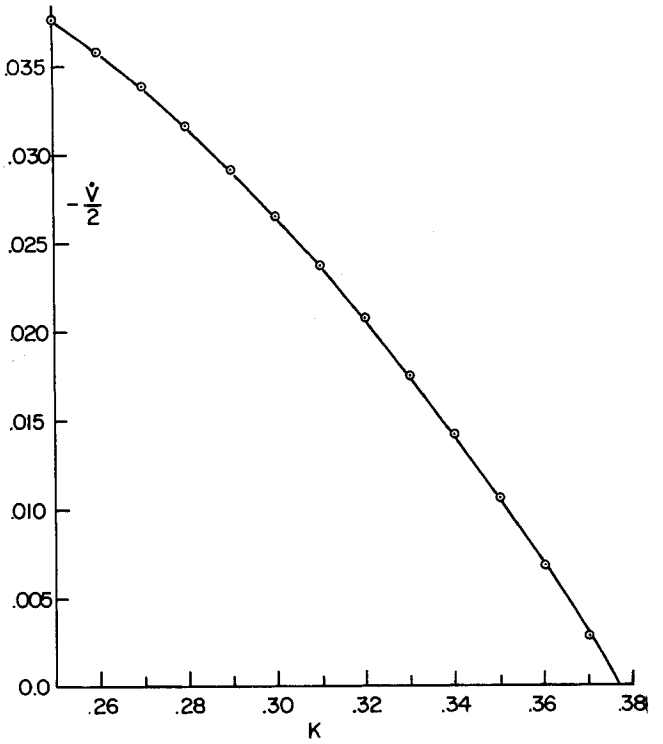

Fig. 2. Single CSTR minimization results.

These parameters yield multiple steady states in each stage with Table 1 indicating the results for the low conversion steady state.

Table 1. The Steady State of Low Conversion for the Three CSTR System

	Stage 1	Stage 2	Stage 3
T, °R.	534.69	538.52	541.68
C, lb. mole/cu. ft.	0.1965	0.1924	0.1879

For the computer minimization calculation the initial value of K was taken to be $K = 0.001$ and the K value was increased and decreased by steps of 0.0002 during the computation. As in the first example the initial guess of the state variables was taken to be 1.01 times their steady state values. Using this starting value only a constant increase in $-\dot{V}(\mathbf{x})/2$ was observed as K was increased. Since we know that $-\dot{V}(\mathbf{x})/2$ should decrease to zero as K is made larger and larger it can be concluded that in this case the initial guess of the state variables needs to be modified. Here, the constant increase in $-\dot{V}(\mathbf{x})/2$ is a consequence of the nonlinear minimization procedure being only local in its ability to find an extremum and the local extremum which is determined is dependent on the choice of the initial values of the state variables. By changing the initial guess of the state variables to $x_i = (1.02)(x_{iss})$ for $i = 1, 3, 5$ and $x_i = (0.98)(x_{iss})$ for $i = 2, 4, 6$ the minimum solution to the problem was obtained. The minimization was performed for approximately 100 different $V(\mathbf{x}) = K$ surfaces, and the total computation time was approximately 5 min. on an IBM 7094 computer.

Figure 3 shows the results of the minimization procedure with $C' = 10^6$. At a value of $K = 0.00189$, $\dot{V}(\mathbf{x}) = 0$, and this K represents the largest RAS for the given form of Liapunov function. It is interesting to note, as illustrated by Figure 3, that $-\dot{V}(\mathbf{x})/2$ first increases and then decreases to zero. This is due to $\dot{V}(\mathbf{x})$ being equal to zero at

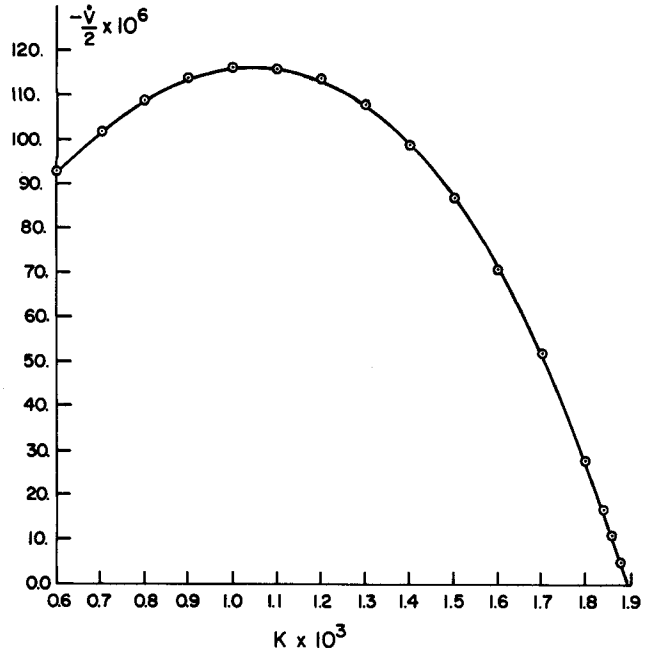

Fig. 3. Three stage CSTR minimization results.

the steady state point and again zero at the point of contact of $\dot{V}(\mathbf{x}) = 0$ with $V(\mathbf{x}) = 0.00189$.

In order to understand the meaning of a K value of 0.00189 in six dimensional space all the temperatures and concentrations except the temperature in the first stage were set equal to their steady state values. The temperature of the first stage was incrementally increased from its steady state value until the system satisfied the equation $V(\mathbf{x}) = 0.00189$. The temperature in the first stage which led to the equation $V(\mathbf{x}) = 0.00189$ being satisfied corresponds to the maximum stable positive deviation of that temperature for the three stage system as predicted by the given form of the Liapunov function. This temperature deviation was 11.2°R. Since the Liapunov method only supplies a sufficient condition for stability it is expected that this deviation is conservative and the system will actually be stable for a larger temperature deviation. The actual largest stable deviation as compared with that predicted by the Liapunov function is a measure of the predictive capability of the Krasovskii type function. To compute just how conservative the 11.2°R. deviation is the transient equations for the three stage system were numerically integrated. The stability limit of the system was found to be at a deviation of +79.2°R. or 7.1 times that predicted by the Liapunov function. Considering the sufficient nature of the Liapunov function this result appears to be an excellent one. The complete integration to steady state of this system of six equations for one value of the initial perturbation took approximately 20 sec. on an IBM 7094 computer. The integration was carried out using Hamming's predictor-corrector method. Therefore, the determination of the stability limit of this one form of perturbation took approximately the same computing time as the determination of the general RAS which applies to all possible perturbations.

Sixteen Stage Model of an Adiabatic Tubular Reactor

It has been shown (*5, 14*) that a tubular reactor in which axial diffusion is taking place can be modeled satisfactorily by a series of feed forward CSTR. This type of modeling is valid in both adiabatic and nonadiabatic situations as well as for steady state and transient systems. This model is quite accurate when the effect of backmixing in the tubular reactor is small. Our concern here will not be with any radial diffusion effects nor with the fact that the nonadiabatic tubular reactor can be modeled without any additional difficulty. The purpose here is to show the necessary relationship between an adiabatic tubular reactor and its corresponding CSTR model and then to determine an RAS for the CSTR model.

The number of stages which is needed to model the tubular reactor is a function of the reactor's Peclet Number. Levenspiel (*14*) has shown that the number of tanks is determined by equating the variances of the output to a pulse input applied to both the exact diffusion model and the CSTR model. The results of his work indicated that the number of stages was related to N_{Pe} by the following relationship:

$$\frac{1}{n} = \frac{2}{N_{Pe}} - \frac{2}{N_{Pe}^2}\left(1 - \exp\left(-N_{Pe}\right)\right) \tag{22}$$

By equating the proper terms the following state perturbation equations (heat and mass) are obtained for an adiabatic CSTR model

for the j^{th} stage, $j = 1, 2, \ldots,$ and $i = 2j - 1$

$$\frac{dx_i}{dt} = \frac{r_j}{C_o} - \frac{r_{jss}}{C_o} + \frac{v}{\Delta x_j}\left(x_{i-2} - x_{i-2ss} - x_i + x_{iss}\right) \tag{23}$$

$$\frac{dx_{i+1}}{dt} = \frac{-r_j}{C_o} + \frac{r_{jss}}{C_o} - \frac{v}{\Delta x_j}\left(x_{i+1} - x_{i+1ss} - x_{i-1} + x_{i-1ss}\right) \tag{24}$$

Here v is the velocity of the fluid in the tubular reactor and Δx_j is the length of stage j of unit cross sectional area. Using (22) it follows that

$$\frac{v}{\Delta x_i A} = \frac{N_{Pe}^2}{2\alpha\left(1 - \dfrac{\left(1 - \exp\left(-N_{Pe}\right)\right)}{N_{Pe}}\right)} \tag{25}$$

where $\alpha = Al^2/D$, l = the length of the reactor, D is the axial diffusivity and A is the reaction rate factor. In (25) we assume that all of the stages are of the same length. If the number of stages predicted by (22) is not close to an integral value then (25) will have to be modified for the final stage which is less than unit length. In Equations (23) and (24) the temperatures and concentrations have been normalized to be consistent with the form of normalization used in the case of the single CSTR. For the usual reaction rate term for r_j, Equations (23) and (24) yield for $j = 1, 2, \ldots,$ and $i = 2j - 1$.

$$\frac{1}{A}\frac{dx_i}{dt} = x_{i+1}\exp\left(-Q/x_i\right) - x_{i+1ss}\exp\left(-Q/x_{iss}\right) - \frac{v}{A\Delta x_j}\left(x_i - x_{iss} - x_{i-2} + x_{i-2ss}\right) \tag{26}$$

$$\frac{1}{A}\frac{dx_{i+1}}{dt} = -x_{i+1}\exp\left(-Q/x_i\right) + x_{i+1ss}\exp\left(-Q/x_{iss}\right) - \frac{v}{A\Delta x_j}\left(x_{i+1} - x_{i+1ss} - x_{i-1} + x_{i-1ss}\right) \tag{27}$$

Equations (26) and (27) need to be multiplied through by a scale factor in order to take into account the division of these equations by the reaction rate frequency factor. This scale factor was arbitrarily chosen as 10^{12}. On this basis the system of equations is properly formulated for the minimization method.

An adiabatic tubular reactor which exhibits multiple steady state profiles has been discussed by Raymond and Amundson (*18*) and a set of physical parameters which yields multiple steady state profiles is

$$N_{Pe} = 30,\ Q = 30/0.4,\ n = 15\tfrac{1}{2},\ T_{\max}/T_o = 1.4$$

$$\frac{v}{A\Delta x_j} = \begin{cases} \text{Equation (25) for } j = 1, 2, \ldots, 15 \\ 2\left[\dfrac{v}{A\Delta x_j}\right] \quad \text{for } j = 16 \end{cases}$$

Figure 4 illustrates the steady state of low conversion for both the integrated steady state diffusion equation and the 16 stage CSTR model of the adiabatic tubular reactor. This confirms that the CSTR accurately models the adiabatic diffusion reactor. The staging model results were determined by Coste's procedure (5).

Turning now to the computer minimization of this 16-stage, 32-variable problem, the starting value for K was taken as $K = 0.0012$ and initial state was $x_i = 1.01\ x_{iss}$. Figure 5 shows the results using a penalty function constant of $C' = 10^8$. This figure exhibits the characteristic initial rise of the minimization curve and then its decrease to zero. For each K the computation time was approximately 8 minutes on an IBM 7094 computer.

In Figure 5 a value of $K = 0.00195$ corresponds to the largest RAS of the given Liapunov function for this 32 variable problem. As in the case of the three stage example it is important to interpret what this region means as far as certain types of perturbations are concerned. Again, we will fix all the state variables at their steady state values except the one being investigated. For instance the K value of 0.00195 leads to certain permissible perturbations in the temperature of a given stage. Table 2 presents the values of some permissible perturbations.

TABLE 2. PERMISSIBLE PERTURBATIONS 16 STAGE MODEL

Stage no.	Perturbation in x_i	Perturbation as T_i/T_o	Perturbation for $T_o = 700°R.$
1	0.00062	0.000248	0.17°R.
9	0.00063	0.000252	0.18°R.
14	0.00065	0.000260	0.18°R.

The last column of Table 2 presents the maximum permitted deviation for an arbitrary inlet temperature of 700°R. It is apparent from this table that the predicted RAS is extremely small and probably considerably smaller than the actual RAS. In order to estimate what are the actual stability characteristics of this system, a perturbation in the temperature of stage no. 9 was made, and the resulting transient equations for the system integrated. A perturbation of +0.00063 produced only an asymptotically stable response from the series of stages. In order for the series of stages to become unstable and go to another steady state operating point it was necessary to make a perturbation in stage 9 of +0.106 or 168 times that predicted by the Liapunov function. Thus we have arrived at

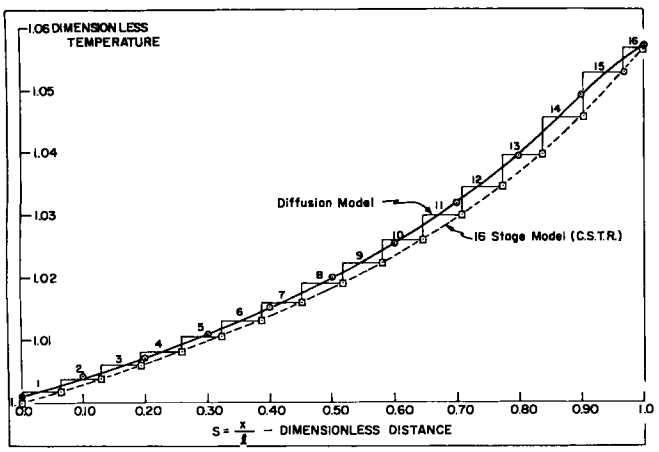

Fig. 4. Comparative temperature profiles for the adiabatic tubular reactor.

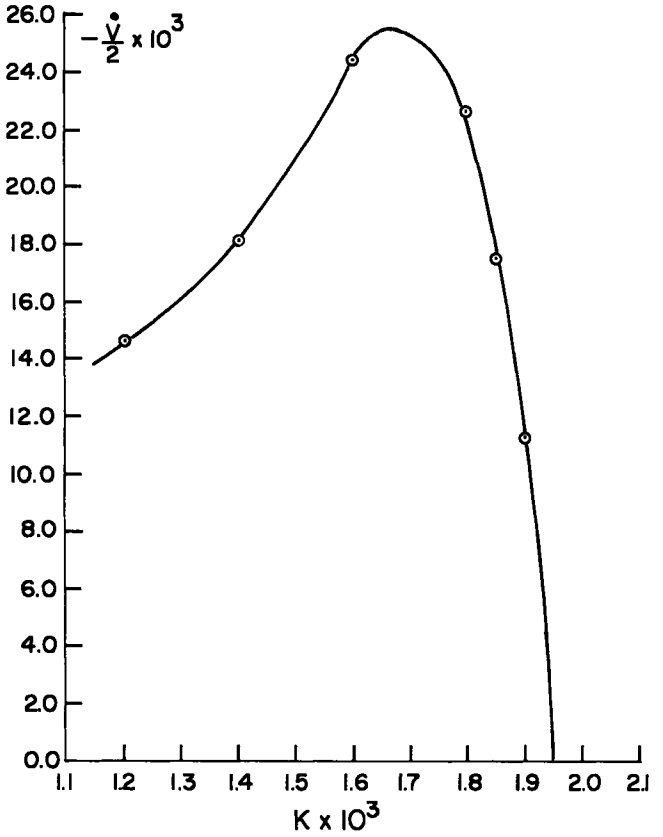

Fig. 5. Sixteen stage CSTR minimization results.

an extremely conservative but finite RAS for this approximation to a distributed parameter system.

In summary, the results of this paper have shown that the determination of a finite RAS for a nonlinear system may be mapped into the problem of minimizing a nonlinear function subject to a constraint. This new problem is then solved via an iterative algorithm. Because the Liapunov RAS is merely a sufficient condition the method predicts regions of asymptotic stability which are conservative; this conservative feature becomes more pronounced as the dimensionality of the original system increases. As a result the method as presented here should have its optimum utility in the treatment of problems having a maximum of 5 to 10 variables. However, one would expect that the stability limits could be increased for any system by varying the weighting matrix A in the Liapunov function and perhaps by using a different type of Liapunov function.

The iterative algorithm used is not guaranteed to converge for every starting value of the state vector. However, this is not unusual for the type of systems considered; in one case reported here where a difficulty with convergence is encountered a small alteration of the initial state was sufficient to achieve convergence.

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NOTATION

A = frequency factor
$\mathbf{A}$ = positive definite symmetric matrix
a = defined by Equation (13)
A_r = heat transfer area
b = defined by Equation (13)
C = concentration

C' = penalty function constant
c_p = heat capacity
D = effective axial diffusivity
F = augmented function to be minimized
$\mathbf{f(x)}$ = nonlinear vector function
ΔH = heat of reaction
$\mathbf{I}$ = identity matrix
$\mathbf{J}$ = Jacobian matrix
K = Liapunov constant
l = length of reactor
N = number of stages
N_{Pe} = vl/D Peclet Number
Q = dimensionless activation energy
Q' = defined by Equation (17)
q = flow rate
r = reaction rate
T = temperature
t = time
U = heat transfer coefficient
V = reactor volume
$V(\mathbf{x})$ = Liapunov function
$\dot{V}(\mathbf{x})$ = time derivative—Liapunov function
v = fluid velocity
$\mathbf{x}$ = state vector
Δx_j = j^{th} length increment
y = defined by Equation (13)

Greek Letters

α = defined by Equation (25)
η = defined by Equation (13)
ρ = density
τ = defined by Equation (13)
τ_o = defined by Equation (13)

Subscripts

o = inlet
A = ambient
ss = steady state

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Network Rupture and the Flow of Concentrated Polymer Solutions

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Entanglement theories for polymer solutions resemble those developed for solid rubbers. These rubberlike theories are extremely successful qualitatively; they give a good indication of the type of response observed experimentally in concentrated solutions. Quantitatively the theories are not so useful; in general they predict constant viscosities in simple shearing motions and ever-increasing tensile stress in steady elongational flow.

If it is supposed that the lifetime of the entanglements is limited partly by a maximum allowable strain magnitude, and that the network ruptures locally whenever this magnitude is exceeded, greatly improved quantitative predictions are observed. For polyisobutylene-cetane solutions, where the critical strain magnitude appears to be about 3, excellent prediction of the steady shearing viscosity curve is available starting from the measured dynamical response to small sinusoidal strains and the critical strain magnitude. Normal stress effects are also well represented; in elongational flow the tensile stress shows a slight maximum. It thus appears that the notion of network rupture is useful in guiding the selection of continuum theories for polymer fluid description.

CONTINUUM THEORY FOR THE DESCRIPTION OF POLYMER FLUIDS

The hunt for nonlinear constitutive relations giving a realistic description of polymer melts and solution has been in progress since 1948; however, if one considers the early pioneering studies of variable viscosity, the search would date back to about 1920. To be acceptable, a constitutive equation is required to predict realistic results for