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Turing Instability in Inhomogeneous Arrays of Diffusively Coupled Reactors

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We study the competition between the Turing instability to steady patterns and the Hopf instability to oscillations in diffusively coupled open reactors. Our approach is based on exact, analytical criteria for the occurrence of these instabilities in arrays of coupled reactors. We consider a general two-variable kinetic model that represents an activator−inhibitor scheme with a complexing agent or substrate for the activator. We apply our results to the Lengyel−Epstein model of the chlorine dioxide−iodine−malonic acid reaction. Using symbolic computation software, we derive exact conditions for the Turing and Hopf bifurcations in small, linear arrays of coupled reactors with an inhomogeneous concentration profile of the substrate. Our main result is the determination of the critical substrate concentration profile, above which the Turing instability occurs before the Hopf instability. This provides the condition for stationary Turing patterns to be experimentally observable in arrays of coupled reactors.

1. Introduction

A wide variety of phenomena in chemistry, biology, physics, and other fields involve coupling between nonlinear, discrete units. Living cells, for example, often interact with adjacent cells by mass transfer via gap junctions. In specific applications, the number of discrete units involved can be quite large. However, insight into the dynamical behavior of coupled nonlinear elements can be gained already from the study of small arrays, consisting of as few as two units. The study of two coupled continuous-flow stirred tank reactors (CSTRs) has a history of more than twenty five years and has had considerable theoretical and practical impact; see, for example, refs 1−20. In most studies, the reactors are coupled via passive diffusion-like mass transfer, though some have considered electrical coupling[6,17,18] and flow rate coupling.[10,13,15] Most theoretical and experimental investigations of coupled CSTRs have focused on coupled chemical oscillators, and many different types of dynamical behavior were observed. Only a few studies have considered coupled steady state reactors.[4,7,21−23]

The first studies of coupled chemical cells were theoretical investigations and focused on the diffusion-induced instability to nonuniform steady states.[24,25] As Turing showed five decades ago, diffusion can destabilize the homogeneous steady state and generate stable, stationary concentration patterns in chemical systems with appropriate nonlinear kinetics.[26] Turing's work has given rise to an extensive literature on chemical pattern formation in chemistry and biology; for reviews, see, for instance, refs 27−29. Though chemical pattern formation is most commonly studied in continuous reaction−diffusion systems, instead of discrete systems of coupled reactors, Turing already showed that the diffusion-induced instability, now called Turing instability or Turing bifurcation, can also occur in two coupled reactors. The earliest studies of the Turing instability in two homogeneous reactors employed the Brusselator model for the kinetics,[24,25] whereas recent studies have used the more realistic Lengyel−Epstein model.[30,31] The latter is a simplified two-variable model[32] for the chlorite−iodide−malonic acid (CIMA) reaction and its variant, the chlorine dioxide−iodine−malonic acid (CDIMA) reaction.[33] These reactions have claimed a prominent place in nonlinear chemical dynamics, since the first conclusive experimental evidence of Turing patterns, in reaction−diffusion systems, was obtained with the CIMA and CDIMA reactions thirteen years ago; see, for example, refs 34−37.

True Turing patterns can only occur in open systems, and their experimental realization requires appropriate flow reactors. Such reactors were developed fifteen years ago, and the continuously fed unstirred reactor (CFUR),[38,39] consisting of a gel layer coupled to one or two CSTRs, has become the main experimental tool. Further, a Turing instability can only occur if the inhibitor species has a diffusion coefficient that is larger than the activator species. For the CIMA and CDIMA reactions, this necessary condition is achieved by introducing a complexing agent or substrate, for example, starch or poly(vinyl alcohol), for the activator species, iodide ion. The substrate is either embedded in the gel of the CFUR in the case of starch or can be used as the gel itself in the case of poly(vinyl alcohol) or polyacrylamide. Consequently, the substrate−activator complex is immobile, which leads to a significant reduction in the effective diffusion coefficient of the activator species. The CIMA and CDIMA reactions can oscillate in a CSTR, and an analysis of their kinetics shows that the concentration of the

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substrate determines if in a CFUR the oscillatory instability or the Turing instability occurs first, i.e., is the primary bifurcation, as a control parameter is varied.[32,40,41] If the substrate concentration is higher than some critical value, the Turing instability is the primary bifurcation, whereas at lower substrate concentrations the oscillatory instability occurs first. This raises the question of the effect of spatially nonuniform substrate concentrations on the formation of Turing patterns, because it is experimentally very difficult to achieve a completely uniform gel. The theory of Pearson and Bruno[41] leads to the conclusion that as long as the substrate concentration is everywhere higher than the critical value, the Turing instability will occur first, and Turing patterns are observable. However, this is only a sufficient condition, not a necessary one. We expect that as long as those regions with a substrate concentration below the critical value are not too large in size, the Turing bifurcation should still be the primary bifurcation.

The effect of spatial inhomogeneities on chemical pattern formation is an important open problem. Chemical or biological systems are rarely completely uniform. Pattern formation in the *Drosophila* egg, for example, occurs in the presence of maternally imposed gradients of gene products.[42] The experimental studies of Turing patterns in the CIMA and CDIMA reactions mentioned above all used CFURs, which unavoidably exhibit gradients in the concentrations of the feed reactants. Theoretical studies of spatially nonuniform reaction−diffusion systems are rare, and little is known about the effects of gradients on the formation of patterns. Except for spatial variations in the diffusion coefficient,[43,44] inhomogeneities in parameters of the reaction−diffusion system typically lead to nonuniform steady states. No general analytical tools exist for the stability analysis of such states. Perturbation techniques can be used for weak nonuniformities, as in refs 45−47. Lengyel and co-workers[48] used an approximation of the reaction−diffusion equation to study the effect of the gradients in CFURs on the position and the possible three-dimensional character of the Turing structures. In general, numerical studies are required to address the problem; see for example, refs 49−53. Voroney and co-workers[54] have carried out numerical simulations of the Sel’kov model with a complexing reaction. They considered the case where the immobile complexing species is confined to disks or stripes. If the spatial scales of the inhomogeneities and the reaction−diffusion system are comparable, interactions between oscillatory behavior and Turing patterns generate spatiotemporal dynamics not observed in a homogeneous medium.

Although the analysis of inhomogeneous reaction−diffusion systems presents serious challenges, the situation is considerably more favorable for inhomogeneous arrays of diffusively coupled reactors. These systems can be studied with the standard methods of stability analysis and bifurcation theory for systems of coupled ordinary differential equations. Using these tools, we derive a general condition for the observability of Turing patterns in inhomogeneous arrays of coupled reactors. We study the effect of inhomogeneities in the substrate concentration for linear arrays of two, three, and four reactors. The paper is organized as follows. In section 2 we briefly review the Lengyel−Epstein model for the CDIMA reaction in a well-stirred reactor and in a reaction−diffusion setting. The general condition for the Turing instability to be the primary bifurcation in arrays of coupled reactors is formulated in section 3. We apply our results to small, linear, inhomogeneous arrays of coupled reactors with Lengyel−Epstein kinetics in section 4. We discuss the implications of our results in section 5.

2. Lengyel−Epstein Model and Turing Bifurcation in a Reaction−Diffusion System

The effect of the complexing agent on the activator species can be taken into account in a simplified two-variable model by “renormalizing” the time scale on which the free activator concentration evolves.[32,41] For the CDIMA reaction in a CSTR, the kinetic equations of the two-variable Lengyel−Epstein model (LE model) are

$$\sigma\frac{\mathrm{d}u}{\mathrm{d}t} = f(u,v) = a - u - 4\frac{uv}{1+u^2} \tag{1}$$

$$\frac{\mathrm{d}v}{\mathrm{d}t} = g(u,v) = b\left(u - \frac{uv}{1+u^2}\right) \tag{2}$$

Here u and v are the dimensionless concentrations of I^- and ClO_2^-, respectively. The constant a is proportional to $[CH_2(COOH)_2]/[ClO_2]$ and the constant b to $[I_2]/[ClO_2]$. The parameter σ depends on the concentration of the complexing agent S according to $\sigma = 1 + K[S]_0[I_2]$, where K is the association constant of the substrate−activator complex. Acceptable experimental values lie in the range $1 \le \sigma < 1000$.[37] Note that $\sigma = 1$ corresponds to no complexing agent. The CDIMA reaction in a CSTR, described by the LE model, has only one steady state given by

$$\bar{u} = \frac{a}{5} \qquad \bar{v} = 1 + \frac{a^2}{25} \tag{3}$$

This state undergoes a Hopf bifurcation to oscillatory behavior at

$$b_H = \frac{3a^2 - 125}{5a\sigma} \tag{4}$$

For $a > \sqrt{125/3}$, the unique steady state of the CDIMA reaction in a CSTR is stable for $b > b_H$, and the reaction oscillates for $b < b_H$.

When the LE model is studied in the setting of a one-dimensional reaction−diffusion system,

$$\sigma\frac{\partial u(x,t)}{\partial t} = f(u,v) + \frac{\partial^2 u}{\partial x^2} \tag{5}$$

$$\frac{\partial v(x,t)}{\partial t} = g(u,v) + d\frac{\partial^2 v}{\partial x^2} \tag{6}$$

where d is the ratio of diffusion coefficients $D_{ClO_2^-}/D_{I^-}$, it is found that the homogeneous steady state undergoes a Turing bifurcation to a nonuniform steady state, as b is decreased, at (see, for instance, ref 37)

$$b_T = \frac{d}{5a}(13a^2 - 4\sqrt{10}a\sqrt{25 + a^2} + 125) \tag{7}$$

The critical value b_T for a bifurcation to Turing patterns is independent of σ, whereas the critical value b_H for a bifurcation to homogeneous oscillations is inversely proportional to σ. To observe the formation of Turing patterns, one must ensure that the Turing bifurcation occurs before the Hopf bifurcation. For a given value of a, this can be achieved by using a sufficiently large concentration of complexing agent such that $\sigma > \sigma_c^*(a)$, where $\sigma_c^*(a)$ is given by $b_T = b_H$.

As is clear from the form of the reaction−diffusion system, steady states and stationary bifurcations are completely independent of σ. It is only time-dependent states, such as oscillations, and nonstationary bifurcations that are affected by σ or the concentration of the complexing agent. Because stationary states are independent of σ, they are not affected by spatial inhomogeneities in the substrate concentration. The theory of Pearson and Bruno[41] leads to the expected conclusion that $\sigma(x) > \sigma_c^*(a)$ everywhere is a sufficient condition for the homogeneous steady state to undergo a Turing bifurcation before a Hopf bifurcation. This raises the interesting question of what happens if $\sigma(x) < \sigma_c^*$ in some regions of the reactor. We expect that as long as those regions are not too large in size or as long as $|\sigma(x) - \sigma_c^*(a)|$ is sufficiently small in those regions, the Turing bifurcation should still occur first.

3. Inhomogeneous Linear Arrays of Coupled Reactors

Although the analytical study of the stability of reaction–diffusion systems with spatial nonuniformities is difficult, as mentioned in section 1, analytical criteria can be derived for the observability of Turing patterns in inhomogeneous arrays of coupled reactors, as we show in this section. Not only are arrays of coupled reactors interesting in their own right as explained in the Introduction, but they can also be understood as a more or less crude discretization of the reaction–diffusion system (5) and (6). We consider a linear array of m reactors containing all components of the CDIMA reaction, including the complexing agent, and linked by diffusive coupling via semipermeable membranes. The reactors are identical with the exception of the complexing agent concentration. The membranes are impermeable to the complexing agent, and individual reactors may be loaded with different concentrations of substrate, i.e., have different values of σ. A linear array of such coupled reactors is described by the following set of coupled ordinary differential equations:

$$\sigma_1 \frac{du_1}{dt} = f(u_1,v_1) + u_2 - u_1 \tag{8}$$

$$\frac{dv_1}{dt} = g(u_1,v_1) + d(v_2 - v_1) \tag{9}$$

$$\sigma_i \frac{du_i}{dt} = f(u_i,v_i) + u_{i+1} + u_{i-1} - 2u_i \qquad i = 2, ..., m-1 \tag{10}$$

$$\frac{dv_i}{dt} = g(u_i,v_i) + d(v_{i+1} + v_{i-1} - 2v_i) \qquad i = 2, ..., m-1 \tag{11}$$

$$\sigma_m \frac{du_m}{dt} = f(u_m,v_m) + u_{m-1} - u_m \tag{12}$$

$$\frac{dv_m}{dt} = g(u_m,v_m) + d(v_{m-1} - v_m) \tag{13}$$

The unique homogeneous steady state of the linear array of CDIMA reactions is given by $(\bar{u}_i, \bar{v}_i) = (\bar{u}, \bar{v})$ for $i = 1, ..., m$. The stability of this state is determined by the eigenvalues ω of an $n \times n$ Jacobian matrix J, $n = 2m$, which are the roots of the nth order characteristic polynomial, $\det(\mathrm{J} - \omega \mathrm{I}) = 0$ (I is the identity matrix):

$$\omega^n + c_1\omega^{n-1} + c_2\omega^{n-2} + ... + c_{n-1}\omega + c_n = 0 \tag{14}$$

The homogeneous steady state is stable, if all roots ω of (14) have a negative real part. The necessary and sufficient conditions for this to hold are the Routh–Hurwitz conditions, see, for example, refs 55–57,

$$\Delta_k = \begin{vmatrix} c_1 & c_3 & \cdot & \cdot & \cdot & \cdot \\ 1 & c_2 & c_4 & \cdot & \cdot & \cdot \\ 0 & c_1 & c_3 & \cdot & \cdot & \cdot \\ 0 & 1 & c_2 & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & \cdot & \cdot & \cdot & c_k \end{vmatrix} > 0 \qquad k = 1, 2, ..., n \tag{15}$$

together with the condition

$$c_n > 0 \tag{16}$$

(Set $c_i = 0$ in (15) for $i > n$.) A stationary bifurcation, which corresponds to a vanishing real eigenvalue, occurs if condition (16) is violated, i.e., $c_n = 0$. The CDIMA reaction in a CSTR cannot undergo a stationary bifurcation; see section 2. Therefore, spatially homogeneous perturbations cannot have a vanishing real eigenvalue for an array of CDIMA reactions, and $c_n = 0$ (with $\Delta_k > 0$) is a necessary and sufficient condition for a Turing instability to occur. Orlando's formula implies that $\Delta_{n-1} = 0$ (with $c_n > 0$, $\Delta_k > 0$, $k = 1, ..., n-2$) is a necessary and sufficient condition for a conjugate pair of purely imaginary eigenvalues,[56,58] i.e., for a Hopf bifurcation.

The Turing bifurcation and the Hopf bifurcation occur together, if

$$c_n = 0 \qquad \text{and} \qquad \Delta_{n-1} = 0 \tag{17}$$

which determines the critical profile $\sigma_{i,c}(a)$. (Because $\Delta_{n-1} = \Delta_{n-2}c_{n-1} - M_{n-2,n-1}c_n$, where $M_{i,j}$ is the minor of the (i, j) element of the Hurwitz determinant Δ_{n-1}, condition (17) implies that $\Delta_{n-2} = 0$ also, if $c_{n-1} \neq 0$, which is the generic case.) Note that we have obtained a fully analytical criterion for the critical substrate concentration profile. This has the great advantage that we can determine the condition where the Turing bifurcation ceases to be the primary bifurcation without having to resort to a time-consuming numerical search of a large parameter space.

Evaluating the various quantities by hand is already a very cumbersome task for two coupled reactors. We have therefore used symbolic computation software, namely MATHEMATICA (Wolfram Research, Inc., Champaign, IL, 2002) and MAPLE (Waterloo Maple Inc., Waterloo, Ontario, 2002), to obtain exact, analytical expressions for the coefficients c_i of the characteristic polynomial (14) and the Hurwitz determinants Δ_k for arrays of up to four coupled reactors.

4. Small Linear Arrays with Lengyel–Epstein Kinetics

4.1. Two Coupled Reactors. For two coupled reactors, the Jacobian is given by

$$\mathbf{J} = \begin{pmatrix} \mathbf{R}_1 & \mathbf{D}_1 \\ \mathbf{D}_2 & \mathbf{R}_2 \end{pmatrix} \tag{18}$$

where

$$\mathbf{R}_i = \begin{pmatrix} (A_{11} - 1)/\sigma_i & A_{12}/\sigma_i \\ A_{21} & A_{22} - d \end{pmatrix} \quad \text{and} \quad \mathbf{D}_i = \begin{pmatrix} 1/\sigma_i & 0 \\ 0 & d \end{pmatrix} \tag{19}$$

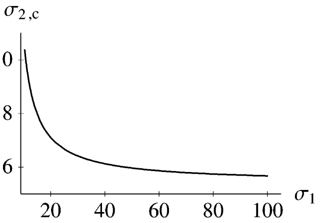

Figure 1. Critical profile, $\sigma_{2,c}$ as a function of σ_1, for two coupled reactors with Lengyel−Epstein kinetics for $a = 50.0$ and $d = 1.07$.

Here

$$A_{11} = \left.\frac{\partial f}{\partial u}\right|_{(\bar{u},\bar{v})} \quad A_{12} = \left.\frac{\partial f}{\partial v}\right|_{(\bar{u},\bar{v})} \quad A_{21} = \left.\frac{\partial g}{\partial u}\right|_{(\bar{u},\bar{v})} \quad A_{22} = \left.\frac{\partial g}{\partial v}\right|_{(\bar{u},\bar{v})} \tag{20}$$

Already for two reactors, the expressions for the coefficients c_i of the characteristic polynomial and the Hurwitz determinants Δ_k in terms of a, b, d, σ_1, and σ_2 are very lengthy and will not be given here. Solving $c_4 = 0$, we find

$$b_T = \frac{2d(a^2 - 175)}{35a} \tag{21}$$

and a Turing bifurcation exists if $a > a_{\min} = \sqrt{175} = 13.228756$. For a homogeneous array, i.e., $\sigma_1 = \sigma_2 = \sigma$, the Turing bifurcation occurs before the Hopf bifurcation if $\sigma > \sigma_c^*(a;2)$ (the argument after the semicolon denotes the number of coupled reactors), where

$$\sigma_c^*(a;2) = \frac{7(3a^2 - 125)}{2d(a^2 - 175)} \tag{22}$$

In an inhomogeneous two-reactor array, the substrate concentration profile is necessarily asymmetric. Let reactor 1 be the high-substrate reactor, $\sigma_1 > \sigma_c^*(a;2)$, and let reactor 2 be the low-substrate reactor, $\sigma_2 < \sigma_c^*(a;2)$. We vary σ_1 in reactor 1 and determine the critical concentration $\sigma_{2,c}(\sigma_1,a,d)$ in reactor 2, as a function of σ_1. For $\sigma_2 > \sigma_{2,c}(\sigma_1,a,d)$ the Turing bifurcation occurs first, whereas for $\sigma_2 < \sigma_{2,c}(\sigma_1,a,d)$ the Hopf bifurcation is the primary bifurcation. We obtain the critical concentration in reactor 2, $\sigma_{2,c}(\sigma_1,a,d)$, by solving (17). We set $b = b_T$, which ensures that the first condition of (17) holds, and use MATHEMATICA to solve $\Delta_3 = 0$ in terms of σ_2. The resulting expression for $\sigma_{2,c}$ takes up about twelve lines. It is not enlightening at all and will therefore not be displayed here. We will instead illustrate the behavior by choosing specific values for a and d and plot $\sigma_{2,c}$ as a function of σ_1. Following ref 37, we use the experimental value $d = 1.07$ for the ratio of diffusion coefficients in all calculations in this paper. (Below, we will no longer explicitly denote the dependence on d of quantities like $\sigma_{2,c}$, etc.) For the parameter a we choose the value $a = 50.0$; however, the behavior is qualitatively the same for other values. For these conditions, $b_T = 2.84314$, and $\sigma_c^*(50;2) = 10.3758$. For a very large concentration of substrate in reactor 1, $\sigma_1 \rightarrow \infty$, the Turing instability will occur first, if $\sigma_2 > \sigma_{2,c}(\infty,50) = 5.41038$. As σ_1 decreases, $\sigma_{2,c}$ increases monotonely, as can be seen from Figure 1. As σ_1 approaches $\sigma_c^* = 10.3758$, so does $\sigma_{2,c}$.

These results show that the Hopf bifurcation is more destabilizing than the Turing bifurcation. If half of the system, i.e., one reactor, contains no substrate, $\sigma_2 = 1$, then the Hopf bifurcation is the primary bifurcation of the coupled array, no matter how large the substrate concentration σ_1 is in the other reactor. In fact, for $a = 50.0$ the two coupled reactors will undergo a transition to oscillations first as b is decreased as long as $\sigma_2 < 5.41038$. Further, the arithmetic mean of the critical profile, $\bar{\sigma}_c = \sigma_1 + \sigma_{2,c}(\sigma_1,a)$, as well as the geometric mean, $\hat{\sigma}_c = \sqrt{\sigma_1 \cdot \sigma_{2,c}(\sigma_1,a)}$, are bigger than the critical value for a homogeneous array $\sigma_c^*(a;2)$, which reinforces the conclusion that the inhomogeneous array is more vulnerable to oscillatory perturbations than to inhomogeneous, stationary perturbations.

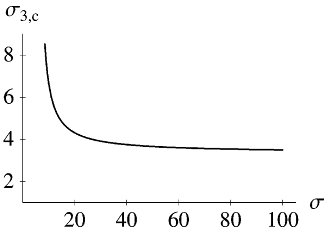

Figure 2. Critical profile, $\sigma_{3,c}$ as a function of σ, for three coupled reactors with Lengyel−Epstein kinetics for case 1: $\sigma_1 = \sigma_2 = \sigma$; $a = 50.0$; $d = 1.07$.

4.2. Three Coupled Reactors. For three coupled reactors, the Jacobian is given by

$$\mathbf{J} = \begin{pmatrix} \mathbf{R}_1 & \mathbf{D}_1 & \mathbf{O} \\ \mathbf{D}_2 & \tilde{\mathbf{R}}_2 & \mathbf{D}_2 \\ \mathbf{O} & \mathbf{D}_3 & \mathbf{R}_3 \end{pmatrix} \tag{23}$$

where

$$\tilde{\mathbf{R}}_i = \begin{pmatrix} (A_{11} - 2)/\sigma_i & A_{12}/\sigma_i \\ A_{21} & A_{22} - 2d \end{pmatrix} \quad \text{and} \quad \mathbf{O} = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix} \tag{24}$$

For an array of three coupled reactors, the Turing condition corresponds to $c_6 = 0$, which yields

$$b_T = \frac{d(a^2 - 75)}{15a} < \tag{25}$$

and a Turing bifurcation exists if $a > a_{\min} = \sqrt{75} = 8.660254$. For a homogeneous array, i.e., $\sigma_1 = \sigma_2 = \sigma_3 = \sigma$, the Turing bifurcation occurs before the Hopf bifurcation if $\sigma > \sigma_c^*(a;3)$, where

$$\sigma_c^*(a;3) = \frac{3(3a^2 - 125)}{d(a^2 - 75)} \tag{26}$$

We will consider two types of inhomogeneous substrate profiles; either an end reactor, e.g., reactor 3, or the middle reactor has a different substrate concentration, i.e., (1) $\sigma_1 = \sigma_2 = \sigma > \sigma_3$ or (2) $\sigma_1 = \sigma_3 = \sigma > \sigma_2$. We determine the critical substrate profile, i.e., $\sigma_{3,c}(\sigma,a)$ in case 1 and $\sigma_{2,c}(\sigma,a)$ in case 2 by solving (17) with $n = 6$ for $\sigma > \sigma_c^*(a;3)$. As for two coupled reactors, we set $b = b_T$, which ensures that the first condition of (17) holds, and use MATHEMATICA to solve Δ_5 in terms of σ_3 or σ_2, respectively. For three or more coupled reactors, the solution of the second equation in (17) can no longer be found in closed, analytical form; $\sigma_{3,c}$ or $\sigma_{2,c}$, respectively, is determined numerically. Note that this is the only numerical step in our approach. Analytical expressions are obtained for all other quantities and conditions. We choose again $a = 50.0$ and find $b_T = 3.45967$ and $\sigma_c^*(50;3) = 8.52683$. The critical profiles for case 1 and 2 are shown in Figures 2 and 3, respectively. Again, $\sigma_{3,c}(\sigma,a)$ and $\sigma_{2,c}(\sigma,a)$ increase monotonely as σ decreases.

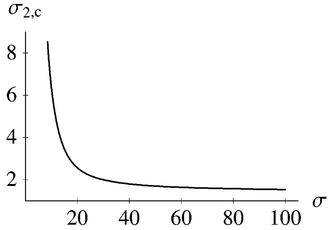

Figure 3. Critical profile, $\sigma_{2,c}$ as a function of σ, for three coupled reactors with Lengyel−Epstein kinetics for case 2: $\sigma_1 = \sigma_3 = \sigma$; $a = 50.0$; $d = 1.07$.

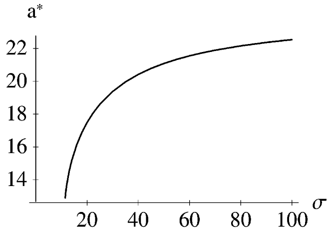

Figure 4. Plot of a^* as a function of σ for three coupled reactors for case 2; $d = 1.07$.

The behavior of the critical substrate concentration is qualitatively the same in both cases and qualitatively the same as for two coupled reactors. The critical values of the substrate concentration are lower for three coupled reactors than for two coupled reactors. This can be easily understood as follows. For three coupled reactors, Turing patterns are favored in two-thirds of the array, because two reactors have a substrate concentration above $\sigma_c^*(50;3)$. For two coupled reactors, Turing patterns are favored only in half the array, explaining the higher critical value. Comparing the two cases for the three-reactor array, we find that the critical substrate concentration is lower for case 2. The Hopf bifurcation to oscillations occurs before the Turing bifurcation more easily if the reactor with a low substrate concentration is an end reactor instead of being a middle reactor. Further, the Hopf bifurcation is the primary bifurcation of the coupled array in both cases, if either $\sigma_3 = 1$ or $\sigma_2 = 1$, respectively, no matter how large the substrate concentration σ is in the other two reactors. These results appear to confirm the conclusion from the previous subsection that the Hopf bifurcation is more destabilizing than the Turing bifurcation. However, for a three-reactor array the situation is more complicated. As a decreases, the critical profile retains the same qualitative form, but it shifts to lower values. For case 1, $\sigma_{3,c}(\sigma,a) > 1$ for $a > a_{\min}$, and if $\sigma_3 = 1$, then the Hopf instability is the primary bifurcation for all values of a and σ. The same is not true for case 2. Given a value of $\sigma_1 = \sigma_3 = \sigma$, there exists an $a^* > a_{\min}$, such that for $a < a^*$ we find $\sigma_{2,c}(\sigma,a) < 1$, which is unacceptable, because experimentally σ cannot be smaller than one. The behavior of a^* as a function of σ is shown in Fig. 4. As σ increases, a^* increases and approaches an asymptotic value of 24.2072. For the largest experimentally acceptable value of the substrate concentration, $\sigma = 1000$, we find $a^* = 24.029$. For $a > 24.2072$, the Hopf bifurcation will occur before the Turing bifurcation, if $1 \leq \sigma_2 < \sigma_{2,c}(\sigma,a)$. For $a < 24.2072$ and σ sufficiently large, the Turing bifurcation always occurs first, even if the middle reactor contains no substrate. This clearly illustrates that an inhomogeneous reactor array, where the reactor with the low substrate concentration is in the middle, provides more favorable conditions for observing Turing patterns than an array where the reactor with the low substrate concentration is located at the end.

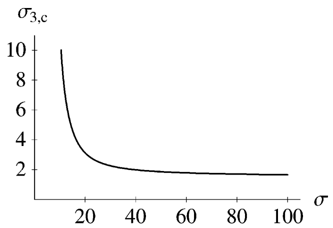

Figure 5. Critical profile, $\sigma_{3,c}$ as a function of σ for four coupled reactors with Lengyel−Epstein kinetics for case 2: $\sigma_1 = \sigma_2 = \sigma_4 = \sigma$; $a = 50.0$; $d = 1.07$.

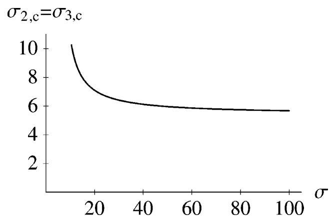

Figure 6. Critical profile, $\sigma_{2,c} = \sigma_{3,c}$ as a function of σ, for four coupled reactors with Lengyel−Epstein kinetics for case 4: $\sigma_1 = \sigma_4 = \sigma$; $a = 50.0$; $d = 1.07$.

4.3. Four Coupled Reactors. For four coupled reactors, the Jacobian is given by

$$\mathbf{J} = \begin{pmatrix} \mathbf{R}_1 & \mathbf{D}_1 & \mathbf{O} & \mathbf{O} \\ \mathbf{D}_2 & \tilde{\mathbf{R}}_2 & \mathbf{D}_2 & \mathbf{O} \\ \mathbf{O} & \mathbf{D}_3 & \tilde{\mathbf{R}}_3 & \mathbf{D}_3 \\ \mathbf{O} & \mathbf{O} & \mathbf{D}_4 & \mathbf{R}_4 \end{pmatrix} \qquad (27)$$

Two Turing bifurcations occur in a linear four-reactor array. One Turing condition is

$$b_{T1} = \frac{2d}{35a}(a^2 - 175) \qquad (28)$$

with $a > a_{\min} = \sqrt{175} = 13.228756$, and the other is

$$b_{T2} = \frac{d}{235a}(2a^2 + 7\sqrt{2}a^2 - 2350 + 1175\sqrt{2}) \qquad (29)$$

with $a > a_{\min} = 7.60544$. These two Turing bifurcations are degenerate at $a_{T0} = 32.96566389$, and for $a \neq a_{T0}$, the difference between b_{T1} and b_{T2} is small. For $a = 50.0$, the Turing instability corresponding to b_{T1} occurs first, $b_T = b_{T1} = 2.84314$, and $\sigma_c^*(50;4) = 10.3758$. We have determined the critical substrate concentration profile for four cases following the same procedure as used for two and three coupled reactors: (1) $\sigma_1 = \sigma_2 = \sigma_3 = \sigma > \sigma_4$; (2) $\sigma_1 = \sigma_2 = \sigma_4 = \sigma > \sigma_3$; (3) $\sigma_1 = \sigma_2 = \sigma > \sigma_3 = \sigma_4$; (4) $\sigma_1 = \sigma_4 = \sigma > \sigma_2 = \sigma_3$. The behavior of the critical substrate concentration is again qualitatively the same in all four cases and qualitatively the same as for two- and three-reactor arrays. Therefore we show only the two cases most favorable to Turing patterns, Figures 5 and 6, which as expected are case 2 and case 4, where the low-substrate reactors are located in the interior of the array.

As for a linear array of three reactors, we find in case 2 that for a small enough and σ large enough, the Turing bifurcation always occurs first, even if the reactor 3 contains no substrate. We define, as for three coupled reactors, the critical value a^* by the condition that $\sigma_{3,c}(\sigma,a^*) = 1$. The behavior of a^* as function of σ is shown in Figure 7. For $\sigma < 17.7$, two curves of Hopf bifurcation points approach each other, merge and vanish as a is decreased. This results in a jump of $\sigma_{3,c}$ from a value larger than 1 to a value smaller than 1, and the definition

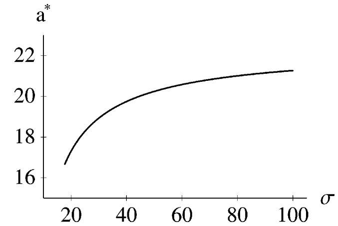

Figure 7. Plot of a^* as a function of σ for four coupled reactors for case 2; $d = 1.07$.

of a^* is no longer applicable. This region in parameter space exhibits rich dynamics, which will be reported elsewhere.[59]

5. Discussion

Using methods of stability analysis and bifurcation theory for coupled ordinary differential equations, we have shown that it is possible to derive exact, analytical conditions for the Turing instability and the Hopf instability in arrays of coupled reactors. This approach has allowed us to assess the effect of spatial inhomogeneities in the substrate concentration on the observability of Turing patterns in diffusively coupled reactors. We found that the Turing bifurcation in the CDIMA reaction is moderately robust to spatial nonuniformities. The concentration of the activator complexing agent can drop to about half of the homogeneous critical value in half of the array, and the Turing bifurcation will still occur before the Hopf bifurcation, if the substrate concentration is moderately large ($\sigma \approx 100$) in the other half of the array. We also find that inhomogeneous arrays are less vulnerable to oscillatory perturbations, if the low-substrate reactors are in the middle of the array. In fact, for three or four coupled reactors, the Turing instability will occur first, even if a reactor in the middle of the array has no substrate at all, if a is low enough and σ is high enough. These results show that, as conjectured in sections 1 and 2, the Pearson and Bruno result, $\sigma(x) > \sigma_c^*(a)$ everywhere, is indeed only a sufficient condition for the Turing bifurcation to occur first; it is not a necessary condition.

The main advantage of our approach is that it avoids time-consuming numerical searches of a large parameter space to find the critical concentration profile. Instead, it relies on symbolic computation software to obtain exact, analytical expressions for the coefficients of the characteristic polynomial, the Hurwitz determinants, the Turing condition, and the Hopf condition. Though in principle any number of coupled reactors can be studied, in practice, the number is limited by the performance of the computational software and hardware. Arrays of up to four reactors can easily be studied on a regular desktop computer—part of the calculations were carried out with MATHEMATICA on a Macintosh 867 MHz PowerPC G4 with 512 MB RAM, and we have obtained reliable results in a reasonable amount of time for up to six reactors using MAPLE on a Compaq ES 40 with 32GB RAM.

Our theoretical analyses show that arrays of coupled reactors can provide a very useful experimental tool to study the formation of spatial chemical patterns. They represent an attractive alternative to CFURs, which so far have been the only type of reactor employed in the study of Turing patterns. Arrays of coupled reactors are particularly well suited to investigate the effect of spatial inhomogeneities on Turing instabilities. It is easy to change the substrate concentration in individual CSTRs and to generate specific inhomogeneous substrate concentration profiles in arrays of coupled reactors. The same task is more difficult in a CFUR; there the substrate is either embedded in the gel or is the gel itself. Arrays of coupled reactors also avoid the gradients in the feed reactant concentrations that occur in CFURs.

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