T = temperature, °K
u = temperature characteristic of biological reaction rate constants, cal/gm·mole
X = biomass concentration, mg/l
Y = biological yield coefficient, mg biomass/mg NO_3^--N
μ = specific nitrate-nitrogen removal rate, mg NO_3^--N removed/mg biomass·hr

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Process Design in a Dynamic Environment:

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Part I. A Decomposition Technique to Study the Stability of Chemical Engineering Systems

The stability of various chemical engineering systems is studied through the use of vector Lyapunov functions. A decomposition technique is employed which reduces the problem to small, independent, free subsystems that can be analyzed through Lyapunov's second method. The stability characteristics of the overall system are then related to the behavior of a linear system which is easily analyzed.

SCOPE

The aim of the stability analysis of a system is to determine the number of steady states in the system and to understand the effect of disturbances on these states. Regions of stability are developed which guarantee the stable operation of the system once the operating conditions fall into this region.

The chemical engineering systems, being nonlinear in their majority, cannot be effectively analyzed through the popular approaches of the eigenvalue structure analysis or Lyapunov's second method. All the reported methods

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have serious drawbacks with respect to their range of applicability or the degree of their effectiveness. Furthermore, the difficulty of the stability analysis is amplified as the dimensionality of the system increases.

The intent of this study was to examine the use of the vector Lyapunov functions in developing an approach to study the stability analysis of large scale chemical engineering systems. A large scale system is decomposed into a number of free independent subsystems. The stability of these subsystems can be analyzed by using the available techniques and is expressed through Lyapunov functions. Then, a linear system of dimension N is constructed, where N is the number of the free subsystems, and the stability of the initial system is examined through the analysis of this linear system. The basic result comes from a lemma that provides an upper bound for the solution of a set of inequalities (Beckenbach and Bellman, 1961).

This decomposition technique can be also applied to systems that have low dimensionality and which can be decomposed into linear free independent subsystems with nonlinear interconnection constraints. Very strong sufficiency conditions can be established for the free subsystems because of their linear nature, and the effectiveness of the method depends only on how strong upper bounds for the interconnection terms can be established.

This characteristic is of particular interest to the stability analysis of tubular reactors and catalyst pellets with diffusion and reaction. Thus, an extension of the suggested approach was developed for distributed systems with particular emphasis on the tubular reactors. It is easily understood that similar analysis can be applied to study the stability of catalyst pellets.

CONCLUSIONS AND SIGNIFICANCE

The decomposition technique employing the vector Lyapunov functions is shown to be a very effective tool to study the stability of large scale systems in chemical engineering. Two examples demonstrate this feature. In the first one, a four-component open system with reaction and diffusion was analyzed. While an eigenvalue structure analysis is intractable and a direct application of Lyapunov's second method encounters serious numerical problems, the decomposition technique exploiting the stability characteristics of the subsystems which were easily established, developed tractable sufficient conditions which allow a parametric stability analysis of the system. In the second example, the stability characteristics of a polymerization reactor were developed. In this case, both the dimensionality and the nonlinearity of the system were handled in a very effective way. Thus, the stability analysis of three 2×2 linear subsystems was required instead of one 6×6, thus reducing significantly the numerical problems. Furthermore, the linearity of the subsystems helped to develop very strong sufficiency conditions which finally produced wider ranges of the stability regions from the ones reported in the literature.

An extension of the decomposition technique to distributed parameter systems was developed, with particular emphasis on the tubular reactors. It provides a tool for an effective stability analysis independently of the number of reacting components. Since the system of dynamic equations describing the heat and mass balances in a tubular reactor is largely linear, with the reaction rate term the only nonlinear coupling term, the decomposition method yielded strong results and when applied to a nonadiabatic tubular reactor with axial mixing and recycle. It predicted the stability of both the stable steady states, something that the direct application of Lyapunov's second method failed to provide.

STABILITY OF INTERCONNECTED SYSTEMS WITH VECTOR LYAPUNOV FUNCTIONS USED

Let us consider a continuous dynamic system S described by the vector differential equation

$$\frac{dx}{dt} = f(t, x) \tag{1}$$

where $x(t) \in R^n$ is the state of the system, and the function f satisfies a global Lipschitz condition so that the solution $x(t; t_o, x_o)$ of Equation (1) exist and are unique and continuous for all initial conditions (t_o, x_o).

Let the system S be composed of N dynamic subsystems S_i described by vector differential equations

$$\frac{dx_i}{dt} = f_i(t, x_i) + g_i(t, e_{i1}x_1, \ldots, e_{iN}x_N) \tag{2}$$

where

$$e_{ij} = \begin{cases} 1 & \text{if subsystem } j \text{ affects through its state the state of subsystem } i \\ 0 & \text{otherwise} \end{cases}$$

In Equation (2) x_i is the state of subsystem S_i, and the functions g_i are such that

$$||g_i(t, e_{i1}x_1, \ldots, e_{iN}x_N)|| \leq \sum_{j=1}^{N} e_{ij}\, \xi_{ij}\, ||x_j|| \tag{3}$$

for $\forall\ t \geq t_o$ and $i = 1, 2, \ldots, N$, where ξ_{ij} are nonnegative numbers.

Consider now the unforced subsystems S_i described by

$$\frac{dx_i}{dt} = f_i(t, x_i) \quad i = 1, 2, \ldots, N \tag{4}$$

It is then assumed that the stability property of each unforced subsystem S_i can be concluded by using a scalar function $v_i(x_i): R^{n_i} \rightarrow R_+^1$ such that $v_i(x_i) \in C^1$ and which satisfies the following inequalities:

$$\phi_{1i}(||x_i||) \leq v_i(x_i) \leq \phi_{2i}(||x_i||)$$

$$\mu_i\phi_{3i}(||x_i||) \leq \dot{v}_i(x_i) \leq \mu_i\phi_{4i}(||x_i||)$$

where $\phi_{ik} = R_+^1 \rightarrow R_+^1$ are comparison functions which belong to the class $\mathcal{L}$: $\phi_{ik}(\rho) \in C^0$; $\phi_{ik}(0) = 0$, $\phi_{ik}(\rho_1) < \phi_{ik}(\rho_2)$ V $\rho_1, \rho_2 : 0 < \rho_1 < \rho_2 < +\infty$ and $\phi_{ik}(\rho) \rightarrow +\infty$ as $\rho \rightarrow +\infty$. Furthermore, μ_i is defined as

$$\mu_i = \begin{cases} -1 & \text{for a stable subsystem } S_i \\ +1 & \text{for an unstable subsystem } S_i \end{cases}$$

For asymptotically stable subsystems, the comparison functions take a simple form as seen in the following theorem of Krasovskii (1963).

Theorem 1

The equilibrium state $x_i = 0$ of a dynamic subsystem $\dot{x}_i = f_i(t, x_i)$ is exponentially stable if and only if there exists a positive definite function $v_i(x_i)$ on R^n such that

$$c_{1i} ||x_i|| \leqq v_i \leqq c_{2i} ||x_i||$$
$$\dot{v}_i \leqq - c_{3i} ||x_i||$$
$$||\text{grad } v_i|| \leqq c_{4i}$$

where c_{1i}, c_{2i}, c_{3i}, and c_{4i} are positive numbers, and we have used $v_i^{1/2}$ instead of v_i, as it was originally stated.

Bailey (1966) examined the stability of a composite system consisting of nonlinear subsystems connected with linear interconnection terms. The following two theorems provide sufficient conditions for a composite system to be asymptotically stable, when the subsystems are asymptotically stable, and for the cases where the composite system forms a chain or a closed loop.

Theorem 2

Consider a composite system that forms a simple chain. If the unforced subsystems S_i, $i = 1, 2, \ldots, N$ [described by Equation (4)] are asymptotically stable, then the null solution of the composite system is asymptotically stable.

Theorem 3

Consider a composite system that forms a simple closed loop. If the unforced subsystems S_i, $i = 1, 2, \ldots, N$ are asymptotically stable with gain estimates η_i, $i = 1, 2, \ldots, N$, then the null solution of the composite system is asymptotically stable if $\prod_{i=1}^{N} \eta_i < 1$.

The gain η_i is defined as the ratio of a bound on the norm of the vector x_i associated with the subsystem S_i to a bound on the norm of the vector of the elements x_i's associated with all the other subsystems which affect subsystem S_i; that is

$$\eta_i = \frac{\sup_{t \geqq t_0} ||x_i||}{\sup_{t \geqq t_0} ||\overline{x}_i||}$$

where $\overline{x}_i^T = [x_1^T, x_2^T, \ldots, x_{i-1}^T, x_{i+1}^T, \ldots, x_N^T]$. For a simple closed loop, evidently

$$\overline{x}_i^T = x_{i-1}^T$$

Theorems 2 and 3 provide easily implementable criteria, and the question of stability of the overall system is actually reduced to the stability of the individual subsystems. For composite systems with structures more complicated than the simple chain or simple closed loop, the sufficiency criteria for stability of the composite system became more involved. Bailey, in the same work and Grujic and Siljak (1973), has provided the conditions for stability of the composite system in the general case.

Theorem 4

Let S be a general composite made up of N subsystems S_i of order n_i, $i = 1, 2, \ldots, N$. Assume that each subsystem S_i is asymptotically stable and has a Lyapunov function v_i satisfying the conditions of theorem 1. Consider the N^{th} order linear system of auxiliary equations

$$\dot{r} = Br$$

where B is an $N \times N$ matrix of elements

$$b_{ij} = - \delta_{ij} c_{3i}/2 c_{2i} + e_{ij} \xi_{ij} c_{4i}/c_{1j}$$

where ξ_{ij} are the nonnegative numbers of relationship (3). The null solution of the composite system will be asymptotically stable if the null solution $r = 0$ of the auxiliary system is asymptotically stable.

The following lemma due to Sevastyanov (1951) provides the necessary and sufficient conditions for the auxiliary system to be asymptotically stable.

Lemma. A real $N \times N$ matrix B with $b_{ij} \geqq 0$ for $\forall\, i,j = 1, 2, \ldots, N$ and $i \neq j$ has all eigenvalues $\lambda_K(B)$ with negative real parts if and only if the following inequalities are satisfied:

$$b_{11} < 0, \quad \begin{vmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{vmatrix} > 0, \ldots, (-1)^N \begin{vmatrix} b_{11} & b_{12} \ldots b_{1N} \\ b_{21} & b_{22} \ldots b_{2N} \\ b_{N1} & b_{N2} \ldots b_{NN} \end{vmatrix} > 0$$

A composite system may be asymptotically stable despite the fact that one of its subsystems may be asymptotically unstable. The stabilizing effect in the composite system is accomplished in a natural way by the interactions among its subsystems. Grujic and Siljak (1973) developed sufficiency conditions for the stability of a composite system with unstable subsystems. The following theorem presents their principal result.

Theorem 5

The equilibrium state of a composite system S consisted of asymptotically stable and unstable subsystems. It is asymptotically stable in the large if there exists a symmetric positive definite $N \times N$ matrix $G = (g_{ij})$ such that the symmetric positive definite $N \times N$ matrix $H = (h_{ij})$ which is the solution of the Lyapunov matrix equation

$$B^T H + HB = - G$$

has all elements specified as

$$h_{ij} \begin{cases} > 0 & i = j \\ \geqq 0 & i \neq j \end{cases}$$

where B is the matrix of the auxiliary linear system of theorem 4.

There are two basic premises for success of the decomposition technique. First, there is the construction of a Lyapunov function which can predict effectively the stability characteristics of the free subsystems. Therefore, the method is promising if the independent subsystems are linear, since very efficient Lyapunov functions can be constructed. Second, there is the development of effective upper bounds for the interconnection terms among the subsystems. The interconnection terms do not have to be linear, but if they are, they facilitate significantly the process of bounding the interconnection terms. Therefore, a close examination of the physical system under consideration will be proved very useful. For the chemical engineering systems considered in the following sections, this proved to be very helpful without creating any unrealistic situations.

Example 1: The Parametric Analysis of the Stability Characteristics of an Open System with Reaction and Diffusion

Synergism of reaction and diffusion in a multicomponent open system brings instability of the nonequilibrium stationary states (NESS) (Turing, 1952; Prigogine and Nicolis, 1967). Othmer and Scriven (1969) presented the results of the linear stability analysis of uniform NESSes for two- and three-component systems. The parametric analysis of the eigenvalue structure of an n ($n > 3$) component system is intractable (as a matter of fact, even for $n = 3$ the results of such parametric analysis are very poor, see Othmer and Scriven, 1969).

In this section we will present an alternative to the eigenvalue analysis, which is particularly suited for systems with $n \geqq 3$. The system to be considered is an autocatalytic mechanism introduced and discussed by Turing (1952) in his work on the morphogenesis in multicellular organisms. Two initial products A and B are transformed into the final or waste products D and E through the intermediate products X and Y and by the action of the catalysts C, W, V, V' following the general scheme shown in Figure 1.

The equations of change in the active species within the system are as follows:

$$\frac{\partial C}{\partial t} = - \nabla \cdot J + N + R(C) \quad (5)$$

where $J = - D \nabla C$ is the vector of diffusive flux density vectors, $N = H(C^o - C)$ is the vector of exchange fluxes, and $R(C)$ is the vector of production rates. The concentrations of the initial and final products A, B, D, and E will be considered constant. Also, for presentation purposes, the concentrations of the two catalysts W and Y' are considered constant. Substituting N and J by their equals given above and linearizing the resulting equation around the stationary state $C = C^{(s)}$, we can derive the following vector which expresses the excursion of the concentrations of the remaining four species from the stationary state:

$$\frac{\partial x}{\partial t} = Kx + D \nabla^2 x$$

where $x \equiv C - C^{(s)}$ and

$$K \equiv \left.\frac{\partial R_i}{\partial C_j}\right|_{C_j=C_j^{(s)}} - H_{ij}^{(s)} + \sum_l \left.\frac{\partial H_{il}}{\partial C_j}\right|_{C_j=C_j^{(s)}} [C_l^o - C_l^{(s)}] \quad (6)$$

Considering in the general case that K and D do not commute, we expand the excursion in those eigenfunctions of the Laplace operator that are appropriate to the system configuration, thus obtaining the following system of ordinary differential equations:

$$\frac{dy}{dt} = (K - k^2 D)y \quad (7)$$

where $y^T = [y_X y_C y_Y y_V]$ is the amplitude function of the Fourier components of wave number k of the excursion, and

$$K - k^2D = \begin{Bmatrix} -k_2X_o - k^2D_X & k_3 & -k_2 & 0 \\ k_2Y_o & -(k_3 + k_4 + k_5B_o + k^2D_C) & k_2X_o & 0 \\ -k_2Y_o & k_3 & -(k_7 + k_2X_o + k_8V_o + k^2D_Y) & -k_8Y_o \\ 0 & 0 & -k_8V_o & -k_8Y_o - k^2D_V \end{Bmatrix}$$

with X_o, Y_o, B_o, and V_o the NESS concentrations.

The four-component system is decomposed into two interacting subsystems:

Subsystem 1

$$\frac{d}{dt}\begin{bmatrix} y_X \\ y_C \end{bmatrix} = \begin{bmatrix} -k_2X_o - k^2D_X & k_3 \\ k_2Y_o & -(k_3 + k_4 + k_5B_o + k^2D_C) \end{bmatrix} \begin{bmatrix} y_X \\ y_C \end{bmatrix} + \begin{bmatrix} -k_2 & 0 \\ k_2X_o & 0 \end{bmatrix} \begin{bmatrix} y_Y \\ y_V \end{bmatrix}$$

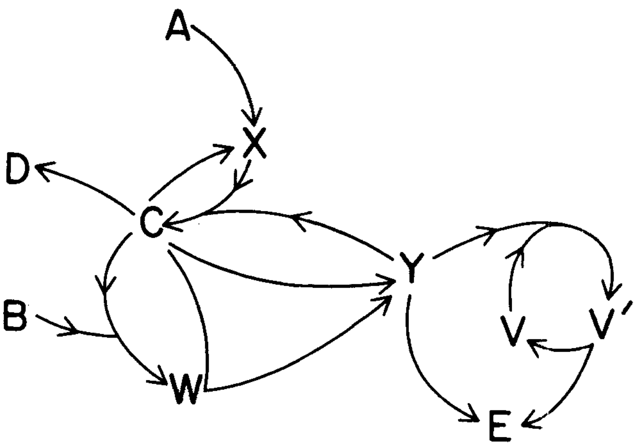


Fig. 1. The autocatalytic mechanism used to demonstrate the parametric stability analysis of open systems with reaction and diffusion.

Subsystem 2:

$$\frac{d}{dt}\begin{bmatrix} y_Y \\ y_V \end{bmatrix} = \begin{bmatrix} -(k_7 + k_2X_o + k_8V_o + k^2D_Y) & -k_8Y_o \\ -k_8V_o & -k_8Y_o - k^2D_V \end{bmatrix} \begin{bmatrix} y_Y \\ y_V \end{bmatrix} + \begin{bmatrix} -k_2Y_o & k_3 \\ 0 & 0 \end{bmatrix} \begin{bmatrix} y_X \\ y_C \end{bmatrix}$$

The unforced, free subsystems are taken by neglecting the interaction terms. The stability characteristics of each unforced subsystem are easily derived through an analysis of the eigenvalue structure of the linearized reaction-diffusion matrices. The results for the stability of each subsystem are summarized in the Tables 1 and 2 (for further details see Othmer and Scriven, 1969). The stability characteristics of the composite system will now be examined for the two distinct cases, namely, when all the unforced subsystems are stable and when one at least is unstable.

Case 1: All subsystems asymptotically stable. In this case, there is a function v_i for each subsystem i, $i = 1, 2$ that satisfies the conditions of theorem 1. By following the usual construction of Lyapunov functions for linear systems, it is easily found that

$$v_1(y_X, y_C) = \left[p_{11}^{(1)} y_X^2 + p_{22}^{(1)} y_C^2 + 2 p_{12}^{(1)} y_X y_C \right]^{1/2} \quad (8)$$

and

$$v_2(y_Y, y_V) = \left[p_{11}^{(2)} y_Y^2 + p_{22}^{(2)} y_V^2 + 2 p_{12}^{(2)} y_Y y_V \right]^{1/2} \quad (9)$$

where $p_{11}^{(i)}$, $p_{22}^{(i)}$, and $p_{12}^{(i)}$ for $i = 1, 2$ are the elements of two 2×2 symmetric and positive definite matrices $P^{(i)}$, $i = 1, 2$, satisfying the relationships

$$A^{(i)T}P^{(i)} + P^{(i)} A^{(i)} = - I \quad i = 1, 2$$

The matrices $A^{(1)}$ and $A^{(2)}$ are the reaction-diffusion matrices for the two unforced subsystems.

Since the subsystems are asymptotically stable, the conditions of theorem 1 should be satisfied. By using the

Lyapunov functions v_1 and v_2 given by Equations (8) and (9), the following constants for the comparison functions of theorem 1 are derived:

$$c_{i1} = \left\{ \min \left[p_{11}^{(i)}, p_{22}^{(i)} \right] \right\}^{1/2}$$

$$c_{i2} = \left\{ \left(p_{11}^{(i)} + p_{22}^{(i)} + \left[p_{11}^{(i)} - p_{22}^{(i)} \right]^2 + 4p_{12}^{(i)2} \right) / 2 \right\}^{1/2}$$

$$c_{i3} = \left\{ \left(p_{11}^{(i)} + p_{22}^{(i)} - \left[p_{11}^{(i)} - p_{12}^{(i)} \right]^2 + 4p_{12}^{(i)2} \right) \Big/ \left(8 \left[p_{11}^{(i)} p_{22}^{(i)} - p_{12}^{(i)} \right] \right) \right\}$$

$$c_{i4} = c_{i2}$$

Following theorem 4, the matrix B of the auxiliary linear system is constructed next:

$$B = \begin{bmatrix} -\dfrac{1}{2c_{21}} & \xi_{12} & \dfrac{c_{41}}{c_{12}} \\ \xi_{21} & \dfrac{c_{42}}{c_{11}} & -\dfrac{1}{2c_{22}} \end{bmatrix}$$

where

$$\xi_{12} = k_2 X_o \quad \text{since} \quad X_o > 1.0$$

and

$$\xi_{21} = \max \{k_2 y_o, k_3\}$$

Therefore, the composite system is asymptotically stable when the following conditions are satisfied (see lemma in previous section):

$$-\frac{1}{2\,c_{21}} < 0 \tag{10}$$

$$\frac{c_{13}}{c_{12}} \frac{c_{23}}{c_{22}} - \xi_{12}\,\xi_{21} \frac{c_{14}\,c_{24}}{c_{11}\,c_{21}} < 0 \tag{11}$$

Condition (10) is always satisfied since c_{21} is positive. Condition (11) imposes a further restriction on the reaction-diffusion parameters of the system that has to be satisfied, in addition to the conditions desired for the asymptotic stability of each unforced subsystem (Tables 1 and 2).

Case 2: One of the subsystems is asymptotically unstable. In this case, theorem 5 provides the sufficient conditions for the composite system to be asymptotically stable. To use theorem 5 effectively, one should determine the properties of the matrix B of the auxiliary system, which guarantees that there exist matrices H and G specified by the theorem. One property of B is certainly the Hurwitz property, and it is required that the matrix B has nonnegative off-diagonal elements and that it satisfies the conditions of Sevastyanov's lemma. For Turing's reaction scheme, the matrix B developed earlier has these properties, and thus it is a Hurwitz matrix. In this case, by choosing a positive definite symmetric matrix G, a positive definite and symmetric matrix H can be computed as a solution of the corresponding Lyapunov matrix equation:

$$B^T H + HB = -G$$

In the present problem, we put $G = I$, and the sufficient conditions for asymptotic stability of the composite system according to theorem 5 are

$$b_{12} b_{21} < b_{21}^2 + b_{22}^2 + b_{11} b_{22} \tag{12}$$

$$b_{12} b_{21} < b_{12}^2 + b_{11}^2 + b_{11} b_{22} \tag{13}$$

and

$$-b_{12} b_{22} - b_{11} b_{21} \geqq 0 \tag{14}$$

The condition (14) is always satisfied; thus conditions (12) and (13) are the sufficiency conditions for asymptotic stability of the composite system.

The sufficient conditions developed earlier were tested to a particular situation for the Turing's mechanism. It is easily found (Prigogine and Nicolis, 1967) that there exists a unique steady state for the system under consid-

TABLE 1. STABILITY CHARACTERISTICS OF THE UNFORCED SUBSYSTEMS 1 AND 2

Case		Conditions		Stability characteristics
1		$T^K < 0, T^D > 0, t^K > 0, t^D > 0$ $T^{KD} - T^K T^D > -2\sqrt{t^K t^D}$		Asymptotically stable for all μ
2		$\gamma_o, \gamma_2 < 0$		Asymptotically stable if $\mu > -T_K/T_D$
3	$\gamma_o, \gamma_2 > 0$	$\gamma_1 < 2\sqrt{\gamma_o \gamma_2}$ $\gamma_1 > 2\sqrt{\gamma_o \gamma_2}$	$t^D > 0$	Asymptotically stable $\forall \mu$ if $\gamma_1 < 2T^D\sqrt{\gamma_2}$ Asymptotically stable for $\mu > \frac{1}{T^D}[T^K + \sqrt{\Delta}]$ if $\gamma_1 > 2T^D\sqrt{\gamma_2}$
4	$\gamma_o, \gamma_2 > 0$	$\dot{\gamma}_1 > 2\sqrt{\gamma_o \gamma_2}$	$t^D = 0$	Asymptotically stable $\forall \mu$
5	$\gamma_o, \gamma_2 > 0$	$-2\sqrt{\gamma_o \gamma_2} < \gamma_1 < 2\sqrt{\gamma_o \gamma_2}$	$t^D > 0$	Asymptotically stable for $\mu > \frac{1}{T^D}[T^K + \sqrt{\Delta}]$
6	$\gamma_o, \gamma_2 > 0$	$0 < \gamma_1 < 2\sqrt{\gamma_o \gamma_2}$	$t^D < 0$	Asymptotically stable for $\mu > \frac{1}{T^D}[T^K + \sqrt{\Delta}]$ if $\gamma_1 > 2T^D\sqrt{\gamma_2}$
7	$\gamma_o, \gamma_2 > 0$	$-2\sqrt{\gamma_o \gamma_2} < \gamma_1 < 0$	$t^D < 0$	Asymptotically stable for $\mu > \frac{1}{T^D}[T^K + \sqrt{\Delta}]$ if $\gamma_1 > 2T^D\sqrt{\gamma_2}$
8	$\gamma_o, \gamma_2 > 0$	$\gamma_1 = \pm 2\sqrt{\gamma_o \gamma_2}$	$t^D > 0$	Asymptotically unstable $\forall \mu$
9	$\gamma_o, \gamma_2 > 0$	$\gamma_1 = \pm 2\sqrt{\gamma_o \gamma_2}$	$t^D < 0$	Asymptotically stable for $\mu > \frac{1}{T^D}[T^K + \sqrt{\Delta}]$
10	$\gamma_o, \gamma_2 > 0$	$-2\sqrt{\gamma_o \gamma_2} < \gamma_1 < 2\sqrt{\gamma_o \gamma_2}$	$t^D = 0$	Asymptotically unstable for $\forall \mu$

Table 2. Notation used in Table 1 for the Stability Characteristics of Subsystems 1 and 2

$$\Delta = \gamma_o\mu^2 + \gamma_1\mu + \gamma_2$$

Subsystem 1

$$T^K = -k_2X_o - (k_3 + k_4 + k_5B_o)$$
$$T^D = D_X + D_C$$
$$T^{KD} = -k_2X_oD_X - (k_3 + k_4 + k_5B_o)D_Y$$
$$t^k = (k_2X_o)(k_3 + k_4 + k_5B_o) - k_2Y_ok_3$$
$$t^D = D_XD_C$$
$$\gamma_o = (D_X - D_C)^2$$
$$\gamma_1 = 2[-k_2X_o + (k_3 + k_4 + k_5B_o)](D_C - D_X)$$
$$\gamma_2 = [-k_2X_o + (k_3 + k_4 + k_5B_o)]^2 + 4k_2k_3Y_o$$

Subsystem 2

$$T^K = -(k_7 + k_2X_o + k_8V_o) - k_8Y_o$$
$$T^D = D_Y + D_V$$
$$T^{KD} = -(k_7 + k_2X_o + k_8V_o)D_Y - k_8Y_oD_V$$
$$t^K = +(k_7 + k_2X_o + k_8V_o)(k_8Y_o) - k_3^2V_oY_o$$
$$t^D = D_YD_V$$
$$\gamma_o = (D_Y - D_V)^2$$
$$\gamma_1 = 2(k_8Y_o - k_7 - k_2X_o - k_8V_o)(D_V - D_Y)$$
$$\gamma_2 = [-(k_7 + k_2X_o + k_8V_o) + (k_8Y_o)]^2 + 4k_8^2Y_o$$

$$\mu \equiv k^2\delta/K \quad \text{where} \quad \delta = D_X \text{ or } D_Y, \quad K = \max_{ij}|K_{ij}|$$

Note: All the elements of the reaction and diffusion matrixes have been normalized with respect to the largest element.

eration. This solution is

$$X_o = \frac{k_1(k_3 + k_4)}{k_2k_4}$$

$$\frac{A}{(-k_9/k_7)V_o' + (k_1/k_4k_7)A(k_5B - k_4)}$$

$$Y_o = \frac{k_9}{k_7}V_o' + (k_1/k_4k_7)(k_5B - k_4)A$$

$$C_o = (k/k_4)A$$

$$V_o = \frac{k_9}{k_8} \cdot \frac{V_o'}{(-k_9/k_7)V_o' + (k_1/k_4)A(k_5B - k_4)}$$

where $w = k_1k_5/k_4k_6$ $AB = w_o =$ const, and $V_o' = V = 10^{-3}\beta$ with $\beta =$ arbitrary parameter. The rate constants k_i, the diffusion coefficients, and the composition of B were given the following values:

$k_1 = 10^{-3}$ $k_2 = 10^3$ $k_3 = 10^6$ $k_4 = 62.5$

$k_5 = 0.125$ $k_6 = 10^8$ $k_7 = 0.0625$ $k_8 = 10^8$

$k_9 = 62.5$ $D_X = D_V = 1/4$ $D_C = D_Y = 1/16$ $B = 10^3$

The concentration of A will be $A = 10^3 \cdot \zeta$, and the concentration of $V' = 10^{-3}\beta$ where β and ζ are *arbitrary* parameters.

Using the expressions in Table 2 and the numerical values for the parameters given above, we can easily see that

$$\gamma_1 < 2\sqrt{\gamma_o\gamma_2}$$

for both the subsystems and for all $\beta, \zeta > 0$. Since also $T^D > 0$ for both subsystems, it is concluded that each subsystem is asymptotically stable for ware numbers larger than a critical value (case 5 in Table 1). For ware numbers larger than the critical value, both the subsystems are asymptotically stable, and the overall system is guaranteed to be stable if condition (11) is satisfied. By using the numerical values of the parameters given previously, condition (11) takes the following form:

(a) If $\frac{10^{-3}\beta}{16} < \zeta < \frac{10^3 + \beta}{16}$, then

$\xi_{12} = k_2X_o = 10^3X_o$ $\quad \xi_{21} = k_3 = 10^6$

$p_{11}^{(1)} > p_{22}^{(1)}$ $\quad p_{11}^{(2)} > p_{22}^{(2)}$

and condition (11) yields

$$(\zeta - 5 \cdot \beta)\mu^2 + \frac{16\zeta^2 - \beta - 4\beta\zeta - 10^2\zeta}{\beta + \zeta}\mu + 10^3\beta\zeta - (16\zeta - \beta) > 0 \quad (11a)$$

Similar expressions for condition (11) can be derived when

(b) $\zeta < \frac{10^{-3}\beta}{16}$ and then $\xi_{12} = k_2X_o$, $\xi_{21} = k_3$

and

(c) $\zeta > \frac{10^3 + \beta}{16}$ and then $\xi_{12} = k_2$, $\xi_{21} = k_2Y_o$

For wave numbers smaller than the critical value, at least one of the systems is asymptotically unstable. Thus, when $\mu < 0.1$, subsystem 1 is unstable, and when $\mu < 0.25$, subsystem 2 is unstable. In these cases conditions (12) and (13) were employed.

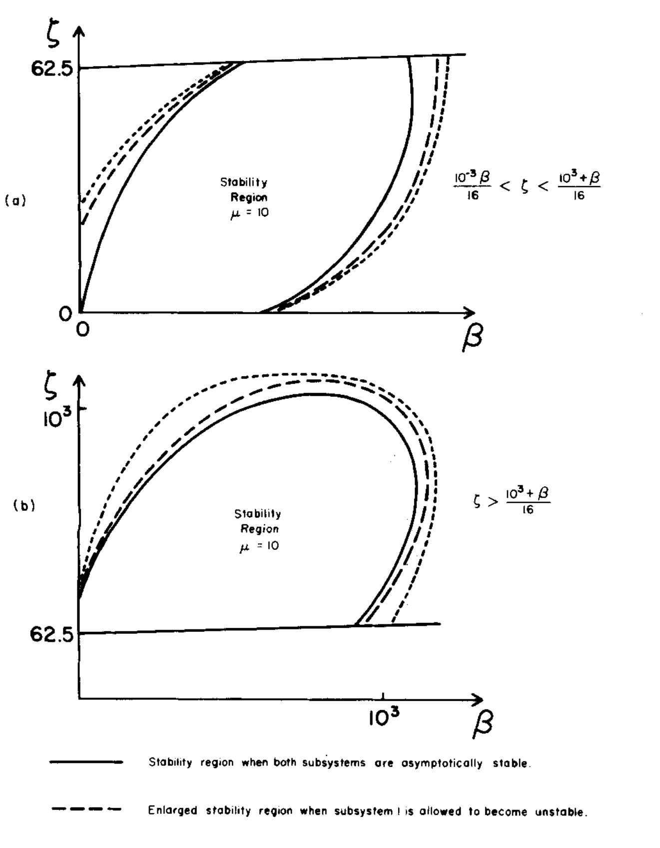


Fig. 2. Stability regions for example 1.

In Figure 2 the stability regions in terms of β and ζ are indicated for the various relationships between β and ζ (cases a and b above). In the previous papers by Prigogine and Nicolis (1967) and Turing (1952), the algebraic simplifications needed to reduce the criteria into manageable forms seriously restricted their numerical results. Thus, instability of the system is possible for a larger range of values β and certainly depends on the value of ζ; for example, if $\zeta = 10^{-3}$, the system is unstable when

$$10.1 \leq \beta \leq 18.7$$

In this example, we tried to demonstrate how the decomposition technique was applied to study the parametric stability of a system where the eigenvalue structure analysis is intractable and where a direct application of Lyapunov's second method encounters serious numerical hurdles. The linearization of the initial reaction-diffusion equations results in the construction of rather conservative stability regions, but the intent in this example was not to find all the stability region for the Turing's mechanism. Furthermore, as we will see later on, the linearization can be avoided, and we can apply the decomposition technique directly to the initial partial differential equations, describing the n component open system with reaction and diffusion.

Example 2: Stability Analysis of Nonideal Flow Polymerization Reactors

Polymerization reactors cannot be modeled by either plug flow reactors or CSTR because of nonideal flow patterns. Shinnar and Noar (1967) have showed that a tanks-in-series model represents fairly well the behavior of a nonideal flow polymerization reactor, especially its flow patterns. In this example a polymerization reactor was modeled as two CSTR's in series with backflow as shown in Figure 3 (see Shastry and Fan, 1973). For a free-radical polymerization, the following mechanism was considered (Bamsford, Barb, Jenkins, and Onyon, 1958):

$$I \xrightarrow{k_d} 2R^* \quad \text{initiation}$$

$$R^* + M \xrightarrow{k_i} P_i^*$$

$$P_j^* + M \xrightarrow{k_p} P^*_{j+1} \quad \text{propagation}$$

$$P_i^* + P_j^* \xrightarrow{k_t} P^*_{j+i} \quad \text{termination}$$

The rate constants k_d, k_p, k_t have the following exponential form:

$$k_i = k_i^o \exp(-E_i/RT), \quad i = d, p, t$$

The dynamic behavior of the polymerization reactor is described by the following set of differential equations which are the unsteady state mass and heat balances expressed in terms of the monomer concentration (M), the total active polymer concentrations through their first moment $[\lambda^{(o)}]$, and the reduced temperatures $(\eta = pC_pT/\Delta H)$

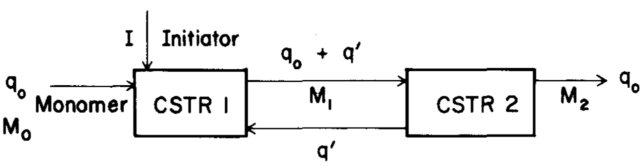


Fig. 3. The schematic representation of two CSTR's used to model the polymerization reactor.

(for further details see Shastry and Fan, 1973, and Billmery, 1971):

$$V_1 \frac{dM_1}{dt} = q_oM_f + q'M_2 - (q_o + q')M_1 - V_1k_pM_1\lambda_1^{(o)} \tag{15}$$

$$V_2 \frac{dM_2}{dt} = (q_o + q')M_1 - (q_o + q')M_2 - V_2k_pM_2\lambda_2^{(o)} \tag{16}$$

$$V_1 \frac{d\eta_1}{dt} = q_o\eta_f + q'\eta_2 - (q_o + q')\eta_1 + V_1k_pM_1\lambda_1^{(o)} + \Phi V_1k_t\{\lambda_1^{(o)}\}^2 - \frac{uA}{\rho C_p}(\eta_1 - \eta_w) \tag{17}$$

$$V_2 \frac{d\eta_2}{dt} = (q_o + q')\eta_1 - (q_o + q')\eta_2 + V_2k_pM_2\lambda_2^{(o)} + \Phi V_2k_t\{\lambda_2^{(o)}\}^2 - \frac{uA}{\rho C_p}(\eta_2 - \eta_w) \tag{18}$$

$$V_1 \frac{d\lambda_1^{(o)}}{dt} = q_o\lambda_f^{(o)} + q'\lambda_2^{(o)} - (q_o + q')\lambda_1^{(o)} + V_2\{2k_dI_1 - k_t[\lambda_1^{(o)}]^2\} \tag{19}$$

$$V_2 \frac{d\lambda_2^{(o)}}{dt} = (q_o + q')\lambda_1^{(o)} - (q_o + q')\lambda_2^{(o)} + V + V_2\{2k_dI_2 - k_t[\lambda_1^{(o)}]^2\} \tag{20}$$

The subscripts 1 and 2 refer to reactors 1 and 2, respectively.

The stability analysis of the system described by Equations (15) through (20), with the eigenvalue structure of the equations above used (after they are linearized around the steady state) is intractable (sixth-order characteristic polynomial) and very restrictive, since it will be applicable only for a conservative region around the steady state. Furthermore, the use of Lyapunov's second method on the system of the nonlinearized equations will yield very conservative stability region. The system will be able to tolerate larger derivations than those predicted by the region of asymptotic stability. The use of a quadratic Lyapunov function of the form

$$V = x^T A x \tag{21}$$

and the transformation of the stability problem into a nonlinear optimization problem (Berger and Lapidus, 1969) to overcome the dimensionality problem has very serious drawbacks. First, it predicts again a very conservative region of asymptotic stability. Second, the conservative nature of the stability region becomes more pronounced as the dimensionality of the problem increases. The latter will happen if we use, for example, more than two CSTR's to model the polymerization reactor. The fact that by manipulating matrix A in Equation (21) we can obtain larger estimates of the region of asymptotic stability is not very helpful, since there are no clear criteria and especially no physical considerations to direct such manipulation of the matrix A.

The decomposition technique demonstrated in the previous example will be used to study the stability of this system. There are two main advantages. First, from Equations (15) through (20) it is clear that if we decompose the system into three subsystems of order 2 each $[\eta_1, M_2; \eta_1, \eta_2; \lambda_1^{(o)}, \lambda_2^{(o)}]$, the free subsystems are linear with nonlinear interconnection terms. Therefore, the use of a quadratic Lyapunov function for each subsystem is recommended and will produce excellent results. Second, the

Table 3. Numerical Values of the Parameters Used in Example 2

	Set 1	Set 2	Units
I_f	0.001534	0.01534	g mole/l
M_f	5.0	5.0	
T_f	300	300	°K
$V_1 = V_2$	1 000	1 000	l
v	3	7.5	Kcal/h m^2 °K
ρ	0.8	0.8	g/cm^3
T_w	300	300	°K
f	0.825	0.825	
E_b	7 100	7 100	
E_t	1 800	1 800	
E_d	29 000	29 000	
k_d^o	1.58×10^{15}	1.58×10^{15}	
k_p^o	5.52×10^7	5.52×10^7	
k_t^o	1.25×10^9	1.25×10^9	
C_p	0.8	0.8	
ΔH_p	−17 500	−17 500	cal/g mole
q	500	500	l/h
A_r	1 000	1 000	cm^2
$\lambda_o^{(o)}$	0.0	0.0	
ΔH_t	−11 000	−11 000	Kcal/g mole

comparison constants required by theorems 4 and 5 can be easily derived through examination of the physical quantities of the system *per se*. Finally, the reduction of the dimensionality of the system facilitates the computation of the needed Lyapunov functions.

In Table 3 two different sets of parameter values are given (Shastry and Fan, 1973). For set 1 there exists only one steady state, while for set 2 there are three steady states. The results of the numerical analysis for CSTR 1 by using the two sets of values given in Table 3 have been summarized in Figures 4 and 5. Similar results can be obtained for CSTR 2. The improvement in the estimation of the regions of asymptotic stability is clear. The decomposition technique has provided larger regions of stability than the direct application of Lyapunov's second method (by using a quadratic form for the Lyapunov's function). In Table 4 the effect of the backflow parameter on the size of the stability region is shown, and it is compared with the values found by Shastry and Fan (1973) using Berger's and Lapidus' (1969) approach. Again the im-

Table 4. The Stability Regions Predicted by Berger and Lapidus' Method and by the Decomposition Technique for Various Values of the Backflow Parameter and for the Set 1 of Parameter Values

Backflow parameter	K by Berger and Lapidus method*	K by the decomposition technique
0	0.006579	0.091320
2	0.006834	0.093051
4	0.007087	0.10064
6	0.007232	0.10292

* These numbers for the example under consideration were derived by Shastry and Fan (1973).

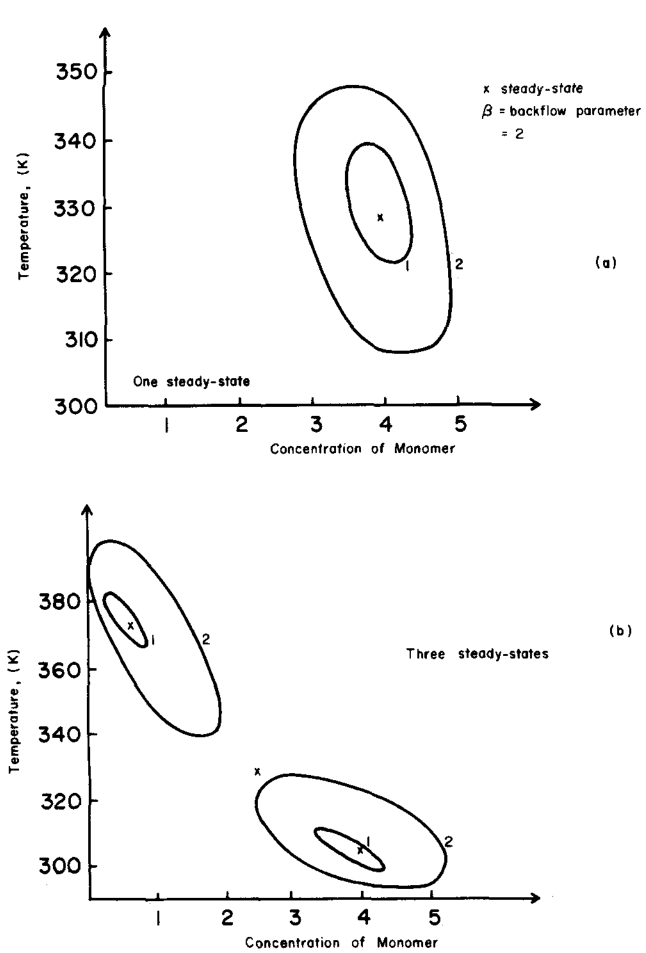


Fig. 4. The stability regions predicted by a quadratic Lyapunov function (curves No. 1) and by the decomposition technique (curves No. 2), for example 2 (both subsystems stable).

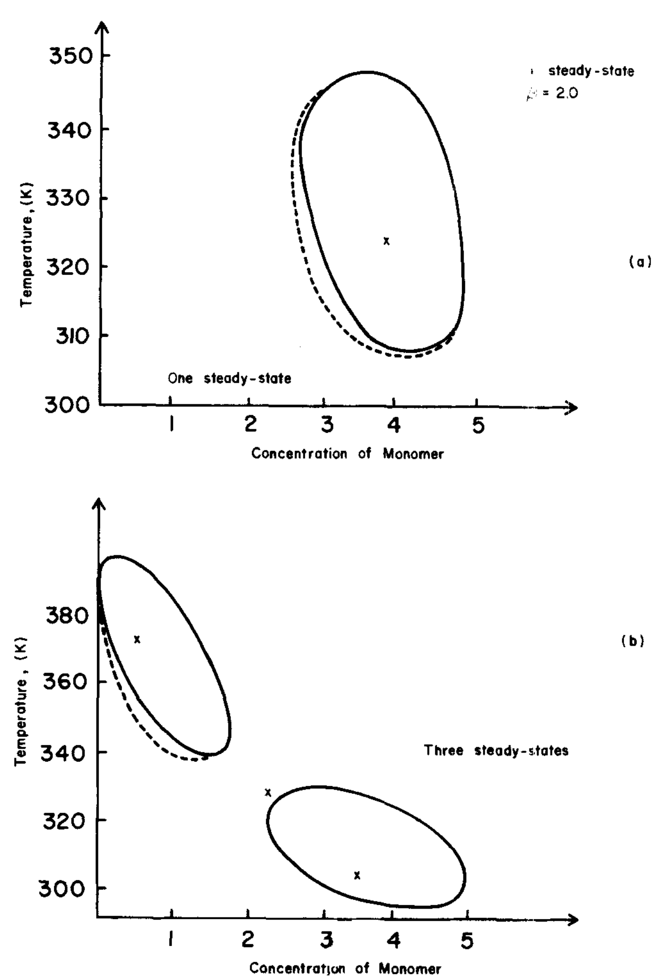


Fig. 5. The enlarged stability regions for example 2 when subsystem 1 is allowed to become unstable.

provement in the stability region is clear when the decomposition technique is used. In Table 4 note that K is a measure of the stability region where $V = K$ (see Shastry and Fan, 1973).

EXTENSION OF THE VECTOR LYAPUNOV FUNCTIONS TO DISTRIBUTED PARAMETER SYSTEMS: STABILITY ANALYSIS OF A TUBULAR REACTOR WITH AXIAL MIXING AND RECYCLE

Stability analysis of distributed systems is very important for a good understanding of many chemical engineering systems. The two problems most treated in the literature are the stability analysis of a tubular reactor with axial diffusion and that of a chemical reaction in a catalyst particle with internal diffusion. As Nishimura and Matsubara (1969) have pointed out, the stability analysis of these systems is equivalent to the analysis of a nonself-adjoint eigenvalue problem related to the linearized system. The sign of the real parts of eigenvalues determines the stability of the equilibrium state. This computation of the eigenvalues is complicated, and easier techniques have been sought.

Wei (1965) introduced the Lyapunov functional as a metric in function space. Further works by Berger and Lapidus (1968), Clough and Ramirez (1972), Yang and Lapidus (1974), Liou, Lim, and Weigand (1974), and others have elaborated in various ways on Lyapunov's method. The results have tended to be conservative. In addition to Lyapunov's method, Luss and Amundson (1967) have used topological methods, and Luss and Lee (1968) have employed the maximum principle for parabolic operators with remarkable results for the cases treated. These methods have certain shortcomings; that is, the former yields rather conservative sufficiency criteria and the latter is applicable in its full strength to a certain class of problems. Other methods suggested by Kuo and Amundson (1967) and Nishimura and Matsubara (1969) require the solution of rather involved computational problems; thus they lose a great deal of their attractiveness.

In this section we will explore the use of the vector Lyapunov functions to study the stability of distributed parameter systems, with particular emphasis to the stability of tubular reactors and catalyst particles.

As a basis for our presentation, we will use a nonadiabatic tubular reactor, with axial mixing and recycle treated numerically by McGowin and Perlmutter (1971) and analytically by Liou, Lim, and Weigand (1974). The dimensionless heat and mass balances for a first-order irreversible reaction taking place are

$$\frac{\partial n}{\partial t} = \frac{p_M}{p_H}\frac{\partial^2 n}{\partial x^2} - p_M\frac{\partial n}{\partial x} + f(n, y) - u_r(n - n_w) \tag{22}$$

$$\frac{\partial y}{\partial t} = \frac{\partial y^2}{\partial x^2} - p_M\frac{\partial y}{\partial x} - \beta f(n, y) \tag{23}$$

where

$$f = D_a y \exp\left[q(n-1)/n\right] \tag{24}$$

and with the following initial and boundary conditions

$$-\frac{\partial n(0)}{\partial x} = p_H\left[1 - \alpha + \alpha n(1) - n(0)\right] \tag{25}$$

$$-\frac{\partial y(0)}{\partial x} = p_M\left[1 - \alpha + \alpha y(1) - y(0)\right] \tag{26}$$

$$\frac{\partial n(1)}{\partial x} = 0 \tag{27}$$

$$\frac{\partial y(1)}{\partial x} = 0 \tag{28}$$

The partial differential Equations (22) and (23) are coupled through the reaction term. Consider the following uncoupled equations, where the reaction terms have been omitted:

$$\frac{\partial n}{\partial t} = \frac{p_M}{p_H}\frac{\partial^2 n}{\partial x^2} - p_M\frac{\partial n}{\partial x} - u_r(n - n_w) \tag{22a}$$

and

$$\frac{\partial y}{\partial t} = \frac{\partial^2 y}{\partial x^2} - p_M\frac{\partial y}{\partial x} \tag{23a}$$

For these equations, consider the same initial and boundary conditions.

Equations (22*a*) and (23*a*) are uncoupled and linear. The stability analysis of each one of them is concerned with the transient solutions in the vicinity of a steady state, and they will be called asymptotically stable at the origin if every nonzero perturbation $\phi(t)$ decays to zero as $t \to \infty$.

Let us consider two positive-definite functionals v_n and v_y determined by the following quadratic forms:

$$v_n = \int_0^1 n^2 dx \quad \text{and} \quad v_y = \int_0^1 y^2 dx$$

If the time derivatives of these functionals are negative-definite functionals, then $v_n \to 0$ and $v_y \to 0$ and consequently $n \to 0$ and $y \to 0$, thus yielding an asymptotically stable origin.

According to theorem 1, the following conditions should be satisfied in order for the system of the uncoupled Equations (22*a*) and (23*a*) to be asymptotically stable:

$$c_{1n}\int_0^1 (n)^2 dx \leq v_n \leq c_{2n}\int_0^1 (n)^2 dx \tag{29}$$

$$\dot{v}_\eta \leq -c_{3n}\int_0^1 (n)^2 dx \tag{30}$$

$$||\text{grad } v_n|| \leq c_{4n}'\left[\int_0^1 (n)^2 dx\right]^{1/2} \leq c_{4n} \tag{31}$$

and

$$c_{1y}\int_0^1 (y)^2 dx \leq v_y \leq c_{2y}\int_0^1 (y)^2 dx \tag{32}$$

$$\dot{v}_y \leq -c_{3y}\int_0^1 (y)^2 dx \tag{33}$$

$$||\text{grad } v_y|| \leq c_{4y}'\left[\int_0^1 (y)^2 dx\right]^{1/2} \leq c_{4y} \tag{34}$$

The quadratic form of the functionals v_n and v_y guarantees their positive definiteness, and therefore

$$c_{1n} = c_{2n} = c_{1y} = c_{2y} = 1$$

In Appendix A,* the values of the constants c_{3n}, c_{3y}, c_{4n}, and c_{4y} are estimated. Equations (A3), (A4), (A5), and (A6) provide very strong bounds, but they are of little help since the behavior of the n and y along the length of the reactor for different time points are not known. There are different ways that someone can proceed from these equations to establish useful and easily estimated values for these constants. In the present work, the steady state information has been exploited, and the following

* Supplementary material has been deposited as Document No. 02841 with the National Auxiliary Publications Service (NAPS), c/o Microfiche Publications, 440 Park Ave. South, New York, N. Y. 10016 and may be obtained for $3.00 for microfiche or $5.00 for photocopies.

equations were developed (see Appendix A):*

$$c_{3n} = \frac{p_M\{[n(0) - n_w]^2 - [n(1) - n_w]^2\} - 2n_s(0)[n(0) - n_w]}{\int_0^1 [(n_{ss} - n_w)^2 + (n_s^2)_{ss}]dx} \quad \text{(A3a)}$$

$$c_{3y} = \frac{y^2(1) - y^2(0) - 2y(0)y_s(0)}{\int_0^1 [y_{ss}^2 + (y_s^2)_{ss}]dx} \quad \text{(A4a)}$$

$$c_{4n} = 2\left(\int_0^1 n_{s\max}^2 dx\right)^{1/2} \quad \text{(A5a)}$$

$$c_{4y} = 2\left(\int_0^1 y_{s\max} dx\right)^{1/2} \quad \text{(A6a)}$$

These constants to be evaluated require the system's parameters and steady state information. Less strong conditions can be developed, based only on the system's parameters.

The most critical point of the decomposition approach is the estimation of a positive constant ξ which will bound from above the magnitude of the interconnection terms; that is

$$||f(y, n)|| \leq \xi \left|\left| \begin{matrix} y \\ n \end{matrix} \right|\right| \quad (35)$$

Close examination of the particular physical system considered will be extremely valuable. In the present example we have

$$f(y, n) = D_a y \exp [q(n - 1)/n]$$

For $n_w < 1$,

$$n_{\max} = 1 + \beta^{-1} [1 - y(1)]$$

and for $n_w \geqq 1$,

$$n_{\max} = 1 + \beta^{-1} [1 - y(1)] + \frac{u_r(n_w - 1)}{p_m(1 - \alpha)}$$

Therefore

$$n_{\max} > 1 \quad \text{and} \quad 0 < \frac{n_{\max} - 1}{n_{\max}} < 1.$$

Thus, we take

$$|f(y, n_{\max})| = |D_a\, y \exp [q(n_{\max} - 1)/n_{\max}]| < |D_a\, y \exp(q)| \leq \xi\, |y|$$

which yields

$$\xi = D_a \exp (q)$$

A priori bounds and the qualitative behavior of the y and n in the reactor are extremely valuable for the decomposition method to study the stability of tubular reactors. Varma (1972) has dealt with this problem, and his results are very strong and effective for stability studies. The development of very sharp bounds in certain occasions can offer tremendous advantages in the decomposition method.

So far we have examined the stability of two uncoupled systems described by the Equations (22*a*) and (23*a*), via Krassovskii's theorem (theorem 1). The values of the constants needed have been established, as well as values for the constant ξ in the bounding relationship for the interconnection term. Nothing can be said for the stability of the system described by the coupled Equations (22) and (23) with the given boundary conditions. To examine the stability of the interconnected system, let us consider the total time derivatives of the functions v_n and v_y along the solution of Equations (22) and (23) with the given boundary conditions. Thus, we take

$$\frac{Dv_n}{Dt} = \int_0^1 2n \left(\frac{\partial n}{\partial t}\right) dx \quad (35)$$

and

$$\frac{Dv_y}{Dt} = \int_0^1 2y \left(\frac{\partial y}{\partial t}\right) dx \quad (36)$$

Along the solution of Equations (22) and (23)

$$\frac{Dv_n}{Dt} = \int_0^1 2n \left[\frac{p_m}{p_H}\frac{\partial^2 n}{\partial x^2} - p_m \frac{\partial n}{\partial x} - u_r(n - n_w)\right] dx + \int_0^1 2n\, f(n, y) dx = \frac{dv_n}{dt} + \int_0^1 2n\, f(n, y) dx \quad (35a)$$

and

$$\frac{Dv_y}{Dt} = \frac{dv_y}{dt} + \int_0^1 2n(-\beta)\, f(n, y) dx \quad (36a)$$

where dv_n/dt and dv_y/dt are the time derivatives of the Lyapunov functionals along the solution of the independent subsystems.

From (35*a*) and (36*a*) we take [by using inequalities (29) through (34)]

$$\frac{Dv_n}{Dt} \leq -\left[\frac{c_{3n}}{c_{2n}} - \frac{c_{4n}}{c_{1n}}\xi\right] v_n + \frac{c_{4n}}{c_{1y}}\xi\, v_y \quad (37)$$

and

$$\frac{Dv_y}{Dt} \leq -\left[\frac{c_{3y}}{c_{2y}} - \frac{c_{4y}}{c_{1y}}\beta\,\xi\right] v_y + \frac{c_{4y}}{c_{1n}}\beta\,\xi\, v_n \quad (38)$$

The solution of the inequalities (37) and (38) is bounded from above by the solution of the following linear system

$$\frac{dV_n}{dt} = -\left[\frac{c_{3n}}{c_{2n}} - \frac{c_{4n}}{c_{1n}}\xi\right] V_n + \frac{c_{4n}}{c_{1y}}\xi\, V_y \quad (39)$$

$$\frac{dV_y}{dt} = -\left[\frac{c_{3y}}{c_{2y}} - \frac{c_{4y}}{c_{1y}}\beta\,\xi\right] V_y + \frac{c_{4n}}{c_{1n}}\beta\,\xi\, V_n \quad (40)$$

according to the theorem (see Beckenbach and Bellman, 1961).

Theorem 6

If $a_{ij} \geqq 0$ for $i \neq j$, then

$$\frac{dx}{dt} \leq Ax \quad \text{with} \quad x(0) = c$$

implies $x \leq y$ where

$$\frac{dy}{dt} = Ay \quad \text{with} \quad y(0) = c$$

Note that $x \leq y$ implies component-by-component majorization, and that for the system of Equations (39) and (40), the terms $\xi \frac{c_{4n}}{c_{1y}}$ and $\beta\,\xi \frac{c_{4y}}{c_{1n}}$ are nonnegative. Therefore, the stability of the tubular reactor with axial mixing and recycle is governed by the stability of the linear system of Equations (39) and (40). According to Sevastyanov's lemma, this system will be stable if

$$-\left[\frac{c_{3n}}{c_{2n}} - \frac{c_{4n}}{c_{1n}}\beta\right] < 0$$

* See footnote on p. 863.

TABLE 5. THE EFFECT OF THE OVERALL HEAT TRANSFER COEFFICIENT ON THE STABILITY OF THE TUBULAR REACTOR

U_r	Comment	
10	Stable when	$D_a < 0.471$ (0.315)*
20	Stable when	0.499 (0.370)
30	Stable when	0.510 (0.412)
40	Stable when	0.583 (0.439)
50	Stable when	0.626 (0.471)

* The results in parenthesis were derived by using Lyapunov's second method directly on the nonlinear system (see Liou, Lim, and Weigand, 1974).

TABLE 6. THE EFFECT OF THE RECYCLE RATIO ON THE STABILITY OF THE TUBULAR REACTOR

Recycle ratio (α)	Comment	
0.02	Stable when	$D_a < 0.598$ (0.427)*
0.04	Stable when	< 0.593 (0.425)
0.08	Stable when	< 0.581 (0.419)
0.10	Stable when	< 0.575 (0.401)
0.20	Stable when	< 0.571 (0.399)
0.30	Stable when	< 0.560 (0.397)

* The results in parenthesis were derived by using Lyapunov's second method directly on the nonlinear system (see Liou, Lim, and Weigand, 1974).

and

$$\left[\frac{c_{3n}}{c_{2n}} - \frac{c_{4n}}{c_{1n}}\xi\right]\left[\frac{c_{3y}}{c_{2y}} - \frac{c_{4y}}{c_{1y}}\beta\xi\right] - \frac{c_{4n}\,c_{4y}}{c_{1n}\,c_{1y}}\beta\xi^2 > 0 \quad (41)$$

The first of the two conditions is always satisfied, thus leaving inequality (41) as the only sufficient condition for asymptotic stability of the tubular reactor.

Similar conditions were developed for the case where the interconnection terms have been linearized around the steady state. The analysis is shown in Appendix B,* and the resulting conditions are very conservative.

Numerical Examples

The strength of the stability criterion was tested on a tubular reactor with axial mixing and recycle with the following parameters (Liou, Lim, and Weigand, 1974):

$$p_M = 10 \quad \alpha = 0.08 \quad \beta = 4 \quad q = 10$$
$$p_H = 5 \quad n_w = 0.8 \quad u_r = 20$$

The effects of the heat transfer coefficient and of the recycle ratio on the stability of the reactor are summarized in the Tables 5 and 6. Qualitatively the results followed the same trends with the ones reported by Liou, Lim, and Weigand; that is, the stability region was enlarged by increasing the u_r (heat transfer coefficient) and by decreasing the recycle ratio α. The regions of stability, though, are enlarged. Criterion (41) has predicted larger stability regions than the simple straightforward application of Lyapunov's second method with variable weighting matrix in the quadratic form of the Lyapunov function used (the numbers in parenthesis).

Furthermore, criterion (41) was tested on a reactor studied numerically by McGowin and Perlmutter (1971) and analytically by Liou, Lim, and Weigand (1974). The following parameters were used:

$$\alpha = 0.5 \qquad p_M = p_H = 4$$
$$\beta = 2.55 \qquad u_r/p_M = 0.20$$
$$\beta n_w = 2.50 \qquad \beta\, D_a \exp(q)/p_M = 10^{11}$$
$$\beta q = 75$$

* See footnote on p. 863.

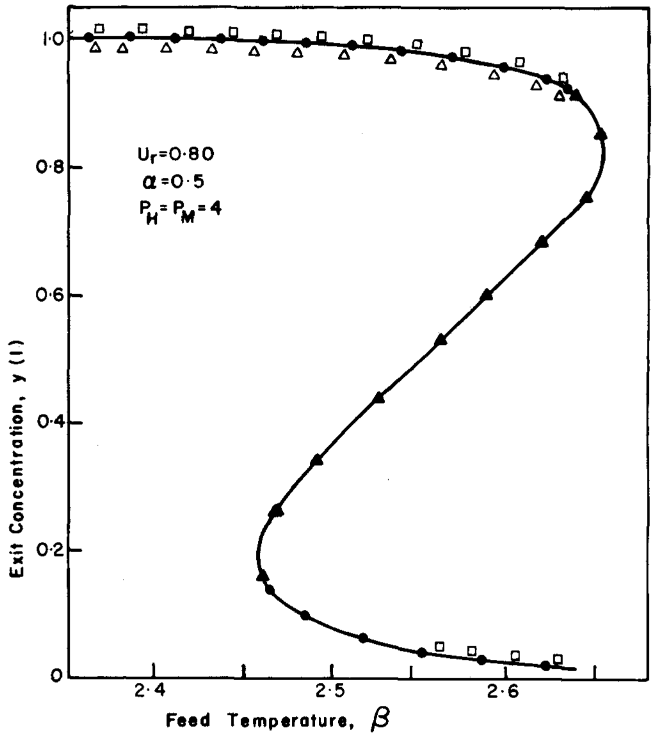


Fig. 6. Stability regions developed by various methods for the nonadiabatic tubular reactor with axial mixing and recycle.

The system has three steady states. McGowin and Perlmutter showed numerically that the high and the low conversion steady states are stable, while the intermediate conversion one is unstable to nonadiabatic perturbations. The criteria used by Liou, Lim, and Weigand failed to recognize the stability of the steady state in the region of high conversion. Criterion (41) guaranteed stability for both stable steady states (Figure 6).

Furthermore, in Figures 7 and 8 the stability regions for the two stable steady states are established. In the same figures, the numerical results reported by McGowin and Perlmutter (1971) are shown. It is clear that the

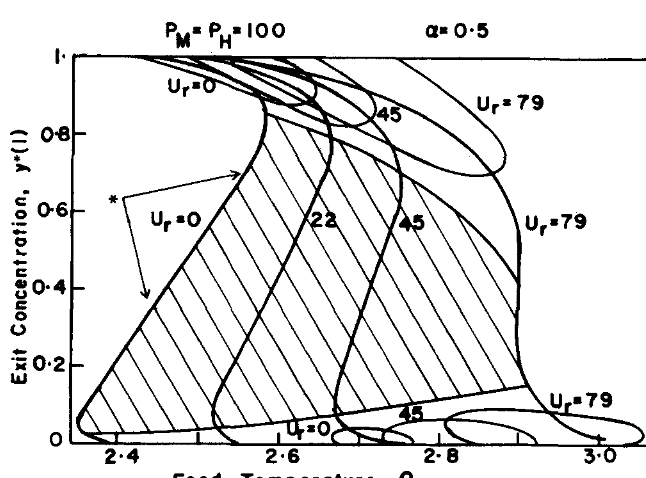
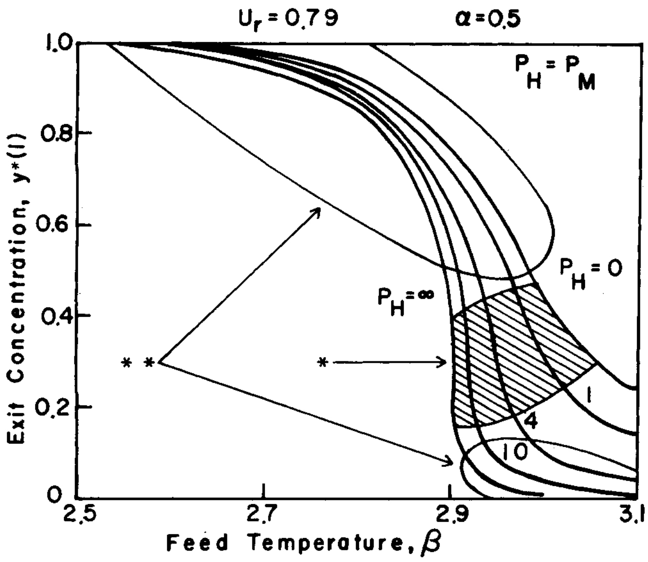


Fig. 7. Comparison of the stability regions computed numerically (McGowin-Perlmutter) and predicted by criterion (41), for various values of u_r.



* Region of Instability,(McGowin & Perlmutter)

* * Region of Stability (Criterion 41) for $P_H = P_M = 1000$.

Fig. 8. Comparison of the stability regions computed numerically (McGowin-Perlmutter) and predicted by criterion (41), for various values of the Peclet numbers.

sufficiency criterion (41) has predicted stability of the tubular reactor over a very satisfactory region of values.

DISCUSSION

A decomposition technique based on Lyapunov's reactor functions has been investigated to study various chemical engineering systems. The results have been encouraging, but the method cannot provide the high quality strong criteria required in many situations. The use of Lyapunov functions to establish the stability characteristics of the free subsystems is the main drawback, since for nonlinear subsystems the results will be very conservative. Therefore, the decomposition technique has certain merits for systems which can be decomposed to linear subsystems. The examined cases fall into this category. Furthermore, it provides a very useful tool to treat systems of high dimensionality despite its conservativeness, since the other available techniques become intractable or computationally cumbersome. An extension of the decomposition technique to distributed parameter systems of interest to chemical engineering is possible, and it has been demonstrated on a tubular reactor. This is a class of problems where many advantages can be drawn from the method. The linearity of the subsystems allows the use of effective Lyapunov functions, and the method is not bogged down by the presence of many reacting and diffusing species. In principle, it can provide a much better tool than is currently available to study tubular reactors with multiple reactions. Examples have to be worked out to demonstrate this statement.

The critical point of the approach is the establishment of effective bounds on the norm of the interconnection terms. The conservativeness of the derived criteria depends on that. Therefore, a close examination of the physical system under consideration can provide very useful information in establishing these bounds. The restriction placed on the interconnection terms depend on the choice of the Lyapunov functions used to prove the stability of the subsystems, as well as the bounds placed on the constraints themselves.

The overall approach provides sufficient criteria only. It is also desirable to establish necessary conditions. Similar analysis can be established to develop sufficient conditions for instability. Such conditions have been developed by Grujic and Siljak (1973), but they are extremely conservative. They can be used as necessary conditions for stability.

This work is a part of a more general effort to study the dynamic characteristics of large-scale interconnected systems, with the purpose to develop design techniques for the synthesis of process flow sheets in a dynamic environment and for the synthesis of control structures. The work which is currently underway aims to accomplish the following tasks: develop stronger conditions of stability by using the maximum principle of the differential equations for the independent subsystems and extend the analysis to develop sufficient criteria for instability.

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NOTATION

C = n component vector of molar concentrations
D = matrix of diffusion coefficients
D_a = parameter defined by $k_o L^2 \exp(-q)/\beta E_a$
E_a = effective mass diffusivity
I = concentration of initiator
k_i = reaction rate constant
k_d, k_p, k_t = rate constants for decomposition of initiator, propagation and termination
L = reactor length
M = concentration of monomer
M_f = feed concentration of monomer into the reactor
n = dimensionless temperature, $n = T/T_f$
p_H = Peclet number for heat transfer, $p_H = \nu L/(\lambda \rho C_p)$
p_M = Peclet number for mass transfer $p_M = \nu L/E_a$
P_i^* = concentration of active polymer of drain of length i
q = dimensionless activation energy, $q = E/RT_f$
q' = backflow rate, rate of flow from tank i to tank $i-1$
q_o = input flow rate into the reactor
R^* = concentration of radices produced from the decomposition of initiator
R = gas constant
U_r = dimensionless heat transfer coefficient, $u_r = 4L^2 u/\rho C_p E_a D$
V = volume of the reactor
y = dimensionless concentrations

Greek Letters

α = recycle ratio
β = term determined by $\beta = \rho C_p T_f/(-\Delta H) C_f$
ΔH = heat of reaction
η = reduced temperature, $\rho C_p T/\Delta H$
λ = effective thermal conductivity
$\lambda^{(o)}$ = first moment of the active polymer concentration
Φ = $\Delta H_t/\Delta H_p$

Subscripts

1 = CSTR 1
2 = CSTR 2
d = decomposition of the initiator
f = feed conditions

p = propagation of the polymerization
t = termination of the polymerization

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Finite Amplitude Equilibrium Waves on the Surface of Nonvertical Falling Films

Experimental data on the frequency and wavelength of finite amplitude equilibrium waves on the surface of nonvertical laminar falling films of mineral oil at moderate Reynolds numbers are correlated successfully on the basis that the frequency of the wave remains constant during the course of its amplification.

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SCOPE

In many practical situations, one has to predict the properties of finite amplitude equilibrium waves on the surface of nonvertical falling films. In spite of many theoretical and experimental investigations that have been conducted on wavy flow in the past, there are many situations where these results are not useful. For example, since the waves are finite in size, the predictions of linear stability theories are not applicable. Also, the results of few nonlinear theories generally are restricted to vertical films and to limiting conditions not necessarily valid in a practical situation. Moreover, most of the experimental investigations have been conducted on vertical films, and not much data are available on the wave properties at small inclination angles. For this reason, an experimental work was undertaken to measure the properties of naturally occurring finite amplitude equilibrium waves on the surface of laminar films at inclination angles considerably different than 90 deg. In this paper, the results that were obtained for wave frequency and wavelength are presented. Since the frequency is the only wave property that is conserved at all the stages of growth, it may be used as a link between the properties of finite amplitude waves and the infinitesimal disturbance at the initial stage of growth. For this reason, data on wave frequency, rarely measured in the past, are used to correlate the properties of finite amplitude waves with the parameters furnished by linear stability theories.