Chemically Driven Convection in a Porous Medium

This paper is focused on the analysis of interaction of free convection and exothermic chemical reaction. As a consequence of the chemical reaction, free convection effects can result. It is difficult to perform an analytical bifurcation analysis of the full nonlinear governing equations; however, Fourier expansion combined with a Galerkin approximation results in a small set of ordinary nonlinear differential equations (initial-value problem) that are amenable to analysis. Conditions for branching of the solution can be determined in an analytical way. A continuation algorithm makes it possible to calculate the branches of stability. The results of the approximative analysis are supported by the numerical integration of the full governing nonlinear equations.

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Introduction

Natural convection effects may influence the course of an exothermic chemical reaction in a critical way. Examples of the interaction of chemical reaction and free convection occur in tubular laboratory reactors, chemical vapor deposition systems, oxidation of solid materials in large containers, synthesis of ceramic materials by a self-propagating reaction, and others. There is little information on the interaction of free convection and chemical reaction in the literature. Merzhanov and Shtessel (1973) investigated the effect of free convection on the explosive characteristics of liquid explosives. Shtessel et al. (1971) solved numerically thermal explosion equations in combination with equations of fluid motion. Since they used only one type of perturbation, only one type of convection solution was found. Kordylewski and Krajewski (1984) solved a similar problem in a cylindrical cavity. For certain values of the parameters they found oscillatory behavior. In order to make the problem more tractable, we introduce two essential approximations. First, we adopt the Boussinesq approximation. Any change in density is assumed negligible except in the external force term of the Navier-Stokes equations. Second, we will consider flow through a porous medium and hence assume that the Darey approximation is valid. We will consider a two-dimensional cavity with insulated side walls and bottom. The top will be kept at a fixed temperature and a zero-order reaction will drive the convection.

The model that describes this situation will be referred to as the original system. We will simplify the original system by approximating the dependent variables with a truncated Fourier series. We will show that the resulting initial-value problem has preserved most of the features of the original system. In the text we will refer to the Fourier-approximated equations as the simplified system.

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Models and Their Bifurcation Behavior

We consider a zero-order exothermic reaction in a rectangular cavity of width-to-height ratio of α. In Figure 1, we state the problem schematically. The continuity, momentum, and energy conservation equations can be written in nondimensional form:

$$\nabla \cdot u = 0 \tag{1}$$

$$\frac{1}{Pr}\left(\frac{\partial u}{\partial t} + \frac{1}{\epsilon} u \cdot \nabla u\right) = -\nabla P - Ra\theta\, \hat{z} - u \tag{2}$$

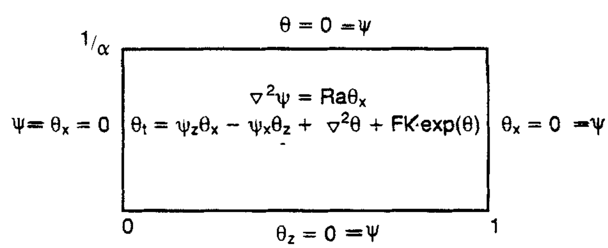


Figure 1. Model equations and boundary conditions.

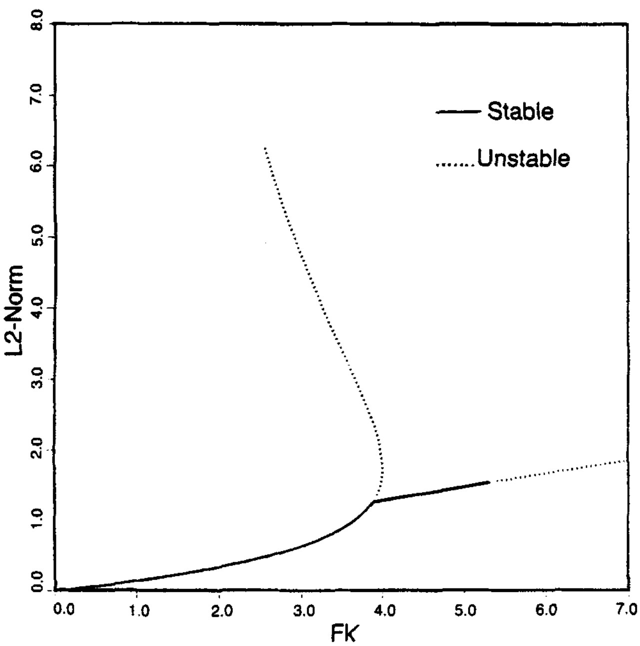


Figure 2. Bifurcation diagram of Eqs. 16 and 17 for *Ra* = 30.

$$\frac{\partial\theta}{\partial t} + u \cdot \nabla\theta = \nabla^2\theta + FK \exp(\theta) \tag{3}$$

where u, P, and θ respectively denote a dimensionless velocity, pressure, and temperature. Pr is the Prandtl number as defined for a porous medium, Ra is the thermal Rayleigh number, and FK is the Frank-Kamenetskii parameter defined in the Notation.

Since we only consider two space dimensions, we can write

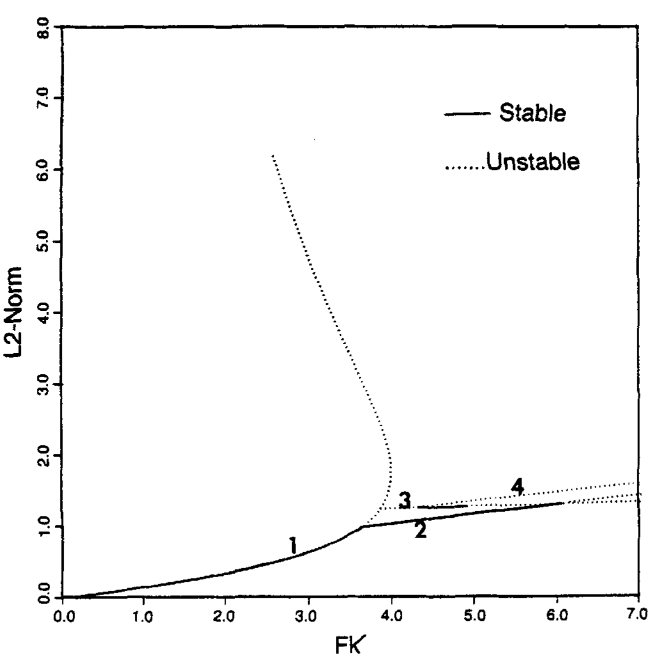


Figure 3. Bifurcation diagram of Eqs. 20–24 for *Ra* = 50.

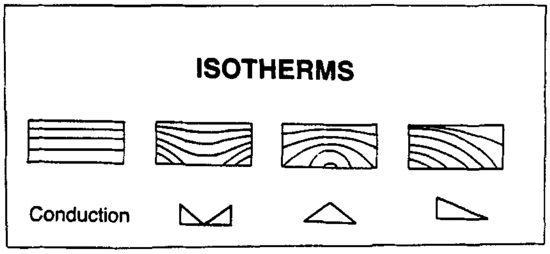


Figure 4. Different types of steady-state solutions.

Eqs. 1–3 in terms of a stream function. Let:

$$\left(-\frac{\partial\psi}{\partial z}, \frac{\partial\psi}{\partial x}\right) = (u_x, u_z) \tag{4}$$

where the subscripts denote the appropriate component. Substituting Eq. 4 into Eqs. 1–3 gives:

$$\frac{1}{Pr}\frac{\partial}{\partial t}(\nabla^2\psi) = -\nabla^2\psi + Ra\frac{\partial\theta}{\partial x} \tag{5}$$

$$\frac{\partial\theta}{\partial t} = \nabla^2\theta - \frac{\partial\psi}{\partial x}\frac{\partial\theta}{\partial z} + \frac{\partial\psi}{\partial z}\frac{\partial\theta}{\partial x} + \text{FK}\exp(\theta) \tag{6}$$

The Prandtl number assumes large values in a great many practical situations, and hence Eqs. 5 and 6 reduce to

$$\nabla^2\psi = Ra\frac{\partial\theta}{\partial x} \tag{7}$$

$$\frac{\partial\theta}{\partial t} = \nabla^2\theta - \frac{\partial\psi}{\partial x}\frac{\partial\theta}{\partial z} + \frac{\partial\psi}{\partial z}\frac{\partial\theta}{\partial x} + \text{FK}\exp(\theta) \tag{8}$$

In the rest of this paper we will refer to Eqs. 7 and 8 as the original system. These equations are supplemented by the boundary conditions shown in Figure 1.

Under conditions of insufficient heat removal, a thermal explosion occurs. Heat removal is facilitated by conduction and convection. If convection is neglected, Eqs. 7 and 8 decouple and a steady state solution of Eq. 8 is only possible for $FK < FK_c$, where FK_c is the critical value; e.g., $FK_c = 0{,}878$ if $\alpha = 1$ (Buckmaster and Ludford, 1983).

Convection stabilizes the reaction to some extent, and steady state solutions of Eqs. 7 and 8 exist for $FK > FK_c$. At the onset of convection, one can consider θ as a solution of the conduction problem with convection superimposed on it. The stream function and temperature can now be approximated by:

$$\psi = \sum_{i=1}^{\infty}\sum_{j=1}^{\infty} A_{ij}(t)\sin\pi ix\sin\pi\alpha jz \tag{9}$$

$$\theta = \cos\left(\frac{\pi\alpha}{2}z\right) \wedge \sum_{\kappa=0}^{\infty} D_k(t)\cos\pi kx \tag{10}$$

The first term of Eq. 10 is purely an approximation of the steady-state conduction solution, and one could have considered here the exact solution given by Buckmaster and Ludford (1983). Note that the conduction solution depends only on z.

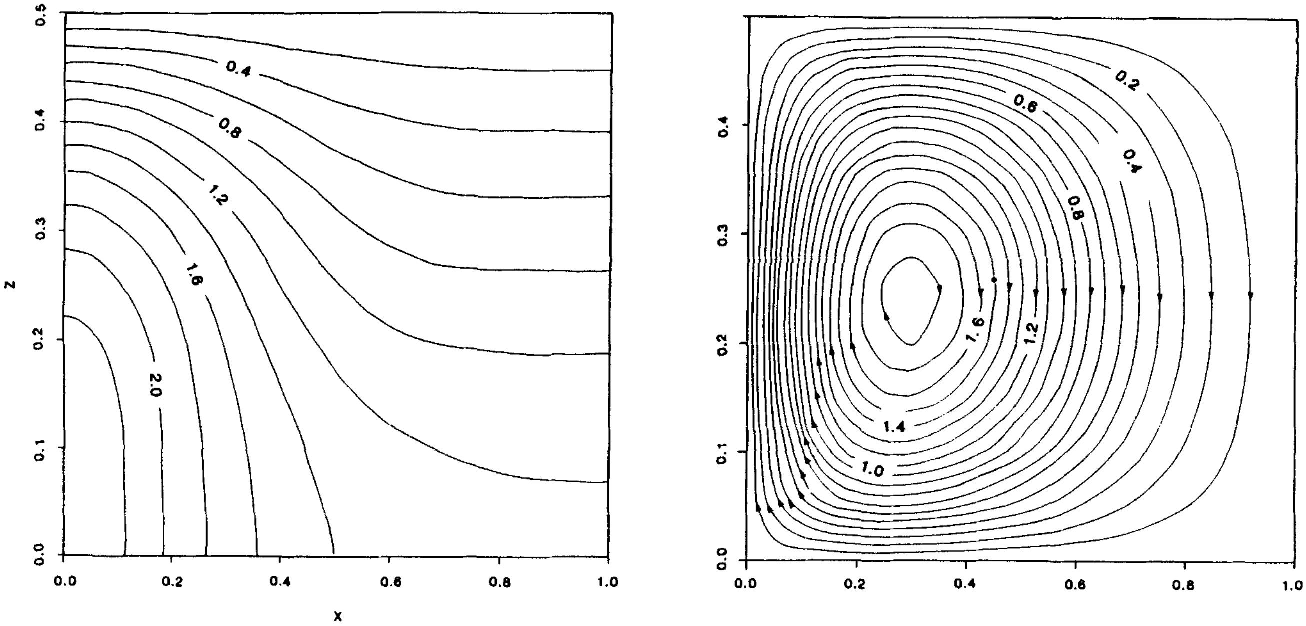


Figure 5. Isotherms and stream function values for FK/FK_c = 1.281 and Ra = 50.

The higher terms contain the lateral effects of convection. Substituting Eqs. 9 and 10 into Eqs. 7 and 8, truncating after one and two terms, respectively, and integrating the product of the residual and its approximation functions, one has a Galerkin approximation of Eqs. 7 and 8. For $\alpha = 2$, one gets the following:

$$0 = -A_{11} + \frac{8}{15\pi^2} Ra D_1 \tag{11}$$

$$\frac{d}{dt} D_0 = -\pi^2 D_0 - \frac{\pi^2 A_{11} D_1}{4} + 4FK\left(\frac{1}{\pi} + \frac{D_0}{4} + \frac{D_0^2}{3\pi} + \frac{D_1^2}{6\pi}\right) \tag{12}$$

$$\frac{d}{dt} D_1 = -2\pi^2 D_1 + \frac{\pi^2 A_{11} D_0}{2} + 8FK\left(\frac{D_1}{8} + \frac{D_0 D_1}{3\pi}\right) \tag{13}$$

Later we will use two and three terms, respectively, to approximate ψ and θ. But in both cases, we will refer to the Galerkin approximation as the simplified system.

Let us first consider the conduction behavior of Eqs. 11–13 alone. Now these equations take the form:

$$\pi^2 D_0 = 4FK\left\{\frac{1}{\pi} + \frac{D_0}{4} + \frac{D_0^2}{3\pi}\right\} \tag{14}$$

and $A_{11} = D_1 = 0$. Equation 14 has two solutions for

$$0 < FK < \pi^2/[1 + 8/(\pi\sqrt{3})] \tag{15}$$

with the result $FK = 3.995$, which compares reasonably with the analytical value of $FK_c = 3.512$.

If convection is considered, Eqs. 11–13 can be written as:

$$\frac{d}{dt} D_0 = -\pi^2 D_0 - \frac{2RaD_1^2}{15} + 4FK\left(\frac{1}{\pi} + \frac{D_0}{4} + \frac{D_0^2}{3\pi} + \frac{D_1^2}{6\pi}\right) \tag{16}$$

$$\frac{d}{dt} D_1 = -2\pi^2 D_1 + \frac{4RaD_0D_1}{15} + 8FK\left(\frac{D_1}{8} + \frac{D_0 D_1}{3\pi}\right) \tag{17}$$

In Figure 2, a complete bifurcation diagram of Eqs. 16 and 17 is shown. One can immediately recognize the conduction branch. We have chosen a fixed value of $Ra = 30$ and used FK as the variable parameter. Branching of a simple bifurcation type (Keller, 1977) occurs at $FK = 3.8757$. At this bifurcation point, two branches emanate and they have solutions (D_0; D_1) and (D_0; $-D_1$), respectively. Since we use the Euclidean norm in Figure 2, these two branches coincide in the figure. The two solutions can be interpreted as asymmetrical solutions with hot spots in the lower left and lower right corners of the cavity with clockwise and counterclockwise rotation of each vortex, respectively. The limit point on the conduction branch occurs at $FK = 3.995$, see Eq. 15. The convection branch is stable, but at $FK = 5.2011$ a Hopf bifurcation point is found. Exchange of stability occurs at this point and the convection solution is not stable anymore. We have thus reached the point where convection can no longer stabilize the chemical reaction. One expects that a thermal explosion will occur beyond this point, and the program we have used to compute the bifurcation diagram was unable to find any other solution emanating from the Hopf point. A natural extension of Eqs. 11–13 for $\alpha = 2$ is

$$\psi = A_{11}(t)\sin 2\pi z \sin \pi x + A_{12}(t) \sin 2\pi z \sin 2\pi x \tag{18}$$

$$\theta = D_0(t)\cos \pi z + D_1(t)\cos \pi z \cos \pi x + D_2(t) \cos \pi z \cos 2\pi x \tag{19}$$

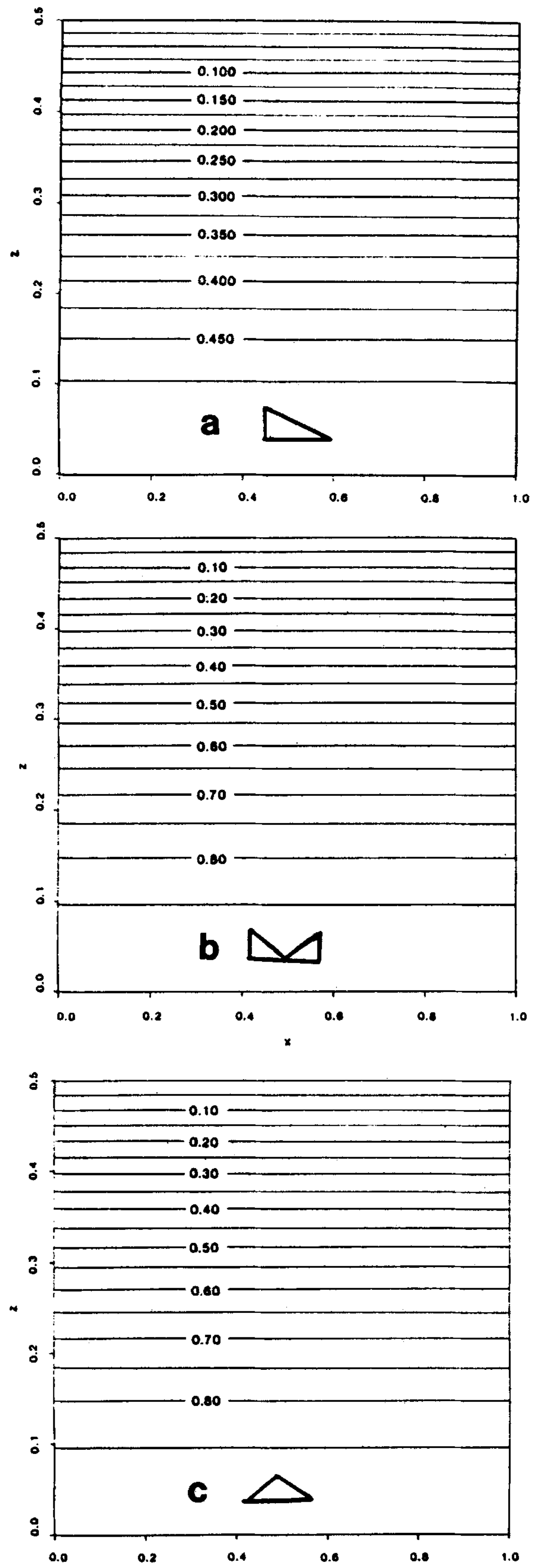


Figure 6. Steady state solutions for different perturbations.

Substituting Eqs. 18 and 19 into Eqs. 7 and 8, the resulting Galerkin approximation is:

$$0 = -A_{11} + \frac{8}{15\pi^2} Ra D_1 \tag{20}$$

$$0 = -A_{12} + \frac{2}{3\pi^2} Ra D_2 \tag{21}$$

$$\frac{dD_0}{dt} = -\pi^2 D_0 - \frac{\pi^2}{4} A_{11} D_1 - \frac{\pi^2}{2} A_{12} D_2 + 4FK \cdot \left(\frac{1}{\pi} + \frac{D_0}{4} + \frac{D_0^2}{3\pi} + \frac{D_1^2}{6\pi} + \frac{D_2^2}{6\pi}\right) \tag{22}$$

$$\frac{dD_1}{dt} = -2\pi^2 D_1 + \frac{\pi^2}{2} A_{11} D_0 - \frac{3\pi^2}{4} A_{11} D_2 + 8FK \cdot \left(\frac{D_1}{8} + \frac{D_0 D_1}{3\pi} + \frac{D_1 D_2}{6\pi}\right) \tag{23}$$

$$\frac{dD_2}{dt} = -5\pi^2 D_2 + \pi^2 A_{12} D_0 + 8FK\left(\frac{D_2}{8} + \frac{D_0 D_2}{3\pi}\right) \tag{24}$$

In this approximation the convection contribution of the temperature solution consists of two terms, and we will be able to follow the interaction between the two flow patterns.

In Figure 3, the bifurcation diagram of Eqs. 20–24 is shown for $Ra = 50$. Branch 1 is the conduction solution. The first convection branches (branch 2) emanate from the conduction solution at $FK = 3.6359$ in a way analogous to Eqs. 16 and 17. The same exchange of stability to thermal explosion, as in Figure 2, occurs at $FK = 6.061$. A second pair of unstable convection branches (branch 3) emanate from the conduction solution at $FK = 3.867$. These solutions are of the type (D_0; 0; $\pm D_2$) and they can be interpreted as two-vortex solutions with two hot spots and one hot spot, respectively. Branch 4 denotes a solution where D_0, D_1 and D_2 are nonzero. In Figure 4, we present the solutions qualitatively. A further bifurcation point is found on the (D_0; 0; D_2) branch at $FK = 4.2671$, and this branch is now stable until a Hopf point at $FK = 4.9217$. The tertiary branch that emanates from (D_0; 0; $-D_2$) at $FK = 4.2671$ is also unstable on the interval $4.2671 < FK < 7$. The crossing of the first branches (D_0; $+D_1$; 0) and second branches (D_0; 0; $+D_2$) at $FK = 6$ is purely coincidental and a result of the norm we have chosen. At this crossing point, the solutions are (0.746; +1.0679; 0) and (1.1278; 0.0; +0.65).

Numerical Verification

To check the validity of the diagrams of Figures 2 and 3 we have integrated the original system at certain points on the bifurcation diagrams. Since the simplified system gives a different value for FK_c, we will compare results between the original and the simplified systems on a basis of FK/FK_c. For our numerical investigation we will thus use $FK = FK_{\text{simplified}}\, FK_c / FK_c^*$ where FK_c denotes the critical value for the original system and FK_c^* is the critical value for the simplified system. We have used an explicit finite-difference method and time steps have varied between 1×10^{-4} and 5×10^{-4}. Poisson's equation was solved by the method of successive overrelaxation. We will use

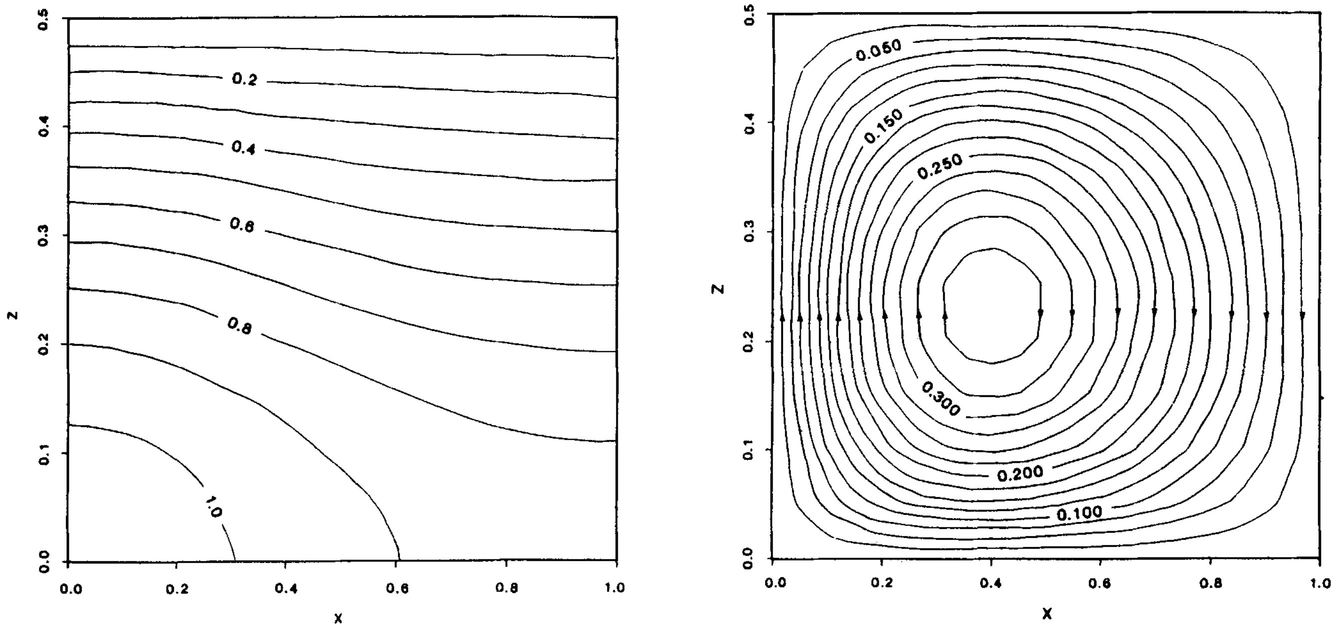


Figure 7. Isotherms and stream function values for $FK/FK_c = 1.0$ and $Ra = 50$.

the following notation to indicate the type of perturbation and steady-state solution:

1. asymmetrical, e.g., initial heating in lower left corner
2. symmetrical double hot spot
3. symmetrical single hot spot

In Figure 5, we show the steady-state solution for $FK/FK_c = 1.281$, $Ra = 30$, and an initial perturbation . Both solutions verify the predictions made by the bifurcation diagram of Figure 2. We have also integrated the original system at $FK/FK_c = 1.281$ with and perturbations. In both cases thermal explosion resulted.

In Figures 6 to 9, we show solutions of the original system for the set of parameters and type of perturbations shown in Table 1. Figures 6a–c are all conduction solutions.

The solutions of the original system verify the bifurcation diagram of Figure 3. Even the stability behavior is correctly predicted. Consider branch 3 of type (D_0; 0; $-D_2$) which is unstable. The original system, with an initial perturbation , is unstable and Figure 9 shows how the evolution to a steady-state solution of type occurs.

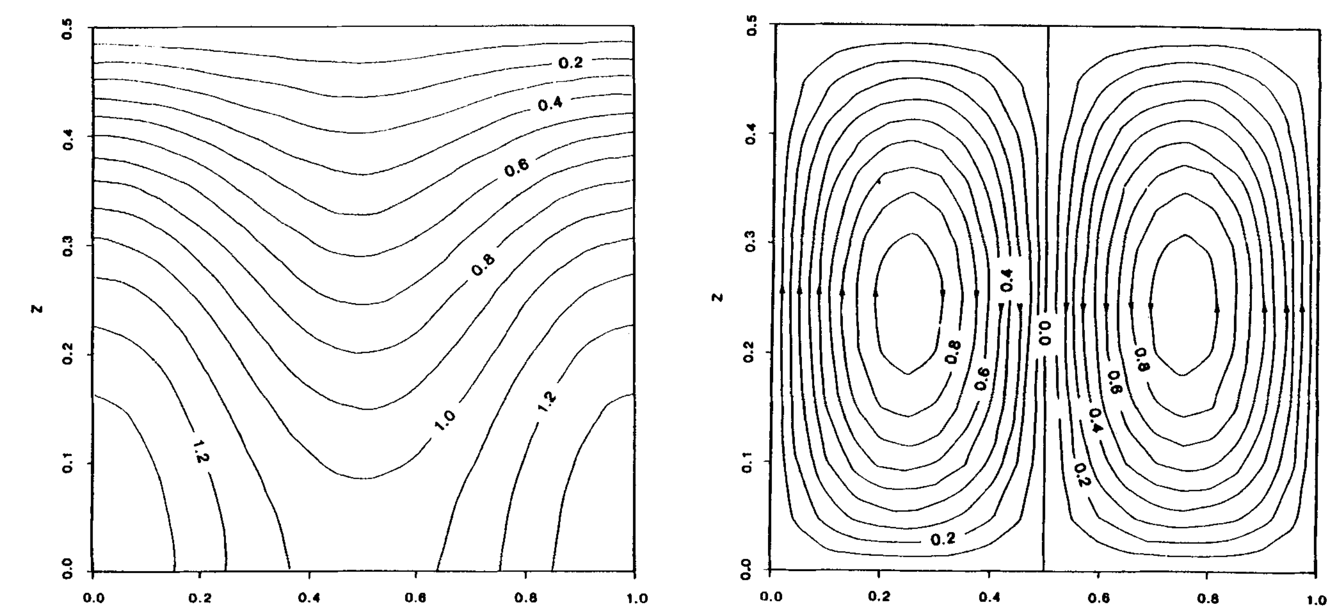


Figure 8. Isotherms and stream function values for $FK/FK_c = 1.189$ and $Ra = 50$.

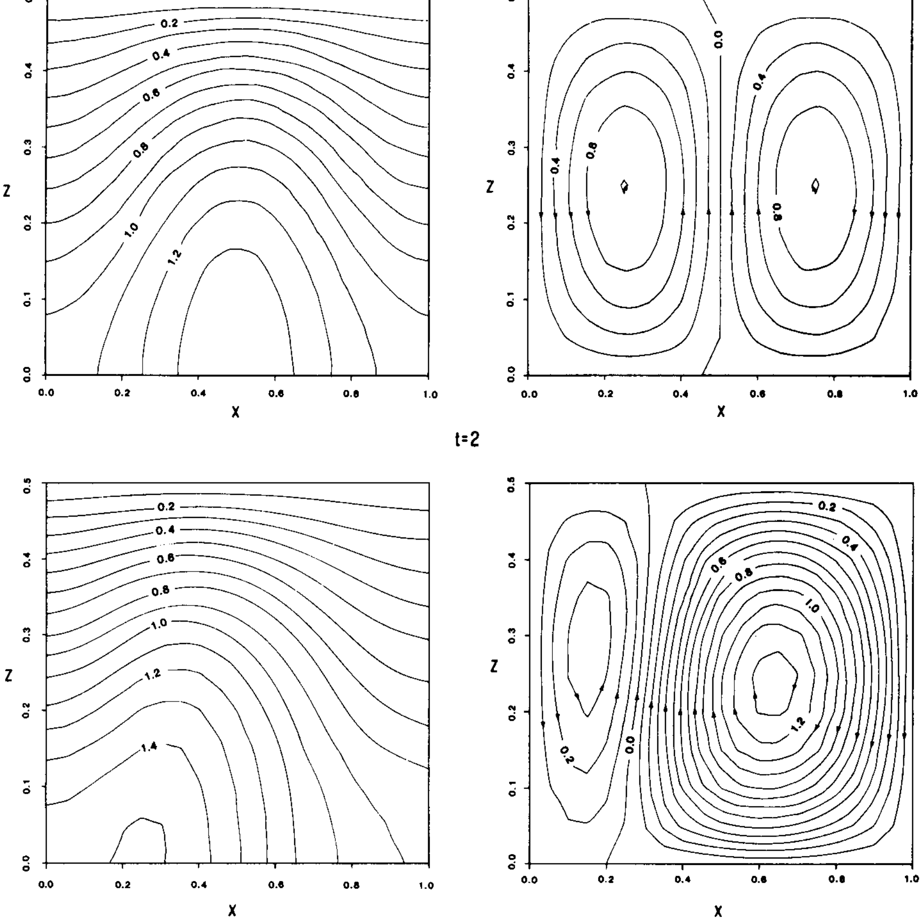


Figure 9a. Isotherms and stream function values for FK/FK_c = 1.189 and Ra = 50: t = 2 and 3.5.

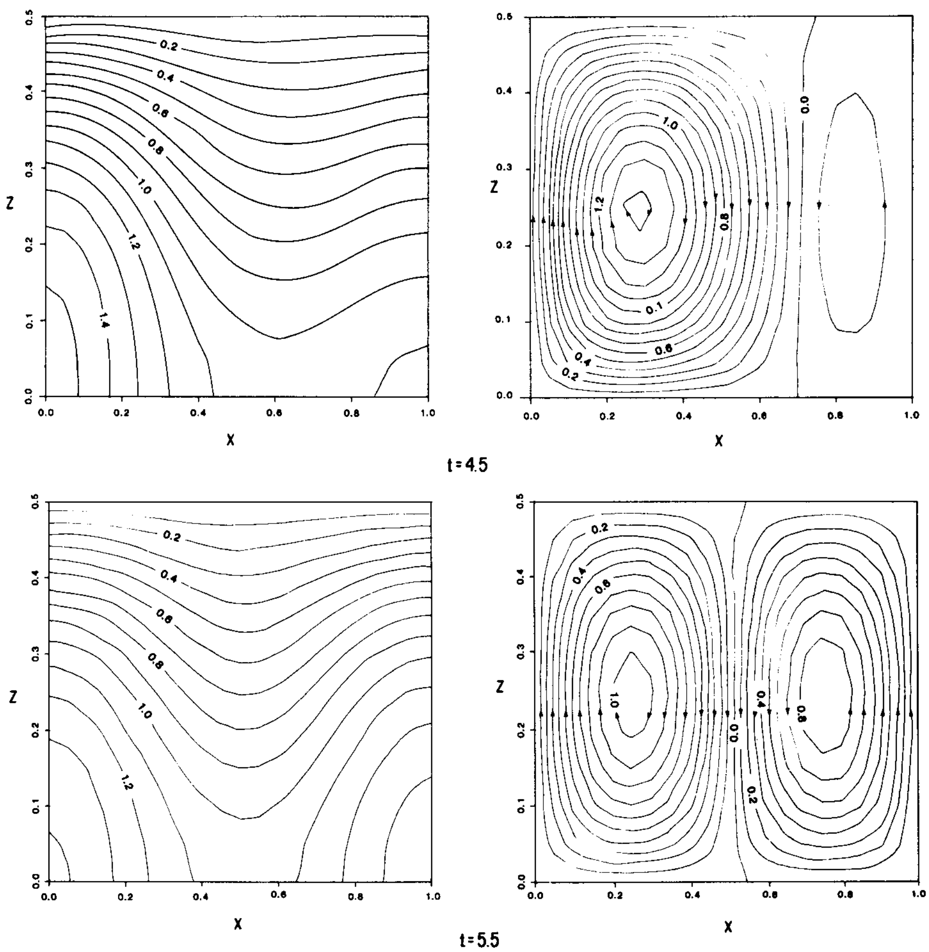
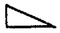
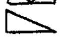
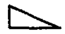


Figure 9b. Isotherms and stream function values for FK/FK_c = 1.189 and Ra = 50: t = 4.5 and 5.5.

Table 1. Parameters and Perturbations for Fig. 6–9 Solutions, $Ra = 50$

Figure No.	FK	Perturbation	Stable Solution Original	Stable Solution Simplified
6a	2.6373		Conduction	Conduction
6b	3.428		Conduction	Conduction
6c	3.428		Conduction	Conduction
7	3.512			
8	4.1757			
9	4.1757			 or 

The method of analysis by means of a truncated Fourier series seems to retain the most important properties of the original system, and the bifurcation and stability behavior are correctly predicted by the simplified system. This is a remarkable result especially in light of the fact that Eqs. 1–3 are not very tractable.

Acknowledgment

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Notation

- C_p – heat capacity
- d – width
- D – diffusion coefficient
- E – activation energy
- FK – Frank-Kamenetskii number, $FK = (Q/k)(E/RT_0^2)\, d^2 k_0 \exp(-E/RT_0)$
- g – gravity constant
- H – height
- K – permeability
- k – thermal conductivity
- k_o – preexponent factor
- P – pressure $p'\epsilon K/\mu\kappa$
- p' – pressure
- Pr – Prandtl number $\nu\epsilon^2 d^2/\kappa K$
- Q – heat of reaction
- R – universal gas constant
- Ra – Rayleigh number, $(\epsilon\beta g K d/\nu\kappa)(RT_0^2/E)$
- T – temperature
- t – time
- u – velocity vector
- x – width
- z – height

Greek letters

- α – aspect ratio, width/height
- β – expansion coefficient, $\partial\rho/\partial T$
- ϵ – porosity
- κ – thermal diffusivity, $k/(\rho C_p)_f$
- μ – dynamic viscosity
- θ – temperature, $(T - T_o)/(RT_o^2/E)$
- ρ – density
- ν – kinematic viscosity, μ/ρ_f

Subscripts

- f – fluid phase
- o – reference state

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