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Modeling of complex dynamics in reaction-diffusion-convection model of cross-flow reactor with thermokinetic autocatalysis

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Abstract

We examine wave patterns occurring in a simple reaction-diffusion-convection model describing a tubular cross-flow reactor with exothermic first order reaction. First, only reaction-diffusion equations are solved by numerical integration to find characteristic spatiotemporal patterns. Then the effects of convection on these patterns are examined. It is found, that most of the resulting patterns are either steady state non-moving waves, or upstream traveling periodic waves. The analysis of this system includes determination of stability and bifurcations of spatially homogeneous steady state, which leads to a dispersion relation, and a direct application of numerical continuation method to the spatially distributed model.

Keywords: reaction-diffusion-convection systems, cross-flow reactor, chemical waves, nonlinear dynamics, bifurcation

1. Introduction

Traveling chemical waves appear due to interplay of autocatalytic chemical reaction and diffusion (Kapral and Showalter, Eds., 1995). Pulse waves can travel through spatially homogeneous but excitable medium, while traveling front waves represent a switch from one homogeneous steady state to another. Near the borderline of excitability and bistable steady states in a parameter space, there may be a zone where more complex dynamics occur, including spatiotemporal chaotic structures (Merkin et al., 1996). Also, periodic phase waves may occur, when the homogenous system is spontaneously oscillatory. All these phenomena are present in the simple model of a cross-flow reactor with exothermic first order reaction studied in this paper when the longitudinal convective flow is absent (Vaníčková et. al., 2003, Trávníčková et. al., 2004]. We have also partly examined effects of added convective flow (i.e., advection along the reactor) (Kohout et al., 2003, Trávníčková et. al., 2004), in particular when the Lewis number *Le* is equal to 1. This corresponds either to a homogeneous reactor (Chang and Schmitz, 1975) or to a packed bed reactor with reaction in liquid phase. When *Le* is different

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from one, a differential convective flow occurs (Yakhnin et al., 1994) leading to convective instabilities (Yakhnin et al., 1995). On the other hand, interaction of reaction and convection in the absence of diffusion/dispersion generates steady state patterns (Nekhamkina et al., 2000), which become dynamic and complex as the dispersion is added (Nekhamkina et al., 2001, Sheintuch and Nekhamkina, 2001). The aim of this paper is to further examine effects of added convective flow on spatiotemporal reaction-diffusion structures for varying values of *Le*.

2. Model Equations

We use a simple one-dimensional model of a cross-flow reactor with exothermic first order reaction (Yakhnin et al., 1994, Nekhamkina et al., 2000). The cross-flow reactor is a membrane tubular reactor (tube within a tube), which enables continuous supply of the reactant not only at the inlet but also through the membrane that forms the outer shell. The reactor is cooled through its inner shell. Although not used in current applications, this arrangement holds a promise of better control over the course of the reaction. The dimensionless mass and energy balance equations govern the spatiotemporal dynamics of the conversion x and dimensionless temperature y as follows,

$$\frac{\partial x}{\partial \tau} = -v\frac{\partial x}{\partial \xi} - \alpha_x (x - x_w) + Da(1-x)e^{\frac{\gamma y}{\gamma + y}}, \tag{1}$$

$$Le\frac{\partial y}{\partial \tau} = d\frac{\partial^2 y}{\partial \xi^2} - v\frac{\partial y}{\partial \xi} - \alpha_y (y - y_w) + BDa(1-x)e^{\frac{\gamma y}{\gamma + y}}. \tag{2}$$

The parameters in Eqs. (1-2) are: the dimensionless convection velocity v, the dimensionless thermal diffusivity d, the Damköhler number Da, the Lewis number Le, the mass and heat transfer coefficients α_x and α_y, respectively, the dimensionless reaction heat B, and the dimensionless activation energy γ. The parameters x_w and y_w are ambient values of x and y. We set $\alpha_x = 0.5$, $x_w = y_w = 0$, $B/Le = 10$, $d/Le = 1$, $\gamma = 1000$ and use v, α_y, Da and Le as variable or adjustable parameters.

The system in the presence of flow is subject to Danckwerts boundary conditions,

$$\xi = 0: \quad x = 0,\ d\frac{\partial y}{\partial \xi} = \frac{v\,y}{Le}; \qquad \xi = L: \quad \frac{\partial y}{\partial \xi} = 0, \tag{3}$$

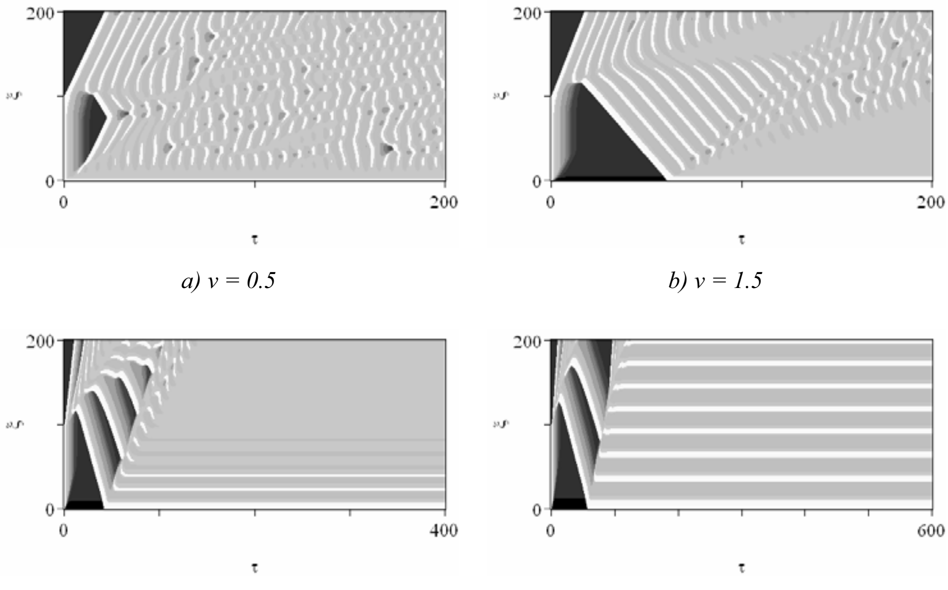
while Neumann boundary conditions are used in the absence of the convective flow,

$$\xi = 0: \quad \frac{\partial y}{\partial \xi} = 0; \qquad \xi = L: \quad \frac{\partial y}{\partial \xi} = 0, \tag{4}$$

where L is the dimensionless length of the reactor.

3. Effect of varying *v* at Le = 1

The homogeneous system (equivalent to a stirred packed bed reactor fed through the membrane only) shows a bifurcation diagram in $Da - \alpha_y$ plane where the region of bistability meets the region of excitability along a Hopf bifurcation curve (Vaníčková et al., 2003). Here a chaotic spatiotemporal structure occurs, which we call triangular chaos. The effect of the flow is shown in Fig. 1. At first, the chaotic pattern persists (Fig. 1a), but as the flow is increased, a high-conversion steady state occurs which is nearly spatially homogeneous (Fig. 1b) with the exception of a narrow zone at the input. Next, this steady state develops small waves near the inlet (Fig.1c) that become regularly spread along the reactor as the flow is increased (Fig. 1d). For still higher *v*, the pattern breaks, and the low-conversion steady state is observed (not shown).



a) v = 0.5 *b) v = 1.5*

c) v = 3.0 *d) v = 4.0*

Figure 1. Effects of convection on triangular chaotic pattern Le = 1.0, Da = 0.039558, $\alpha_y = 1.0$*, shades of grey code conversion from dark (x=0) to light (x=1)*

To understand the nature of these transitions we used continuation method and linear stability analysis of Eqs. (1-3), followed the steady state as *v* is varied, and generated a solution diagram (e.g., Kohout et al., 2002) in Fig. 2. It turns out that there are two Hopf bifurcations on the branch delimiting a range where the steady state is stable. The first one corresponds to the transition from Fig. 1a to Fig. 1b, and the second one corresponds to disappearance of the wavy pattern. Within the range of stable steady state the wave number is decreased as the convective flow is increased.

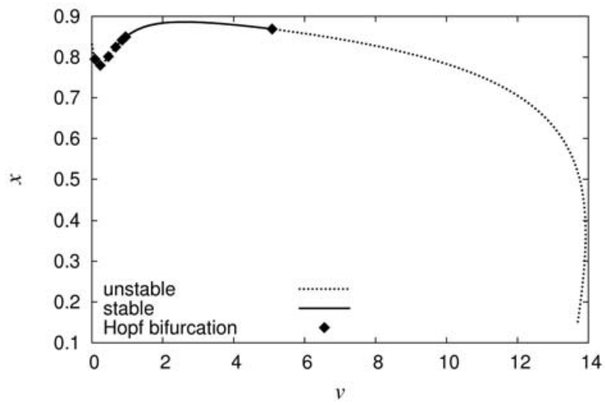
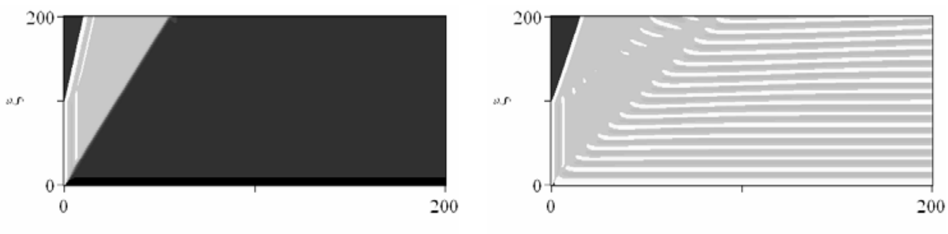


Figure 2. Dependence of the conversion x at position ξ near the inlet on the convection velocity v shows effects of convective flow on the stability of high conversion steady state

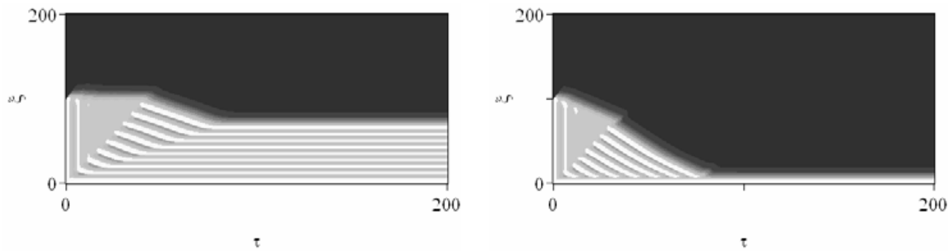
4. Effect of varying Le at v = const

The effect of changing the Lewis number is studied for conditions that keep the same phase portrait in the reaction-diffusion system, that is, α_y/Le, B/Le and d/Le have to be kept constant and equal to the values for $Le = 1$. We chose to study the front wave at $v = 3$. For Le = 1 there are two coexisting fronts, the faster one is an ignition front, the slower one is an extinction front (Fig. 3a). Initially, the change in *Le* does not affect the ignition front, but has a drastic effect on the extinction front, which is converted into a steady state wavy pattern (Fig. 3b). Next, the ignition front is frozen, and the steady state pattern exists only in a part of the reactor (Fig. 3c). Finally, the ignition front is reverted and becomes an upstream extinction front, which pushes the wavy pattern toward the inlet so that only a narrow high-conversion zone remains (Fig.3d).

By performing a linear stability analysis of the homogeneous steady state in an unbounded system we obtain a dispersion relation (Yakhnin et al., 1995, Nekhamkina et al., 2000) implying existence of a neutral curve corresponding to appearance of periodic waves with certain wave number k at various flow velocities v, see Fig. 4. When the frequency of these waves becomes zero, standing waves appear, indicated by a Hopf-Turing point in Fig. 4. This observation suggests, that even in the bounded system the steady state pattern in Fig. 3b occurs due to this Hopf-Turing point.



a) $Le = 1.0$, $\alpha_y = 0.99$, $d = 1$, $B = 10$　　*b) $Le = 1.2$, $\alpha_y = 1.188$, $d = 1.2$, $B = 12$*



c) Le = 1.5, α_y = 1.485, d = 1.5, B = 15

d) Le =2.0, α_y = 1.98, d = 2, B = 20

Figure 3. Effects of Lewis number on front wave Da = 0.04, v=3.0

5. Effect of varying *v* at Le = 600

The last case examined here is the effect of convective flow on reaction-diffusion patterns when *Le* is large. The parameters *Da*, *B* and α_y are adjusted so that the corresponding homogeneous system is near the borderline between a high-conversion steady state and limit cycle oscillations, and the reaction-diffusion system displays chaotic dynamics that we call an undulating pattern (Fig. 5a). When the flow is slightly increased, this pattern is still chaotic and takes the form of upstream moving ripples (Fig. 5b). Then, after a transient, the moving waves become periodic (Fig. 5c). Further increase in velocity (Fig. 5d) causes the upstream waves to move faster, and an alternating pattern of one- and two-packet waves form during the transient, which eventually evolves into regular periodic waves. These waves have lower wave number as well as frequency than the earlier ones.

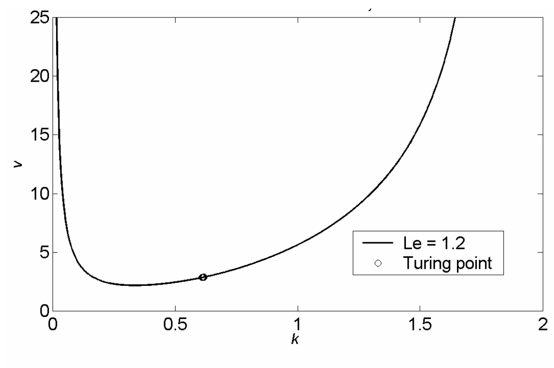


Figure 4. Neutral curves corresponding to case b) from the Figure 3

6. Conclusions

We have shown that the effect of convection on reaction-diffusion waves in a cross-flow tubular reactor may lead either to a steady state wavy pattern for the Lewis number close to one or to periodic waves for large values of *Le*. It is known that reaction-

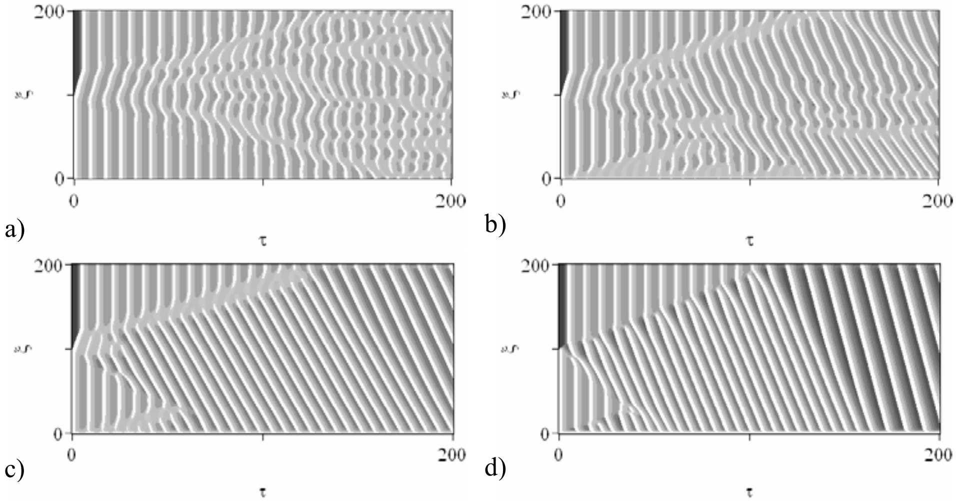


Figure 5. Effects of convection on undulating chaotic pattern Le = 600, Da = 0.064, α_y = 690. a) v = 0.0, b) v = 0.1, c) v = 0.5, d) v = 1.5

convection steady state wavy patterns are related to periodic oscillations of the homogeneous system with *Le* = 1 (Nekhamkina et al., 2000). Since the reaction-diffusion patterns examined here are far from this condition when *Le* is large, convection cannot contribute to steady state pattern and periodic waves occur instead.

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