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Complex Dynamics Resulting from Coupling between Oregonators in a Series of Two CSTRs with Recycle

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Complex periodic and aperiodic dynamics for the coupling between simple oscillators in a series of two CSTRs with recycle has been investigated. Numerical results are reported with flow rate and recycle ratio as bifurcation parameters. A new route following 1^j bifurcation (j can be odd or even numbers depending on the space time and recycle ratio) to chaos has been identified. The so-called "well-mixed limit" depends on the chemical kinetics involved.

Introduction

The Belousov−Zhabontinskii (BZ) reaction is a well-known example of a chemical reaction exhibiting both temporal and spatial instabilities far from equilibrium (see ref 1 and references cited therein). The first comprehensive mechanism for the BZ reaction was proposed by Field, Koros, and Noyes[2], from which an abstract model, the so-called three-variable irreversible Oregonator, was derived.[3] Within the unstable region of the stability diagram, the Oregonator in a flow reactor could only exhibit limit cycle behavior.[4]

Mixing may alter the complex system dynamics both quantitatively and qualitatively.[5,6] Macromixing effects on complex chemical dynamic systems have been investigated in several studies.[4,7−14] Two-compartment systems are the most commonly employed flow model in these studies. One of the most striking conclusions drawn from these studies is that complex dynamics may result from the coupling between incomplete mixing and nonlinear chemical kinetics.

Gyorgyi and Field[9] had modeled the dead space within a stirred tank via a flow model with two CSTRs located in parallel. They had demonstrated that due to the coupling between the two oscillators (the four-variable, partially reversible Oregonator model as discussed in ref 15), complex periodic or aperiodic oscillations could result by varying the input flow rate. A sequence of period doubling bifurcation to chaos was identified. Doumbouya et al.[16] and Doumbouya and Schneider[17] had investigated the coupling between two oscillators (BZ reactions) located in parallel as well. Complex dynamics such as quasiperiodicity, phase locking, and chaos are observed experimentally and theoretically.

Nonideal flow patterns may exist in different ways in a stirred tank, which could be modeled via various flow models. One example is the tanks-in-a-series model,[18] which is a one-parameter model useful in modeling the inflow port effect or the fluid dispersion effect in the reactor. In a flow reactor the reactants would enter first into an input zone then flow into the bulk phase of the reactor, which resemble a tanks-in-a-series configuration.

The focus of this work is to investigate the possible role of macromixing effect on the interference between simple oscillators in two tanks in a series. Numerical results show that, owing to the coupling of the two three-variable irreversible Oregonator oscillators (abbreviated as Oregonator hereafter) in two CSTRs in a series, complex dynamic behavior will occur. A new bifurcation sequence to chaos is identified.

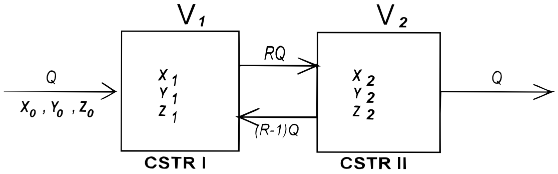

Figure 1. Schematics of the flow system.

The Models

Figure 1 illustrates schematically the flow system under consideration, which consists of two perfectly mixed CSTRs in a series. The volumes were both set as 400. Due to the action of the stirrer, there exists a recycle flow at a flow rate of $(R - 1)Q$ between the two CSTRs. $R - 1$ is the recycle ratio and an increase in R is equivalent to increasing mixing intensity. The underlying dynamics is described by the following six simultaneous ODEs (note: the relationship between the actual phenomenological equations and the rate constants with the following dimensionless chemical kinetics has been provided in ref 4 and is not shown here for brevity's sake):

$$\frac{\mathrm{d}X_1}{\mathrm{d}t} = \frac{X_0 - RX_1 + (R-1)X_2}{\tau_1} + s(Y_1 - X_1Y_1 + X_1 - qX_1^{\,2}) \tag{1}$$

$$\frac{\mathrm{d}Y_1}{\mathrm{d}t} = \frac{Y_0 - RY_1 + (R-1)Y_2}{\tau_1} + \frac{1}{s}(Y_1 - X_1Y_1 + fZ_1) \tag{2}$$

$$\frac{\mathrm{d}Z_1}{\mathrm{d}t} = \frac{Z_0 - RZ_1 + (R-1)Z_2}{\tau_1} + \omega(X_1 - Z_1) \tag{3}$$

$$\frac{\mathrm{d}X_2}{\mathrm{d}t} = \frac{R(X_1 - X_2)}{\tau_2} + s(Y_2 - X_2Y_2 + X_2 - qX_2^{\,2}) \tag{4}$$

$$\frac{\mathrm{d}Y_2}{\mathrm{d}t} = \frac{R(Y_1 - Y_2)}{\tau_2} + \frac{1}{s}(-Y_2 - X_2Y_2 + fZ_2) \tag{5}$$

$$\frac{\mathrm{d}Z_2}{\mathrm{d}t} = \frac{R(Z_1 - Z_2)}{\tau_2} + \omega(X_2 - Z_2) \tag{6}$$

where τ_1 and τ_2 are the same and are equal to V_1/Q ($=V_2/Q$). Other parameters are listed in Table 1. Notably, the input concentration of Y ($Y_0 = 10.0$) is much higher than the threshold

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TABLE 1: Parameters and Input Concentrations in the Two Reactors Described by Eqs 1–6

$X_0 = 0.01$	$Y_0 = 10.0$	$Z_0 = 0.01$	
$Q = 0.2$	$V_1 = 400$	$V_2 = 400$	
$f = 1$	$s = 77.27$	$q = 8.375 \times 10^{-6}$	$\omega = 32.2$

concentration (approximately 0.95 in this system) required to trigger the oscillation.[4]

At $R = 1$, no recycling is considered. Under perfect mixing limit (R approaches infinity), it is easy to show that the dynamic behavior for CSTR I and II would coincide and reduce to the following equations:

$$\frac{dX}{dt} = \frac{X_0 - X}{\tau} + s(Y - XY + X - qX^2) \tag{7}$$

$$\frac{dY}{dt} = \frac{Y_0 - Y}{\tau} + \frac{1}{s}(-Y - XY + fZ) \tag{8}$$

$$\frac{dZ}{dt} = \frac{Z_0 - Z}{\tau} + \omega(X - Z) \tag{9}$$

where $\tau = 2\tau_1$.

The Gear method was employed as the integration tool with a maximum relative error of 10^{-8}. Numerical results were immaterial even the relative error was set as low as 10^{-10}.

Results

Figure 2 summarizes the system stability with the notation described in ref 9, i.e., I^j denotes that I large-amplitude peaks and j small-amplitude peaks comprise a cycle. Detailed structures in the boxes shown in Figure 2a are represented in Figure 2, b and c. The time sequences for X_1 corresponding to the triangle and square symbols in Figure 2 are shown in Figure 3, a and b. Figure 3a represents an 1^3 oscillation pattern; while for Figure 3b, an 1^4 oscillation pattern.

At $R = 1$, simple oscillation patterns are observed for both CSTRs, however, the period for X_1 is apparently larger than X_2. Since the key component for the occurrence of oscillation is Y (Br^-), this result is expected since the input concentration for CSTR II (Y_1) would be varying while in most cases much less than that for CSTR I ($Y_0 = 10.0$). For simplicity, the periodicity for X_1 and X_2 are denoted as (1^0, 1^0).

As R is beyond unity the interactions between CSTR I and II result in an 1^1 periodicity in both CSTRs (region I in Figure 2). Notably in CSTR I, the large-amplitude peaks for X_1 are self-generated, while the small-amplitude peaks are induced from the large-amplitude peaks for X_2. Similar situations are also observed for X_2 in CSTR II. Synchrony thereby occurs between the two CSTRs, while the interaction intensity grows as R increases.

Moving further into region II in Figure 2, for example, R ranges between 48.22 and 48.99 at $Q = 0.2$, and within each cycle there exist two 1^1 periodicities for X_1, and a 3^1 periodicity for X_2, denoted by (($1^1)^2$, 3^1) periodicity.

In region III in Figure 2a, for example, R ranges between 49.00 and 63.15 at $Q = 0.2$, and the small-amplitude peaks for X_2 have grown to large-amplitude peaks. The state thereby becomes (1^1, 2^0) periodicity.

As the state moves to the narrow region between region III and IV in Figure 2, complex oscillations occur. A different bifurcation pattern takes place for Q higher than or less than and equal to 0.2. Consider first $Q = 0.2$. As R increases to the region between 63.15 and 63.241, a sequence of bifurcation occurs from (1^1, 2^0) → (1^3, 4^0) → (1^5, 6^0) → (1^7, 8^0) and so on. The X_1 sequence for (1^3, 4^0) has been demonstrated in Figure 3a. The bifurcation sequence is an 1^{2n-1} route to chaos. When R is beyond 63.245, the number of small-amplitude peaks accompanied with the single large-amplitude peak in a cycle for X_1 becomes unpredictable. Chaotic dynamic behavior is observed, as demonstrated in Figure 3c ($R = 63.2460$). This corresponds to the chaos region B in Figure 2a.

After R increases beyond 63.28, the situation suddenly changes into simple oscillation patterns, in which the two CSTRs oscillate synchronously. However, the amplitude in X_1 is much smaller than that for X_2, which gives a state of (0^1, 1^0) (region IV in Figure 2a). The amplitude and the period both grow with the increase in R. For R larger than approximately 2000, the outputs for X_1 and X_2 are the same as that described by eqs

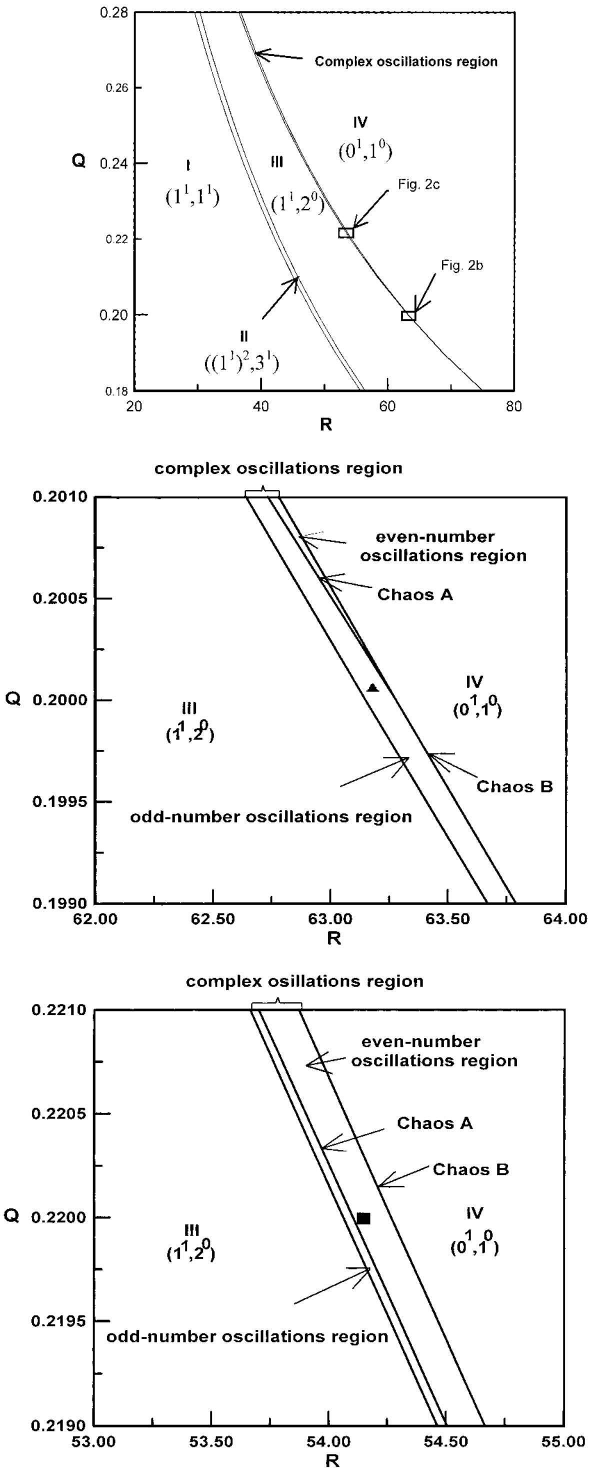

Figure 2. Stability diagram for the present dynamic system.

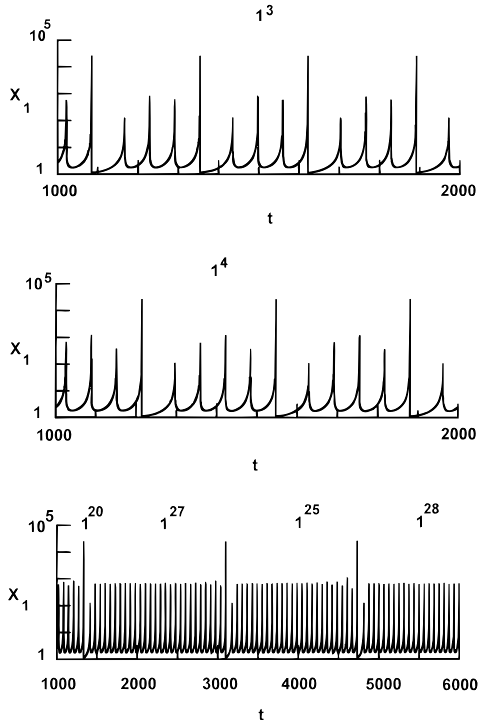

Figure 3. Time evolution for reactant X_1: (a) 1^3 periodicity, $Q = 0.2$, $R = 63.18$; (b) 1^4 periodicity, $Q = 0.22$, $R = 54.13$; (c) chaos, $Q = 0.2$, $R = 63.2436$.

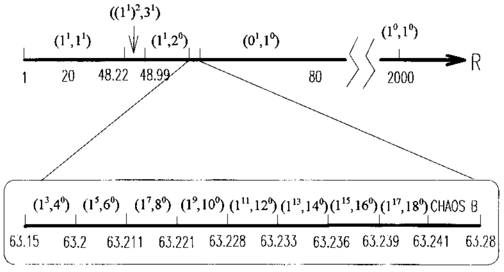

Figure 4. Bifurcation sequence for $Q = 0.2$.

7−9, the infinite R limit. As a result, the stirred tank can be taken as a perfectly mixed CSTR when R is larger than 2000.

Figure 4 depicts the bifurcation sequence with $Q = 0.2$. The odd-number oscillations region in Figure 2a corresponds to the 1^{2n-1} bifurcation sequence to chaos in Figure 4. All cases with $Q < 0.2$ behave similarly to the $Q = 0.2$ case.

Next consider $Q = 0.22$ as a representative for all cases with Q larger than 0.2. Between regions III and IV a more complicated oscillation pattern than that for $Q = 0.2$ exists. There is an odd-number oscillations region such as that for $Q = 0.2$ between $R = 54.061$ and 54.099. As R increases further (between 54.1 and 54.103), complex oscillations with both 1^{2n-1} and 1^{2n} take place. For example, the X_1 sequence for $R = 54.102$ follows: $1^4 \rightarrow 1^6 \rightarrow 1^4 \rightarrow 1^6 \rightarrow 1^4 \rightarrow 1^9 \rightarrow 1^4 \rightarrow 1^6 \rightarrow 1^7 \rightarrow 1^4 \rightarrow 1^5 \rightarrow 1^4 \rightarrow 1^5$, and so on. Figure 5, a and b demonstrates the corresponding phase plane portraits. The sequence is unpredictable and thereby ensembles the chaotic region A denoted in Figure 2b,c.

Increasing further the R value moves the state into the even-number oscillations region. First between 54.103 and 54.132 is the (1^4, 5^0) periodicity state. What follows is the complex oscillations including both (1^2, 3^0) and (1^4, 5^0), denoted as region $C_2{}^4$. After then the sequence becomes (1^2, 3^0) → $C_2{}^4$ → (1^4, 5^0) → $C_4{}^6$ → (1^6, 7^0) → $C_6{}^8$ → (1^8, 9^0) → $C_8{}^{10}$ and so on. The X_1 sequence for the (1^4, 5^0) periodicity has been shown in Figure 3b. As R increases beyond 54.266, the number of small-amplitude peaks accompanied by the single large-amplitude peak in a cycle for X_1 becomes unpredictable. Figure 6 depicts the bifurcation sequence for $Q = 0.22$. An 1^{2n} bifurcation sequence to chaos is noted.

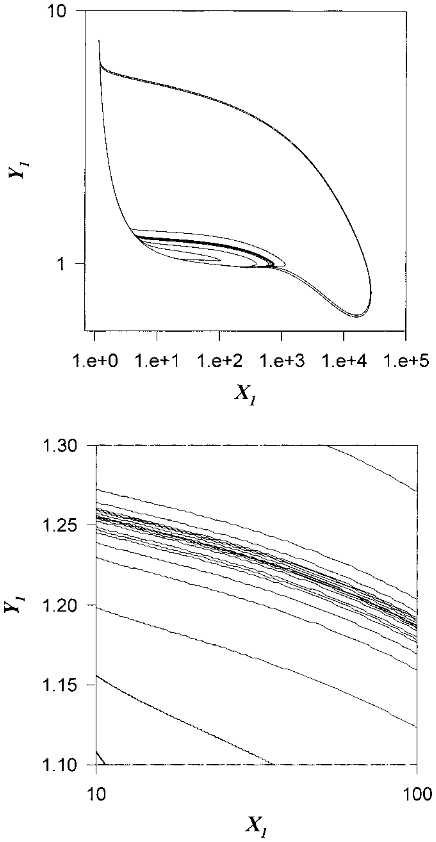

Figure 5. Phase plane portraits for chaos A region. $Q = 0.22$, $R = 54.102$.

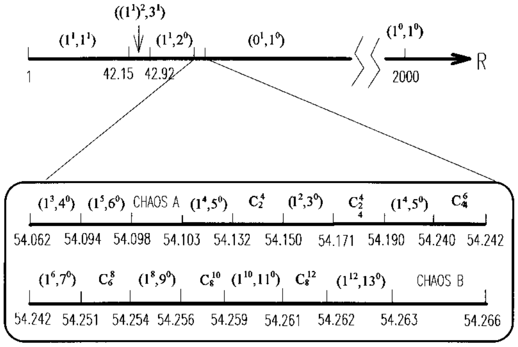

Figure 6. Bifurcation sequence for $Q = 0.22$.

Discussion

In the Oregonator the depletion of component Y in both CSTRs is the key factor affecting the system dynamics. In region I in Figure 2, the two oscillators interact mutually, as evidenced by the small- and large-amplitude peaks appear in both CSTRs. However, owing to the depletion of Y_1, the oscillations for CSTR II are fully excited in region II. On the other hand, the oscillations for CSTR I is suppressed to an extent for the high concentration input of Y_0.

The bifurcation to chaos occurs in a sequence of 1^n periodicity bifurcations, where n is an odd number when $Q < 0.2$ (with a space time greater than or equal to 4000), or an even number when $Q > 0.2$. Such a kind of bifurcation route had not been reported previously for the Oregonator-related processes and is totally different from the period-doubling route reported for

CSTRs in parallel.[9] The transition between the two regions with different odd-number periodicities (e.g., 1^3 and 1^5) is rather sharp that an intermediate state cannot be detected even the recycle ratio change is set as low as 10^{-6}. This is also different from the dynamics for most complex chemical systems.

On the other hand, the transition between regions with even-number periodicities becomes not so sharp as that for odd-number periodicities. For example, the $C_2{}^4$ region existing between (1^4, 5^0) and (1^2, 3^0) in Figure 6 actually comprises many combinations of the 1^4 and 1^2 periodicities, such as $(1^2)(1^4)$, $(1^2)(1^2)(1^4)$, and so on. And finally, all states evolve as 1^2 periodicity. The transition between the other even-number periodicity regions reveals a similar character.

Within the chaotic region, although the oscillation patterns are unpredictable, there exists a trend that the number of small-amplitude peaks on an average increases with the recycle ratio R. For example, the X_1 sequence at $R = 63.245$, $Q = 0.2$ is $1^{22} \rightarrow 1^{38} \rightarrow 1^{33} \rightarrow 1^{29} \rightarrow ...$, while for $R = 63.28$ the sequence becomes $1^{58} \rightarrow 1^{64} \rightarrow 1^{64} \rightarrow 1^{62} \rightarrow ....$ Finally, CSTR II takes over the process and only the induced small-amplitude peaks survive in CSTR I. After the chaotic region (region IV), all large-amplitude peaks in CSTR I are killed suddenly, without a detectable bifurcation region behind it. This is also not usually observed in most complex dynamic systems.

Notably, the present Oregonator model can only exhibit simple limit cycle behavior in a perfect CSTR with the parameter set used. The dynamics observed here is owing to the coupling between the two simple oscillators, whose oscillation period is affected by the recycle ratio, or the mixing intensity. When the recycle ratio is close to zero, coupling is diminished. When the recycle approaches infinity, the coupling becomes too strong that both oscillators will be forced to behave like a single oscillator. In between there is a recycle ratio region where the coupling is strong enough but both oscillators still have their own patterns. Synchronous oscillations result when their periods can find common multiple. When this is not possible, chaotic oscillations result.

We have also changed the tank volumes V_1 and V_2 to 8 and 792, so that tank I occupies only 1% of the total reactor volume. Similar dynamic behavior as mentioned above is observed for this situation (with a smaller $Q = 0.01$) as well. As a result, the input port region, even though the occupied volume can be relatively small when compared with the total reactor volume, can function as a source of complex dynamic behavior in an incompletely macromixed reactor.

For diagnosing the mixing in a flow reactor, it is a common practice to inject some inert tracer into a flow reactor and to trace the outflow tracer concentration continuously.[18] The tracer concentration versus time data resemble the so-called residence time distribution (RTD) of the reactor. If the RTD is close to that for a CSTR, the reactor is usually accepted as well macromixed. Notably, no chemistry is involved in such a diagnosis scheme. We have here conducted a series of simulations considering a step-change input of some inert tracer into the initially tracer-free reactor shown in Figure 1. Figure 7 illustrates the response curves. Apparently, on the basis of the RTD obtained, the flow system shown in Figure 1 can be taken as well macromixed only if R is greater than 10. This value is, however, much less than that found for the present Oregonator model (2000). The so-called "well-mixed limit" thereby depends strongly on the chemical kinetics involved.[13,14]

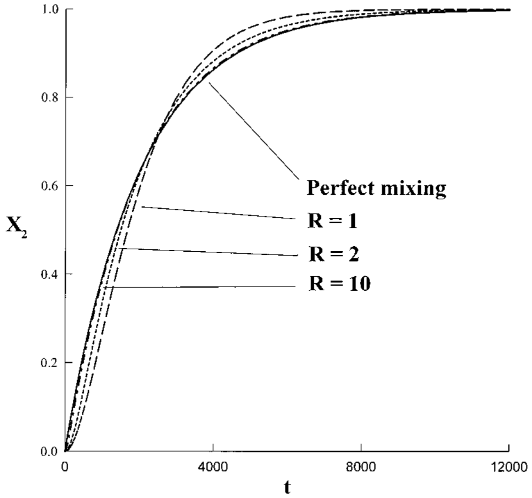

Figure 7. Response curve of flow system shown in Figure 1 for a step-change input of an inert tracer under various R.

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