

## PATTERN FORMATION IN INTERACTING CONTINUOUS STIRRED TANK REACTORS

Sang Hwan KIM

Inorganic Chemistry Department, Korea Research Institute of Chemical Technology, Daejeon 302-343, Korea

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**Abstract**—The dynamic behavior of coupled continuous stirred tank reactors in which the nonisothermal Langmuir-Hinshelwood type reactions occur, exhibits several types of pattern formation. The regular and irregular multipeak patterns are detected for the endothermic reaction of a Langmuir-Hinshelwood type when the heat communication between the neighboring cells is larger than the mass interaction. These observations may imply the possible existence of spatial structure in a matrix of catalysts, the non-uniform distribution of concentration and temperature in packed bed reactors, and corrugated propagating fronts in combustion problems.

### INTRODUCTION

During the past decades the non-uniform steady states emerging from a perfectly homogeneous steady state, have received a great deal of attention. Pattern formation in developmental biology, Benard convection in fluid dynamics, formation of coherent light in the laser, and occurrence of spatio-temporal concentration and/or temperature waves in chemically reacting systems are well-known examples of stable ordered structures evolving from an unstable uniform state.

The pioneering work on pattern formation was performed by Turing[1]. He studied a mathematical model of a growing embryo and suggested that a system of chemical substances, called morphogens, reacting together and diffusing through a tissue, is adequate to account for the main phenomena of morphogenesis. Such a system, although it may originally be quite homogeneous, may develop a pattern of structures due to the instability of homogeneous equilibrium, which is triggered off by random disturbances.

Since then a plethora of papers have appeared to use Turing's idea toward structure formation phenomena in various disciplines. Goodwin[2] proposed a phase-shift model for spatial and temporal organization in developing systems. Goldbeter[3] studied one-dimensional pattern formation for an allosteric enzyme reaction and detected standing as well as propagating concentration waves. The parameter domain of spatial structures for several models in an attempt to elucidate the Turing's pattern formation, was investigated by Murray[4]. Catalano et al.[5]

demonstrated various types of pattern formation for allosteric enzyme reactions in the one-and two-dimensional space.

It should be noted that all authors mentioned above considered isothermal systems. In this paper we consider an array of nonisothermal continuous stirred tank reactors in which a Langmuir-Hinshelwood type reaction occurs. The spatial structures are investigated for the geometry of multiple cells in the one-and two-dimensional space. The effect of geometry and system size on pattern formation will be also discussed.

### GOVERNING EQUATIONS

Consider an one-dimensional array of CSTRs with a string and ring configuration (see Fig. 1). The mass and energy balances for these systems, in which a Langmuir-Hinshelwood type reaction occurs, are represented by coupled differential equations in the dimensionless form:

$$\frac{dX}{d\tau} = 1 - X - R(X, Y) + \mu_m \Delta X \quad (1)$$

$$\frac{dY}{d\tau} = 1 - Y + \beta R(X, Y) + \mu_t \Delta Y \quad (2)$$

where

$$R(X, Y) = \frac{\alpha X}{(1 + LX)^2} e^{-\gamma Y} \quad (3)$$

under the following assumptions:

(1) The cell volume, the feed composition and temperature, and the flow rate to all cells are identical.

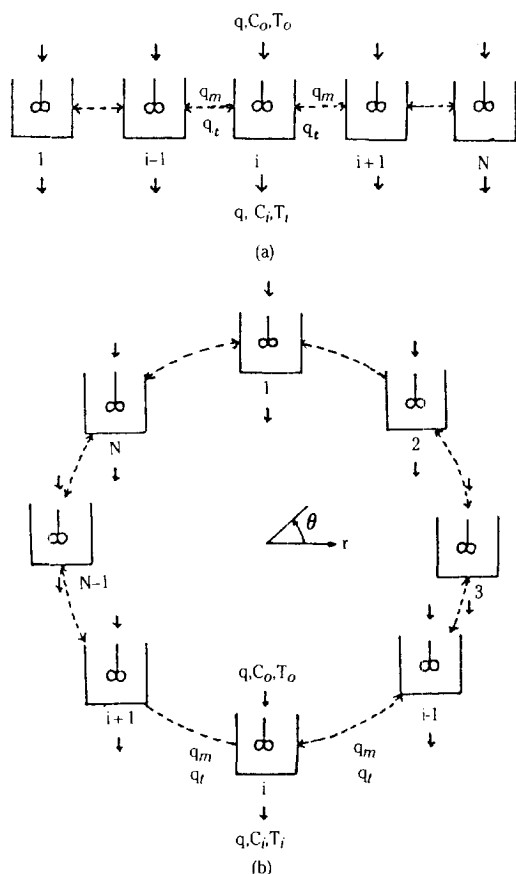


Fig. 1. Schematic diagram of interacting CSTRs.

The geometry is: (a) string (b) ring.

That means every cell in Fig. 1 is exposed to the same surroundings.

(2) A single chemical reaction occurs in each cell, the rate of which differs from one CSTR to another only if the concentration of a single component and the temperature vary.

(3) The rates of exchange of mass and heat between neighboring cells may be described by the product of an exchange coefficient and the concentration and temperature difference.

In this paper the  $i$ -th element of the vector quantities,  $\underline{X}$  and  $\underline{Y}$ , refers to the dimensionless concentration and temperature at the  $i$ -th cell, respectively. We have also denoted  $\beta$  the dimensionless heat of reaction,  $\alpha$  and  $L$  the dimensionless kinetic constants,  $\gamma$  the dimensionless activation energy,  $C_o$  the feed concentration,  $T_o$  the feed temperature,  $q$  the feed flow rate,  $V$  the volume of a CSTR,  $\mu_m$  and  $\mu_t$  the dimensionless exchange coefficients of mass and heat between neighboring cells, respectively and  $\tau$  the dimensionless time

defined by

$$\begin{aligned} X_i &= \frac{C_i}{C_o} & Y_i &= \frac{T_i}{T_o} & \gamma &= \frac{E}{RT_o} \\ \tau &= \frac{q}{V} t & \alpha &= \frac{kV}{q} & \beta &= \frac{(-\Delta H)C_o}{\rho C_p T_o} \\ \mu_m &= \frac{q_m}{q} & \mu_t &= \frac{q_t}{q} \end{aligned} \quad (4)$$

The structure matrix,  $\underline{\Delta}$ , represents the geometry of systems in question. For the one-dimensional configuration shown in Fig. 1, the structure matrices for the string ( $\underline{\Delta}_s$ ) and ring ( $\underline{\Delta}_r$ ) are given by

$$\underline{\Delta}_s = \begin{bmatrix} -1 & 1 & 0 & \cdots & 0 \\ 1 & -2 & 1 & 0 & \cdots & 0 \\ 0 & 1 & -2 & 1 & 0 & \cdots & 0 \\ \vdots & & & \vdots & & \vdots \\ 0 & \cdots & \cdots & 0 & 1 & -1 \end{bmatrix} \quad (5)$$

and

$$\underline{\Delta}_r = \begin{bmatrix} -2 & 1 & 0 & 0 & \cdots & 0 & 1 \\ 1 & -2 & 1 & 0 & \cdots & 0 & 0 \\ 0 & 1 & -2 & 1 & 0 & \cdots & 0 & 0 \\ \vdots & & & \vdots & & \vdots & & \vdots \\ 1 & 0 & \cdots & 0 & \cdots & 1 & -2 \end{bmatrix} \quad (6)$$

Eigenvalues and eigenvectors of these structure matrices are well known and the details are reported in the literature[6,7].

From a chemical engineering viewpoint the description for an assemblage of catalysts can be visualized as an array of CSTRs. The interacting protrusion from catalytic wire (fuzzy wire model) proposed by Jensen and Ray[8] and the monolithic catalytic converter which, by virtue of its design, has a large number of interacting parallel flow channels, are also described by interacting local reactors.

## LINEAR STABILITY ANALYSIS

The number and character of steady states in a single cell are readily reduced from Eqs. (1) and (2). Its mathematical description is obtained by setting the exchange coefficients,  $\mu_m$  and  $\mu_t$ , to zero and changing the vectors to scalar quantities with eliminating the subscript  $i$ . It is obvious that a steady state of a single cell is also a steady state of an array of cells, regardless of the magnitude of  $\mu_m$  and  $\mu_t$ . We shall refer to these states as the "uniform steady states". There are one, three or five uniform steady states[6]; the number corresponds to the number of steady states for a single cell. These uniform steady states arise when the ex-

change coefficients between the neighboring cells have extremely large values.

The stability analysis of uniform steady states in the cellular network was developed in a very elegant way by Othmer and Scriven[7]. Using their approach, the effect of changes in the network topology on the dynamic pattern of interacting multiple cells, can be treated systematically. They also predicted the occurrence of standing or travelling waves. Kennedy and Aris[9] demonstrated the bifurcation of uniform steady states to the asymmetric steady states and homogeneous oscillatory motion.

In order to examine the stability of uniform steady states the linear stability analysis is applied in this work. When the system equations (1) and (2) are linearized about a particular uniform steady state, the stability is determined by the eigenvalues of the following reaction-and-transport matrix,  $\underline{\underline{A}}$ :

$$\underline{\underline{A}} = \begin{pmatrix} -1 - \frac{\partial R}{\partial X} + \mu_m \lambda_s & -\frac{\partial R}{\partial Y} \\ \beta \frac{\partial R}{\partial X} & -1 + \beta \frac{\partial R}{\partial Y} + \mu_t \lambda_s \end{pmatrix} \quad (7)$$

where  $\lambda_s (s = 1, 2, \dots, N)$  are the eigenvalues of the structure matrix ( $\underline{\underline{A}}$ ). The partial derivatives in Eq. (7) are evaluated at a uniform steady state.

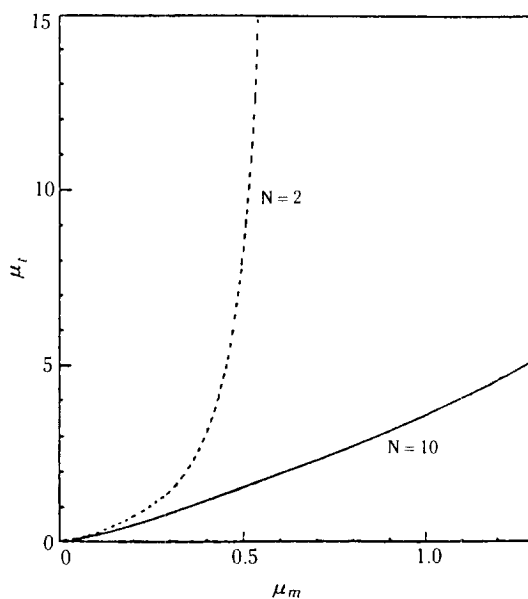
In order to determine the stability of uniform steady states to infinitesimal perturbations, the procedure is first, deduce the structure matrix of the geometry and calculate its eigenvalues  $\lambda_s$ ; and second for each of the  $N$  numbers,  $\lambda_s$ , calculate the eigenvalues  $\epsilon_s$  of the reaction-and-transport matrix,  $\underline{\underline{A}}$ . Then if all  $2N$  eigenvalues,  $\epsilon_s$ , have negative real parts, the uniform steady states are stable. If one or more of these eigenvalues have positive real parts, the uniform steady states are unstable.

## NUMERICAL RESULTS

Numerical computation of symmetry breaking was performed for an array of nonisothermal continuous stirred tank reactors in which the endothermic Langmuir-Hinshelwood type reaction takes place. The values of the governing parameters are reported in Table 1.

**Table 1. The values of governing parameters**

$\alpha = 4.52 \times 10^4$	•
$\beta = -0.2$	
$\gamma = 5.5$	
$L = 15.0$	



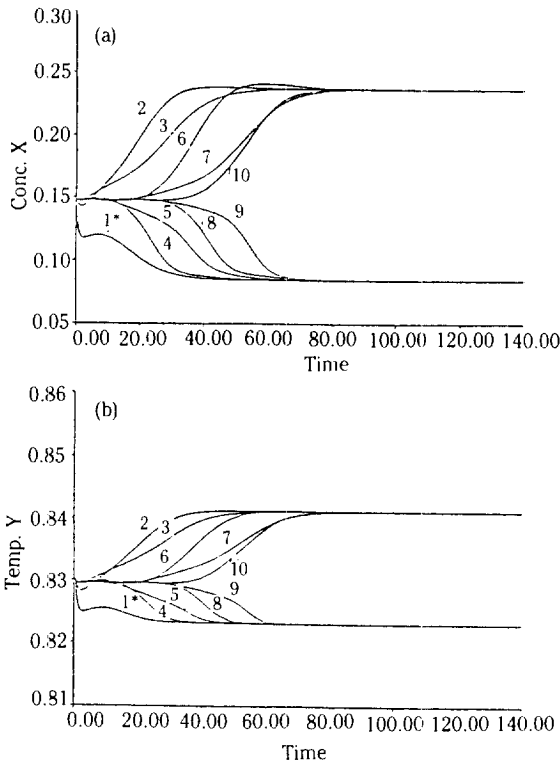
**Fig. 2. Instability region of uniform steady states for the string.**

— total cell number is 2  
 ..... total cell number is 10

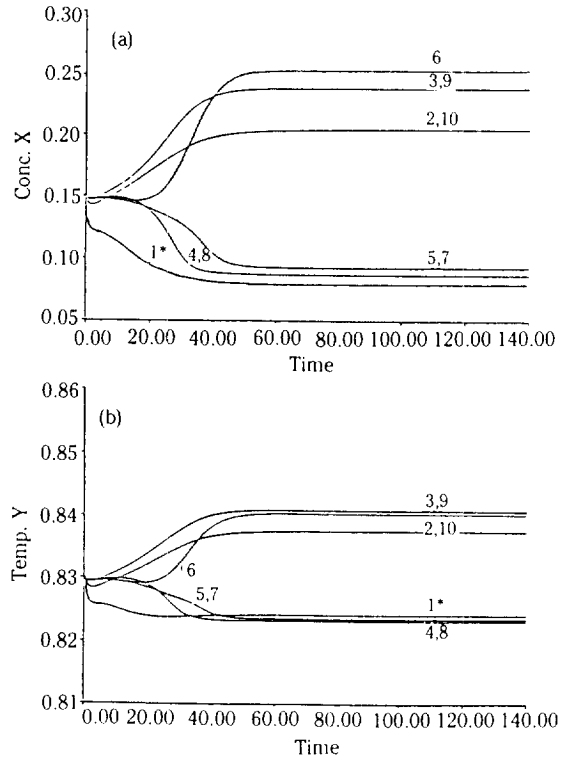
The instability region in  $(\mu_m, \mu_t)$  parameter plane for the string is depicted in Fig. 2. The parameter values of  $\mu_m$  and  $\mu_t$  in the upper part of solid and dotted lines give rise to the instability of uniform steady states for ten and two interacting cells, respectively. The instability region of a uniform steady state is enlarged with the increasing number of cells. This implies that the symmetry-breaking instability strongly depends on the length of the system.

The concentration and temperature histories for an array of ten cells in the configurations of the string and ring with the values of  $\mu_m$  and  $\mu_t$  in the instability region, are depicted in Figs. 3 and 4, respectively. The number in these figures represents the cell number and the perturbed cell is described as the asterisk (\*) on the cell number. The transient concentration and temperature diverge from an initial state, very close state to the uniform one, eventually come to rest at a stable nonuniform state. These results state that if ten cells were extremely well isolated, each would remain in that state for any kind of perturbation. As they are brought into closer communication through the mass and heat transfer, the stability of each cell will be lost spontaneously and every cell will travel to the new steady states.

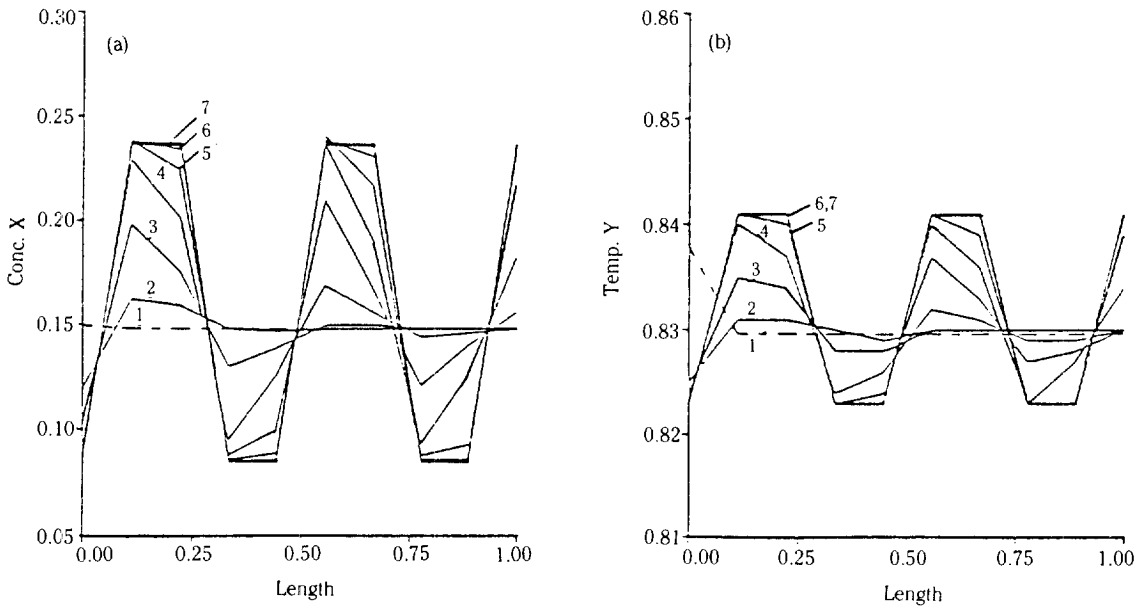
The spatial profiles for the same parameter values as those in Figs. 3 and 4, clearly show the occurrence of spatial structure in the geometry of the string and



**Fig. 3. Transient behavior of unstable uniform steady states in the string: (a) concentration (b) temperature.  $\mu_m = 0.1, \mu_t = 0.5, N = 10$ .**

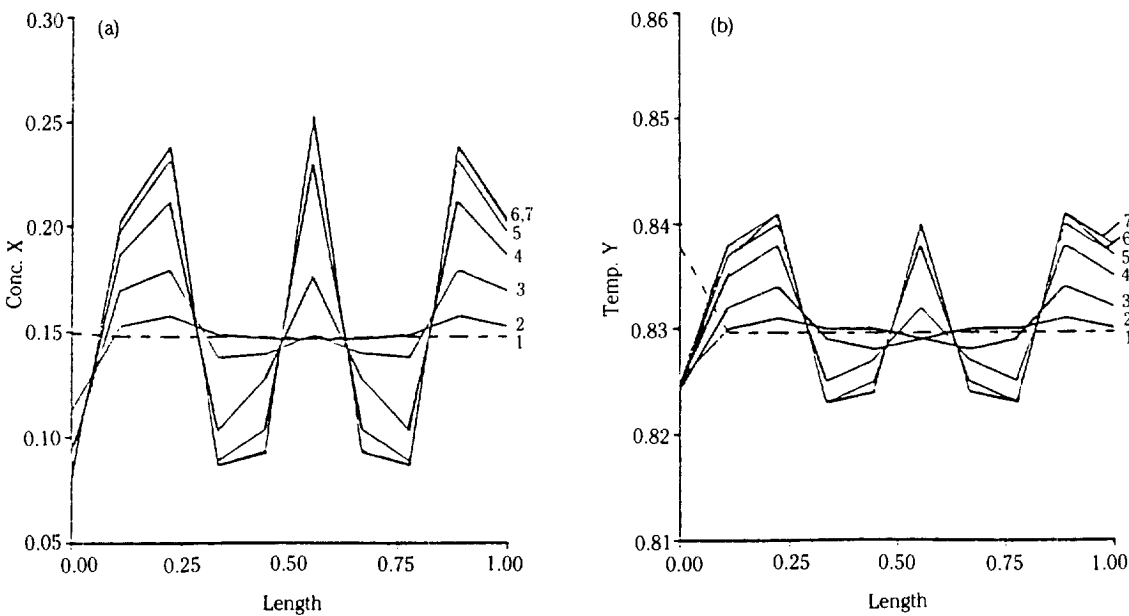


**Fig. 4. Transient behavior of unstable uniform steady states in a ring: (a) concentration (b) temperature.  $\mu_m = 0.1, \mu_t = 0.5, N = 10$ .**

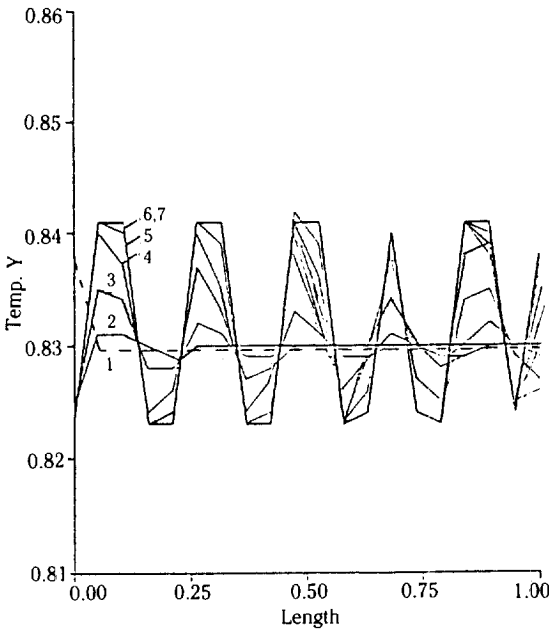


**Fig. 5. Spatial profiles in the string: (a) concentration (b) temperature.  $\mu_m = 0.1, \mu_t = 0.5, N = 10$ .**

Time is: (1) 0.0, (2) 10.0, (3) 20.0, (4) 30.0, (5) 40.0, (6) 50.0, (7) steady state.

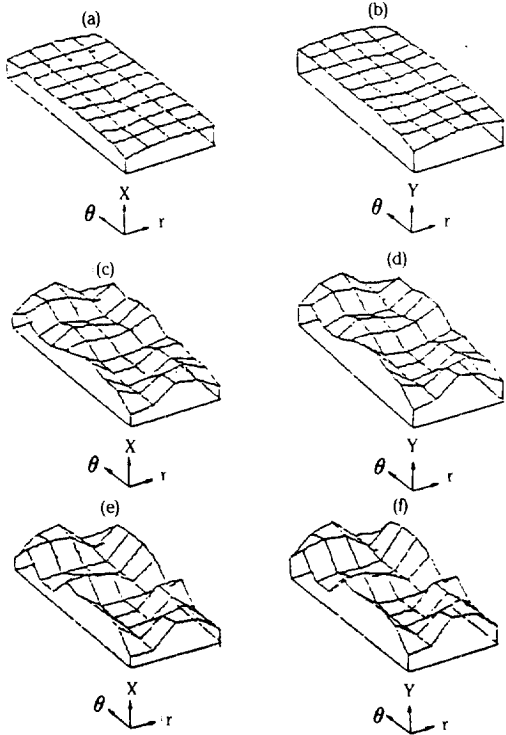


**Fig. 6. Spatial profiles in the ring: (a) concentration (b) temperature.**  $\mu_m=0.1, \mu_t=0.5, N=10$ .  
Time is; (1) 0.0, (2) 10.0, (3) 20.0, (4) 30.0, (5) 40.0, (6) 50.0, (7) steady state.



**Fig. 7. Spatial temperature profiles in the string.**  $\mu_m=0.1, \mu_t=0.5, N=20$ .  
Time is; (1) 0.0, (2) 10.0, (3) 20.0, (4) 30.0, (5) 40.0, (6) 50.0, (7) steady state.

ring, respectively(see Figs. 5 and 6). Of course some difference in the spatial profiles of steady states exists between the geometry of the string and ring. The effect of cell number(or length of the system) on spatial



**Fig. 8. Spatial structures in a two-dimensional circle.**  $\mu=0.1, \mu_t=0.5$  in both directions.

	$\tau = 10$	30	steady state
concentration	(a)	(c)	(e)
temperature	(b)	(d)	(f).

structures is shown in Fig. 7 comparing to the corresponding profiles in Fig. 5. This may imply that the spatial pattern closely connects to the length of the system.

The spatial pattern in the configuration of a circle clearly shows the characteristic of irregular multipeak patterns (see Fig. 8). These multipeak patterns were also detected for allosteric enzyme reactions in two dimensional space by Catalano et al.[5].

## CONCLUSIONS

The possible spatial pattern in the interacting CSTRs where the endothermic reaction of a Langmuir-Hinshelwood type occurs, is studied. The regular and irregular multipeak patterns are detected in the one- and two-dimensional space.

The significance of these results from the chemical engineering viewpoint, may predict the lateral non-uniform distribution of concentration and temperature in packed bed reactors and symmetry-breaking of propagating fronts in combustion problems. The study of the possible symmetry-breaking and the standing and travelling waves for a first-order exothermic reaction when the heat interaction is stronger than the mass communication, deserves further work.

## NOMENCLATURE

$C_i$	: Concentration at the $i$ -th CSTR
$C_o$	: Inlet feed concentration
$C_p$	: Heat capacity of the fluid
$E$	: Activation energy
$\Delta H$	: Heat of reaction
$k$	: Reaction constant
$L$	: Dimensionless chemisorption equilibrium constant
$N$	: Total number of CSTRs
$q$	: Feed flow rate
$q_m$	: Flow rate of mass interaction
$q_t$	: Flow rate of heat interaction
$\underline{R}$	: Reaction rate vector defined in Eq. (3)
$t$	: time
$T_i$	: Temperature at the $i$ -th CSTR
$T_o$	: Inlet feed temperature
$V$	: Volume of a CSTR
$\underline{X}$	: Dimensionless concentration vector

$\underline{Y}$  : Dimensionless temperature vector

## Greek Letters

$\alpha$	: Dimensionless kinetic constant ( $= \frac{kV}{q}$ )
$\beta$	: Dimensionless heat of reaction ( $= \frac{(-\Delta H)C_o}{\rho C_p T_o}$ )
$\gamma$	: Dimensionless activation energy ( $= \frac{E}{RT_o}$ )
$\epsilon$	: Eigenvalues of reaction-and-transport matrix $\underline{A}$
$\underline{\Delta}$	: Structure matrix
$\lambda$	: Eigenvalues of a structure matrix $\underline{\Delta}$
$\mu_m$	: Dimensionless mass interaction rate ( $= \frac{q_m}{q}$ )
$\mu_t$	: Dimensionless heat interaction rate ( $= \frac{q_t}{q}$ )
$\rho$	: Density of the fluid
$\theta$	: Azimuth angle

## Superscript

\* : Perturbed CSTR

## Subscripts

$i$	: Cell number
$s$	: Straight string
$r$	: Ring

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