Steady-State Multiplicity Caused by Nonideal Mixing in Two Isothermal CSTR's

C. T. Liou
Y. S. Chien
Department of Chemical Engineering
National Taiwan Institute of Technology
Taipei, Taiwan 10772, R.O.C.

The existence of multiple steady state in nonlinear models has received considerable attention in reaction engineering literature: since the early work of Liljenroth (1918), there has been much research analyzing this multiplicity in chemical reacting systems. Recent comprehensive reviews of this phenomenon were presented by Mobidelli et al. (1986) and Razon and Schmitz (1987). Thus, the steady state and transient behavior in individual CSTR's (continuously stirred tank reactors) have been thoroughly discussed.[1]

The problem of multiplicity and transient behavior in a couple of CSTR's in series was not the subject of systematical discussion until 1980. Kubicek et al. (1980) used a numerical method to analyze multiplicity and stability in a sequence of two nonadiabatic-nonisothermal CSTR's. They discovered that seven steady states are the maximum number of multiple steady states in such a system. Later, Varma (1980), in a similar study on the number and stability of steady states in a sequence of two CSTR's, showed that its maximum number is seven. Svoronos et al. (1982), in their study on the complex dynamic behaviors of steady state, also found that in such a system its maximum number is seven. In addition, Dangelmayr and Stewart (1984) deduced the pattern of steady-state multiplicity of the system using the singularity theory. However, almost all this research was carried out on the basis that only the ideal mixing takes place in CSTR's. They failed to consider that the ideal mixing of their models cannot be obtained in real CSTR's.

The purpose of this note is to extend the research in the direction of real, nonideal mixing situation. We used the nonideal mixing model developed by Lo and Cholette (1983) to examine how steady-state multiplicity happened in two CSTR's in series where the reaction rate expression is $-\gamma a = kCa/(1 + KCa)^2$. When the two CSTR's are in series and under nonideal mixing situation, the necessary and sufficient conditions for multiple steady states in the individual CSTR's are discussed. We found that, under nonideal mixing in the two CSTR's in series, the maximum number of steady states of multiplicity is nine. This is a remarkable discrepancy as compared to that when such a system is under ideal mixing, the maximum number being seven.

Mathematical Model

We use Cholette's model of two CSTR's coupled in series, as shown in Figure 1. The parameters m_1 and m_2 are the fractions of the total volume that are perfectly mixed in the first and second CSTR's, respectively. The parameters n_1 and n_2 are the fractions of the feed entering the zone of perfect mixing in the first and second CSTR, respectively. When m_1, m_2, n_1 and n_2 are all equal to 1, both CSTR's are in an ideal mixing situation. When any one of above parameter is not equal to 1, the whole system is not under ideal mixing. Here, we assumed these parameters are always known by residence time distribution.

Referring to Figure 1, the mass balance equations for the first CSTR during steady state are written as

$$\frac{n_1}{m_1}\frac{1}{Da_1}(Xa_0 - Xa'_{,1}) = Xa'_{,1}/(1 + Xa'_{,1})^2 \tag{1}$$

and

$$n_1 Xa'_{,1} + (1 - n_1)Xa_0 = Xa_{,1} \tag{2}$$

and for the second CSTR,

$$\frac{n_2}{m_2}\frac{1}{Da_2}(Xa_{,1} - Xa'_{,2}) = Xa'_{,2}/(1 + Xa'_{,2})^2 \tag{3}$$

and

$$n_2 Xa'_{,2} + (1 - n_2)Xa_{,1} = Xa_{,2} \tag{4}$$

Correspondence concerning this paper should be addressed to C. T. Liou.

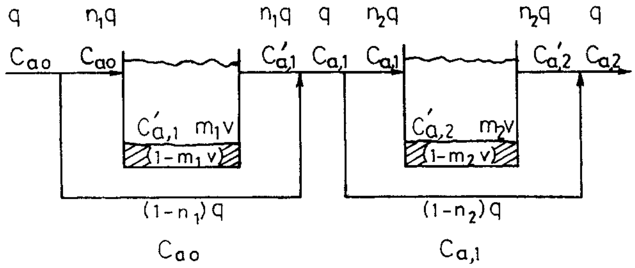

Figure 1. Cholette's model of two CSTR's coupled in series.

where

$$Xa_0 = KCa_0$$
$$Da_i = k\tau_i$$
$$\tau_i = V_i/q_i$$
$$Xa'_{,i} = KCa'_{,i}$$
$$Xa_{,i} = KCa_{,i}$$
$$i = 1, 2$$

The lefthand terms of Eqs. 1 and 3 are the dimensionless net inputs of reactant A into the first and second CSTR, respectively. The righthand terms of those equations are the dimensionless consumption rates of the chemical reaction in each CSTR.

Necessary Conditions for Multiplicity

Using the bifurcation theory, we can derive the necessary conditions for multiplicity in each CSTR. In the first tank, one of the necessary condition is calculated by simultaneously solving Eq. 1 and its derivative with respect to $Xa'_{,1}$. Then it is obtained as,

$$2Xa'^2_{,1} - Xa_0 Xa'_{,1} + Xa_0 = 0. \quad (5)$$

Similarly in the second CSTR,

$$2Xa'^2_{,2} - Xa_{,1} Xa'_{,2} + Xa_{,1} = 0. \quad (6)$$

From Eqs. 5 and 6, we easily find the following roots,

$$Xa'_{,1+}, Xa'_{,1-} = \frac{Xa_0 \pm \sqrt{Xa_0(Xa_0 - 8)}}{4} \quad (7)$$

and

$$Xa'_{,2+}, Xa'_{,2-} = \frac{Xa_{,1} \pm \sqrt{Xa_{,1}(Xa_{,1} - 8)}}{4}. \quad (8)$$

Hence, in each CSTR, one necessary condition for steady-state multiplicity is determined:

In the first tank

$$Xa_0 \geq 8 \quad (9)$$

In the second tank

$$Xa_{,1} \geq 8 \quad (10)$$

Another necessary condition for steady-state multiplicity can be found through the condition according to Perlmutter's method (1972): for the first CSTR, we can simultaneously solve Eq. 1 and its first and second derivative with respect to $Xa'_{,1}$. Thus,

$$Da_1 \geq 27\frac{n_1}{m_1}. \quad (11)$$

Similarly, for the second CSTR,

$$Da_2 \geq 27\frac{n_2}{m_2}. \quad (12)$$

From the above results, we know that the necessary conditions (Eqs. 9 and 10), under nonideal mixing, are the same as those under ideal mixing; however, the other necessary conditions (Eqs. 11 and 12), under nonideal mixing, are different from those under ideal mixing because the condition for ideal mixing is

$$Da_i \geq 27. \quad (i = 1, 2) \quad (13)$$

For the first CSTR, the difference is factor n_1/m_1, and for the second CSTR, n_2/m_2. The values of these factors affect the ordinate values Da_1 and Da_2, respectively, in the exact regions of steady-state multiplicity. In the first CSTR, when the value n_1/m_1 is larger than 1, the exact region of steady-state multiplicity shifts upward. Likewise, when the value of n_1/m_1 is smaller than 1, the exact region of steady-state multiplicity shifts downward. However, when the value of n_1/m_1 is equal to 1, the exact region of steady-state multiplicity does not shift and is the same as that under ideal mixing.

Once again, for the first CSTR, the necessary conditions under nonideal mixing are stated by conditions 9 and 11. For the second CSTR, the necessary conditions under nonideal mixing are stated by conditions 10 and 12. For the two CSTR's in series the conditions under nonideal mixing are the combination of conditions 9 and 10, and the combination of conditions 11 and 12.

Sufficient condition for multiplicity

In the reaction system, when Da_1, n_1, m_1, and Xa_0 do not satisfy the necessary conditions of multiplicity, as in Eqs. 7 and 9, there exists a unique steady state. When Da_1, n_1, m_1, and Xa_0 do satisfy the above necessary conditions, there is a condition that three steady states:

$$\text{the slope of } \overline{A_1Xa_0} \leq -n_1/(m_1Da_1) \leq \text{the slope of } \overline{B_1Xa_0}, \quad (14)$$

where A_1 and B_1 are high and low bifurcation points for Xa_0, $\overline{A_1Xa_0}$ ($\overline{B_1Xa_0}$) is the straight line that connect points A_1, (B_1), and Xa_0.

The abscissas of A_1 and B_1 are obtained through Eq. 7. The ordinate values of A_1 and B_1 are obtained by the righthand term of Eq. 1. The condition is easily identified in Figure 2, whose physical meaning is that the three steady states must occur in the range composed by $\overline{A_1Xa_0}$ and $\overline{B_1Xa_0}$.

In a similar way, the sufficient condition for the second CSTR is defined as

$$\text{the slope of } \overline{A_2Xa_{,1}} \leq -n_2/(m_2Da_2) \leq \text{the slope of } \overline{B_2Xa_{,1}}. \quad (15)$$

So long as there is no multiplicity in the first CSTR, A_2 and B_2 are high and low bifurcation points for $Xa_{,1}$, respectively. The abscissas of A_2 and B_2 are obtained by Eq. 8. The ordinate values of A_2 and B_2 are obtained by the righthand term of Eq. 3.

When multiplicity occurs in the first CSTR, the three steady states $Xa^l_{,1}$, $Xa^m_{,1}$, and $Xa^u_{,1}$, exist. So, sufficient conditions can be given as follows:

$$\text{the slope of } \overline{Xa^l_{,1}A^l_2} \leq -n_2/(m_2Da_2) \leq \text{the slope of } \overline{Xa^l_{,1}B^l_2}; \quad (16)$$

$$\text{the slope of } \overline{Xa^m_{,1}A^m_2} \leq -n_2/(m_2Da_2) \leq \text{the slope of } \overline{Xa^m_{,1}B^m_2} \quad (17)$$

and

$$\text{the slope of } \overline{Xa^u_{,1}A^u_2} \leq -n_2/(m_2Da_2) \leq \text{the slope of } \overline{Xa^u_{,1}B^u_2}. \quad (18)$$

A^l_2, B^l_2, A^m_2, B^m_2, A^u_2, and B^u_2 are high and low bifurcation points for $Xa^l_{,1}$, $Xa^m_{,1}$ and $Xa^u_{,1}$, respectively, The abscissas and ordinates of A^l_2, B^l_2, A^m_2, B^m_2, A^u_2, and B^u_2 are obtained in a similar way.

From the previous discussions, the necessary and sufficient conditions of multiplicity for the first and second CSTR are a combination of conditions 9 to 12, 14, and 16 to 18. A lack in any of the criteria (Eqs. 9 to 12, 14, and 16 to 18) would make the number of steady states smaller than nine.

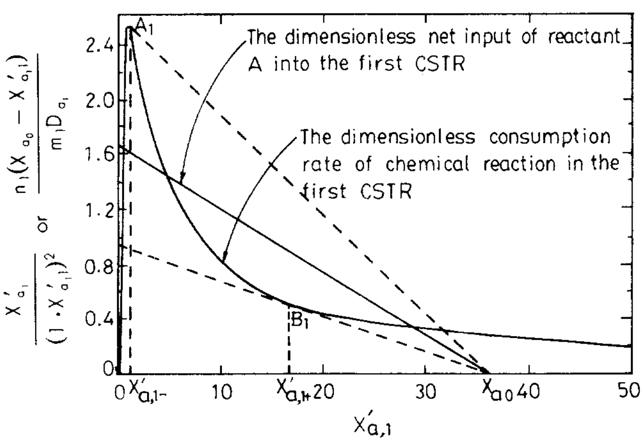

Figure 2. Condition for multiplicity.

Proof of a multiplicity of nine steady states

At steady state, the mass balance in the first CSTR is written as:

$$Da_1 = \frac{(1 + Xa_{,1})^2}{Xa_{,1}}(Xa_0 - Xa_{,1}) = F(Xa_{,1}). \quad (19)$$

Here, $F(0) = \infty$, $F(Xa_0) = 0$; when the derivative of above equation is rearranged through $Xa_{,1}$,

$$F'(Xa_{,1}) = F(Xa_{,1})\left(\frac{2}{(1 + Xa_{,1})} - \frac{1}{(Xa_0 - Xa_{,1})} - \frac{1}{Xa_{,1}}\right) = 0 \quad (20)$$

The roots of Eq. 20 are the roots of the part enclosed in brackets, which can be written as

$$\frac{-2Xa^2_{,1} + Xa_0Xa_{,1} - Xa_0}{(1 + Xa_{,1})(Xa_0 - Xa_{,1})Xa_{,1}} = 0 \quad (21)$$

In Eq. 21, roots of $Xa_{,1+}$, $Xa_{,1-}$ in the numerator are given by Eq. 7 as the whole numerator is equivalent to Eq. 5. From Eq. 7, we see the value of $Xa_{,1-}$ is always $\leq 2 < 8$. If $Xa_0 < 8$, $Xa_{1,-}$ does not exist. Furthermore, as shown in Figure 3, we see the low steady state of $Xa^l_{,1}$ is always smaller than $Xa_{,1-}$; and the order of these values is $Xa^l_{,1} < Xa_{,1-} < Xa^m_{,1} < Xa_{,1+} < Xa^u_{,1}$. So, the outlet of steady state, $Xa^l_{,1}$, is always smaller than 8, as $Xa^l_{,1} < Xa_{,1-} < 8$. It means that for $Xa^l_{,1}$ in the first CSTR multiplicity does not occur in the second CSTR because the necessary condition of multiplicity $Xa_{,1}$ is larger than 8 in the second

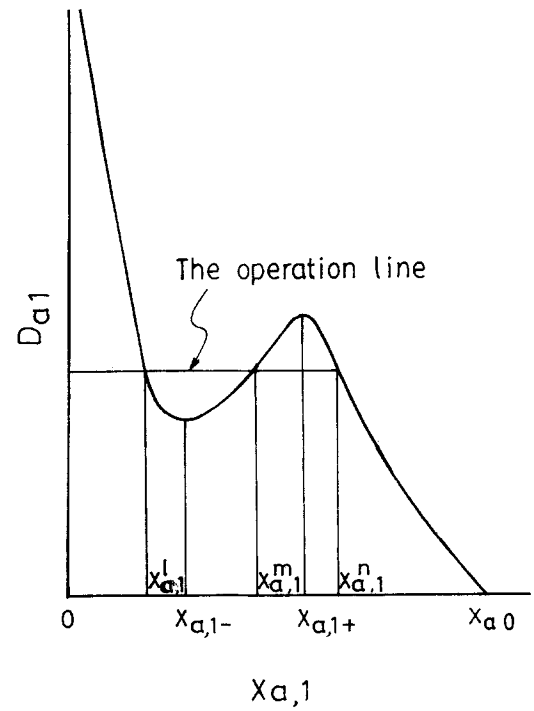

Figure 3. Low steady state of $Xa^l_{,1}$.

CSTR. However, the values of $Xa_{,1}^{m}$ and $Xa_{,1}^{u}$ may be greater than 8, equal to 8, or smaller than 8. Hence, multiplicity occurs, when the values of $Xa_{,1}^{m}$ and $Xa_{,1}^{u}$ are larger than 8. Thus, under ideal mixing in two CSTR's in series, the maximum number of steady states is seven.

Turning to nonideal mixing, $Xa'_{,1}$ corresponds to $Xa_{,1}$, so, $Xa'_{,1}$ is always smaller than 8. However, when $Xa'_{,1}$ is shifted by Eq. 2, it can make $Xa_{,1} > 8$. Thus, under nonideal mixing in two CSTR's in series, multiplicity will occur. The maximum number of steady states is nine.

Finally the sufficient conditions for multiplicity in this system are expressed as follows:

$$Da_{1*} = F(Xa'_{,1-}) \le \frac{m_1 Da_1}{n_1} \le F(Xa'_{,1+}) = Da_1^* \quad (22)$$

$$Da_{21*} = F(Xa'_{,21-}) \le \frac{m_2 Da_2}{n_2} \le F(Xa'_{,21+}) = Da_{21}^* \quad (23)$$

$$Da_{22*} = F(Xa'_{,22-}) \le \frac{m_2 Da_2}{n_2} \le F(Xa'_{,22+}) = Da_{22}^* \quad (24)$$

$$Da_{23*} = F(Xa'_{,23-}) \le \frac{m_2 Da_2}{n_2} \le F(Xa'_{,23+}) = Da_{23}^* \quad (25)$$

where Da_* and Da^* are the ordinate values at the bifurcation points ($Xa_{,-}$ and $Xa_{,+}$).

Notation

A = low bifurcation point
B = high bifurcation point
Ca = outlet concentration of reactant A of CSTR, mol/L
Ca' = concentration of reactant A in active space of CSTR, mol/L
Ca_0 = feed concentration of reactant A, mol/L
Da = Damkohler number, dimensionless = $k\tau$
F = function, defined in Eq. 19
K = constant, mol/L^{-1}
k = reaction rate constant, s^{-1}
m = fraction of the total volume which is perfectly mixed
n = fraction of the feed entering the zone of perfect mixing
q = flow rate, L/s
V = reactor volume, L
Xa_0 = KCa_0, dimensionless
Xa' = KCa', dimensionless
Xa = KCa, dimensionless

Greek letters

τ = reactor holdup time, s

Superscripts

l = lower steady state
m = middle steady state
u = upper steady state
$*$ = at the abscissa $Xa_{,i+}$ ($i = 1, 2$)

Subscripts

1 = first CSTR
2 = second CSTR
$_*$ = at the abscissa $Xa_{,i-}$ ($i = 1, 2$)
ij = steady state within the ith CSTR caused by the jth steady state in the $(i-1)$th CSTR (j = 1, 2 and 3 for lower, middle and upper steady state)

Literature Cited

Dangelmayr, G., and I. Stewart, "Sequential Bifurcation in Continuous Stirred Tank Chemical Reactors Coupled in Series," *SIAM J. Appl. Math.* **45**, 895 (1985).

Kubicek, M., H. Hofmann, V. Hlavacek, and J. Sinkule, "Multiplicity and Stability in a Sequence of Two Nonadiabatic, Nonisothermal CSTR's," *Chem. Eng. Sci.*, **35**, 987 (1980).

Liljenroth, F. G., "Starting and Stability Phenomena of Ammonia Oxidation and Similar Reactions," *Chem. Met. Eng.*, **19**, 287 (1918).

Lo, S. N., and A. Cholette, "Multiplicity of a Conversion in a Cascade of Imperfectly Stirred Tank Reactors," *Chem. Eng. Sci.*, **38**, 367 (1983).

Morbidelli, M., A. Varma, and R. Aris, "Reactor Steady State Multiplicity and Stability," *Chemical Reaction and Reactor Engineering*, eds., J. J. Carberry and A. Varma, Chap. 14, Chemical Industries/26, Marcel Dekker, New York (1986).

Perlmutter, D. D., *Stability of Chemical Reactors*, Prentice-Hall, Englewoods Cliffs, NJ (1972).

Razon, L. F., and R. A. Schmitz, "Multiplicity and Instability in Chemical Reacting Systems: a Review," *Chem. Eng. Sci.*, **43**, 1005 (1987).

Svoronos, S. R., R. Aris, and G. Stephenpoulos, "On the Behavior of Two Stirred Tanks in Series," *Chem. Eng. Sci.*, **37**, 357 (1982).

Varma, A., "On the Number and Stability of State States of a Sequence of Continuous Stirred Tank Reactors," *Ind. Eng. Chem. Fundam.*, **19**, 316 (1980).

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