Local Stability of Tubular Reactors

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Liapunov analysis techniques employing a general quadratic functional are used to derive stability conditions for tubular reactor systems. The adiabatic tubular reactor without axial dispersion is shown to be locally stable, which excludes the possibility of multiple steady states, and the reactor with axial dispersion is proven locally stable if a condition involving only system parameters and steady state values is satisfied. Peclet numbers for heat and mass transfer are not specified equal for the latter proof.

Results of simulation studies are used to confirm the validity of the derived stability condition, and it is shown that the parametric region of multiplicity is quite well defined. For the nonlinear equations, single steady state cases appear to possess nonuniform stability.

This paper investigates the stability of tubular reactors using both theoretical and computational techniques. Liapunov's direct method employing a functional based on a general quadratic norm is used as the theoretical method. The theoretical analysis yields through straightforward algebraic manipulation stability results without the need for a solution of the partial differential equations describing the system. Dynamic simulations were computationally carried out by finite differencing the describing equations and using the quasilinearization technique.

In the literature much attention has recently been devoted to stability studies of distributed parameter systems. Murphy and Crandall (*19*) applied Liapunov stability theory to the catalyst particle problem using a theorem somewhat similar to that to be presented here. Their analysis yielded stability conditions depending on system parameters and steady state values. Han and Meyer (*15*) used bounded-input-bounded-output concepts to analyze the stability of a nondispersive, catalytic bed reactor. They obtained a stability condition based on discretized nonlinear equations which was different from previous results based on linearized equations. Other work has been done on nondispersive models, and an example is the recent article by Agnew and Narsimhan (*1*).

Based on original work by Amundson and Raymond (*2*, *3*) and separately, van Heerden (*22*), several recent articles (*14*, *16*, *17*) have treated the adiabatic tubular reactor with heat and mass transfer Peclet numbers set equal. This restriction will not apply here.

McGowin and Perlmutter (*18*) have included a heat transfer term in the modeling equations but still assumed equal Peclet numbers. Nishimura and Matsubara (*20*) have considered the case of unequal Peclet numbers, but in order to apply their method which uses an L_2 norm Liapunov functional a nontrivial definition of state variables must be introduced.

The second or direct method of Liapunov avoids determining the solution of differential equations in order to study the stability characteristics of those equations. A function which is positive definite in the state variables, that is, positive away from a given steady state and zero only at the steady state is specified, and stability is ensured if it can be shown that the time derivative of this function is negative definite. This time derivative involves time derivatives of the state variables, and these are conveniently available in the system differential equations.

Liapunov's first method, according to Bertram and Kalman (*7*), "deals with stability questions via an explicit representation of the solutions of a differential equation," whereas Aris (*4*) is more specific in stating, "His so-called first method shows how the process of linearization about the steady state may be justified and exploited."

The difficulty in the application of the second method is usually found in the search for the Liapunov function. An inverse formulation involving first the specification of a negative definite Liapunov function derivative has been widely used for linear lumped systems. Recently via a double integral theorem (*6*), application has been possible for linear distributed systems. The inverse technique eliminates the search.

A valid point of criticism of the second method is that its use in determination of regions of stability for nonlinear systems often yields weak or conservative results (*21*).

The basis for the theoretical analysis which follows is the use of a Liapunov functional of a general quadratic norm

$$V = \| \underline{u}_b \|^2_{\underline{\underline{P}}} = \int_0^1 \underline{u}_b' \, \underline{\underline{P}}(x) \, \underline{u}_b \, dx$$

The matrix $\underline{\underline{P}}(x)$ is positive definite and of the following block diagonal form

$$\underline{\underline{P}}(x) = \left[\begin{array}{c|c} \underline{\underline{P}}_{ss}(x) & \underline{\underline{O}} \\ \hline \underline{\underline{O}} & \underline{\underline{P}}_{ff}(x) \end{array}\right]$$

and $\underline{u}_b$ is a vector of all state variables except those introduced to reduce higher order items (*5*). The subscripts *ss* and *ff* indicate that these partitioned matrices treat second- and first-order state variables respectively, and $\underline{u}_b = \mathrm{col}(\underline{u}_s, \underline{u}_f)$. The use of this general quadratic norm eliminates *a priori* searches for Liapunov functionals. The exact

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form that works for a particular problem is a result of applying the Liapunov analysis.

Using the general quadratic Liapunov functional, the following theorem can be proved.

An unforced second-order distributed parameter system of the form

$$\frac{\partial \hat{\underline{u}}}{\partial t} = \underline{\underline{A}}(\underline{u}, x, t) \frac{\partial \underline{u}}{\partial x} + \underline{B}(\underline{u}, x, t)$$

is uniformly asymptotically stable in the large if for all $t > 0$ and $x \epsilon [0, 1]$

1. $\underline{u}' \underline{\underline{F}} \underline{u} \Big|_0^1 \leq 0$ and
2. the matrix $\underline{\underline{C}}$ is negative definite

where

$$\underline{\underline{F}} = \left[\begin{array}{c|c|c} \underline{\underline{P}}\underline{\underline{A}}_{bb} & \multicolumn{2}{c}{\underline{\underline{P}}_{ss}} \\ \cline{2-3} & \multicolumn{2}{c}{\underline{\underline{O}}} \\ \hline \underline{\underline{P}}_{ss} & \underline{\underline{O}} & \underline{\underline{O}} \end{array}\right],$$

$$\left[\begin{array}{c|c|c} \multicolumn{2}{c|}{\underline{\underline{C}}_{bb}} & -\dfrac{\partial \underline{\underline{P}}_{ss}}{\partial x} \\ \cline{3-3} \multicolumn{2}{c|}{} & \underline{\underline{O}} \\ \hline -\dfrac{\partial \underline{\underline{P}}_{ss}}{\partial x} & \underline{\underline{O}} & -2R\underline{\underline{P}}_{ss} \end{array}\right]$$

and

$$\underline{\underline{C}}_{bb} = -\underline{\underline{P}} \frac{\partial \underline{\underline{A}}_{bb}}{\partial x} - \frac{\partial \underline{\underline{P}}}{\partial x} \underline{\underline{A}}_{bb} + 2\underline{\underline{P}}\, \underline{\underline{B}}_{bb}$$

Here $\hat{\underline{u}} = \text{col}(\underline{u}_b, \underline{O}_a)$ and $\underline{u} = \text{col}(\underline{u}_b, \underline{u}_a)$ where $\underline{u}_a$ represent auxiliary variables defined to reduce a higher order system to the form required by the theorem. The proof of this theorem was first presented by Baker (*5*), and its applications to countercurrent and parallel heat exchangers with and without dispersive effects are also available elsewhere (*10, 11*). A short outline of the proof is given in Appendix A.

In order to use the theorem, one must formulate his system in the above form, derive the two key matrices $\underline{\underline{C}}$ and $\underline{\underline{F}}$ and attempt to satisfy the two conditions by suitable choice of $\underline{\underline{P}}(x)$. These steps will be illustrated in the following examples.

NONDISPERSIVE TUBULAR REACTOR

Assuming that a first-order reaction takes place in a single phase adiabatic tubular reactor, that there is a significant heat of reaction and the rate can be expressed in Arrhenius form, and that axial dispersion and radial gradients are negligible, the energy and material balances are described by the following equations and their boundary conditions:

$$\rho c_p \frac{\partial T}{\partial \theta} = -\rho c_p\, v \frac{\partial T}{\partial z} + (-\Delta H)\, kC \exp\left(-\frac{E}{R_g T}\right), \quad T(0, \theta) = T_0 \quad (1)$$

$$\frac{\partial C}{\partial \theta} = -v \frac{\partial C}{\partial z} - kC \exp\left(-\frac{E}{R_g T}\right), \quad C(0, \theta) = C_0 \quad (2)$$

With substitutions of $y = C/C_0$, $x = z/L$, $t = v\theta/L$, and $n = T/T_0$, the above become

$$\frac{\partial n}{\partial t} = -\frac{\partial n}{\partial x} + \frac{(-\Delta H) k C_0 L}{\rho c_p v\, T_0}\, y \exp\left(-\frac{E}{R_g T_0 n}\right), \quad n(0) = 1 \quad (3)$$

$$\frac{\partial y}{\partial t} = -\frac{\partial y}{\partial x} - \frac{kL}{v}\, y \exp\left(-\frac{E}{R_g T_0 n}\right), \quad y(0) = 1 \quad (4)$$

Defining for simplification $q = E/R_g T_0$, $B_y = kL/v$, $B_n = \dfrac{(-\Delta H)\, k C_0 L}{\rho c_p\, v\, T_0}$, and $R = y \exp(-q/n)$, Equations (3) and (4) are

$$\frac{\partial n}{\partial t} = -\frac{\partial n}{\partial x} + B_n R, \quad n(0) = 1 \quad (5)$$

$$\frac{\partial y}{\partial t} = -\frac{\partial y}{\partial x} - B_y R, \quad y(0) = 1 \quad (6)$$

Past experience has shown (*10, 12*) that the system can be proved stable for endothermic reactions, but that the application of the theorem to the nonlinear equations for exothermic reactions yields no conclusive results; therefore, the equations will be linearized here in order to gain information about local stability for exothermic reactions. Equations (5) and (6) are linearized about a given steady state and by the substitution of

$$R_1 = \left.\frac{\partial R}{\partial n}\right|_{st} \quad R_2 = \left.\frac{\partial R}{\partial n}\right|_{st},$$

$$u_1 = n - n_{st}, \quad \text{and} \quad u_2 = y - y_{st}$$

the following are obtained

$$\frac{\partial u_1}{\partial t} = -\frac{\partial u_1}{\partial x} + B_n R_1 u_1 + B_n R_2 u_2, \quad u_1(0) = 0 \quad (7)$$

$$\frac{\partial u_2}{\partial t} = -\frac{\partial u_2}{\partial x} - B_y R_1 u_1 - B_y R_2 u_2, \quad u_2(0) = 0 \quad (8)$$

At this point, it is noted that

$$R_1 = \frac{y_{st} q}{n^2_{st}} \exp\left(-\frac{q}{n_{st}}\right) > 0 \quad (9)$$

$$R_2 = \exp\left(-\frac{q}{n_{st}}\right) > 0 \quad (10)$$

Inequality (9) may not be true in a few cases; for example, decomposition of NO_2 for which the rate varies inversely with temperature.

Equations (7) and (8) can now be written in the form demanded by the theorem, that is,

$$\frac{\partial \underline{u}}{\partial t} = \underline{\underline{A}} \frac{\partial \underline{u}}{\partial x} + \underline{\underline{B}}\, \underline{u}$$

where

$$\underline{\underline{A}} = \begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix} \quad \text{and} \quad \underline{\underline{B}} = \begin{bmatrix} B_n R_1 & B_n R_2 \\ -B_y R_1 & -B_y R_2 \end{bmatrix}$$

In this case,

$$P = \begin{bmatrix} P_1 & 0 \\ 0 & P_2 \end{bmatrix}$$

and there are no second-order variables, so

$$\underline{\underline{F}} = \underline{\underline{P}}\underline{\underline{A}}_{bb} = \underline{\underline{P}}\underline{\underline{A}} = -\underline{\underline{P}} \quad \text{and}$$

$$\underline{\underline{C}} = \underline{\underline{C}}_{bb} = -\frac{\partial P}{\partial x}\underline{\underline{A}} + 2\underline{\underline{PB}}$$

$$= \begin{bmatrix} \dfrac{\partial P_1}{\partial x} + 2B_nR_1P_1 & 2B_nR_2P_1 \\ -2B_yR_1P_2 & \dfrac{\partial P_2}{\partial x} - 2B_yR_2P_2 \end{bmatrix}$$

The first condition of the theorem is that $\underline{u}'\underline{\underline{F}}\underline{u}|_0^1 \leq 0$. Here

$$\underline{u}'\underline{\underline{F}}\underline{u}|_0^1 = -P_1(1)u_1^2(1) - P_2(1)u_2^2(1) \leq 0,$$

and the condition is satisfied without any restriction on P_1 or P_2 except that they be positive at $x = 1$ and bounded. So that the matrix $\underline{\underline{C}}$ above can be made negative definite

$$\frac{\partial P_1}{\partial x} + 2B_nR_1P_1 < 0 \tag{11}$$

and

$$\left(\frac{\partial P_1}{\partial x} + 2B_nR_1P_1\right)\left(\frac{\partial P_2}{\partial x} - 2B_yR_2P_2\right) + 4P_1P_2B_yB_nR_1R_2 > 0 \tag{12}$$

For inequality (11) to hold, let $P_1 = \exp(-Kx)$ and then $-K + 2B_nR_1 < 0$ so K should be chosen such that $K > 2B_nR_1$. The additional specification of $P_2 = \exp(-x)$ ensures that inequality (12) will be true, and the proof is complete.

Therefore, the linearized Equations (7) and (8) have been proved globally asymptotically stable which implies local asymptotic stability for the nonlinear Equations (1) and (2). This in turn indicates (*16*) that multiple steady states, at least one of which is unstable, cannot exist for this system.

DISPERSIVE TUBULAR REACTOR

Axial dispersion is included in the model by the addition of second-order terms to Equations (1) and (2) of the previous section. The dimensionless linearized equations are

$$\frac{\partial u_1}{\partial t} = \frac{\alpha}{D}\frac{\partial^2 u_1}{\partial x^2} - r_2\frac{\partial u_1}{\partial x} + B_1R_1u_1 + B_1R_2u_2 \tag{13}$$

with B.C.

$$\frac{\partial u_1}{\partial x}(0) = r_1u_1(0); \quad \frac{\partial u_1}{\partial x}(1) = 0$$

$$\frac{\partial u_2}{\partial t} = \frac{\partial^2 u_2}{\partial x^2} - r_2\frac{\partial u_2}{\partial x} - B_2R_1u_1 - B_2R_2u_2 \tag{14}$$

with B.C.

$$\frac{\partial u_2}{\partial x}(0) = r_2u_2(0) \quad \text{and} \quad \frac{\partial u_2}{\partial x}(1) = 0$$

Auxiliary variables are defined in order for the system equations to fit the general hyperbolic form for use in the stability theorem. Then the matrices $\underline{\underline{F}}$ and $\underline{\underline{C}}$ are formed in order to test the condition of the theorem. The details of the analysis are given in Appendix *B* while the results are presented below.

The reactor system can be proved stable using the Liapunov functional

$$V = \int_0^1 \underline{u}'\,\underline{\underline{P}}(x)\underline{u}\;dx$$

where

$$\underline{\underline{P}}(x) = \begin{bmatrix} \exp(-K_1X) & 0 \\ 0 & \exp(-K_2X) \end{bmatrix}$$

with the restrictions that

i. $K_1 >$ but $\approx 2B_1R_1/r_2$, (15)

ii. $\dfrac{B_1R_1}{r_1r_2} < 1$, and (16)

iii. $K_2 < \dfrac{2r_1B_2R_2}{B_1R_1}\left(1 - \dfrac{B_1R_1}{r_1r_2}\right)$. (17)

Only inequality (16) is a key condition here since the others involve only specification of the Liapunov function. It is noted that as either or both of the Peclet numbers become very large, that is, nondispersive flow is approached, inequality (16) would tend to be satisfied. This corroborates the stability proof for the nondispersive reactor. Inequality (16) also indicates that if R_1 is a large number, that is, the reaction rate is highly temperature sensitive, stability is more difficult to prove.

STEADY STATE DETERMINATION

A numerical solution of the steady state forms of Equations (13) and (14) is desired. Following the technique used by Amundson and Raymond (3), the steady state profiles may be approximated to desired accuracy. It should be noted that this method assumes equal Peclet numbers for heat and mass axial dispersion and is only used here as a convenient means of testing the proof of the previous section which places no such restrictions on the Peclet numbers.

With the assumption that $r_1 = r_2$, and defining $PE = r_1 = r_2$, the nonlinear describing Equations (B4) and (B5) can be combined (3) to give in steady state form

$$\frac{d^2n}{dx^2} - PE\frac{dn}{dx} + \frac{L^2K}{D}(n_{\lim} - n)\exp\left(-\frac{q}{n}\right) = 0 \tag{18}$$

with the boundary conditions

$$1 - n(0) = -\frac{1}{PE}\frac{dn}{dx}(0) \tag{19}$$

and

$$\frac{dn}{dx}(1) = 0 \tag{20}$$

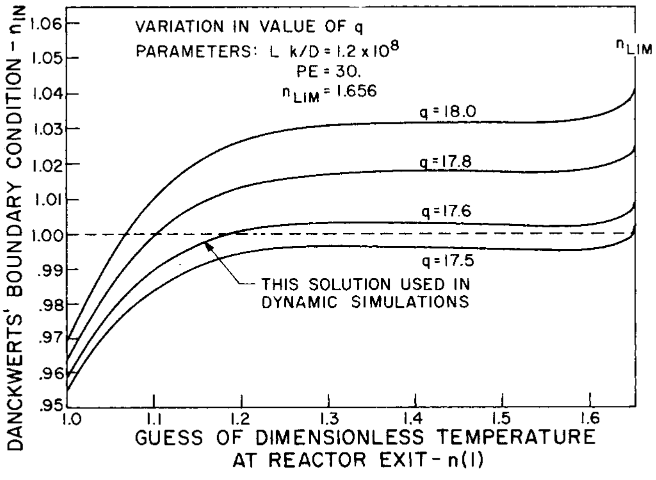

Fig. 1. Steady state determination of adiabatic tubular reactor.

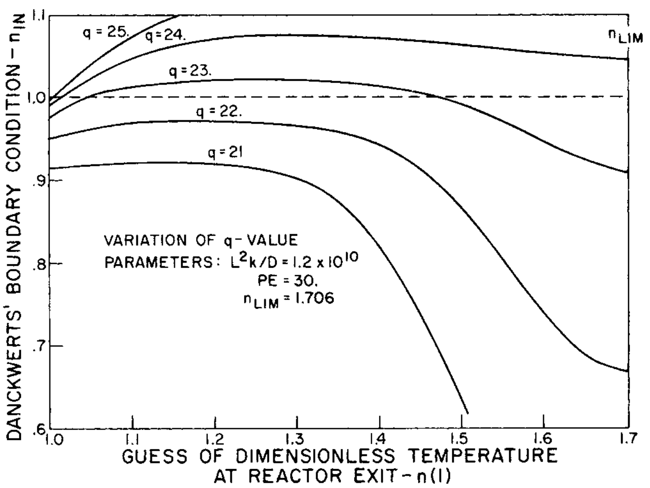

Fig. 2. Steady state determination of adiabatic tubular rector.

The quantity $n_{\rm lim}$ is the limiting dimensionless temperature in the reactor, that is, that temperature reached at complete conversion.

The solution technique is to pick a value of $n(1)$, and with Equation (20), integrate Equation (18) backwards to $x = 0$. Equation (19) is then tested to see if it is satisfied to desired accuracy, and if not another guess is made for $n(1)$, and the process is repeated. It is convenient to define the quantity n_{in} as

$$n_{in} = n(0) - \frac{1}{PE}\frac{dn}{dx}(0) \qquad (21)$$

therefore when $n_{in} = 1$ the Danckwerts boundary condition [Equation (20)] is satisfied and the steady state has been found.

The behavior of the solution steady state for arbitrary ranges of the parameters PE, L^2k/D, and q can be found in (9) and (11). Figure 1 illustrates graphically the determination of the proper $n(1)$ for $L^2k/D = 1.2 \times 10^8$, $PE = 30$, and $n_{\rm lim} = 1.656$ with the value of q ranging from 17.5 to 18.0. These values are based on the following system parameters (8):

$$r_1 = r_2 = 30, \quad \alpha = D = 1 \text{ sq.cm./sec.}, \quad C_0 = 0.5 \text{ lb.-mole/cu.ft.}$$

$$T_0 = 510\ ^\circ\text{R.}, \quad \rho = 60 \text{ lb./cu.ft.}, \quad c_p = 1 \text{ B.t.u./lb.-mole/}^\circ\text{F.}$$

$$L = 100 \text{ cm.}, \quad k = 1.2 \times 10^4 \text{ sec.}^{-1}, \quad (-\Delta H) = 4 \times 10^4 \text{ B.t.u./lb.-mole}$$

If the value of the quantity B_1R_1/r_1r_2 is computed based on these parameters and the steady state solution for $q = 17.6$, the result ranges monotonically from 0.028 at the reactor entrance to 0.264 at the exit. Therefore, the stability proof is valid for this case, and the given steady state is locally stable. This implies only stability of this steady state, whereas Figure 1 indicates there is only one solution.

The system parameters above are modified by specifying $(-\Delta H) = 4.32 \times 10^4$ B.t.u./lb.-mole, $k = 1.2 \times 10^6$ sec.$^{-1}$, and q is ranged between 21 and 25. Figure 2 illustrates steady state solutions for this case. For the value $q = 23$, three solutions exist. This is more clearly shown in Figure 3 where the vertical scale is expanded. For steady state II noted on that figure, the quantity B_1R_1/r_1r_2 evaluated at the reactor entrance is equal to 0.018 and at the exit is 4.99. The condition is violated, and conclusions about stability cannot be made. However, for $q = 24$ (see Figure 2) and above, $B_1R_1/r_1r_2 < 1$, and local stability can be proved.

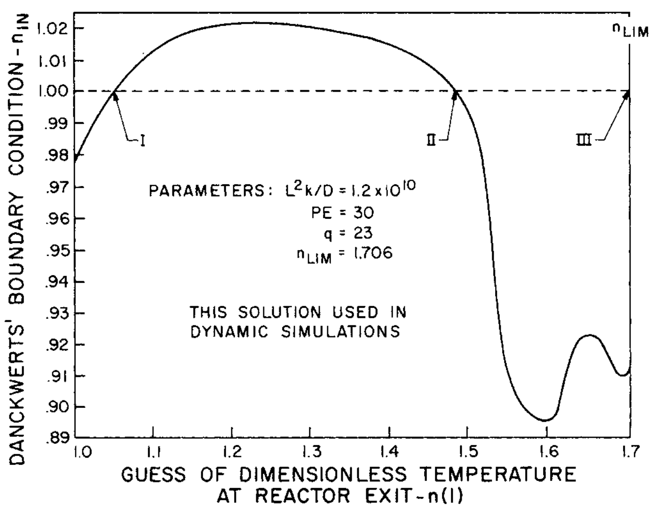

Fig. 3. Steady state determination of adiabatic tubular reactor.

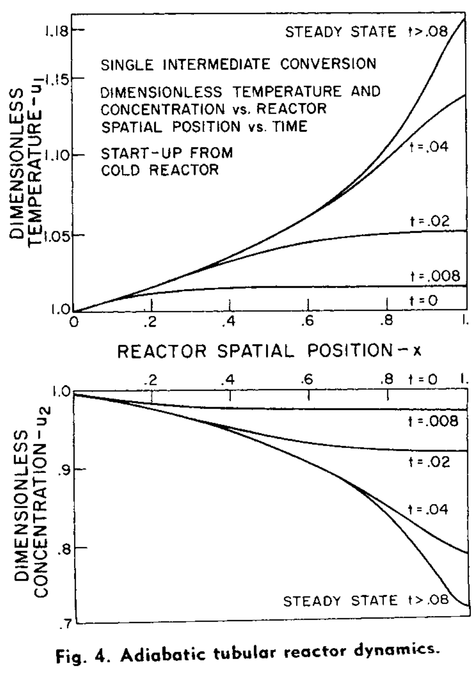

Fig. 4. Adiabatic tubular reactor dynamics.

At values less than $q = 23$, no conclusion is attained; however, heuristic arguments for local stability can be made on the basis that the spatial region in the reactor where the condition is not satisfied is quite limited and, thus, is given little weight in the Liapunov function integral. In any case, the transition to multiplicity is well defined from the one side.

DYNAMIC SIMULATION

The partial differential Equations (1) and (2) have been solved numerically for the two cases discussed in the previous section. The solution technique used was quasilinearization, and details of its application are available elsewhere (*10, 12*). This technique proved to be very efficient in the solution of these highly nonlinear equations.

Figures 4 to 7 are based on the single steady state indicated on Figure 1 with a value of $q = 17.6$. Figure 4 shows the response of temperature and concentration in a cold start-up situation. The stable convergence to the steady state here is further emphasized by Figure 5 which shows the behavior of a computed Liapunov function (L_2 norm) and its derivative.

For this same case, nonuniform stability is illustrated in Figure 6 for an initial linear profile in temperature above the steady state. The perturbation is first amplified by reaction before it is convected out of the reactor. A Liapunov technique which considers only uniform stability will certainly fail here. Success was attained in the application to the linearized equations because the nonuniform nature was lost in the linearization process.

This nonuniform behavior is also illustrated by the dynamics of the Liapunov function as shown in Figure 7.

The multiple steady state case chosen was that of Figure 3. Figure 8 shows the three steady state profiles and a dynamic simulation from an initial constant profile just above the low conversion steady state. The high conversion steady state is rapidly attained.

Local nonuniform stability about the low steady state is illustrated in Figure 9, and local instability appears to be the case for the intermediate conversion steady state in Figure 10.

CONCLUSIONS

Through the application of a theorem based on a general norm Liapunov functional, the following have been demonstrated.

1. The adiabatic tubular reactor with no axial dispersion is locally stable. This implies that multiple steady states cannot exist.
2. The adiabatic tubular reactor with independent mass and heat axial dispersion can be proven stable if a condition based only on system parameters and steady state information is satisfied.
3. Steady state simulations indicate that this stability condition is valid and that it defines well the range of parameters for which multiple steady states occur.
4. The simulations of nonlinear dynamics show that the system exhibits nonuniform stability about stable steady states in multiple and even single cases.

NOTATION

$\underline{\underline{A}}$ = coefficients of state spatial derivative terms

$\underline{\underline{B}}$ = coefficients of state terms

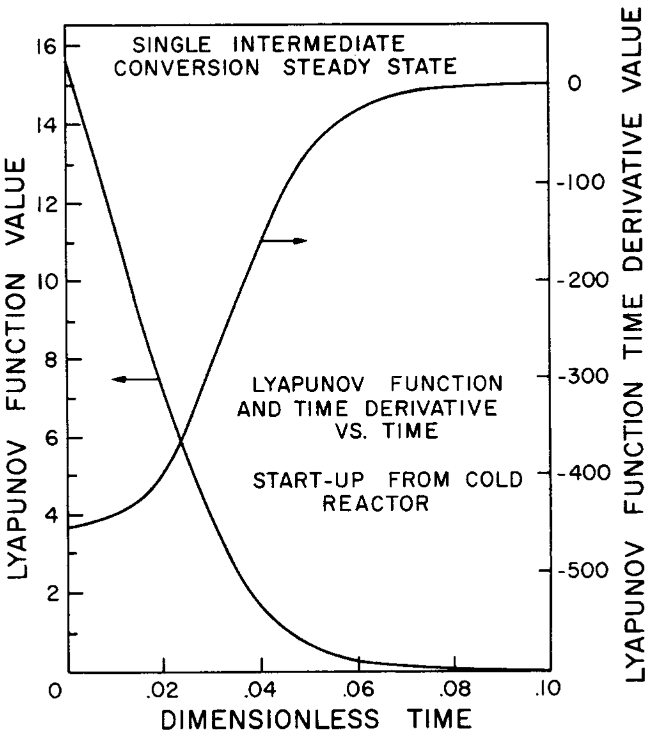

Fig. 5. Adiabatic tubular reactor dynamics.

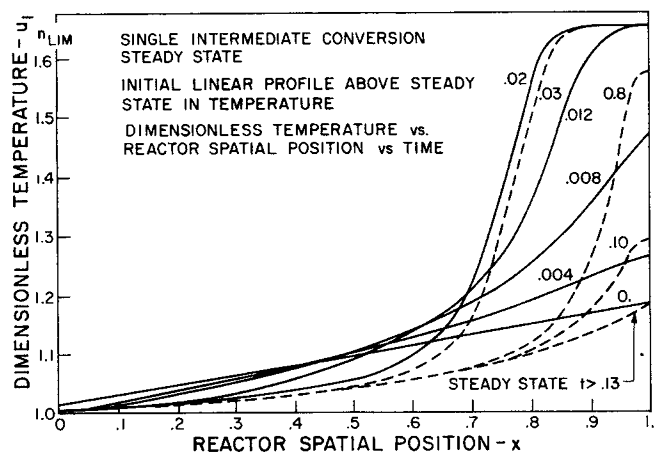

Fig. 6. Adiabatic tubular reactor dynamics.

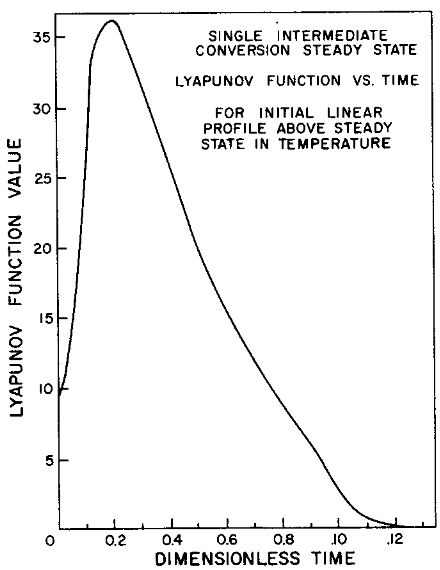

Fig. 7. Adiabatic tubular reactor dynamics.

$\bar{\bar{C}}$ = matrix for Liapunov analysis
$\bar{\bar{F}}$ = matrix for Liapunov analysis
$\bar{\bar{I}}$ = identity matrix
$\bar{\bar{O}}$ = null matrix
$\bar{\bar{P}}$ = Liapunov function general norm matrix
$\bar{\bar{R}}$ = diagonal matrix involving Peclet numbers
$\underset{\sim}{\bar{u}}$ = all state variables
$\underset{\sim}{\hat{u}}$ = composite vector of basic state variables and null vector
O = null vector

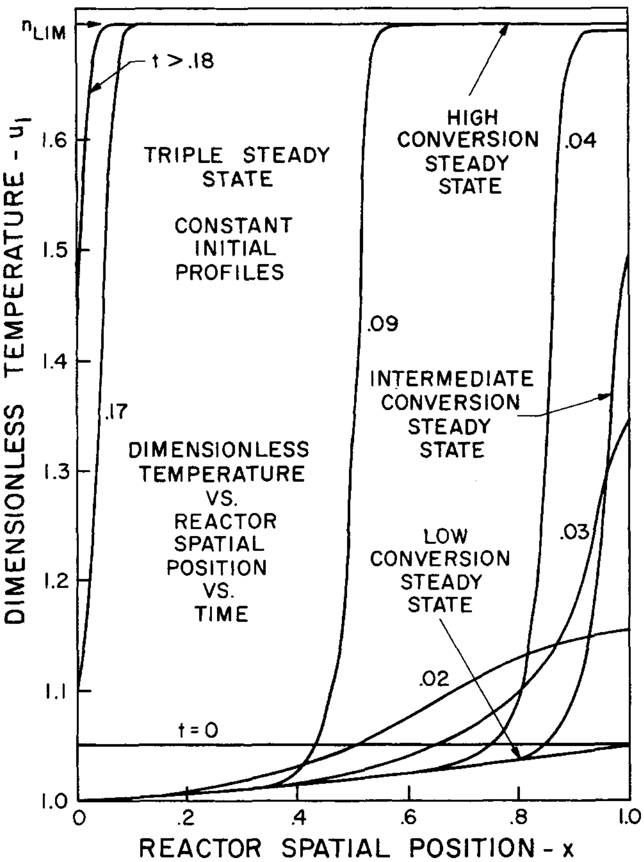

Fig. 8. Adiabatic tubular reactor dynamics.

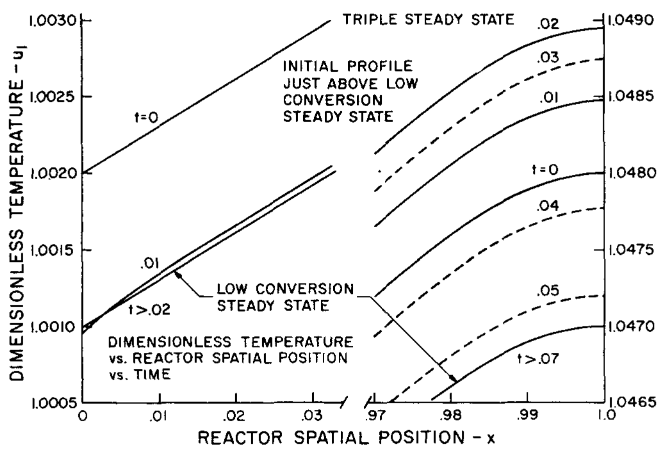

Fig. 9. Adiabatic tubular reactor dynamics.

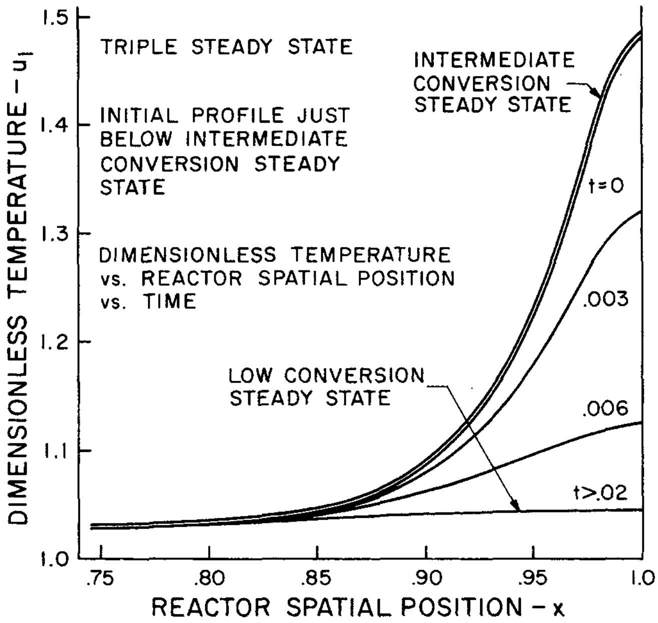

Fig. 10. Adiabatic tubular reactor dynamics.

$\bar{B}_n$ = term defined for simplification of Equations (3) and (4)
B_y = term defined for simplification of Equations (3) and (4)
B_1 = term similar to B_n, but for dispersive case
B_2 = term similar to B_y, but for dispersive case
C = concentration of reactant
c_p = heat capacity of fluid
D = effective mass diffusivity
E = activation energy
k = frequency factor
K = constant used in Liapunov function for nondispersive case
K_1 = constant used in Liapunov function for dispersive case
K_2 = constant used in Liapunov function for dispersive case
L = real length of reactor
n = dimensionless temperature
n_{in} = defined term for steady state determination
n_{lim} = dimensionless limiting temperature for reactor
PE = Peclet number for mass and heat transfer, when equal
q = dimensionless activation energy
R = dimensionless reaction rate
R_g = gas law constant
R_1 = partial derivative of R with respect to temperature
R_2 = partial derivative of R with respect to concentration
r_1 = Peclet number for heat transfer
r_2 = Peclet number for mass transfer
T = temperature of fluid
t = dimensionless time
v = linear velocity of fluid
x = dimensionless spatial (axial) variable
y = dimensionless concentration
z = spatial (axial) variable
$(-\Delta H)$ = heat of reaction
α = thermal diffusivity, effective
θ = real time
ρ = density of fluid
λ = effective thermal conductivity

Subscripts

a	= auxiliary variable
b	= basic variable
bb	= $b \times b$ square matrix and pertaining to basic variables
f	= first-order only variable
ff	= $f \times f$ square matrix and pertaining to first-order variables
n	= pertaining to dimensionless temperature
o	= inlet condition
s	= second-order variable (can be first also)
ss	= $s \times s$ square and pertaining to second-order variables
st	= steady state conditions
y	= pertaining to dimensionless concentration

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APPENDIX A: STABILITY THEOREM EMPLOYING A GENERAL QUADRATIC NORM

A second-order system can be written as

$$\frac{\partial \underline{u}_b}{\partial t} = \mathcal{L}_b(\underline{u}) \tag{A1}$$

where

$$\mathcal{L}_b(\cdot) = \underline{\underline{A}}_b \frac{\partial}{\partial x}(\cdot) + \underline{\underline{B}}_b(\cdot) \tag{A2}$$

$$\frac{\partial \underline{u}_s}{\partial t} = \underline{\underline{R}}\underline{u}_a \tag{A3}$$

and $\underline{\underline{A}}_b$ and $\underline{\underline{B}}_b$ are $b \times n$ matrices which are the first b rows of $\underline{\underline{A}}$ and $\underline{\underline{B}}$ respectively.

For

$$V = \int_D (\underline{u}'_b\, \underline{\underline{P}}\, \underline{u}_b)\, dx \tag{A4}$$

then

$$\dot{V} = \int_D \left(\frac{\partial \underline{u}'_b}{\partial t} \underline{\underline{P}}\, \underline{u}_b + \underline{u}'_b\, \underline{\underline{P}} \frac{\partial \underline{u}_b}{\partial t} \right) dx \tag{A5}$$

but since $\underline{\underline{P}}$ is symmetric,

$$\dot{V} = 2 \int_D \left(\underline{u}'_b\, \underline{\underline{P}} \frac{\partial \underline{u}_b}{\partial t} \right) dx \tag{A6}$$

Substituting for $\frac{\partial \underline{u}_b}{\partial t}$,

$$\dot{V} = 2 \int_D \left(\underline{u}'_b\, \underline{\underline{PA}}_b \frac{\partial \underline{u}}{\partial x} \right) dx + \int_D 2 \quad (\underline{u}'_b\, \underline{\underline{PB}}_b\, \underline{u})\, dx \tag{A7}$$

In terms of partitioned matrices we have

$$\dot{V} = 2 \int_D \left(\underline{u}'_s\, \underline{\underline{P}}_{ss} \frac{\partial \underline{u}_a}{\partial x} \right) dx + 2 \int_D \left(\underline{u}'_b\, \underline{\underline{PA}}_{bb} \frac{\partial \underline{u}_b}{\partial x} \right) dx + 2 \int_D (\underline{u}'_b\, \underline{\underline{PB}}_{bb}\, \underline{u}_b)\, dx \tag{A8}$$

Since $\underline{\underline{P}}_{ss}$ is symmetric, then the first term of the right-hand side may be integrated by parts as follows:

$$2 \int_D \left(\underline{u}'_s\, \underline{\underline{P}}_{ss} \frac{\partial \underline{u}_a}{\partial x} \right) dx = 2(\underline{u}'_s\, \underline{\underline{P}}_{ss}\, \underline{u}_a)\Big|_0^1 - 2 \int_D \left(\underline{u}'_s \frac{\partial \underline{\underline{P}}_{ss}}{\partial x} \underline{u}_a \right) dx - 2 \int_D \left(\frac{\partial \underline{u}'_s}{\partial x} \underline{\underline{P}}_{ss}\, \underline{u}_a \right) dx \tag{A9}$$

From the description of the second-order system

$$\frac{\partial \underline{u}_s}{\partial x} = \underline{\underline{R}}\, \underline{u}_a, \quad \underline{\underline{R}} \text{ is symmetric, then } \frac{\partial \underline{u}'_s}{dx} = \underline{u}'_a \underline{\underline{R}}.$$

Now, the third term on the right-hand side of Equation (A8) becomes

$$-2 \int_D \left(\frac{\partial \underline{u}'_s}{\partial x} \underline{\underline{P}}_{ss}\, \underline{u}_a \right) dx = -2 \int_D (\underline{u}'_a\, \underline{\underline{RP}}_{ss}\, \underline{u}_a)\, dx \tag{A10}$$

Since $\underline{\underline{PA}}_{bb}$ is symmetric, the second integral of Equation (A8) may also be integrated by parts, giving

$$2 \int_D \left(\underline{u}'_b\, \underline{\underline{PA}}_{bb} \frac{\partial \underline{u}_b}{\partial x} \right) dx = 2(\underline{u}'_b\, \underline{\underline{PA}}_{bb}\, \underline{u}_b)\Big|_0^1 - 2 \int_D \left(\underline{u}'_b \left(\frac{\partial \underline{\underline{P}}}{\partial x} \underline{\underline{A}}_{bb} + \underline{\underline{P}} \frac{\partial \underline{\underline{A}}_{bb}}{\partial x} \right) \underline{u}_b \right) dx - 2 \int_D \left(\frac{\partial \underline{u}'_b}{\partial x} \underline{\underline{PA}}_{bb}\, \underline{u}_b \right) dx, \tag{A11}$$

but

$$\frac{\partial \underline{u}'_b}{\partial x} \underline{\underline{PA}}_{bb}\, \underline{u}_b = \underline{u}'_b\, \underline{\underline{PA}}_{bb} \frac{\partial \underline{u}_b}{\partial x},$$

so the last term of Equation (A1) may be transposed to the left-hand side and combined to give

$$2 \int_D \left(\underline{u}'_b\, \underline{\underline{PA}}_{bb} \frac{\partial \underline{u}_b}{\partial x} \right) dx = (\underline{u}'_b\, \underline{\underline{PA}}\, \underline{u}_b)\big|_0^1 - \int_D \left(\underline{u}'_b \left(\frac{\partial \underline{\underline{P}}}{\partial x} \underline{\underline{A}}_{bb} + \underline{\underline{P}} \frac{\partial \underline{\underline{A}}_{bb}}{\partial x} \right) \underline{u}_b \right) dx \quad \text{(A12)}$$

Combining terms, the equation for $\dot{V}$ becomes

$$\dot{V} = 2(\underline{u}'_s\, \underline{\underline{P}}_{ss}\, \underline{u}_a)\big|_0^1 - 2 \int_D \left(\underline{u}'_s \frac{\partial \underline{\underline{P}}_{ss}}{\partial x} \underline{u}_a \right) dx - 2 \int_D (\underline{u}'_a\, \underline{\underline{RP}}_s\, \underline{u}_a)\, dx + (\underline{u}'_b\, \underline{\underline{PA}}_{bb}\, \underline{u}_b)\big|_0^1 - \int_D \left(\underline{u}'_b \left(\frac{\partial \underline{\underline{P}}}{\partial x} \underline{\underline{A}}_{bb} + \underline{\underline{P}} \frac{\partial \underline{\underline{A}}_{bb}}{\partial x} \right) \underline{u}_b \right) dx + 2 \int_D (\underline{u}'_b\, \underline{\underline{PB}}_{bb}\, \underline{u}_b)\, dx \quad \text{(A13)}$$

then defining

$$\underline{\underline{C}}_{bb} = - \underline{\underline{P}} \frac{\partial \underline{\underline{A}}_{bb}}{\partial x} - \frac{\partial \underline{\underline{P}}}{\partial x} \underline{\underline{A}}_{bb} + 2\underline{\underline{PB}}_{bb},$$

$$\dot{V} = 2(\underline{u}_s\, \underline{\underline{P}}_{ss}\, \underline{u}_a)\big|_0^1 + \int_D (\underline{u}'_b\, \underline{\underline{C}}_{bb}\, \underline{u}_b)\, dx + (\underline{u}_a\, \underline{\underline{PA}}_{bb}\, \underline{u}_b)\big|_0^1 - 2 \int_D \left(\underline{u}'_s \frac{\partial \underline{\underline{P}}_{ss}}{\partial x} \underline{u}_a \right) - 2 \int_D (\underline{u}'_a\, \underline{\underline{RP}}_{ss}\, \underline{u}_a)\, dx. \quad \text{(A14)}$$

The matrices may be compounded as follows:

$$\underline{\underline{F}} = \left(\begin{array}{cc|c} \multicolumn{2}{c|}{\underline{\underline{PA}}_{bb}} & \begin{array}{c} \underline{\underline{P}}_{ss} \\ \hline \underline{\underline{O}} \end{array} \\ \hline \underline{\underline{P}}_{ss} & \underline{\underline{O}} & \underline{\underline{O}} \end{array} \right), \qquad \underline{\underline{C}} = \left(\begin{array}{cc|c} \multicolumn{2}{c|}{\underline{\underline{C}}_{bb}} & \begin{array}{c} -\dfrac{\partial \underline{\underline{P}}_{ss}}{\partial x} \\ \hline \underline{\underline{O}} \end{array} \\ \hline -\dfrac{\partial \underline{\underline{P}}_{ss}}{\partial x} & \underline{\underline{O}} & -2\underline{\underline{RP}}_{ss} \end{array} \right)$$

and the above equation becomes

$$\dot{V} = (\underline{u}'\, \underline{\underline{F}}\, \underline{u})\big|_0^1 + \int_D (\underline{u}'\, \underline{\underline{C}}\, \underline{u})\, dx. \quad \text{(A15)}$$

Therefore, if $(\underline{u}'\, \underline{\underline{F}}\underline{u})\big|_0^1 \leq 0$ and the matrix $\underline{\underline{C}}$ is negative definite, then $\dot{V} < 0$, and the system is uniformly asymptotically stable in the large.

APPENDIX B: DISPERSIVE TUBULAR REACTOR DETAILS

Axial dispersion is included in the model by the addition of second-order terms to Equations (1) and (2). The energy and material balances are then

$$\rho c_p \frac{\partial T}{\partial \theta} = \lambda \frac{\partial^2 T}{\partial Z^2} - \rho v c_p \frac{\partial T}{\partial Z} + (-\Delta H)\, kC \exp\left(- \frac{E}{R_g T} \right) \quad \text{(B1)}$$

$$\frac{\partial C}{\partial \theta} = D \frac{\partial^2 C}{\partial Z^2} - v \frac{\partial C}{\partial Z} - kC \exp\left(- \frac{E}{R_g T} \right) \quad \text{(B2)}$$

and the boundary conditions are

$$- \lambda \frac{\partial T}{\partial Z}(0, \theta) = \rho v c_p (T_0 - T(0, \theta)) \quad \frac{\partial T}{\partial Z}(L, \theta) = 0, \quad \text{(B3)}$$

$$- D \frac{\partial C}{\partial Z}(0, \theta) = v(C_0 - C(0, \theta)), \quad \frac{\partial C}{\partial Z}(L, \theta) = 0.$$

Equations (B3) are known as the Danckwerts boundary conditions (*13*) and whether it be more appropriate to define T_0 and C_0 as taken at $z = -\infty$ or $z = 0^-$ does not change their form (9).

Equations (B1), (B2), and (B3) are nondimensionalized and simplified with the following definitions: $x = z/L$, $n = T/T_0$, $y = C/C_0$, $t = D\theta/L^2$, $r_1 = vL/\alpha$, $r_2 = vL/D$, $q = E/R_gT_0$, $B_1 = \dfrac{(-\Delta H)kC_0L^2}{\rho c_p T_0 D}$, $B_2 = kL^2/D$, $\alpha = \lambda/\rho c_p$, $R = y \exp(-q/n)$. The Peclet numbers for heat and mass dispersion are recognized as r_1 and r_2 above with α being the effective thermal diffusivity. The results are

$$\frac{\partial n}{\partial t} = \frac{\alpha}{D} \frac{\partial^2 n}{\partial x^2} - r_2 \frac{\partial n}{\partial x} + B_1 R, \quad \frac{-\partial n}{\partial x}(0) = r_1(1 - n(0)), \quad \frac{\partial n}{\partial x}(1) = 0 \quad \text{(B4)}$$

$$\frac{\partial y}{\partial t} = \frac{\partial^2 y}{\partial x^2} - r_2 \frac{\partial y}{\partial x} - B_2 R, \quad - \frac{\partial y}{\partial x}(0) = r_2(1 - y(0)), \quad \frac{\partial y}{\partial x}(1) = 0 \quad \text{(B5)}$$

Equations (B4) and (B5) are now linearized in the same manner as were (5) and (6) by defining $u_1 = n - n_{st}$, $u_2 = y - y_{st}$, $R_1 = \dfrac{\partial R}{\partial n}\Big|_{st}$, and $R_2 = \dfrac{\partial R}{\partial y}\Big|_{st}$ so that

$$\frac{\partial u_1}{\partial t} = \frac{\alpha}{D} \frac{\partial^2 u_1}{\partial x^2} - r_2 \frac{\partial u_1}{\partial x} + B_1 R_1 u_1 + B_1 R_2 u_2, \quad \text{(B6)}$$

$$\frac{\partial u_1}{\partial x}(0) = r_1 u_1(0), \quad \frac{\partial u_1}{\partial x}(1) = 0$$

$$\frac{\partial u_2}{\partial t} = \frac{\partial^2 u_2}{\partial x^2} - r_2 \frac{\partial u_2}{\partial x} - B_2 R_1 u_1 - B_2 R_2 u_2, \quad \text{(B7)}$$

$$\frac{\partial u_2}{\partial x}(0) = r_2\, u_2(0), \quad \text{and} \quad \frac{\partial u_2}{\partial x}(1) = 0.$$

In order to reduce the order or Equations (B6) and (B7), the auxiliary variables $u_3 = \dfrac{\alpha}{D} \dfrac{\partial u_1}{\partial x}$ and $u_4 = \dfrac{\partial u_2}{\partial x}$ are introduced

$$\frac{\partial u_1}{\partial t} = -r_2 \frac{\partial u_1}{\partial x} + \frac{\partial u_3}{\partial x} + B_1 R_1 u_1 + B_1 R_2 u_2, \quad u_3(0) = r_2 u_1(0), \quad \text{(B8)}$$

$$\frac{\partial u_2}{\partial t} = -r_2 \frac{\partial u_2}{\partial x} + \frac{\partial u_4}{\partial x} - B_2 R_1 u_1 - B_2 R_2 u_2, \quad u_4(0) = r_2 u_2(0), \quad \text{(B9)}$$

$$0 = \frac{\partial u_1}{\partial x} - \frac{D}{\alpha} u_3, \quad u_3(1) = 0 \quad \text{(B10)}$$

$$0 = \frac{\partial u_2}{\partial x} - u_4, \quad u_4(1) = 0 \quad \text{(B11)}$$

Now Equations (B8) to (B11) can be written in form for use with the theorem

$$\frac{\partial \hat{\underline{u}}}{\partial t} = \underline{\underline{A}} \frac{\partial \underline{u}}{\partial x} + \underline{\underline{B}}\, \underline{u}$$

where

$$\underline{u} = \begin{bmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \end{bmatrix}, \quad \hat{\underline{u}} = \begin{bmatrix} u_1 \\ u_2 \\ 0 \\ 0 \end{bmatrix}, \quad \underline{\underline{A}} = \left[\begin{array}{c|c} A_{bb} & \underline{\underline{I_2}} \\ \hline \underline{\underline{I_2}} & \underline{\underline{O_2}} \end{array}\right],$$

and

$$\underline{\underline{B}} = \left[\begin{array}{c|cc} \underline{\underline{B_{bb}}} & \multicolumn{2}{c}{\underline{\underline{O_2}}} \\ \hline & -r_1/r_2 & 0 \\ \underline{\underline{O_2}} & 0 & -1 \end{array}\right]$$

Further,

$$\underline{\underline{A_{bb}}} = \begin{bmatrix} -r_2 & 0 \\ 0 & -r_2 \end{bmatrix}, \quad \underline{\underline{B_{bb}}} = \begin{bmatrix} B_1R_1 & B_1R_2 \\ -B_2R_1 & -B_2R_2 \end{bmatrix},$$

$$\underline{\underline{I_2}} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \text{ and } \underline{\underline{O_2}} = \begin{bmatrix} 0 & 0 \\ 0 & 0 \end{bmatrix}$$

The matrices $\underline{\underline{F}}$ and $\underline{\underline{C}}$ are now formed in order to test the conditions of the theorem:

$$\underline{\underline{F}} = \begin{bmatrix} -P_1r_2 & 0 & P_1 & 0 \\ 0 & -P_2r_2 & 0 & P_2 \\ P_1 & 0 & 0 & 0 \\ 0 & P_2 & 0 & 0 \end{bmatrix}$$

The first condition is that $\underline{u}'\underline{\underline{F}}\underline{u}\big|_0^1 \leq 0$. Here, $\underline{u}'\underline{\underline{F}}\underline{u} = -P_1r_2u_1^2 - P_2r_2u_2^2 + 2P_1u_1u_3 + 2P_2u_2u_4$, then $\underline{u}'\underline{\underline{F}}\underline{u}\big|_0^1 = -P_1(1)r_2u_1^2(1) - P_2(1)r_2u_2^2(1) - P_1(0)r_2u_1^2(0) - P_2(0)r_2u_2^2(0) \leq 0$. Therefore the condition is satisfied as long as P_1 and P_2 are positive at both $x = 0$ and $x = 1$.

The matrix $\underline{\underline{C}}$ is as follows:

$$\begin{bmatrix} r_2\frac{\partial P_1}{\partial x} + 2P_1B_1R_1 & 2P_1B_1R_2 & -\frac{\partial P_1}{\partial x} & 0 \\ -2P_2B_2R_1 & r_2\frac{\partial P_2}{\partial x} + 2P_2B_2R_2 & 0 & -\frac{\partial P_2}{\partial x} \\ -\frac{\partial P_1}{\partial x} & 0 & -2\frac{r_1}{r_2}P_1 & 0 \\ 0 & -\frac{\partial P_2}{\partial x} & 0 & -2P_2 \end{bmatrix}$$

Four conditions must be met so that $\underline{\underline{C}}$ be negative definite.

1.
$$r_2\frac{\partial P_1}{\partial x} + 2P_1B_1R_1 < 0 \tag{B12}$$

This will hold if $P_1 = \exp(-K_1x)$ and K_1 is chosen such that $K_1 > 2B_1R_1/r_2$.

2.
$$\left(r_2\frac{\partial P_1}{\partial x} + 2P_1B_1R_1\right)\left(r_2\frac{\partial P_2}{\partial x} - 2P_2B_2R_2\right) + 4P_1P_2B_1B_2R_1R_2 > 0 \tag{B13}$$

The expression within the first parentheses is that of inequality (B12) which was made negative above: therefore, if P_2 is chosen so that

$$r_2\frac{\partial P_2}{\partial x} - 2P_2B_2R_2 < 0, \tag{B14}$$

inequality B13 will be true. By defining $P_2 = \exp(-K_2x)$, inequality (B14) holds, and no restrictions have to be placed on K_2.

3. It is now necessary to evaluate the determinant of the third principal minor of $\underline{\underline{C}}$ and ensure that it be negative. This condition is

$$-2\frac{r_1}{r_2}P_1\left(r_2\frac{\partial P_1}{\partial x} + 2P_1B_1R_1\right)\left(r_2\frac{\partial P_2}{\partial x} - 2P_2B_2R_2\right) - \left(\frac{\partial P_1}{\partial x}\right)^2\left(r_2\frac{\partial P_2}{\partial x} - 2P_2B_2R_2\right) - 2\frac{r_1}{r_2}P_1(4P_1P_2B_1B_2R_1R_2) < 0 \tag{B15}$$

Substituting $P_1 = \exp(-K_1x)$ and $P_2 = \exp(-K_2x)$, and dividing by $\exp(-K_1x)^2\exp(-K_2x)$, inequality (B15) becomes

$$2\frac{r_1}{r_2}(-r_2K_1 + 2B_1R_1)(-r_2K_2 - 2B_2R_2) + K_1^2(-r_2K_2 - 2B_2R_2) + 2\frac{r_1}{r_2}(4B_1B_2R_1R_2) > 0 \tag{B16}$$

The above is simplified to

$$2r_1r_2K_1K_2 + 4r_1K_1B_2R_2 > 4r_1K_2B_1R_1 + r_2K_1^2K_2 + 2K_1^2B_2R_2 \tag{B17}$$

Recalling the condition that $K_1 > 2B_1R_1/r_2$, K_1 is chosen arbitrarily close to the quantity $2B_1R_1/r_2$, and a substitution of $K_1 = 2B_1R_1/r_2$ is made in inequality (B17) for further evaluation. The result is

$$K_2 < \frac{2r_1B_2R_2}{B_1R_1}\left(1 - \frac{B_1R_1}{r_1r_2}\right) \tag{B18}$$

Since the value of K_2 can be made small, inequality (B18) and this third condition will hold if

$$\frac{B_1R_1}{r_1r_2} < 1 \tag{B19}$$

This is a restriction based on system parameters and steady state information only.

4. The determinant of the whole matrix $\underline{\underline{C}}$ must now be shown to be positive in order to complete the proof. This determinant is expanded by minors along the fourth row, and the result is

$$\det \underline{\underline{C}} = -2P_2 \det(\text{3rd PRINCIPAL MINOR OF } \underline{\underline{C}})$$

$$-\frac{\partial P_1}{\partial x}\left\{-\left(\frac{\partial P_1}{\partial x}\right)^2\frac{\partial P_2}{\partial x} - 2\frac{r_1}{r_2}P_1\frac{\partial P_2}{\partial x}\left(r_2\frac{\partial P_1}{\partial x} + 2P_1B_1R_1\right)\right\} > 0 \tag{B20}$$

It is noted that the term involving the third principle minor of $\underline{\underline{C}}$ is positive, so assuring that the other term is positive also will satisfy inequality (B20). If the former term is then dropped and the forms for P_1 and P_2 substituted, inequality (B20) reduces to

$$K_1^2 > 2\frac{r_1}{r_2}\left(K_1 - \frac{2B_1R_1}{r_2}\right) \tag{B21}$$

This condition is already satisfied by the specifications of section 3.

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