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CHAOTIC BEHAVIOR IN TUBULAR FLOW REACTORS WITH $A \rightarrow B \rightarrow C$ REACTIONS

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Abstract— A tubular nonisothermal-nonadiabatic chemical reactor with consecutive reactions described by a set of three nonlinear parabolic equations, shows a sequence of period doubling bifurcations of a limit cycle. A numerical examination of the model reveals that complex periodic and irregular oscillations are possible. With increasing values of the Peclet number, regular and irregular oscillations are suppressed and disappear. The results of this numerical study may be used to explain turbulization of laminar flames.

INTRODUCTION

The pattern of multiple steady states and their dynamic behavior in chemically exothermic reacting systems has been known for some time to be complex[1]. By far, the most extensively investigated and best understood exothermic reacting system is the stirred tank reactor in which simple[2-4] and complex[5-8] chemical reactions have been studied. The model of a stirred tank reactor is represented by a set of nonlinear ordinary differential equations. Far less attention has been paid to tubular reacting systems which are described by a set of nonlinear parabolic differential equations. Hlavacek et al.[9-10] and Varma and Amundson[11] observed multiple steady states and periodic oscillations of concentration and temperature fields.

Recently Puszynski and Hlavacek[12] observed experimentally complex and irregular temperature oscillations in a long tubular packed bed. Major new results in nonlinear dynamics have given great insight into the behavior of nonlinear systems. Many reacting systems display motion which is, in a certain sense, well-ordered and regular. By this we mean that the associated trajectories are forever confined to well defined regions of phase space and show little changes in character when small changes in initial conditions are made. In the irregular regime, the trajectories are very sensitive to small perturbations in inital conditions and can wander in an erratic-looking manner. The irregular regimes have been observed in some chemically reacting systems[7,8]. The study of irregular behavior was performed only for systems which are perfectly mixed, i.e., which do not feature any space gradients. To our knowledge, irregular oscillations in chemically reacting systems with space gradients (e.g. tubular flow reactors) have not been discovered so far. Since the presence of irregular regime is of great importance in the flame theory, the aim of our effort was to perform a numerical search which hopefully could locate interesting bifurcation phenomena and irregular dynamic behavior in reacting systems with space gradients.

The goal of this paper is twofold:

(1) To show that consecutive chemical reactions occurring in a tubular flow reactor may give rise to period doubling bifurcations and eventually to irregular oscillations.

(2) To show that for higher values of the Peclet number (i.e. for strongly convective systems) all type of oscillations disappear.

GOVERNING EQUATIONS

For homogeneous consecutive first order reactions $A \rightarrow B \rightarrow C$ occurring in a tubular nonadiabatic-nonisothermal system, the transient equations can be written in the following dimensionless form:

$$\frac{\partial u}{\partial \tau} = \frac{1}{Pe}\frac{\partial^2 u}{\partial x^2} - \frac{\partial u}{\partial x} - Da\, u \exp\left(\frac{w}{1+\varepsilon w}\right) \quad (1)$$

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$$\frac{\partial v}{\partial \tau}=\frac{1}{Pe}\frac{\partial^2 v}{\partial x^2}-\frac{\partial v}{\partial x}+Da\,u\ \exp\left(\frac{w}{1+\varepsilon w}\right)$$

$$-Da\,S\,v\ \exp\left(\frac{kw}{1+\varepsilon w}\right) \quad (2)$$

$$\frac{\partial w}{\partial \tau}=\frac{1}{Pe}\frac{\partial^2 w}{\partial x^2}-\frac{\partial w}{\partial x}+Da\,B\ u\exp\left(\frac{w}{1+\varepsilon w}\right)$$

$$-Da\,B\,\alpha\,S\ v\ \exp\left(\frac{kw}{1+\varepsilon w}\right)-\beta(w-w_c) \quad (3)$$

subject to boundary conditions

$$x=0:\ 1=u-\frac{1}{Pe}\frac{\partial u}{\partial x} \quad (4)$$

$$v=\frac{1}{Pe}\frac{\partial v}{\partial x}$$

$$w=\frac{1}{Pe}\frac{\partial w}{\partial x}$$

$$x=1:\ \frac{\partial u}{\partial x}=\frac{\partial v}{\partial x}=\frac{\partial w}{\partial x}=0. \quad (5)$$

The details of the development of this model can be found elsewhere[9]. The variables u, v, and w, represent dimensionless concentrations of component A, component B, and temperature, respectively.

In the text above, we have denoted: Pe is the Peclet number, Da the Damköhler numer, ε the dimensionless activation energy, B the dimensionless adiabatic temperature rise, α the ratio of heat effects, β the dimensionless heat transfer coefficient, S the selectivity, w_c the dimensionless temperature of cooling medium, and k the ratio of activation energies[9].

PERIOD DOUBLING BIFURCATIONS

The set of nonlinear parabolic equations, Eqs. (1)-(5), was integrated by a Crank-Nicolson method with an automatic time step adjustment. The error of integration was controlled to four decimal places.

Irregular behavior of reacting systems has been described for a number of isothermal[13,14] and nonisothermal[7,8] systems. However, to our knowledge, no example of irregular oscillations in reacting systems described by partial differential equations has been reported so far.

For our study, we have chosen the system of two consecutive reactions studied by Kahlert, Rössler, and Varma[7]. They have shown that in a continuous stirred tank reactor, a sequence of period-doubling bifurcations of a limit cycle may occur which leads into a pattern of periodic and irregular behavior. This system is represented by a set of three nonlinear ordinary differential equations. It is noted that the equations describing the stirred tank reactors are the limiting cases of Eqs.(1)-(5) describing a tubular flow reactor, for $Pe \rightarrow 0$.

Table 1. The values of governing parameters

Da	= 0.26
ε	= 0.0
B	= 57.77
α	= 0.426
β	= 7.995
S	= 0.5
w_c	= 0.0
k	= 1.0

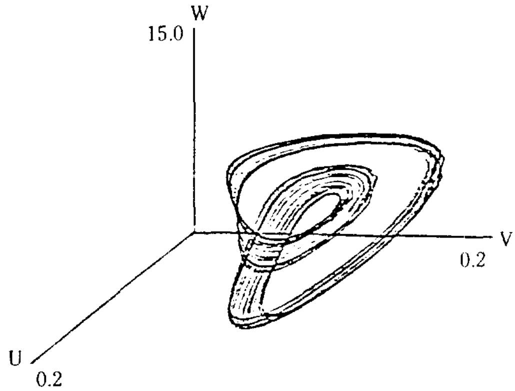

Fig. 1. Chaotic behavior at $Pe=0.04$.

It is obviously impossible to vary all nine parameters to analyze the dynamic behavior of the model in Eqs.(1)-(5). To rationalize the search in the parametric space, we have used the results presented by Kahlert et al.[7] and chose the Peclet number as the bifurcation parameter. The values of the governing parameters are reported in Table 1.

For the system under consideration, we have calculated the integral mean values of the variables u, v, and w and plotted these values in the following figures. For the values from Table 1 and for $Pe \rightarrow 0$, Kahlert et al.[7] reported chaotic behavior of the system described by Eqs.(1)-(5). We started the numerical simulation of the model for $Pe=0.01$. For $Pe=0.04$ the model reveals the chaotic behavior as shown in Fig. 1. Increasing the value of Pe, $Pe=0.043$, the model gives rise to a period-sixteen limit cycle (Fig. 2).

For $Pe=0.0488$, the numerical solution of the parabolic equations results in a limit cycle with the

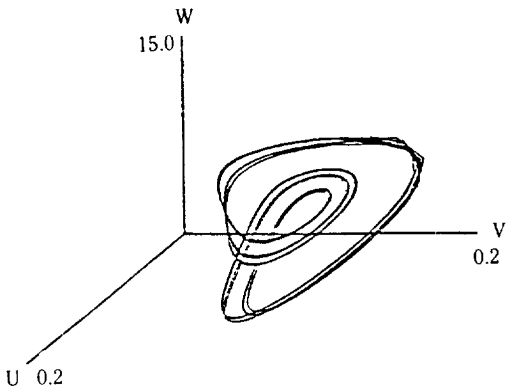

Fig. 2. Period sixteen limit cycle at *Pe*=0.043.

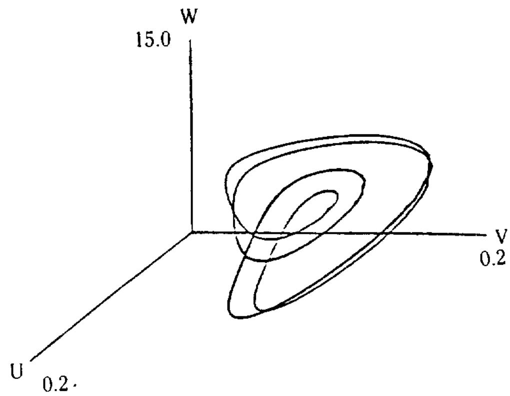

Fig. 4. Period four limit cycle at *Pe*=0.05.

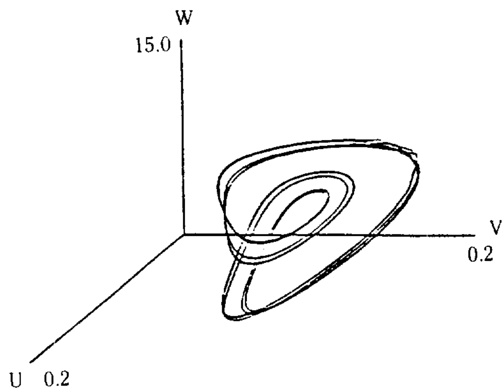

Fig. 3. Period eight limit cycle at *Pe*=0.0488.

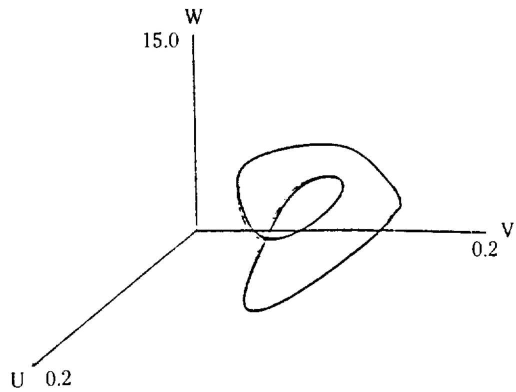

Fig. 5. Period two limit cycle at *Pe*=0.16.

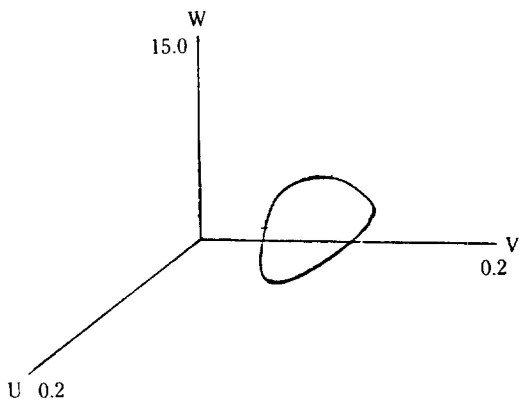

Fig. 6. Period one limit cycle at *Pe*=0.21.

period eight as depicted in Fig. 3. For $Pe=0.05$ the model gives rise to a period four limit cycle as shown in Fig. 4. For $Pe=0.16$ the numerical solution of the system results in a limit cycle with the period two (Fig. 5). The bifurcation to a period one limit cycle occurs at $Pe \approx 0.21$ (Fig. 6). With increasing value of Peclet number the limit cycle shrinks and at a certain value of Peclet number disappears; from the model we can estimate $Pe \approx 0.33$ as depicted in Fig. 7. These calculations are in agreement with the results[9], the higher is the Peclet number the lower is the probability of the occurrence of any type of oscillations.

One of the routes to chaos is a sequence of period doubling bifurcation of a limit cycle which has been observed in the experiments on Rayleigh-Benard convection[15], nonlinear electrical oscillators[16], shallow water waves[17], and the Belousov-Zhabotinski reaction. As the parameter is varied, the system changes from simple periodic to complex aperiodic motion. In the limit of aperiodic behavior, there is a unique and hence universal solution common to all systems undergoing period doubling bifurcations. This fact implies remarkable consequences. For a given system, if we denote by a_n the value of the parameter at which its period doubles for the nth time, the sequence of successive bifurcation values of a in the limit behaves like a geometric series, that is to say, the ratio between two subsequent differences between

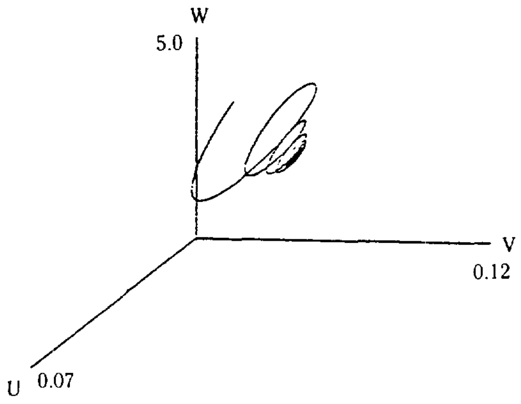

Fig. 7. Steady state at $Pe = 0.33$.

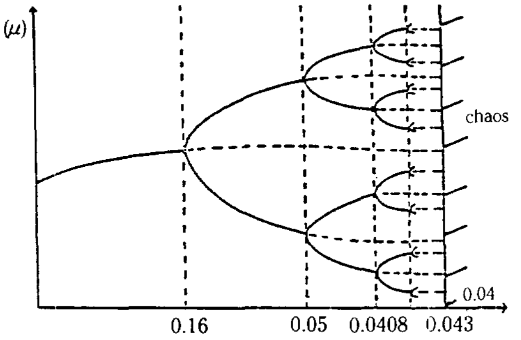

Fig. 8. Feigenbaum sequence of the model.

adjacent values converges towards a fixed value:

$$\delta_n = \frac{a_{n+1} - a_n}{a_n - a_{n-1}} \approx 4.6692016. \tag{16}$$

This definite number (Feigenbaum number) must appear as a natural constant in all systems exhibiting a period-doubling route to chaos. Fig. 8 illustrates period doubling bifurcations of a limit cycle in the model as the Peclet number decreases. The ratio between two subsequent differences between adjacent Peclet numbers in the model $\delta_n = \frac{0.043 - 0.0488}{0.0488 - 0.05} = 4.83$ seems to be close to the natural Feigenbaum number.

CONCLUSIONS

The numerical results reported here indicated that period doubling bifurcations may exist also for a set of nonlinear parabolic equations. It has been shown that the irregular behavior of the system disappears for higher values of the Peclet number. With increasing values of Pe we have observed the following sequence: irregular behavior→period sixteen→period eight→period four→period two→period one→stable steady state. It is well established experimental fact that flame fronts may show the irregular pulsations[18]. Based on our results, these pulsations can be explained by interaction of heat and mass transfer and a chemical reaction. However, for higher values of the Peclet number, the irregular behavior is suppressed and disappears. We have performed an analysis for the Lewis number $Le = Pe_M/Pe_H = 1$. Based on results reported for examples in the Aris book[1], we can expect that for $Le > 1$ complex oscillations may exist in a larger domain of parameters.

NOMENCLATURE

a : bifurcation parameter
B : dimensionless adiabatic temperature rise $[= \frac{(-\Delta H) C_o}{\rho C_p T_o} \frac{E}{RT_o}]$
Da : Damköhler number $[= k_o L/U]$
k : ratio of activation energy $[= E_2/E_1]$
Le : Lewis number $[= Pe_M/Pe_H]$
Pe : Peclet number $[= UL/D]$
S : selectivity $[= k_{20}/k_{10}]$
u : dimensionless concentration of A
v : dimensionless concentration of B
w : dimensionless temperature $[= E/RT_0^2 (T - T_0)]$
w_c : dimensionless temperature of cooling medium
x : axial coordinate

Greek Letters

α : ratio of heat effects $[= \Delta H_2/\Delta H_1]$
β : dimensionless heat transfer coefficient
ε : dimensionless activation energy $[= (E_1/RT_0)^{-1}]$

Subscripts

H : heat transfer
M : mass transfer
n : nth time period doubling

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