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Manuscript received April 6, 1972; revision received July 11, 1972; note accepted July 12, 1972.

Sufficient Conditions for Uniqueness and the Local Asymptotic Stability of Adiabatic Tubular Reactors

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The stability of adiabatic tubular reactor with axial mixing (ATRAM) has been studied first numerically by Raymond and Amundson (1964) and later by a number of investigators (Amundson, 1965; Nishimura and Matsubara, 1969; Berger and Lapidus, 1968; Clough and Ramirez, 1972) by solving a set of ordinary differential equations, an integral equation, or an inequality condition, all of which require the steady state profiles. Thus, their methods must also rely upon numerical solutions. The uniqueness of the steady state has been investigated by Luss and Amundson (1967) and Luss (1968) for an ATRAM and by Matsuyama (1970) for an ATRAM with recycle. The objective of this study is to obtain, using the approach used by Clough and Ramirez (1972), more convenient stability and uniqueness conditions than those currently available, that is, in terms of inlet or outlet temperature and/or system parameters. We also consider the case of equal Peclet number as a special case of the more general case of unequal Peclet numbers.

SUFFICIENT CONDITION FOR STABILITY IN TERMS OF STEADY STATE PROFILES

Consider an adiabatic tubular reactor with axial mixing (ATRAM) in which a single first-order, irreversible reaction is taking place. The dimensionless heat and mass balance equations are (Clough and Ramirez, 1972)

$$\frac{\partial n}{\partial t} = \frac{p_M}{p_H}\frac{\partial^2 n}{\partial x^2} - p_M\frac{\partial n}{\partial x} + B_1 f \tag{1}$$

$$\frac{\partial y}{\partial t} = \frac{\partial^2 y}{\partial x^2} - p_M\frac{\partial y}{\partial x} - B_2 f \tag{2}$$

with boundary conditions

$$-\frac{\partial n(0)}{\partial x} = p_H\,[1 - n(0)] \qquad -\frac{\partial y(0)}{\partial x} = p_M\,[1 - y(0)] \tag{3}$$

$$\frac{\partial n(1)}{\partial x} = 0 \quad \frac{\partial y(1)}{\partial x} = 0 \tag{4}$$

The sufficient condition for stability as derived by Clough and Ramirez (1972) and corrected by Liou et al. (1972) is

$$Q(x) = B_1 f_n(x)/p_H p_M < 1/4 \quad \text{for all } x \in [0, 1] \tag{5}$$

where

$$f_n(x) = \left.\frac{\partial f}{\partial n}\right|_{s.s.} = \frac{q y_s(x)}{n_s^2(x)}\, e^{-q/n_s(x)} \tag{6}$$

It is noted that $f_n(x)$ is determined from the steady state solutions of Equations (1) through (4).

Clough and Ramirez (1972) and Nishimura and Matsubara (1969) carried their stability criteria to this point, that is, in terms of steady state profiles. Starting from this point we further develop criteria in terms of exit or inlet temperature and also in terms of system parameters only. We do this by estimating the supremum of $Q(x)$ from the steady state equations.

Considering Inequality (5) we have

$$\operatorname*{Sup}_{0 \leq x \leq 1} f_n(x) \leq \frac{p_H p_M}{4\,B_1} \tag{7}$$

Therefore, the problem is reduced to the estimation of $\operatorname{Sup} f_n(x)$.

SUFFICIENT CONDITION FOR STABILITY IN TERMS OF THE EXIT OR INLET TEMPERATURE

Two different cases are considered, Cases I and II.

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Case I: Equal heat- and mass-transfer Peclet numbers, that is, $p_H = p_M = p_e$

It is noted that at steady state [Raymond and Amundson (1964)],

$$y = \frac{B_2}{B_1} (n_{\lim} - n) \quad (8)$$

where

$$n_{\lim} = 1 + \frac{B_1}{B_2} \quad (9)$$

Substituting Equation (8) into Equation (6) we obtain

$$f_n(x) = \frac{B_2 q}{B_1} \cdot \frac{n_{\lim} - n}{n^2} e^{-q/n} \quad (10)$$

The necessary condition for the maximum value of $f_n(x)$ is $[df_n(x)/dx]|_{x=x^*} = 0$, that is, either

$$n(x^*) = \left(n_{\lim} + \frac{q}{2}\right) - \left[n^2_{\lim} + \left(\frac{q}{2}\right)^2\right]^{1/2} \triangleq \bar{n} \quad (11)$$

or

$$n(x^*) = n(1) \quad (12)$$

For this system $n(x)$ is a monotonically increasing function, $n(1) \geqq n(x)$, and the sufficient condition must be examined for three cases,

(i) If $n(1) < \bar{n}$, then $x^* = 1$ and $d^2f_n(x)/dx^2|_{x=1} < 0$

The supremum occurs at the exit, $x = 1$.

(ii) If $n(1) \geqq \bar{n} \geqq n(0)$, then $d^2f_n(x)/dx^2|_{x=1} > 0$
$d^2f_n(x)/dx^2|_{n(x)=\bar{n}} < 0$

The supremum occurs at $n(x) = \bar{n}$.

and (iii) If $\bar{n} \leqq n(0)$, the supremum occurs at $n(x) = n(0)$ because $df_n(x)/dx$ is always negative for all $x \in (0, 1)$. Therefore, the following statement is true.

The reactor system, Equation (1) through (4), with equal heat- and mass-transfer Peclet numbers, is locally stable, if the inequality condition

$$Q^* = \frac{B_2 q}{p_e^2} \cdot \frac{n_{\lim} - n}{n^2} e^{-q/n} < 1/4 \quad (13)$$

is satisfied where

$$n = \begin{cases} n(0) & \text{if } n(0) \geqq \bar{n} \\ n(1) & \text{if } n(1) < \bar{n} \\ \bar{n} & \text{if } n(1) \geqq \bar{n} \geqq n(0) \end{cases} \quad (14)$$

Case II: Unequal heat- and mass-transfer Peclet numbers, that is, $p_H \neq p_M$

The necessary condition is

$$\frac{df_n(x^*)}{dx} = \frac{q}{n^2} e^{-q/n} \left[\frac{dy}{dx} + \frac{y(q-2n)}{n^2} \frac{dn}{dx}\right] \Bigg|_{x=x^*} = 0 \quad (15)$$

In general, the solutions of Equation (15) are not unique. One of these solutions is $x^* = 1$, the others may be at $x = \xi$, where $\xi \in (0, 1)$. Since $p_H \neq p_M$, we cannot derive an analytical relationship between $y(x)$ and $n(x)$. However, for some limiting cases, for example,

If $\quad E \leqq 2\,RT_0$

then $\quad q = \dfrac{E}{RT_0} \leqq 2 \leqq 2n(x)$

and $\quad \dfrac{dy}{dx} + \dfrac{y(q-2n)}{n^2} \dfrac{dn}{dx} \leqq 0$

For this limiting case, $df_n(x)/dx < 0$ for all $x \in (0, 1)$, and the supremum occurs at $x = 0$. Therefore, we can state the following:

If the reactor system, Equations (1) through (4), has the constraint $E \leqq 2\,RT_0$, the sufficient condition for local asymptotic stability is

$$Q^* = \frac{B_1 q}{p_H p_M} \cdot \frac{y(0)}{n^2(0)} e^{-q/n(0)} < 1/4 \quad (16)$$

A SUFFICIENT CONDITION FOR UNIQUENESS IN TERMS OF SYSTEM PARAMETERS ONLY

Sufficient condition for stability, Inequality (5), is extended to determine the uniqueness of the steady state solution. The sufficient condition is based on system parameters only.

Case I: $p_M = p_H = p_e$

For this case we have

$$Q^* = \sup_{1 \leqq n \leqq n_{\lim}} \frac{B_2 q}{p_e^2} \cdot \frac{n_{\lim} - n}{n^2} e^{-q/n} < 1/4$$

It is easy to show that the supremum occurs at

$$n = \begin{cases} 1 & \text{if } \bar{n} \leqq 1 \\ \bar{n} & \text{if } \bar{n} > 1 \end{cases} \quad (17)$$

Therefore, Inequality (13) can be modified as follows. The reactor system with equal heat- and mass-transfer Peclet numbers is locally stable, if the sufficient condition

$$Q^* = \frac{B_2 q}{p_e^2} \cdot \frac{n_{\lim} - n}{n^2} e^{-q/n} < 1/4 \quad (18)$$

is satisfied, where n satisfies Equation (17).

Note that Inequality (18) is independent of steady state profiles. Since at least one of the multisteady states is unstable (Ivanov et al., 1967), the solution of the steady state equations for a system which has been proved stable must be unique. Thus, Inequality (18) is also a sufficient condition for uniqueness.

Case II: $p_H \neq p_M$

For this case, the sufficient condition for local asymptotic stability is given by Inequality (5),

$$Q^* = \sup_{0 \leqq x \leqq 1} \frac{B_1 q}{p_H p_M} \cdot \frac{y}{n^2} e^{-q/n} < 1/4$$

Note that

$$Q^* \leqq \frac{B_1 q}{p_M p_M} \cdot \sup_{0 \leqq y \leqq 1} y \cdot \sup_{1 \leqq n \leqq n_{\lim}} e^{-q/n}/n^2$$

$$= \frac{B_1 q}{p_M p_H} \sup_{1 \leqq n \leqq n_{\lim}} e^{-q/n}/n^2$$

It can be shown that the supremum occurs at

$$n = \begin{cases} 1 & \text{if } q/2 < 1 \\ q/2 & \text{if } 1 < q/2 < n_{\lim} \\ n_{\lim} & \text{if } q/2 > n_{\lim} \end{cases} \quad (19)$$

Therefore the sufficient condition for uniqueness is

$$\frac{B_1 q}{p_M p_H} \cdot \frac{1}{n^2} \cdot e^{-q/n} < 1/4 \quad (20)$$

where n satisfies Equation (19).

THE EFFECT OF SYSTEM PARAMETERS ON THE SUFFICIENT CONDITION FOR UNIQUENESS

It is noted that when some of the system parameters change, it is not necessary to resolve the steady state equations as discussed below.

1. If the reactor length L is changed, B_2, p_H and p_M are changed. But Q^* does not change, thus the sufficient condition for uniqueness, Inequality (18) or (20), is independent of reactor length. This is a conservative result due to the extension of the stability condition to obtain the uniqueness condition and corresponds to the case in which the reactor is operated at a very high conversion. However, the sufficient condition for stability, Inequality (13), or (16), shows that the possibility of multiple steady states can be eliminated by decreasing the reactor length.

2. If the linear velocity is changed from v_1 to v_2 then the effective thermal diffusivity α is changed and Q_2^* is given by

$$Q_2^* = \frac{v_1^2}{v_2^2} \frac{\alpha_2}{\alpha_1} Q_1^*$$

For highly turbulent flow where the thermal diffusivity is proportional to velocity [Kramers and Westerterp, 1963], Q^* is inversely proportional to the velocity and thus uniqueness of steady state can be assured by increasing the velocity.

3. If inlet conditions c_0 and T_0 are changed, it is no longer possible to obtain by inspection Q_2^* from the known Q_1^*. However, it can be shown that the possibility of multiple steady states can be eliminated by diluting the feed or by decreasing the inlet temperature.

DISCUSSION

A Liapunov technique has been used to derive a stability condition for adiabatic tubular reactors with axial dispersion. A sufficient condition is obtained, and the sufficient condition is extended to determine the criterion of uniqueness.

The stability condition in terms of the steady state profiles and system parameters, Inequality (5), applies as well to the case of unequal Peclet numbers. This condition is reduced to stability conditions in terms of system parameters and the steady state outlet or inlet temperature, Inequalities (13) and (16). Inequality (16) applies to the case of unequal Peclet numbers under a restriction, $E \leq 2\, RT_0$. However, the steady state exit or inlet temperature can only be obtained by solving for the entire steady state profiles.

Our results for uniqueness, in terms of system parameters only, apply as well to the case of unequal Peclet numbers and correspond to the result of Luss and Amundson (1967) when Peclet numbers are equal. However, the result of Luss and Amundson [their Equation (85)] is left in terms of a yet to-be-determined supremum of a complicated function of dimensionless temperature.

For highly turbulent flow in which the mechanisms of mass and heat transfer are the same (convective), mass- and heat-transfer Peclet numbers become equal, but in general they are not equal as pointed out by Klinkenberg and Mooy (1948). While we have obtained results for the general case of unequal Peclet numbers, most of the previous work took advantage of equal Peclet numbers, an assumption under which the system equations become uncoupled and hence lead to a mathematically more convenient problem. However, this is not the universal physical situation.

ACKNOWLEDGMENT

Purdue Research Foundation provided a fellowship for C. T. Liou.

NOTATION

B_1	=	parameter group, $\dfrac{(-\Delta H) c_0 k_0 L^2}{\rho\, C_p\, E_a\, T_0}$
B_2	=	parameter group, $k_0\, L^2/E_a$
f	=	dimensionless reaction rate, $f = y\, e^{-q/n}$
n	=	dimensionless temperature, $n = T/T_0$
p_M	=	Peclet number for mass transfer, $p_M = vL/E_a$
p_H	=	Peclet number for heat transfer, $p_H = vL/\alpha$
p_e	=	Peclet number for mass and heat transfer, when equal
q	=	dimensionless activation energy, $q = E/RT_0$
t	=	dimensionless time $t = E_a\theta/L^2$
x	=	dimensionless spatial variable, $x = z/L$
y	=	dimensionless concentration, $y = c/c_0$
$*$	=	referred to optimal quantities

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Manuscript received June 22, 1972; communication accepted June 23, 1972.