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Chaos control in the cerium-catalyzed Belousov–Zhabotinsky reaction using recurrence quantification analysis measures

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ABSTRACT

Chaos control in the Belousov–Zhabotinsky-CSTR system was investigated theoretically and experimentally by reconstructing the phase space of the cerium (IV) ions concentration time series and then optimizing recurrence quantification analysis measures. The devised feedback loop acting on the reactor inlet flow rate was able to experimentally suppress chaos and drive the system to an almost predictable state with approximately 93% determinism. Similar theoretical results have also been demonstrated in numerical simulations using the four-variable Montanator model as solved by the multistage Adomian decomposition method.

1. Introduction

Complex dynamic behaviors have been reported for a number of chemical reaction systems including the Belousov–Zhabotinsky (BZ) [1], the Briggs–Rauscher (BR) [2], the Bray–Liebhafsky (BL) [3], the chlorine dioxide–iodide [4] reactions, etc. Particularly, the BZ system has been extensively investigated and was found to exhibit limit cycle behavior, hysteresis and chaos under certain conditions in well-mixed, as well as unstirred, batch and continuous reactors [5,6]. In fact, a BZ reaction consists of simultaneous oxidation and bromination of an organic compound, such as malonic acid, by bromate ions catalyzed by the ions of a transition-metal, such as cerium or manganese, in a strongly acidic environment [7].

The first elaborate mechanism for the BZ reaction was proposed by Field, Körös and Noyes in 1972 [8], which is now widely accepted, and involves three main processes: (1) consumption of bromide ion, (2) autocatalytic reaction of bromous acid with oxidation of the catalyst, and (3) organic reaction with reduction of the catalyst. In 1974, Field and Noyes simplified the FKN mechanism by retaining only five key reactions and developed a mathematical model dubbed the Oregonator, named after the University of Oregon, where the research was conducted [9]. The Oregonator model is formulated as a system of coupled nonlinear ODEs, which captures the essential features of the FKN mechanism. Györgyi, Rempe and Field provided further insights into the BZ reaction in a continuous-flow, stirred tank reactor (CSTR) by developing an 11-state variable model with three adjustment parameters [10]. A simplified version of the latter model, with a substantially reduced computational burden, was then proposed by Györgyi and Field, which is now recognized as the four-variable Montanator model in deference to the University of Montana [11]. The four-variable Montanator model can satisfactorily account for chaos formation in

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BZ-CSTR systems, which has been demonstrated by experiment [12,13].

The recurrence quantification analysis (RQA) has emerged as a powerful tool for investigation of the dynamics of a given system through means of a reconstructed phase space. The salient feature of the RQA is that it provides a wealth of useful information even in the case of short, non-stationary and extremely noisy data where previous time series analysis strategies fail to yield reliable results. Moreover, by using the RQA, one may partition the whole time history into consecutive epochs and thus better investigate the system behavior step by step [14,15]. For example, the RQA-based measures have been employed to successfully interpret electromyography data [16], data of human postural fluctuations [17], electroencephalographic time series [18], neuronal signals [19], cardiovascular variability signals [20,21], molecular dynamics simulation results [22], pressure signals of fluidized bed reactors [23–27], stock market time series [28]. For a review see [29].

Most recently, we have shown that a number of control designs, involving nonlinear, dislocated and speed feedback laws, can stabilize the periodic oscillations of the BZ reaction under batch conditions in theory [30].

Petrov et al. [31] have experimentally stabilized periodic oscillations in a BZ-CSTR system by perturbing the flow rates of cerium and bromate solutions into the reactor and monitoring according to the phase-portrait of the system. Our work is mainly different from their approach in that we here investigate the application of the RQA-based measures to feedback control the chemical chaos for the first time to the best of our knowledge. Moreover, as it will be discussed in the next parts, we have measured ceric ions concentration by means of a spectrophotometer instead of the potentiometric method. In what follows, we develop a systematic approach for controlling the BZ-CSTR chaos by means of two RQA-based measures, namely the recurrence rate and determinism. As it will be shown in the sequel, a feedback law that locally maximizes any of these measures can realize chaos suppression, both in theory and practice.

2. The four-variable Montanator model

The four-variable Montanator model focuses on the molar concentration of particular species, namely Br^-, $HBrO_2$, Ce^{4+} and BrMA in a single CSTR. For convenient reference, we assign $y_1 = [Br^-]$, $y_2 = [HBrO_2]$, $y_3 = [Ce^{4+}]$ and $y_4 = [\mathrm{BrMA}]$, and, by custom, the coupled nonlinear terms are incorporated into the reaction rates. Thus, this model consists of a system of four coupled strongly nonlinear ODEs as follows:

$$\begin{cases} \frac{dy_1}{dt} = -r_1 - r_2 + r_7 + r_8 + \frac{1}{\tau}(y_{1,in} - y_1), \\ \frac{dy_2}{dt} = -r_1 + r_2 - 2r_3 + 0.5(r_4 - r_5) + \frac{1}{\tau}(y_{2,in} - y_2), \\ \frac{dy_3}{dt} = r_4 - r_5 - r_6 - r_7 + \frac{1}{\tau}(y_{3,in} - y_3), \\ \frac{dy_4}{dt} = 2r_1 + r_2 + r_3 - r_7 - r_8 + \frac{1}{\tau}(y_{4,in} - y_4), \end{cases} \tag{1}$$

where the subscript "in" denotes the mixed feed at a specific reactor inlet and τ is the reactor residence time, i.e. the reactor volume divided by the volumetric flow rate entering the reactor. The kinetic rate expressions for reactions r_1 to r_8 are given in Table 1.

The quasi-steady-state concentration of the radical species $MA^\bullet$ is defined as

$$[MA^\bullet]_{QSS} = \frac{-k_1[\mathrm{BrMA}] + \sqrt{(k_1[\mathrm{BrMA}])^2 + 8k_2k_3[\mathrm{MA}][Ce^{4+}]}}{4k_3}, \tag{2}$$

and we can estimate the molarity of $BrO_2^\bullet$ radicals by assuming that they are in a long-lasting chemical equilibrium with the species BrO_3^- and $HBrO_2$ as

$$[BrO_2^\bullet]_{est} = [BrO_2^\bullet]_{EQ} = \sqrt{k_4[HBrO_2]/k_5}. \tag{3}$$

The numeric values for the kinetic rate coefficients of the two latter equations are as follows [11]:

$$k_1 = 2.4 \times 10^4 M^{-1}\,s^{-1}, \quad k_2 = 0.3 M^{-1}\,s^{-1},$$
$$k_3 = 3.0 \times 10^9\ M^{-1}\,s^{-1}, \quad k_4 = 0.858\ s^{-1},$$
$$k_5 = 4.2 \times 10^7\ M^{-1}\,s^{-1}.$$

The initial concentrations of the four state variables as well as the values for the molar concentrations $[H^+]$, $[BrO_3^-]$, [MA] and $[\mathrm{Ce}]_{tot}$ are considered the same as in [32].

3. The numerical solver

Not every numerical integration scheme can be trusted for the analysis of mathematical models, especially those involving chaotic dynamics. As indicated in [33], certain popular numerical methods, such as finite difference schemes and Euler's method, might lead to grossly erroneous outcomes known as ghost solutions in the treatment of stiff ODEs, or sometimes even non-stiff ODEs, unless an

Table 1
Chemical reactions included in the four-variable Montanator model and their kinetic rate formulas.

Reaction steps	Kinetic rate expressions ($M\,s^{-1}$)
$Br^- + HBrO_2 + \{H^+\} \rightarrow 2\mathrm{BrMA}$	$r_1 = 2.0 \times 10^6[H^+][Br^-][HBrO_2]$
$Br^- + \{BrO_3^-\} + \{2H^+\} \rightarrow \mathrm{BrMA} + HBrO_2$	$r_2 = 2.0[BrO_3^-][H^+]^2[Br^-]$
$2HBrO_2 \rightarrow \mathrm{BrMA}$	$r_3 = 3.0 \times 10^3[HBrO_2]^2$
$0.5HBrO_2 + \{BrO_3^-\} + \{H^+\} \rightarrow HBrO_2 + Ce^{4+}$	$r_4 = 6.2 \times 10^4[H^+]([\mathrm{Ce}]_{tot} - [Ce^{4+}])[BrO_2^\bullet]_{est}$
$HBrO_2 + Ce^{4+} \rightarrow 0.5HBrO_2$	$r_5 = 7.0 \times 10^3[HBrO_2][Ce^{4+}]$
$Ce^{4+} + \{\mathrm{MA}\} \rightarrow \{\mathrm{products}\}$	$r_6 = 0.3[\mathrm{MA}][Ce^{4+}]$
$\mathrm{BrMA} + \mathrm{Ce(IV)} \rightarrow Br^-$	$r_7 = 30.0[Ce^{4+}][\mathrm{BrMA}]$
$\mathrm{BrMA} \rightarrow Br^-$	$r_8 = 2.4 \times 10^4[\mathrm{BrMA}][MA^\bullet]_{QSS}$