Local Stability of Tubular Reactors

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Some difficulties, which existed due to the nonsymmetric nature of matrix $\underline{\underline{C}}$, in a recent paper of the above title by Clough and Ramirez (1972) have been aptly noted by Liou et al. (1972a) who attacked these and presented suitably modified stability criteria. Unfortunately, however, there are still some problems in the case of the tubular reactor with axial dispersion (point 3 of Liou et al., 1972a) and the stability criterion reached for this case, inequality (6) of Liou et al. (1972a), is incomplete. We obtain new stability criteria in this note and show that this inequality is only one of the two that must actually hold to ensure asymptotic stability of the steady state in the general case of $r_1 \neq r_2$ and the other implies this one. This whole approach is, in fact, shown to yield more conservative stability criteria than those of Varma and Amundson (1972). Conclusions of Liou et al. (1972b), since they were based on their earlier work, are therefore also incorrect for $r_1 \neq r_2$.

In the notation of Clough and Ramirez (1972), the negative definiteness of the symmetric matrix $\hat{\underline{\underline{C}}}$ corresponding to the unsymmetric matrix $\underline{\underline{C}}$, that is, $\hat{\underline{\underline{C}}} = (\underline{\underline{C}} + \underline{\underline{C}}^T)/2$, is assured if and only if the following inequalities hold:

$$\Delta_1 \equiv -r_2 \frac{dP_1}{dx} - 2B_1R_1P_1 > 0 \tag{1a}$$

and defining

$$\Delta_2 \equiv -r_2 \frac{dP_2}{dx} + 2B_2R_2P_2 \tag{1b}$$

$$\Delta_3 \equiv \Delta_1\Delta_2 - (B_2R_1P_2 - B_1R_2P_1)^2 > 0 \tag{2}$$

$$\Delta_4 \equiv -\Delta_2 \left(\frac{dP_1}{dx}\right)^2 + 2\frac{r_1}{r_2} P_1\Delta_3 > 0 \tag{3}$$

$$\Delta_5 \equiv -\left(\frac{dP_2}{dx}\right)^2 \left[2\frac{r_1}{r_2} P_1\Delta_1 - \left(\frac{dP_1}{dx}\right)^2\right] + 2P_2\Delta_4 > 0 \tag{4}$$

where $P_i(x) = \exp(-K_ix)$, with K_i being positive constants, are the functions used in defining the Liapunov functional

$$V(t) = \int_0^1 \underline{u}^T \underline{\underline{P}}\, \underline{u}\, dx \tag{5}$$

and

$$\underline{\underline{P}} = \begin{bmatrix} P_1 & 0 \\ 0 & P_2 \end{bmatrix} \tag{6}$$

The idea of Clough and Ramirez (1972) was to choose the constants K_i in a manner such that the most liberal stability condition is reached. We will show here that the best choice is $K_1 = r_1$, $K_2 = r_2$ where r_1 and r_2 are the Peclet numbers for heat and mass transfer, respectively. To arrive at this conclusion, we note that in the case of an exothermic chemical reaction $B_i \geqq 0$, $R_i(x) \geqq 0$ for the class of reaction rate expressions under consideration and with $P_i(x)$ as defined above, $\Delta_2 > 0$ always while (1a) holds if

$$K_1 > 2(B_1/r_2)R_{1,m} \tag{7}$$

In what follows

$$R_{i,m} = \underset{x\epsilon[0,1]}{\text{Max}}\ R_i(x), \quad R_{i,n} = \underset{x\epsilon[0,1]}{\text{Min}}\ R_i(x) \tag{8}$$

$\Delta_4 > 0$ implies that $\Delta_3 > 0$; so that attention need be focussed only on inequalities (3) and (4), with the choice of K_1 as in (7). The necessary (though not sufficient) condition for inequality (3) to hold is

$$K_1^2 - 2K_1r_1 + 4B_1R_1(r_1/r_2) < 0\ , \tag{9}$$

but under this restriction, $\Delta_5 > 0$ implies $\Delta_4 > 0$; so that we now only need to satisfy inequality (4) with K_1 satisfying both (7) and (9). The difficulty of Liou et al. (1972a) is that they satisfy (9) but assume that $\Delta_4 > 0$ implies $\Delta_5 > 0$; this is not true.

Since (9) may be rearranged as

$$(K_1 - r_1)^2 - r_1^2[1 - (4B_1R_1/r_1r_2)] < 0 \tag{10}$$

the least restrictive way to satisfy (10) is to take $K_1 = r_1$ and then

$$B_1R_{1,m}/r_1r_2 < 1/4 \tag{11}$$

satisfies both (7) and (9).

We must now simply find conditions so that inequality (4) holds with $K_1 = r_1$ and under the restriction (11). A rearrangement of (4) reveals that it cannot be satisfied unless

$$-(K_2 - r_2)^2 + r_2^2 + 4B_2R_2 > 0 \tag{12}$$

With the choice $K_2 = r_2$, (12) is satisfied in the least restrictive manner; all our choices are now over but we must still satisfy (4) which now takes the form

$$\left(1 - \frac{4B_1R_1}{r_1r_2}\right)(r_2^2 + 4B_2R_2) - \frac{4}{P_1P_2r_1r_2}(B_2R_1P_2 - B_1R_2P_1)^2 > 0 \tag{13}$$

Note that (13) implies (11); so the final stability criteria is (13). In terms of parameters, the final stability condition is the satisfaction of inequality (13) over the entire range of the a priori bounds on concentration and temperature:

$$0 \leqq y \leqq 1, \quad 1 \leqq n \leqq 1 + (B_1/B_2) \tag{14}$$

A derivation of these (rate independent) a priori bounds for the adiabatic and the nonadiabatic tubular reactors is in preparation and will be published elsewhere.

Let us now pause and see what has been done. The above analysis implies that if the choice of functions $P_i(x) = \exp(-K_ix)$ is made in defining the matrix $\underline{\underline{P}}$ for the Liapunov functional in Equation (5), the best that can possibly be done is to take $K_i = r_i$; but with this choice

$$V(t) = \int_0^1 [\{u_1 \exp(-r_1x/2)\}^2 + \{u_2 \exp(-r_2x/2)\}^2]\, dx \quad (15)$$

The transformations

$$\tilde{u} = u_1 \exp(-r_1x/2), \quad \tilde{v} = u_2 \exp(-r_2x/2) \quad (16)$$

are frequently made (compare Berger and Lapidus, 1968; Varma and Amundson, 1972) to make the spatial differential operators in Equations (B6) and (B7) of Clough and Ramirez (1972) self-adjoint. In the transformed variables, the Liapunov functional in Equation (15) takes the form

$$V(t) = \int_0^1 [\tilde{u}^2 + \tilde{v}^2]\, dx \quad (17)$$

which is the simplest Liapunov functional that comes to mind. We can then summarize that if the approach of Clough and Ramirez (1972) is to give better stability conditions than the ones that can be obtained by the most obvious choice of a Liapunov functional, one must look for functions $P_i(x)$ other than $\exp(-K_ix)$.

Varma and Amundson (1972) have recently considered several problems concerning the nonadiabatic tubular reactors, including those concerning uniqueness and asymptotic stability of the steady states. It was shown that by considering Liapunov functionals of the form

$$\overline{V}(t) = \int_0^1 [\tilde{u}^2 + p\tilde{v}^2]\, dx \quad (18)$$

where p is a positive constant, to be chosen later appropriately, sufficient conditions ensuring uniqueness and asymptotic stability of the steady state can be derived. This approach was suggested by the work of Padmanabhan et al. (1971). Note that the Liapunov functional $V(t)$ of Clough and Ramirez (1972) in Equation (17) takes $p \equiv 1$. In the present notation, the approach of Varma and Amundson (1972) leads to the result that the conditions

$$\underset{x\epsilon[0,1]}{\text{Min}} \left[\frac{4\lambda_{1,1}}{r_1^2} + 1 - \frac{4B_1R_1}{r_1r_2} \right] \equiv \underset{x\epsilon[0,1]}{\text{Min}}\; q(x) = q_1 > 0 \quad (19)$$

and with p chosen to satisfy

$$pq(x)[4\lambda_{1,2} + r_2^2 + 4B_2R_2] > [4/(Q_1Q_2r_1r_2)]\,[pB_2R_1Q_2 - B_1R_2Q_1]^2 \quad (20)$$

ensure that the steady state is asymptotically stable. Here

$$Q_i(x) = \exp(-r_ix), \quad (21)$$

while $\lambda_{1,i}$, $i = 1, 2$ are the least eigenvalues of the differential operator, $L[\;] \equiv \frac{d^2}{dx^2}[\;]$ satisfying the boundary conditions

$$B_i[\;] = 0 : \begin{cases} \left(-\frac{d}{dx} + \frac{r_i}{2}\right)[\;] = 0 & ; \; x = 0 \\ \left(\frac{d}{dx} + \frac{r_i}{2}\right)[\;] = 0 & ; \; x = 1 \end{cases} \quad (22)$$

It may be shown that all the eigenvalues $\lambda_{n,i}$ are real, positive, and satisfy the transcendental equation

$$\tan\sqrt{\lambda_{n,i}} = r_i\sqrt{\lambda_{n,i}}/[\lambda_{n,i} - (r_i^2/4)]\,; \quad i = 1, 2\,; \quad 0 < \lambda_{1,i} < \pi^2 \quad (23)$$

Since $\lambda_{1,i}$ are strictly positive, condition (19) is somewhat better than condition (11) obtained by the earlier approach and since the best choices for K_i in the earlier approach are $K_i = r_i$, $P_i(x) \equiv Q_i(x)$ so that even with $p \equiv 1$, condition (20) is better than (13). However, we still have the freedom of choosing p shrewdly; this we do now.

A rearrangement of (20) leads to the result that if

$$2B_1B_2R_{1,n}R_{2,n} + q_1r_1r_2[\lambda_{1,2} + (r_2^2/4) + B_2R_{2,n}] > 2B_1B_2R_{1,m}R_{2,m}\exp(|r_1 - r_2|/2) \quad (24)$$

then p can be chosen such that (20) holds. Since in terms of parameters, $R_{i,m}$ and $R_{i,n}$ must be evaluated over the entire range of the a priori bounds (14); $R_{1,n} \equiv 0$ for the first-order irreversible reaction under consideration by Clough and Ramirez (1972) so that (24) may be replaced by the more conservative condition:

$$q_1r_1r_2[\lambda_{1,2} + (r_2^2/4) + B_2R_{2,n}] > 2B_1B_2R_{1,m}R_{2,m}\exp(|r_1 - r_2|/2) \quad (25)$$

Since (25) implies (19); satisfaction of (25) is enough to ensure that the steady state is asymptotically stable. This reduces to condition (134b) of Varma and Amundson (1972) for zero heat transfer coefficient. (There is a typographical error there in that the 2 in the argument of the exponential is missing.) For $r_1 = r_2$, the case of equal Peclet number for heat and mass transfer, it has been shown (Varma and Amundson, 1972) that condition (19), with

$$R_1(y, n) = \frac{d}{dn}\left[R\left(1 - \frac{B_2}{B_1}(n-1), n\right)\right] \quad (26)$$

is the only one required.

Some remarks deserve mention. The stability criteria developed here, that is, inequality (25), can be used in two different ways. If in numerical computations one finds that a certain steady state satisfies (25) [less conservatively, (24), but let us not belabor this point] with $R_{i,m}$ and $R_{i,n}$ evaluated as in Equation (8), then that steady state will be asymptotically stable. However, for a fixed set of flow and kinetic parameters, there may be more than one steady state which satisfies this inequality; if so, they will all be asymptotically stable. If a certain steady state does not satisfy this inequality, no conclusion concerning its instability can be drawn, for this inequality only represents a sufficient (and not necessary and sufficient) condition for stability. However, if (25) holds over the entire range of the a priori bounds, then the analysis of Varma and Amundson (1972) implies that the steady state will be unique and asymptotically stable. This is, of course, the kind of information that is the most desirable one for the practicing engineer to have. For the case of equal Peclet numbers, satisfaction of (19) alone, with R_1 as in (26), over the entire range of the a priori bounds ensures both the uniqueness of the steady state and its asymptotic stability (Varma and Amundson, 1972).

Since the stability condition reached by Liou et al. (1972a) [their inequality (6), which is the same as inequality (11) above] has been shown above to be incomplete for the general case of $r_1 \neq r_2$, their extension in Liou et al. (1972b) is erroneous for $r_1 \neq r_2$ and is indeed not as good as can be even for $r_1 = r_2$ since neither the identification (26) is made, nor is the term involving λ_1 present in their analysis.

Thus, for $r_1 = r_2 = r$ and $\lambda_{1,1} = \lambda_{1,2} = \lambda_1$, (19) can be analyzed with respect to developing stability criteria in terms of inlet or exit temperatures alone. For the first-order irreversible reaction under consideration,

$$R\left(1 - \frac{B_2}{B_1}(n-1), n\right) \equiv \left[1 - \frac{B_2}{B_1}(n-1)\right] \exp(-q/n) \quad (27)$$

Then

$$R_1 \equiv \frac{dR}{dn} = \left[-\frac{B_2}{B_1} + \left\{1 - \frac{B_2}{B_1}(n-1)\right\}\frac{q}{n^2}\right] \exp(-q/n) \quad (28)$$

The nature of the function R has been investigated by Aris (1969). In the range $1 \leq n \leq 1 + (B_1/B_2)$, the function may have at most one inflexion point, and this, with a positive slope at

$$n \equiv n_i = q\,[1 + (B_1/B_2)]/[q + 2\{1 + (B_1/B_2)\}] \quad (29)$$

The largest value of R_1 occurs at

$$n = \begin{cases} n(1) & \text{if } n(1) \leq n_i \\ n(0) & \text{if } n(0) \geq n_i \\ n_i & \text{if } n(0) \leq n_i \leq n(1) \end{cases} \quad (30)$$

The condition (19) on rearrangement yields that asymptotic stability is assured if

$$(1/n^2)\,[-B_2 n^2 + q\,\{B_1 - B_2(n-1)\}] \exp(-q/n) < (r^2/4) + \lambda_1, \quad (31)$$

with the lhs evaluated at n given by (30). It may be seen by comparison that (31) is a better condition than (13) of Liou et al. (1972b).

As discussed above, if the evaluation of the largest value of R_1 is made over the entire range of the a priori bounds $1 \leq n \leq 1 + (B_1/B_2)$, uniqueness and stability are both ensured by condition (19) above. It is easy to verify that if

$$B_1 q/B_2 < 1, \quad (32)$$

then $R_1 < 0$ always, so that (19) is always satisfied. If (32) is violated, then it is easy to show that R_1 attains its largest value at

$$n = \begin{cases} 1 & \text{if } q \leq 2[1 + (B_2/B_1)] \\ n_i & \text{if } q > 2[1 + (B_2/B_1)] \end{cases} \quad (33)$$

and (31) evaluated for n given by (33) satisfies (19).

Several other uniqueness criteria for the case of $r_1 = r_2$ have been recently summarized (Varma and Amundson, 1973).

For $r_1 \neq r_2$, it does not seem possible to derive information from stability criterion (25) in terms of inlet or exit values. However, if $R_{i,m}$ and $R_{i,n}$ in Equation (8) are evaluated over the entire range of the a priori bounds (14), then (25) may be rearranged as

$$B_2 < \frac{[\mu_1 R_{2,n} - \mu_2 \beta R_{1,m}] + \sqrt{[\mu_1 R_{2,n} + \mu_2 \beta R_{1,m}]^2 + 2\mu_1\mu_2\,|\beta|\,R_{1,m}R_{2,n} \exp(|r_1 - r_2|/2)}}{R_{1,m}[2\beta R_{2,n} + |\beta|\,R_{2,m} \exp(|r_1 - r_2|/2)]} \quad (34)$$

and it is obvious from the above discussion that (34) ensures both uniqueness of the steady state and its asymptotic stability. Here,

$$\mu_i \equiv \lambda_{1,i} + (r_i^2/4) \quad (35)$$

while

$$\beta = (-\Delta H) D C_0/\lambda T_0, \quad (36)$$

where $\beta r_2/r_1 = B_1/B_2$ is the maximum adiabatic temperature rise.

NOTATION

$B[\ ]$ = boundary operator, defined by (22)
B_1 = $(-\Delta H)\,k\,L^2\,C_0/c_p\,\rho\,D\,T_0$
B_2 = $k\,L^2/D$
c_p = fluid heat capacity
C = concentration of key reactant
$\underline{\underline{C}}$ = matrix in stability analysis
$\hat{\underline{\underline{C}}}$ = $(\underline{\underline{C}} + \underline{\underline{C}}^T)/2$
D = effective mass diffusivity
E = activation energy
ΔH = heat of reaction
k = frequency factor
K_i = constants
L = reactor length
n = dimensionless temperature, T/T_0
p = constant
$P_i(x)$ = $\exp(-K_i x)$
$\underline{\underline{P}}$ = matrix, defined by (6)
q = dimensionless activation energy, $E/R_g\,T_0$
$q(x)$ = function, defined by (19)
q_1 = constant, defined by (19)
$Q_i(x)$ = $\exp(-r_i x)$
r_1 = Peclet number for heat transfer, $v\,c_p\,\rho\,L/\lambda$
r_2 = Peclet number for mass transfer, $v\,L/D$
R = dimensionless reaction rate, $y \exp(-q/n)$
R_1 = $\partial R/\partial n|_s$
R_2 = $\partial R/\partial y|_s$
R_g = gas constant
t = dimensionless time, $D\theta/L^2$
u_1 = $n(x,t) - n_s(x)$
u_2 = $y(x,t) - y_s(x)$
$\underline{u}$ = $(u_1, u_2)^T$
$\tilde{u}$ = function, defined by (16)
$\tilde{v}$ = function, defined by (16)
v = flow velocity
V = Liapunov functional
x = dimensionless distance, z/L
y = dimensionless concentration, C/C_0
z = distance from reactor inlet

Greek Letters

β = $(-\Delta H)\,D\,C_0/\lambda\,T_0$
λ = effective thermal conductivity
λ_1 = least eigenvalue satisfying (23)
μ_i = $\lambda_{1,i} + (r_i^2/4)$
ρ = fluid density
θ = time

Subscripts

0 = inlet value

1 = heat transfer
2 = mass transfer
m = maximum value
n = minimum value
s = steady state

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Multicomponent Mass Transfer in Turbulent Flow

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The purpose of this note is to give a method for predicting multicomponent eddy diffusivities and to correct the recent analysis of von Behren et al. (1972). The new results are simpler and more accurate.

PREDICTION OF EDDY DIFFUSIVITIES

The diffusion equations of a nonreacting fluid in laminar or turbulent flow can be written in an uncoupled form (Stewart and Prober, 1964; Toor, 1964):

$$\frac{\partial \check{x}_i}{\partial t} + (\nabla \bullet v^\star \check{x}_i) = \check{D}_i \nabla^2 \check{x}_i \quad i = 1, \dots n-1 \quad (1)$$

Here the $\check{D}_i$ are the inverted eigenvalues of Stewart and Prober's matrix $[A]$, and the $\check{x}_i$ are the corresponding transformed compositions. The $\bar{x}_i$ of that paper are written as $\check{x}_i$ here, to distinguish them from time-smoothed quantities.

Time-smoothing Equation (1), we get

$$\frac{\partial \bar{\check{x}}_i}{\partial t} + (\nabla \bullet \bar{v}^\star \bar{\check{x}}_i) = \check{D}_i \nabla^2 \bar{\check{x}}_i - (\nabla \bullet \overline{v^{\star\prime} \check{x}_i'}) \quad i = 1, \dots n-1 \quad (2)$$

If the correlation term is rewritten with an eddy diffusivity tensor $\check{\mathbf{D}}_i^{(t)}$, Equation (2) becomes

$$\frac{\partial \bar{\check{x}}_i}{\partial t} + (\nabla \bullet \bar{v}^\star \check{x}_i) = \check{D}_i \nabla^2 \bar{\check{x}}_i + (\nabla \bullet \check{\mathbf{D}}_i^{(t)} \bullet \nabla \bar{\check{x}}_i) \quad i = 1, \dots n-1 \quad (3)$$

Equations (1), (2), and (3) are analogous to the following equations of binary systems:

$$\frac{\partial x_A}{\partial t} + (\nabla \bullet v^\star x_A) = \mathcal{D}_{AB} \nabla^2 x_A \quad (4)$$

$$\frac{\partial \bar{x}_A}{\partial t} + (\nabla \bullet \bar{v}^\star \bar{x}_A) = \mathcal{D}_{AB} \nabla^2 \bar{x}_A - (\nabla \bullet \overline{v^{\star\prime} x'_A}) \quad (5)$$

$$\frac{\partial \bar{x}_A}{\partial t} + (\nabla \bullet \bar{v}^\star \bar{x}_A) = \mathcal{D}_{AB} \nabla^2 \bar{x}_A + (\nabla \bullet \mathbf{D}_{AB}^{(t)} \bullet \nabla \bar{x}_A) \quad (6)$$

Thus, any solution of Equation (4), (5), or (6) provides a solution of Equation (1), (2), or (3) in the same flow field, satisfying equivalent boundary conditions. The