

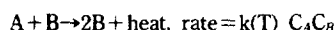
# APPLICATION OF SINGULARITY THEORY TO A NON-ISOTHERMAL CSTR WITH AN AUTOCATALYTIC REACTION

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**Abstract**—The steady-state behavior is investigated for a non-isothermal, non-adiabatic CSTR in which an autocatalytic reaction takes place with kinetic scheme



Singularity theory is applied to find the maximal number of steady-state solutions and to determine the regions in the parameter space corresponding to these solutions. The parameter space is divided into four regions corresponding to four types of different steady-state structure and it is shown that multiple steady-states (up to three) exist for some set of parameter values.

**Key words:** Singularity Theory, Autocatalytic Reaction, Steady-State Multiplicity, Bifurcation Diagram, Non-Isotherm CSTR

## INTRODUCTION

Steady-state multiplicity can be observed in many chemically reacting systems. It has been thought that steady-state multiplicity is very important for the optimum operation and control of chemical reactors. While this phenomenon can be found in various types of chemical reactors, lumped-parameter systems such as CSTR have been the main subject due to their ease of analysis. The multiplicity features of systems in which a single chemical reaction takes place have been studied extensively in both theoretical and experimental aspects [1-3]. However, as the chemical reaction system becomes more complicated [4-6], it becomes more difficult to analyze the system because a large number of parameters are involved.

To overcome such difficulties, Golubitsky and Keyfitz [7] introduced the singularity theory which is a powerful method for determining the multiplicity features of a chemically reacting system. More recently, Balakotaiah and Luss [8-11] developed a systematic method of applying the singularity theory to various chemical reacting systems.

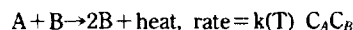
Meanwhile, the autocatalytic reaction has been considered as an important subject in many works [12-24]. Singularity theory has been applied to this autocatalytic reaction to examine the steady-state multiplicity features [25-31]. Previous works on this system have not considered the non-isothermal case until Kay et al. [26] who analyzed the steady-state behavior with some simplifying assumptions concerning the temperature dependence and the operating conditions.

In this work, the singularity theory is applied to the non-isothermal CSTR in which a quadratic autocatalysis is taking place. It will be shown that a rather simple steady-state behavior can be obtained without the simplifying assumptions which were introduced

by Kay et al. [26].

## MATERIAL AND ENERGY BALANCES

The quadratic autocatalytic reaction which is to be considered in this study has the following kinetic scheme:



When this reaction is taking place in a non-isothermal, non-adiabatic CSTR, the material balance equation for each of the reactants may be written in the form

$$V \frac{dC_A}{dt} = q(C_{A_f} - C_A) - V k C_A C_B \quad (1)$$

$$V \frac{dC_B}{dt} = q(C_{B_f} - C_B) + V k C_A C_B \quad (2)$$

and the energy balance equation becomes

$$\rho C_p V \frac{dT}{dt} = q \rho C_p (T_f - T) - U a (T - T_c) + (-\Delta H) V k C_A C_B \quad (3)$$

where  $k$  is the Arrhenius rate constant expressed as

$$k = k_0 \exp(-E/RT)$$

Here,  $C_A$  and  $C_B$  denote the concentrations of A and B, respectively, while  $T$ ,  $q$  and  $V$  represent the temperature, the flow rate and the reactor volume, respectively. Other symbols are defined in the nomenclature.

Steady-state equations can be obtained from Eqs. (1) to (3) with the left hand sides equal to zero. At steady-state conditions, Eqs. (1) through (3) may be reduced to a single equation for the temperature, which should be involved with the following dimensionless groups:

$$Y = -\frac{E}{RT}, \quad Da = \frac{V k_0 C_{A_f}}{q}, \quad \mu = \frac{RT_m}{E}$$

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$$\gamma = \frac{C_{Bf}}{C_{Af}}, \quad \beta = \frac{RC_A(-\Delta H)}{E\rho C_p(1+H)} \quad (4)$$

where

$$T_m = \frac{T_f + HT_f}{1+H}, \quad H = \frac{Ua}{q\rho C_p}$$

In this case, the reduced steady-state equation for the dimensionless temperature is

$$F(Y, Da, \mathbf{p}) = Da \exp(Y) \{(\beta + \mu)Y + 1\} \{(\mu - \beta\gamma)Y + 1\} - \beta Y(1 + \mu Y) = 0 \quad (5)$$

where  $\mathbf{p}$  is a vector of three dimensionless parameters  $\mu$ ,  $\beta$  and  $\gamma$ . We note that in the feasible region of the parameter space,  $Da$ ,  $\mu$  and  $\beta$  are positive and  $\gamma$  is non-negative while  $Y$  is negative. The Damköhler number  $Da$  is taken as the bifurcation parameter in this study.

It is to be noted at this point that the way of choosing dimensionless groups in this study is different from that of Kay et al. [26]. While we take the dimensionless temperature as  $Y = -E/RT$ , they defined the dimensionless temperature  $\theta$  as  $\theta = (T - T_0)E/RT_0^2$  ( $T$ : inflow temperature), and made an approximation of  $\varepsilon\theta \ll 1$  (where  $\varepsilon = RT_0/E$ ) to express the exponential term in the Arrhenius rate constant as  $e^\theta$ . This was necessary for an analytic treatment of their model.

### SINGULARITY ANALYSIS

Since the function  $F(Y, Da, \mathbf{p})$  given by Eq. (5) is continuous and differentiable as many times as necessary, we may regard it as a smooth mapping. To determine the local qualitative features of  $F(Y, Da, \mathbf{p})$  in Eq. (5) by applying the singularity theory, it is required to find a simpler mapping  $G$  that is contact equivalent to the mapping  $F$ . The mapping  $G$  can be found by using several equality and inequality conditions about the mapping  $F$ , where the equality conditions are called the defining conditions while the inequality conditions are called the non-degeneracy conditions. The actual procedures of obtaining the mapping  $G$  by applying these conditions have been established by Golubitsky and Keyfitz [7].

The defining conditions of  $F$  can be found by considering the singularity of highest order. In this case the defining conditions are

$$F = \frac{\partial F}{\partial Y} = \frac{\partial^2 F}{\partial Y^2} = \frac{\partial F}{\partial Da} = 0 \quad (6)$$

These simultaneous equations can be solved analytically (but with lengthy manipulations) to give a solution in parametric form:

$$\begin{aligned} Y^\circ &= -1/\mu \\ Da^\circ &= \exp(1/\mu) \\ \gamma^\circ &= 0 \\ \beta^\circ &= \mu^2 \end{aligned} \quad (7)$$

At this singular point,

$$\frac{\partial^3 F}{\partial Y^3} \cdot \frac{\partial^2 F}{\partial Y \partial Da} \neq 0 \quad (8)$$

which is the non-degeneracy condition of  $F$ . Eq. (7) represents the most degenerate singular point that lives in the feasible region. All the possible geometric structures of the function  $F$  are

obtained by certain perturbations of a variable in the neighborhood of this singular point.

According to Golubitsky and Keyfitz [7], the mapping  $F$  is contact equivalent to the mapping  $G$  represented by

$$G(x, \lambda) = x^3 + \lambda x \quad (9)$$

in the neighborhood of this singular point. However, because the mapping  $G$  is contact equivalent to the mapping  $F$  only in the neighborhood of this singular point, all the perturbations of independent direction originating from this point cannot be represented by  $G(x, \lambda)$ . Therefore, we must obtain the universal unfolding that can represent all the perturbations of independent direction. The universal unfolding of  $G(x, \lambda)$  is given by

$$G(x, \lambda, \alpha) = x^3 + \lambda x + \alpha_1 + \alpha_2 x^2 \quad (10)$$

where  $\alpha$  is a vector of parameters. The mapping  $G(x, \lambda)$  is usually called the pitchfork bifurcation.

According to Golubitsky and Schaeffer [32-33], all the possible boundaries of the region in the parameter space corresponding to each of the bifurcation diagrams can be obtained by examining the three types of varieties; i.e., hysteresis, isola and double-limit varieties. In this case, the double-limit variety does not exist. The hysteresis variety is the set of all points in the plane  $(\alpha_1, \alpha_2)$  satisfying the conditions

$$G = \frac{\partial G}{\partial x} = \frac{\partial^2 G}{\partial x^2} = 0 \quad (11)$$

along with Eq. (10). Whereas the isola variety is given by the set of all points satisfying the conditions

$$G = \frac{\partial G}{\partial x} = \frac{\partial G}{\partial \lambda} = 0 \quad (12)$$

The result has been well established as shown in Fig. 1 [8]. From Fig. 1, we see that the maximum number of steady-states is three. Also the bifurcation diagrams in Fig. 1 represent all the possible structures of bifurcation diagram of  $F$ .

The bifurcation sets of  $F$  can be obtained by solving the following hysteresis and isola variety equations.

$$F = \frac{\partial F}{\partial Y} = \frac{\partial^2 F}{\partial Y^2} = 0 \quad (13)$$

$$F = \frac{\partial F}{\partial Y} = \frac{\partial F}{\partial Da} = 0 \quad (14)$$

The hysteresis and isola varieties obtained by Eqs. (13) and (14) are shown in Fig. 2(a). The point (s) in Fig. 2(a) represents the singular point, and the curve originating from this point is a hysteresis variety. Since the hysteresis variety equation cannot be solved analytically, a numerical scheme is adopted here. The isola variety is given by  $\gamma = 0$ , namely, the  $\mu$ -axis. The relation  $\mu = \beta\gamma$  is depicted by the dashed line in Fig. 2(a). When this line is crossed, one isolated curve appears or disappears from the feasible region of  $Y$ . Thus this line acts as an isola variety.

When  $\gamma \rightarrow \infty$ , the hysteresis variety has an asymptotic value of  $\mu$  which is determined from Eq. (13) as

$$\mu^* = \frac{-\beta + \sqrt{\beta(\beta+1)}}{2} \quad (15)$$

On the other hand, the value of  $\mu$  at the singular point of highest order is given by

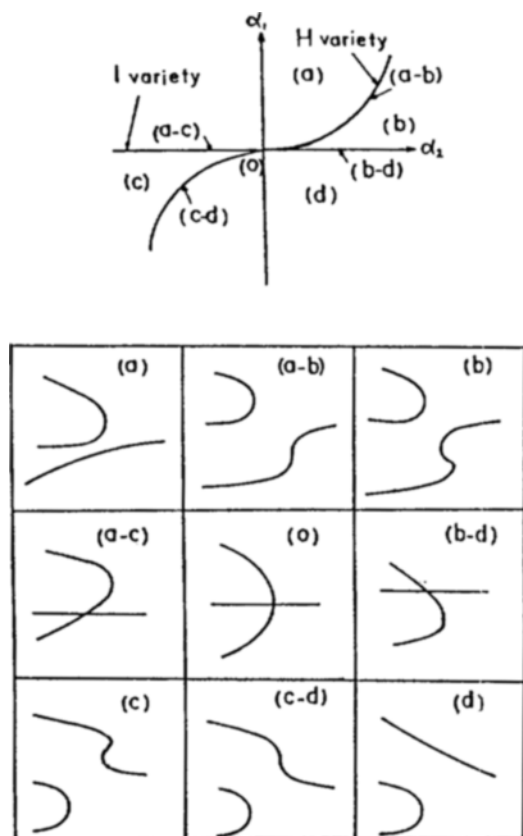


Fig. 1. Classification of the bifurcation diagrams in the case of pitchfork.

$$\mu^0 = \sqrt{\beta} \quad (16)$$

Since  $\mu^* < \mu^0$  for all values of  $\beta > 0$ , we always have the hysteresis variety as shown in Fig. 2(a).

The bifurcation diagrams corresponding to each region of  $(\mu, \gamma)$  plane are shown in Fig. 2(b) in which the vertical axis represents the dimensionless temperature,  $\theta$  ( $=RT/E$ ). It is clearly seen that the maximum number of steady-states is three.

Compared to the results by Kay et al. [26], Fig. 2 shows much simpler bifurcation sets and steady-state behavior. This simpler feature seems to be entirely due to the different way of choosing dimensionless groups. As we use different dimensionless groups and choose the bifurcation parameter so that its variation causes changes in the dimensionless parameters in the model of Kay et al. [26], it is not allowed to compare the steady-state patterns and the shape of bifurcation sets directly with those of Kay et al. [26]. Nevertheless, the maximum number of steady-states remains unchanged by the way of choosing dimensionless groups.

## SPECIAL CASES

### 1. No Catalyst in the Feed ( $\gamma=0$ )

When  $C_{Bf}=0$ , 'no reaction' is one of the possible steady-states. This trivial solution is usually called "washout". On the other hand, non-trivial solutions exist when the catalyst B is charged initially into the reactor as a seed or there is another reaction which produces B, because this originally present or reaction-produced catalyst ignites the autocatalytic reaction. Therefore, multiple steady-states are expected with "washout" as one of the pos-

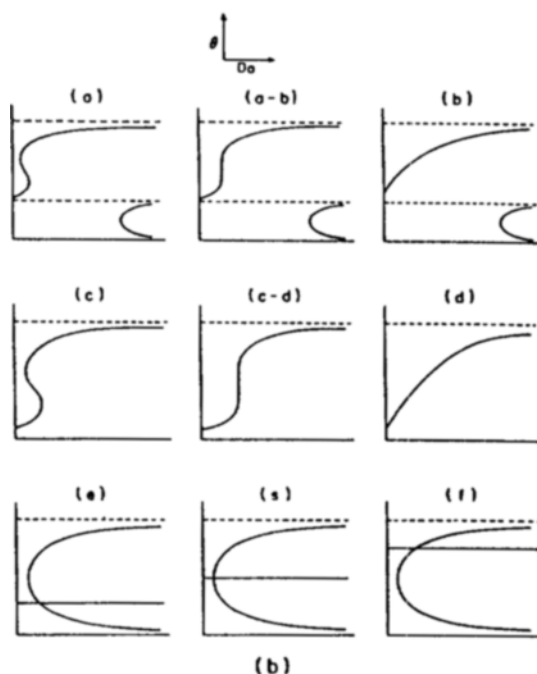
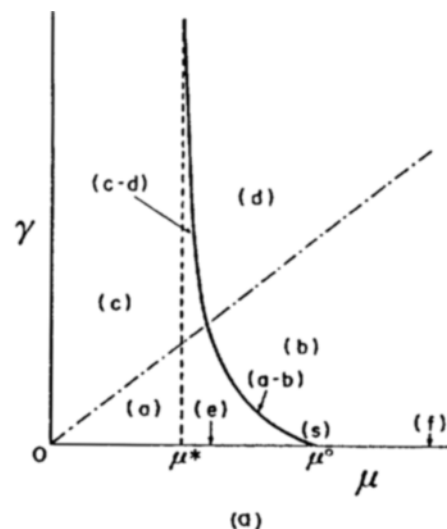


Fig. 2. The bifurcation sets (a) and the corresponding bifurcation diagrams (b) for quadratic autocatalytic reactions (arbitrary value of  $\beta$ ).

sible steady-states. In this case, the possible bifurcation diagrams are given by the parts (e) and (f) of Fig. 2(b).

### 2. Excess Catalyst in the Feed ( $\gamma \gg 1$ )

With an increase in the amount of catalyst B in the feed, autocatalytic effect fades away because a large amount of catalyst B makes feedback effect not so important. Thus, for a sufficiently large value of  $\gamma$ , it behaves like the first-order kinetics. The bifurcation set in Fig. 2(a) shows that the region (a) and (b) becomes smaller and smaller with an increase of  $\gamma$ . Therefore, in the case of excess catalyst in the feed, only two bifurcation diagrams given by the parts (c) and (d) of Fig. 2(b) are observed in the feasible range of  $\mu$  values.

### 3. Isothermal Case

From the material balance equations, the following single steady-state equation for the conversion of A can be obtained.

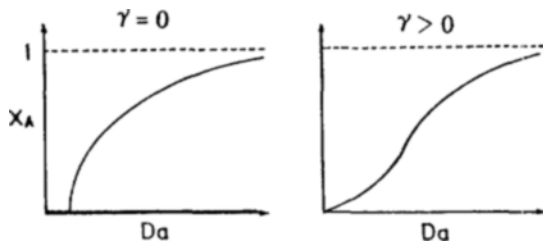


Fig. 3. The bifurcation diagrams in the isothermal case.

$$G(X_A, Da, \gamma) = X_A - Da(1 - X_A)(\gamma + X_A) = 0 \quad (17)$$

The defining and non-degeneracy conditions may be written

$$G = \frac{\partial G}{\partial X_A} = \frac{\partial G}{\partial Da} = 0 \quad (18)$$

$$\frac{\partial^2 G}{\partial X_A^2} \cdot \frac{\partial^2 G}{\partial X_A \partial Da} \neq 0 \quad (19)$$

In this case, the most degenerate singular point is

$$X_A^0 = 1, Da^0 = 1, \gamma^0 = 0 \quad (20)$$

For the mapping  $G$ , only isola variety exists, which is given by  $\gamma = 0$ . The bifurcation diagrams corresponding to the value of  $\gamma$  are shown in Fig. 3. From Fig. 3, we see that two steady-states including "washout" can be obtained in case of  $\gamma = 0$  while only a unique steady-state is obtained when  $\gamma > 0$ . The same result has been reported by Gray and Scott [18].

### CONCLUSION

From the combined use of singularity and bifurcation theories we have found all the possible types of bifurcation diagrams and the boundaries of the region in the parameter space corresponding to each of the bifurcation diagrams for a non-isothermal autocatalytic reaction taking place in a CSTR.

Four types of different steady-state behavior were observed in the feasible region of parameter space and it was shown that multiple steady-states (up to three) exist for some set of parameter values.

The present model has treated the case with different temperatures between the feed and the coolant whereas Kay et al. [26] assumed equal temperatures. It is interesting to note that much simpler steady-state behavior has been obtained without the simplifying assumptions that were introduced by Kay et al. [26].

### NOMENCLATURE

$a$  : heat transfer area [ $\text{cm}^2$ ]  
 $A, B$  : species A, B  
 $C$  : concentration [ $\text{mol}/\text{cm}^3$ ]  
 $C_p$  : heat capacity [ $\text{cal}/(\text{g} \cdot ^\circ\text{K})$ ]  
 $Da$  : Damköhler number  
 $E$  : activation energy [ $\text{cal}/\text{mol}$ ]  
 $-\Delta H$  : heat of reaction [ $\text{cal}/\text{mol}$ ]  
 $H$  : dimensionless heat transfer coefficient  
 $k_0$  : pre-exponential factor  
 $k$  : reaction rate constant [ $l/(\text{mol} \cdot \text{sec})$ ]  
 $\mathbf{p}$  : vector of parameters  
 $q$  : flow rate [ $\text{cm}^3/\text{sec}$ ]

$R$  : universal gas constant [ $\text{cal}/(\text{mol} \cdot ^\circ\text{K})$ ]  
 $T$  : absolute temperature [ $^\circ\text{K}$ ]  
 $T_m$  : reference temperature [ $^\circ\text{K}$ ]  
 $U$  : overall heat transfer coefficient [ $\text{cal}/(^{\circ}\text{K} \cdot \text{cm}^2 \cdot \text{sec})$ ]  
 $V$  : volume of reactor [ $\text{cm}^3$ ]  
 $X$  : conversion  
 $x$  : a state variable  
 $Y$  : dimensionless temperature defined by Eq. (4)

### Greek Letters

$\alpha$  : vector of parameters  
 $\beta$  : dimensionless heat of reaction  
 $\gamma$  : ratio of concentrations defined by Eq. (4)  
 $\theta$  : dimensionless temperature  
 $\lambda$  : bifurcation parameter  
 $\mu$  : dimensionless activation energy  
 $\rho$  : density [ $\text{g}/\text{cm}^3$ ]

### Superscripts

$^0$  : singular point coordinate  
 $*$  : asymptotic value

### Subscripts

$A, B$  : species A, B  
 $c$  : coolant  
 $f$  : feed

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