On-line Runaway Detection in Batch Reactors Using Chaos Theory Techniques

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In this work nonlinear time-series analysis using delay coordinate embedding was applied to simulated temperature data from isoperibolic batch reactors to develop an early-warning detection system of the runaway. In the first part of this study an early-warning detection criterion, that is, when the divergence of the system becomes positive on a segment of the reaction path, was developed and compared with previous criteria. This criterion has the property of being preserved under phase-space reconstruction and, hence, it is possible to calculate it when only temperature data are available. This reconstructed divergence is compared with the theoretically calculated divergence using temperature and conversion data. The comparison demonstrates the validity of such an approach finding a new path, lying between the simple use of measured variables and the complex model-based reconstruction techniques, to assess in advance hazardous situations in chemical reactors.

Introduction

The maintenance of safe operation conditions in chemical reactors is of paramount importance to avoid personal and installation damage and environmental pollution. In general, severe accidents due to runaway reactions can be grouped into one scenario: if, for some reason, the rate of heat generation by chemical reaction exceeds the rate of heat removal of the cooling system, the temperature of the reacting mass will begin to rise. This in turn will cause an increase in the heat-generation rate. This positive-feedback mechanism results in autoacceleration behavior of the heat-generation rate, producing a large amount of heat in a very short time with the possibility of triggering side and chain reactions that eventually can lead to the destruction or inoperability of the plant.

Major safety advancements at the level of a particular chemical process can only be achieved through the long processes of research and engineering experience. Nevertheless, despite the conventional fallback mechanisms, switches, and multilayer control circuitry available today, there is always the possibility of undetected runaway events. A safe reactor is therefore not only characterized by the degree of complexity of its safety measures but also by how soon unexpected potentially dangerous situations can be detected. Early-warning devices are therefore indispensable, irrespective of the detailed mechanism of the reaction and of other safety measures.

An early-warning detection system consists of the following parts (Iserman, 1984): interface with the process to acquire data (monitoring); criteria to distinguish between dangerous situations and nondangerous ones (detection); procedure for triggering the alarms (diagnosis and evaluation). Methods for early warning detection can be divided into two categories, depending upon the quantities being used. The first one consists of only using measurements from the system that in the case of chemical reactors turn out to be temperature measurements, its derivatives, or a combination, which is the case

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of the OLIWA system (Hub, 1977; Hub and Jones, 1986). The second method consists of using a model of the system, the available measurements and, normally, a Kalman filter to estimate the nonmeasurable variables (Gilles and Schuler, 1982; King and Gilles, 1990). Despite all the different approaches, early on-line detection of hazardous states in batch chemical reactors is still an open problem because of the wide range of processes that are carried out on such equipment, their complexity, strong nonlinearity, and time-varying parameters. In this sense, the bottleneck for an on-line detection system is the criterion that distinguishes between dangerous and nondangerous situations. On the one hand, the detection system has to provide sufficient time for plant operators to correct the deviations from safe operation, while on the other hand, it has to avoid false alarms, and, especially for batch and semibatch reactors, the on-line safety criteria have to be as independent of the actual process carried out in the plant as possible.

In this work we have tried to demonstrate that a third approach for early on-line detection of hazardous situations exists, in which you do not need a mathematical model of the process, but in which you try to extract information about the behavior of the reactor by phase-space reconstruction using time-delay embedding of temperature measurements. For a simple isoperibolic (constant jacket temperature) batch reactor trajectories in phase space approach a fixed point for $t \to \infty$, where the reaction has finished and the final reaction mass temperature equals the jacket temperature, that is, trajectories originating from two nearby starting points would eventually end up at the same fixed point. Nevertheless, before reaching this fixed point, the orbits can diverge. If the process parameters are near the runaway boundary, a small change will cause dramatic changes in the behavior of the phase-space trajectories. In chaos theory one is often confronted with a similar divergence of trajectories (Abarbanel, 1996). In fact, the rate of divergence can be quantified using the so-called local Lyapunov exponents (Abarbanel et al., 1993). Although we are not interested in studying chaotic systems, we borrow from chaos theory the idea of characterizing the system using the rate of divergence, or convergence in the nonrunaway case.

Recently, Strozzi and Zaldívar (1994) studied the use of local Lyapunov exponents to calculate the parametric sensitivity of batch reactors, showing that the new method gave similar high-sensitivity regions to those of previous criteria. Furthermore, the dynamic behavior of the sum of local Lyapunov exponents allowed the definition of a new intrinsic criterion (see Alós et al., 1996a) for assessing the thermal stability of semibatch reactors. The advantage of these criteria lies in their simplicity, which makes them more easily applicable to the study of complex situations than the earlier techniques. Furthermore, the experimental verification, in a 2-L bench-scale reaction calorimeter and a 100-L pilot-plant installation, of the safe limits of a batch and semibatch process was carried out using the esterification of 2-butanol with propionic anhydride catalyzed by sulphuric acid (see Strozzi et al., 1994 and Alós et al., 1996b). The theoretical safe limits obtained using the criteria based on Lyapunov exponents were compared with the experimental results, and good agreement between the experimental and theoretical regions of high parametric sensitivity was obtained.

In the first part of this work, we make an attempt, based on the off-line analysis of energy and mass-balance equations, to use the large number of parametric sensitivity studies in chemical reactors (Wilson, 1946; Barkelew, 1959; Thomas, 1961; Adler and Enig, 1964; van Welsenaere and Froment, 1970; Rajadhyaksha et al., 1975; Westerterp and Ptasinski, 1984a,b; Westerterp and Overtoom, 1985; Morbidelli and Varma, 1986, 1987, 1988; Hagan et al., 1987, 1988a,b; Westerink and Westerterp, 1988; Balakotaiah, 1989; Westerterp and Westerink, 1990; Steensma and Westerterp, 1990, 1991; Vajda and Rabitz, 1992; Balakotaiah et al., 1995) to define an on-line criterion. Parametric sensitivity in this context describes the situation in which a small change in the inlet conditions—and/or coolant temperature or flow rate, feed temperature or concentrations—as well as to any of the other physicochemical characteristics of the system, induces a large change in the temperature profile of the reactor. First, a physical interpretation of the sum of local Lyapunov exponents for measuring parametric sensitivity (Strozzi and Zaldívar, 1994) is presented, discussed and compared with previous safety criteria. The dynamic of batch reactors is discussed in terms of phase-space dissipative systems. This allows the connection between the phase-space volume contraction and the sum of Lyapunov exponents and the definition of a suitable on-line criterion, that is, when the divergence of the batch or semibatch reactor becomes positive on a segment of the reaction path. We recall that the divergence is a scalar quantity defined at each point as the sum of the partial derivatives of the mass and energy balances with relation to the correspondent variables—temperature and conversion—that is, $\partial(dT/dt)/\partial T + \partial(dz/dt)/\partial z$.

From this it is possible to perform a comparison with previous criteria. Different kinetic schemes are discussed with special emphasis on the case of autocatalytic reactions that are to be expected when decomposition reactions are involved (Grewer, 1987) and that hardly have been studied. The results show the validity of this criterion, even in the case of autocatalytic reactions, where previously employed on-line criteria (Adler and Enig, 1964; Hub and Jones, 1986) were unable to define a suitable boundary for runaway characterization.

The on-line application of this criterion requires the reconstruction of the phase space through nonlinear time-series analysis using delay coordinate embedding. First, we present the idea of reconstructing the phase space of the system by the use of time delays of observed temperature data. We apply this approach to an isoperibolic batch reactor in which an exothermic first-order reaction takes place. The other methods of determining the appropriate time delay as well as the dimension of the reconstructed phase space from the temperature measurements are discussed. As the techniques used are not standard for a chemical engineer, some basic ideas used along this line are provided. However, the interested reader is referred to the original references for a detailed description.

Once the state space has been reconstructed, it is necessary to compare it with the original phase space. This is accomplished by calculating the invariant quantities that are preserved under phase embedding reconstruction. We use the evolution of the divergence during the transient whose signal is our early-warning criterion to distinguish between safe and runaway. First, we discuss the properties of the reconstructed divergence. Then we perform a theoretical analysis using simulated data for the previously mentioned case.

Preliminary experimental verification has been carried out (Strozzi et al., 1998) showing that there is a suitable way of reconstructing the divergence by measuring the temperature at different points inside the reactor. Our work is currently continuing along these lines, with the objective of creating an early-warning detection prototype.

Taking into account the experimental data necessary for its application (only temperature measurements), this method opens a new route between the simple use of measured variables and the complex model-based state reconstruction techniques to assess in advance hazardous situations in chemical reactors, allowing for the necessary countermeasures to be taken.

Dissipative Systems and Phase-Space Volume Contraction

Let us consider a system of d ordinary differential equations, in our case energy and mass balances, defined as

$$\frac{dx(t)}{dt} = F[x(t)], \tag{1}$$

where $x(t)=[x_1(t), x_2(t), \ldots, x_d(t)]$ in R^d and $F=[F_1, \ldots, F_d]$ is a smooth nonlinear function of x, that is, that the existence and uniqueness properties hold. At time $t>0$ the initial condition $x(0)$ finds itself at some new point $x(t)$. Similarly, all initial conditions lying in a certain region $\Gamma(0)$ find themselves in another region $\Gamma(t)$ after time t. If we let $V(t)$ denote the volume of the region $\Gamma(t)$, then a strong version of Liouville's theorem (Arnold, 1973) states that

$$\frac{dV(t)}{dt} = \int_{\Gamma(t)} \operatorname{div} F[x(t)]\, dx_1(t) \cdots dx_d(t), \tag{2}$$

where

$$\operatorname{div} F[x(t)] = \frac{\partial F_1[x(t)]}{\partial x_1(t)} + \frac{\partial F_2[x(t)]}{\partial x_2(t)} + \cdots + \frac{\partial F_d[x(t)]}{\partial x_d(t)}. \tag{3}$$

Assuming that our d-dimensional volume is small enough that the divergence of the vector field, $\operatorname{div} F(x)$, is constant over $V(t)$, then

$$\frac{dV(t)}{dt} = V(t) \cdot \operatorname{div} F[x(t)], \tag{4}$$

and hence,

$$\int_0^t \frac{dV(\tau)}{V(\tau)} = \int_0^t \operatorname{div} F[x(\tau)]\, d\tau, \tag{5}$$

which means that the initial phase-space volume $V(0)$ shrinks (grows) with time in R^d as

$$V(t) = V(0) e^{\int_0^t \operatorname{div} F[x(\tau)] d\tau}. \tag{6}$$

Hence, for the case of a system given by Eq. 1, the rate of change of an infinitesimal volume $V(t)$ following an orbit $x(t)$ is given by the divergence of the flow, which is locally equivalent to the trace of the Jacobian of F. The integral of a strictly positive (negative) function is itself strictly positive (negative), and the integral of an identically zero function is identically zero. That means if $\operatorname{div} F(x) < 0$ $\forall x$ in the state space, then the flow of trajectories is volume-contracting; if $\operatorname{div} F(x) > 0$ $\forall x$, the flow is volume-expanding, and if $\operatorname{div} F(x) = 0$ $\forall x$, then the flow is volume-preserving. State-space volumes are conserved in Hamiltonian systems, such as those that arise from the Newtonian mechanics of particles moving without friction. That means that if all points in a subset of state space with a positive finite volume progress forward over some time interval, then the resulting set has the same volume as the initial set. Such systems are defined as being conservative. For dissipative systems, what usually happens is that all trajectories converge toward invariant sets of relatively low dimension with simple geometrical features called attractors.

In this work we are interested in studying a dissipative chemical reaction carried out batchwise in isoperibolic conditions, and hence the trajectories in state space—temperature and concentrations—will converge at $t \to \infty$ to a fixed point when all reagents have been consumed and the final temperature of the reaction mass equals that jacket temperature. In other words, we have a system of dimension d—reactor temperature and concentrations of different species—that collapses to a point that has dimension zero. Nevertheless, before reaching the fixed point, the orbits can diverge, and hence we are interested in studying the dynamics of the orbital collapse (see Figure 1).

On the other hand, Lyapunov exponents monitor the behavior of closely adjacent points in the phase space as a func-

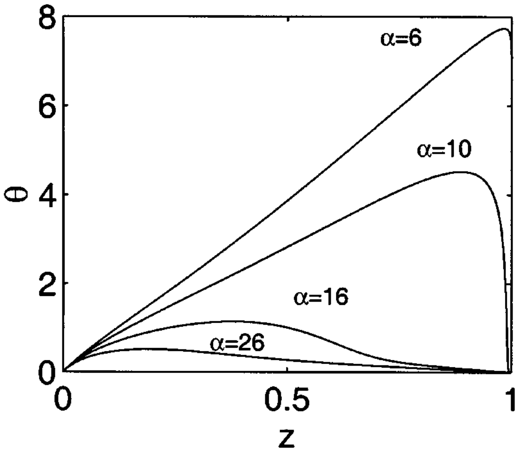


Figure 1. Trajectories in phase space ($\theta - z$) for different values of α.

In this case, $B=10$, $\epsilon=0.05$, and α changes from 26 to 6. The trajectories are for a first-order reaction carried out batchwise in an isoperibolic reactor (starting point $\theta=0$ and $z=0$, final point $\theta=0$ and $z=1$).

tion of time. Let us introduce a local Cartesian coordinate system with origin at $x(0)$ by choosing at random d small vectors coming from $x(0)$ and then orthogonalizing them. These vectors will be denoted by $q(0)=[q_1(0), \ldots, q_d(0)]$, and they can be seen as the principal axis of a unitary d-sphere of initial conditions. Then Lyapunov exponents are defined (Wolf et al., 1985) as

$$\lambda_i = \lim_{t \to \infty} \frac{1}{t} \log_2 \frac{|q_i(t)|}{|q_i(0)|}; \quad i=1,\ldots,d, \tag{7}$$

that is, they measure the mean rate of expansion or contraction of the d axes of the initial sphere. If the points in this d-sphere of initial conditions expand away from each other in the ith direction, the ith Lyapunov exponent will be positive; if they converge, the exponent becomes negative; and if the two points stay the same distance apart, the exponent stays near zero.

Since the orientation of the d-ellipsoid defined by $q(t)$ changes continuously, the directions associated with a given exponent vary, too.

As we said before, in a batch reactor, the orbits starting from near points in the phase space will converge, for $t \to \infty$, to a fixed point when the reaction has finished and the final temperature is the jacket temperature. In this case, the Lyapunov exponents will give information on such a point. Nevertheless, before reaching the fixed point, the orbits can diverge. To study this ''local'' divergence it is necessary to use the Lyapunov exponents at time t, the so-called local Lyapunov exponents (Abarbanel et al., 1993), which are defined as

$$\lambda_i(t) = \frac{1}{t} \log_2 \frac{|q_i(t)|}{|q_i(0)|}; \quad i=1,\ldots,d. \tag{8}$$

When the initial d-sphere evolves, it will become a d-ellipsoid due to the locally deforming nature of the flow, the linear extent of the ellipsoid grows (reduces) as $2^{\lambda_1(t)\cdot t}$, the area defined by the first two principal axes grows (reduces) as $2^{(\lambda_1(t)+\lambda_2(t))\cdot t}$, the volume defined by the first three principal axes grows (reduces) as $2^{(\lambda_1(t)+\lambda_2(t)+\lambda_3(t))\cdot t}$, and so on. In general in a phase space of a higher dimension the calculation of the volume will be

$$V(t) = 2^{(\lambda_1(t)+\lambda_2(t)+\cdots+\lambda_d(t))\cdot t} V(0). \tag{9}$$

For this reason, Strozzi and Zaldívar (1994) defined the sensitivity using Lyapunov exponents as follows

$$s_\phi = \frac{d\left(\max 2^{[\lambda_1(t)+\lambda_2(t)+\cdots+\lambda_d(t)]\cdot t}\right)}{d\phi}, \tag{10}$$

where ϕ is the parameter in relation to which we want to know the sensitivity of the system. In this case, criticality is defined as the value of ϕ for which Lyapunov sensitivity has an extreme.

From Eqs. 6 and 9 it follows that

$$\sum_j \lambda_j(t) = \frac{1}{\log(2)} \frac{1}{t} \int_0^t \operatorname{div} F[x(\tau)]\, d\tau. \tag{11}$$

This means that the sum of the local Lyapunov exponents is proportional to the temporal mean of the divergence of the field F, $\operatorname{div} F[x(t)]$. As is shown, we are interested in the sum of the Lyapunov exponents and not in their individual values. For this reason, we can use the relation given by Eq. 11 to calculate the sum and to apply Eq. 10, and hence integrate over time the divergence or the trace of the Jacobian. Furthermore, as can be seen (see Eq. 11), the inverse of the sum of Lyapunov exponents has time units. Since the divergence of F at time t is equal to the sum of the real part of the eigenvalues of the Jacobian of F at time t, Eq. 11 also gives a relation between the sum of Lyapunov exponents and the eigenvalues of the Jacobian.

Off-Line and On-Line Runaway Criteria

A considerable amount of work has been done in studying the parametric sensitivity of chemical reactors; such studies had sought to define the simple criteria that allowed the establishment of the parametric region—that characterize the algebraic-differential equations describing the mass and energy balances of these reactors—where the operation would be safe. The question that now arises is if it is possible from these studies to extract a safety criterion that may be used on-line as an early-warning criterion. In this section, we compare different procedures for calculating runaway boundaries for batch reactor models. First, we review the boundary criteria for the simpler well-mixed batch reactor model in which a single, irreversible nth-order exothermic reaction occurs. We study the relationships of previous criteria with the criterion based on the sum of Lyapunov exponents (Strozzi and Zaldívar, 1994), using the concepts previously developed. We then extend these results to autocatalytic reactions to study the validity limits of such a criterion. This study allows us to introduce a parameter that can be used on-line to define runaway boundaries.

Runaway boundary for a single nth-order reaction

The pertinent equations representing mass and energy balances, in an ideal well-stirred batch reactor working under isoperibolic conditions (constant jacket temperature, T_e) in which a single irreversible nth-order exothermic reaction $A \to B$ occurs, are

$$\frac{dz}{d\tau} = (1-z)^n \exp\left(\frac{\theta}{1+\epsilon\theta}\right) \tag{12}$$

$$\frac{d\theta}{d\tau} = B(1-z)^n \exp\left(\frac{\theta}{1+\epsilon\theta}\right) - \alpha\theta, \tag{13}$$

with initial conditions

$$z=0, \qquad \theta=0 \quad \text{at} \quad \tau=0, \tag{14}$$

where

$$\tau = \frac{t}{t_R}; \qquad z = 1 - \frac{C_A}{C_{A_0}}; \qquad \theta = \frac{E}{RT_e}\frac{T - T_e}{T_e}$$

$$B = \frac{\Delta T_{\text{ad}}}{\epsilon T_e}; \qquad \epsilon = \frac{RT_e}{E}; \qquad \Delta T_{\text{ad}} = \frac{(-\Delta H)C_{A_0}}{\rho Cp}$$

$$\alpha = \frac{t_R}{t_{\text{co}}}; \qquad t_R = \frac{1}{k(T_e)C_{A_0}^{n-1}}; \qquad t_{\text{co}} = \frac{V\rho Cp}{US}; \qquad t_g = \frac{t_R}{B}.$$

Here, t_R is the characteristic reaction time, t_g is the characteristic heat-generation time, and t_{co} is the characteristic cooling time (Balakotaiah et al., 1995).

Comparison with Previous Criteria. In comparison with previous criteria for parametric sensitivity analysis, it is convenient to consider the system behavior in the temperature-conversion plane. From Eqs. 12–14 it readily follows that

$$\frac{d\theta}{dz} = B - \frac{\alpha\theta}{(1-z)^n \exp\left(\frac{\theta}{1+\epsilon\theta}\right)}, \tag{15}$$

with initial conditions:

$$\theta = 0 \quad \text{at} \quad z = 0. \tag{16}$$

To study reactor stability, Barkelew (1959) introduced the Frank-Kamenetskii exponential approximation for the Arrhenius term: if T is sufficiently close to T_e, then $\epsilon\theta \ll 1$, and

$$\frac{\theta}{1+\epsilon\theta} \approx \theta. \tag{17}$$

With this approximation, Eq. 15 is transformed into

$$\frac{d\theta}{dz} = B - \frac{\alpha\theta \cdot e^{-\theta}}{(1-z)^n}. \tag{18}$$

The calculation of the partial derivative in the temperature function gives

$$\frac{\partial\left(\frac{d\theta}{dz}\right)}{\partial\theta} = \frac{\alpha e^{-\theta}}{(1-z)^n}(\theta - 1). \tag{19}$$

Barkelew's criterion is obtained, assuming that the derivative, Eq. 19, is negative. The group $\alpha e^{-\theta}/(1-z)^n$ is always positive, and hence:

$$\frac{\alpha e^{-\theta}}{(1-z)^n}(\theta - 1) < 0 \Rightarrow \theta - 1 < 0 \Rightarrow \theta < 1 \tag{20}$$

implies no parametric sensitivity or runaway, which means

$$\frac{E}{RT_e^2}(T - T_e) < 1. \tag{21}$$

Condition $\theta < 1$ is equivalent to $\theta_{\max} < 1$. Barkelew (1959) set $\theta_{\max} = 1$ as the boundary criterion for runaway, that is,

$$\frac{E}{RT_e^2}(T_{\max} - T_e) = 1. \tag{22}$$

For $\theta_{\max} < 1$ the reactor temperatures will not runaway; above $\theta_{\max} = 1$ they will runaway or stay very close to runaway conditions.

If the approximation Eq. 17 is not included, the calculation of derivative gives

$$\frac{\partial\left(\frac{d\theta}{dz}\right)}{\partial\theta} = \frac{\alpha \exp\left(\frac{-\theta}{1+\epsilon\theta}\right)}{(1-z)^n}\left(\frac{\theta}{(1+\epsilon\theta)^2} - 1\right). \tag{23}$$

Using the same reasoning as before, the restrictive limit for nonrunaway obtained is

$$\theta < (1+\epsilon\theta)^2, \tag{24}$$

which means

$$\frac{E}{RT^2}(T - T_e) < 1, \tag{25}$$

which is equivalent to the condition to prevent runaway found by Van Welsenaere and Froment (1970):

$$\frac{E}{RT_{\max}^2}(T_{\max} - T_e) < 1. \tag{26}$$

Therefore, Van Welsenaere and Froment's criterion states that the derivative of the flow given by Eq. 15 has to be negative to prevent runaway. The only difference between the previous criteria is that Barkelew uses a simplified expression for the Arrhenius term, which leads to a more restrictive runaway boundary than the one found by applying Van Welsenaere and Froment's criterion.

Using the Lyapunov exponents, the sensitivity criterion, Eq. 10, is obtained after allowing for the divergence of the system given by Eqs. 12–13, that is,

$$\operatorname{div} F(\theta, z) = (1-z)^{n-1}\exp\left(\frac{\theta}{1+\epsilon\theta}\right)\left(\frac{B(1-z)}{(1+\epsilon\theta)^2} - n\right) - \alpha. \tag{27}$$

For a first-order reaction and applying the approximation given by Eq. 17, it readily follows that

$$\operatorname{div} F(\theta, z) = \exp(\theta)[B(1-z) - 1] - \alpha. \tag{28}$$

Let us consider the initial conditions, $\theta = 0$ and $z = 0$; in this case Eqs. 27 and 28 become, $\operatorname{div} F(0,0) = (B - 1 - \alpha)$, which can be expressed in the form of characteristic times as follows: $\operatorname{div} F(0,0) = t_R[1/t_g - 1/t_R - 1/t_{\text{co}}]$. The divergence will be positive if the time constant for the heat generation is higher than the time constants for the cooling and reaction times. The sum of Lyapunov exponents will be equivalent to the integral over time of the Eq. 27, or Eq. 28 if we introduce the Frank-Kamenetskii exponential approximation for the Arrhenius term, Eq. 17.

On-Line Criteria. A first attempt at a definition of an on-line safety criterion was carried out by Hub (1977) and Hub and Jones (1986). They used the increase in the heat expansion as the hazard-identification criterion, that is,

$$\frac{dq_G}{dt} > 0, \tag{29}$$

where q_G is the power generated by chemical reaction. The principle applied is based on a simple energy balance over the reactor:

$$q_G = MCp\frac{dT}{dt} + US(T - T_e). \tag{30}$$

Power generated = power used to increase the temperature of the reaction mixture + power removed by the coolant flowing through the jacket. From Eq. 30 it is possible to obtain:

$$\frac{dq_G}{dt} = MCp\frac{d^2T}{dt^2} + US\frac{d(T - T_e)}{dt}, \tag{31}$$

assuming that MCp and US are constants.

The criterion of Eq. 29 defines two different regions separated by the line $dq_G/dt = 0$. The region in which the heat output of the reaction declines can be considered nonhazardous. In addition, two other zones in the region in which the heat output of the reaction increases can be discarded from the potentially dangerous region. In the former, the power accumulated in the reaction mixture increases and the power removed through the jacket decreases; this is due to deliberate heating of the heat-transfer fluid by the control system and, in principle, is not dangerous. In the latter, the heat removed increases and the heat accumulated decreases, so in this situation the reaction is under control. Hence, for the purpose of hazard recognition, it is sufficient to check the following two expressions:

$$\frac{d^2T}{dt^2} > 0 \quad \text{and} \quad \frac{d(T - T_e)}{dt} > 0. \tag{32}$$

The strength of this criterion is its separate understanding of the supervised process. It is the only on-line method that in principle does not require any setting, adjustment, or information on the process or equipment. Another advantage is that only two temperatures need to be measured for the hazard identification. The disadvantage is that disturbances, always superimposed on the measurement signal, become amplified and considerably affect the result of the evaluation. Hence, digital filters of a high order and various auxiliary algorithms must be employed to smooth out the differential coefficients and to avoid false alarms. In practice, positive values of the derivatives are allowed up to upper limits l_1 and l_2 and the alarm is triggered only if these limits are exceeded by a time interval greater than $\Delta t_{\min}$. The variables l_1, l_2, and $\Delta t_{\min}$ must be adjusted for each process (Casadei, 1977).

Gilles and Schuler (1982) used the criterion previously developed by Adler and Enig (1964) to distinguish between safe and runaway situations. Based mostly on physical intuition, Adler and Enig (1964) proposed a boundary limit in the parameter space; on one side of this boundary (insensitive region) $d^2\theta/dz^2$ is negative everywhere on the reaction path, while on the other side (runaway region), both $d\theta/dz$ and $d^2\theta/dz^2$ are positive on a segment of the reaction path, that is,

$$\frac{d\theta}{dz} > 0 \quad \text{and} \quad \frac{d^2\theta}{dz^2} > 0. \tag{33}$$

To use such a criterion, the conversion must be estimated on-line from the temperature measurements, and hence a mathematical model of the reaction rate, as well as of the reactor, is necessary. Even though this criterion also requires second-order derivatives, provided Kalman filtering techniques are used, there is an integration that leads to signal smoothing (King, 1985). Furthermore, at every point, the Kalman filter gives an estimate of the whole state vector. Therefore, it is possible to use another criterion in combination with Eq. 33 or, assuming no changes on the model parameters, even calculate the future development of the process. Unfortunately, due to the low production levels, time constraints, and the enormous variety of processes, the development of reaction-rate models for batch processes usually is not economically justified, and therefore the application of model-based techniques is not always possible, being reserved to special cases.

Comparison of Runaway Boundaries. Figures 2 and 3 show a comparison between runaway boundaries for a first-order reaction carried out batchwise. As can be seen, Barkelew's criterion is the most conservative one. On the other hand, the local temperature sensitivity (Morbidelli and Varma,

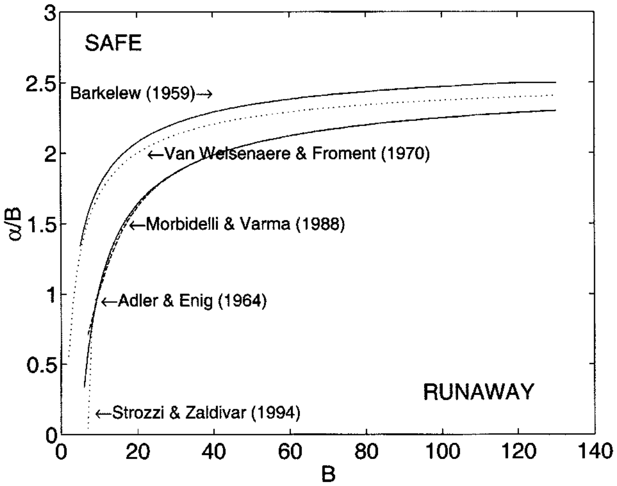


Figure 2. Runaway boundaries using different criteria for a batch reactor in which a first-order reaction takes place ($n = 1$, $\epsilon = 0.05$).

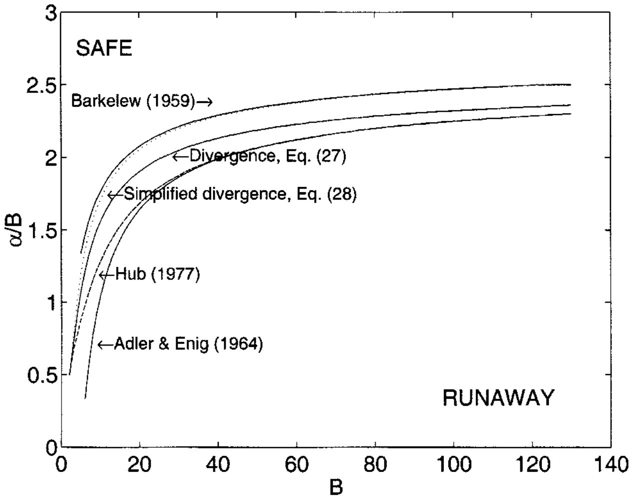


Figure 3. Runaway boundaries using different criteria for a batch reactor in which a first-order reaction takes place ($n = 1$, $\epsilon = 0.05$).

1988), $s_\phi(z) = d\theta_{\max}(z)/d\phi$, the sum of Lyapunov exponents, and the Adler and Enig (1964) criteria give, as was shown previously (Strozzi and Zaldívar, 1994), similar results for $B > 7$ and $\epsilon < 0.1$, these being criteria the least conservative. For low values of B, thermal runaway becomes a quite mild phenomenon and eventually vanishes (Morbidelli and Varma, 1988). Figure 3 shows the comparison between Barkelew's criterion and the criterion based on $\operatorname{div} F(\theta, z) > 0$. As can be seen, both criteria are similar when the simplification given by Eq. 17 is introduced in the divergence. This is in accordance with the findings of Vajda and Rabitz (1992). These authors observed that at criticality the temperature becomes the dominant variable, and that any perturbation in the parameters affects the conversion by altering the temperature and thereby the reaction rate, whereas the direct, quasi-isothermic effects of parameter perturbations on the conversion are negligible. For this reason, similar findings are obtained when working with the temperature-conversion plane rather than in temperature-time and conversion time. In fact, if we use the temperature-conversion system (Eq. 15), Barkelew's and Van Welsenaere and Froment's criteria are related to the divergence in this system—there is an analytical expression that passes from these criteria to the divergence that can be found elsewhere (Strozzi, 1997). The simulated results of the boundary region, between safe operation and runaway, obtained using the different on-line criteria are also shown. As can be seen, for low B values, Eq. 27 gives the same results as Eq. 32, the OLIWA criterion being slightly conservative for higher values of B at which Eqs. 32 and 33 give similar boundary diagram. This means that in the case of a first-order reaction the warning or alarm would occur before using the positive divergence criterion than in the other two on-line criteria.

Runaway boundary for autocatalytic reactions

An important class of reactions is autocatalytic reactions, in which a reaction product increases the rate of reaction in proportion to its concentration, so that, at least in the early stages, the rate of reaction (and the rate of heat generation) increases with time as the reaction proceeds. Clearly, whatever the magnitude of the heat of reaction, the effect of this can never be neglected in the prerunaway stage, because initially, at least, it must exceed the effect of the rising temperature. Even though a considerable number of decomposition reactions show autocatalytic behavior, for example, aromatic nitrocompounds, aliphatic nitroso compounds, thiophosphoric esters, acrylates, sulphones, esters, and chlorides of sulphonic acids (Grewer, 1979), there are only a few parametric sensitivity studies for this type of reaction (Bowes, 1984).

Considering an ideal well-stirred batch reactor working under isoperibolic conditions (constant jacket temperature, T_e) in which a single autocatalytic exothermic reaction $A \rightarrow B$ occurs, the pertinent equations representing mass and energy balances are

$$\frac{dz}{d\tau} = (1 - z)(\delta + z)\exp\left(\frac{\theta}{1 + \epsilon\theta}\right) \tag{34}$$

$$\frac{d\theta}{d\tau} = B(1 - z)(\delta + z)\exp\left(\frac{\theta}{1 + \epsilon\theta}\right) - \alpha\theta, \tag{35}$$

with initial conditions:

$$z = 0, \qquad \theta = 0 \qquad \text{at} \qquad \tau = 0, \tag{36}$$

where δ is a small fractional amount of product to ensure that the reaction can start, so that $dz/d\tau > 0$ when $\tau = 0$.

The time coordinate may be eliminated from Eqs. 34 and 35 by dividing Eq. 35 by Eq. 34. This gives

$$\frac{d\theta}{dz} = B - \frac{\alpha\theta}{(1 - z)(\delta + z)\exp\left(\dfrac{\theta}{1 + \epsilon\theta}\right)}. \tag{37}$$

The calculation of the partial derivative as a function of θ gives:

$$\frac{\partial\left(\dfrac{d\theta}{dz}\right)}{\partial\theta} = \frac{\alpha\exp\left(\dfrac{-\theta}{1 + \epsilon\theta}\right)}{(1 - z)(\delta + z)}\left(\frac{\theta}{(1 + \epsilon\theta)^2} - 1\right). \tag{38}$$

Introducing the approximation given by Eq. 17, Eq. 38 is transformed into

$$\frac{\partial\left(\dfrac{d\theta}{dz}\right)}{\partial\theta} = \frac{\alpha e^{-\theta}}{(1 - z)(\delta + z)}(\theta - 1). \tag{39}$$

The group $\alpha e^{-\theta}/[(1 - z)(\delta + z)]$ is always positive, and hence:

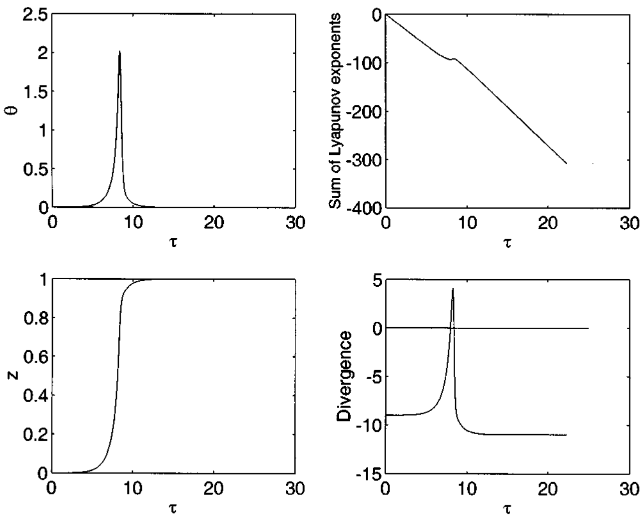
$$\frac{\alpha e^{-\theta}}{(1 - z)(\delta + z)}(\theta - 1) < 0 \Rightarrow \theta - 1 < 0 \Rightarrow \theta < 1 \tag{40}$$

implies no parametric sensitivity or runaway, which means $E(T - T_e)/RT_e^2 < 1$ (see Eq. 21). Using the same considerations as for the nth-order reactions (see Westerterp et al., 1984), it is possible to arrive to the same result for autocatalytic reactions, that is, a criterion for runaway, $\theta_{\max} = 1$. As can be seen, this criterion agrees with the case of Eq. 21, that is, when the reactor temperature and the temperature difference between the reactor and the jacket are maximum. This criterion establishes the value $e/4$ as the upper limit for α/B (Bowes, 1984).

The sensitivity criterion using the Lyapunov exponents, Eq. 10, is obtained when the divergence of the system given by Eqs. 34 and 35 is taken into consideration, that is,

$$\operatorname{div} F(\theta, z) = \left[1 - \delta + 2z + \frac{B\left(\delta + z(1-\delta) + z^2\right)}{(1+\epsilon\theta)^2}\right] \exp\left(\frac{\theta}{1+\epsilon\theta}\right) - \alpha. \tag{41}$$

The initial value of divergence, $1 + \delta(B-1) - \alpha$, is a large negative number, because B vanishes with δ and the sum of Lyapunov exponents, which is the mean of the divergence over time, can underestimate the runaway boundary for this type of reaction (see Figure 4). From numerical simulations it was observed that the sum of the local Lyapunov exponents criterion gives the same results as the maximum of $d\theta_{\max}/d\alpha$ when $\delta > 0.05$, that is, when the initial negative part starts to be small in comparison to the rest. Similar results were obtained when simulating the phase inversion phenomenon in semibatch aromatic nitrations. In that case, the model that describes the overall conversion rate changes suddenly (Zaldívar et al., 1995), but because the Lyapunov exponents criterion uses the integral over time, it is slow to respond to this fast change.



(a) **(b)**

Figure 4. Dimensionless temperature, conversion, sum of Lyapunov exponents and divergence for an autocatalytic reaction ($B = 20$, $\alpha = 10$, $\epsilon = 0.1$, and $\delta = 1.0 \times 10^{-4}$).

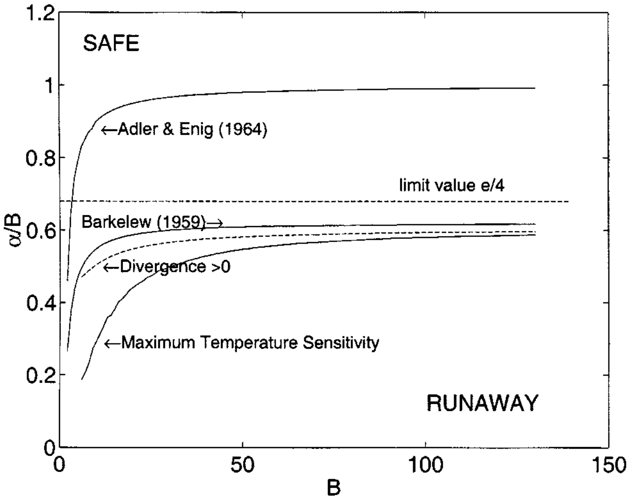


Figure 5. Runaway boundary for batch reactor in which an autocatalytic reaction takes place ($\epsilon = 0.1$, $\delta = 1.0 \times 10^{-4}$).

Figure 5 shows the comparison between the different criteria for the case of the autocatalytic reaction. As can be seen, in this case, for $\epsilon = 0.1$, Barkelew's criterion using the Frank-Kamenetskii exponential approximation for the Arrhenius term, Eq. 17, gives a conservative runaway boundary for the autocatalytic reaction. On the other hand, the maximum sensitivity, $d\theta_{\max}/d\alpha$, gives the lower restrictive criterion, as in the first-order reaction case. Furthermore, under these conditions, the criterion based on the sum of the Lyapunov exponents defined by Eq. 10 does not give a runaway boundary up to $B > 100$. The Adler and Enig (1964) criterion, Eq. 33, would be too conservative, defining a runaway boundary smaller than Barkelew's criterion, and producing unnecessary false alarms. Hub's criterion, Eq. 32, always gives an alarm—if no limits to the first and second derivative are imposed—because of the nature of the behavior of the temperature during autocatalytic reactions, which is autoaccelerated as the conversion increases, even though in some cases this effect is negligible. In this case the positive divergence criterion lies between Barkelew's criterion and the maximum temperature-sensitivity criterion.

The results of this study suggest that instead of using the sum of Lyapunov exponents, which is the mean over the time of the divergence, we could study the divergence. In this case the early-warning criterion should be

$$\operatorname{div} F(\theta, z) > 0. \tag{42}$$

The question that arises at this stage is how it is possible to calculate divergence on-line, that is, if we know only the measurements of the evolution of temperature.

Phase-Space Reconstruction Techniques

Equation 1, which represents the state of a deterministic dynamical system, contains the information necessary to predict the future evolution of the system and reconstruct its past. Let us consider a time series of measurements of an observable quantity over time, which, in the absence of noise, is related to the dynamical system by

$$s(t) = h[x(t)]. \tag{43}$$

The system on which the observable quantity is being measured evolves with time. The phase-space reconstruction problem is that of recreating states when the only information available is contained in a time series, that is, how do we go from the measurement of one variable to the multivariable state space or phase space that is required to study the system? State-space reconstruction is the first step that must be taken to analyze a time series in terms of dynamical systems theory. Typically, the functions F and h are both unknown, so we cannot hope to reconstruct states in their original form. However, we may be able to reconstruct a state space that is equivalent to the original in the sense that differential properties are preserved.

Work by Takens (1981) and improvements by Sauer et al. (1991) have shown that if the dynamics are on a d-dimensional Euclidean space, an embedding of the system, can be obtained with a $2d+1$-dimensional reconstructed state space using derivatives or delay coordinates.

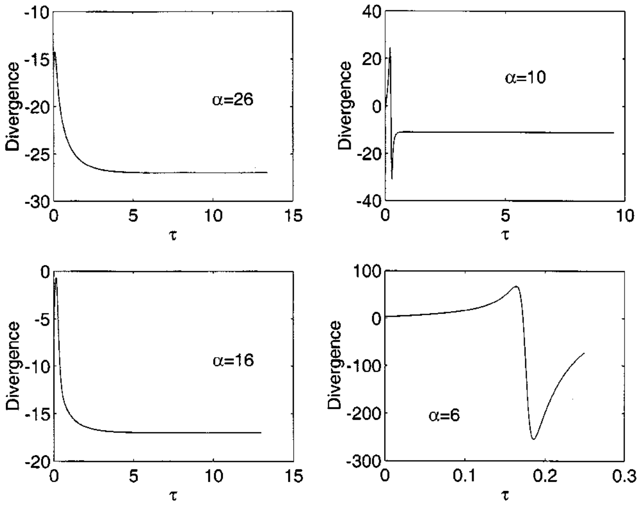
There are several methods of reconstructing state space from the observed quantity (Breeden and Packard, 1994), in our case the temperature $T(t)$. These include delay coordinates, derivative coordinates (Packard et al., 1980), and global principal-value decomposition (Broomhead and King, 1986). The method of reconstruction can make a large difference in the quality of the resulting coordinates, but in general it is not clear which method is the best (Casdagli et al., 1991). The lack of a unique solution for all purposes is due in part to the presence of noise and the finite length of the data set. Even different algorithms for achieving the same goal often have different optimal representations. No single representation will be optimal for all possible objectives.

In the method for reconstructing the phase space using the derivatives, numerically investigated by Packard et al. (1980), the coordinates are derivatives of successively higher order $\{s(t), \dot{s}(t), \ddot{s}(t), \ldots\}$. There are many algorithms for the numerical computation of derivatives, so in this sense the method of derivatives actually defines a family of different methods, depending on the algorithm. However, derivatives are sensitive to noise when approximated from the observed time series. This has led in part to the extensive use of delay coordinates, particularly when higher-dimensional representations are necessary. A delay coordinate, often referred to as a lag, is simply the observed variable some time Δt in the past. Delay coordinates, $\{T(t), T(t-\Delta t), T(t-2\Delta t), \ldots\}$, are easy to work with and can be effective for very high-dimensional cases where it may be not practical to calculate the requisite number of derivatives. The difficulty with them is that in order to use them it is necessary to choose the delay parameter Δt. If Δt is too small, each coordinate is almost the same, and the trajectories of the reconstructed space are squeezed along the identity line; this phenomenon is known as redundance. If Δt is too large when there is chaos and noise, the dynamics at one time become effectively disconnected from the dynamics at a later time, so that even simple geometric objects look extremely complicated; this phenomenon is known as irrelevance. Most of the research on the state-space reconstruction problem has centered on the problems of choosing Δt and the embedding dimension, d_E, which we can call the parameters of the reconstruction for delay coordinates. Principal-value, derivative, and delay coordinates are related to each other by linear transformations. However, the transformation from delay coordinates to the original coordinates is typically nonlinear (Casdagli et al., 1991).

It is necessary to mention that the theory of phase-space reconstruction has been developed for a system that lies on a chaotic attractor, which is not our system, since we have a fixed-point attractor. However, we are interested in rebuilding the trajectory of our system during the transient, before the system has reached the attractor. In this sense, Sauer's version (Sauer et al., 1991) of Takens (1981) Theorem states that we can rebuild the state space whenever the system lies in a compact subset of the Euclidean space, R^d, with $d < \infty$, which is in our system (for a formal demonstration, see Strozzi, 1997). The main problem is that all the algorithms that calculate the parameters of the phase-space reconstruction make use of the dense structure of chaotic attractors, so they are not directly applicable to our problem.

Application to batch reactors

The pertinent equations representing mass and energy balances, in the case of an ideal well-stirred batch reactor working under isoperibolic conditions in which a single irreversible nth-order exothermic reaction $A \rightarrow B$ occurs, are given by Eqs. 12–13, with initial conditions given by Eq. 14. Figure 1 shows four typical $\theta - z$ trajectories for $B = 10$, $\epsilon = 0.05$, and the change of the dimensionless heat-transfer coefficient, α, with low values leading to exothermic runaway, while Figure 6 shows the calculated divergence-time profiles for the preceding simulations. As can be seen, divergence for the low values of the dimensionless heat-transfer coefficients



(a) **(b)**

Figure 6. Divergence profile for the simulations in Figure 1.

B = 10, ϵ = 0.5, and α changes from 26 to 6. First-order reaction carried out batchwise in an isoperibolic reactor.

becomes positive, while in the simulations with a high-dimensionless heat-transfer coefficient it remains negative during all the runs. The final value of the divergence for all simulations is negative, which agrees with the dissipative nature of our system. According to our developed early-warning criterion for runaway detection, Eq. 42, when the divergence of the batch reactor becomes positive on a segment of the reaction path, we are in a runaway situation. Hence, simulation runs with $\alpha = 36$ and 26 are safe, and $\alpha = 6$ and 10 can be defined as runaways.

As was said earlier, normally the only available measurement is the temperature, and hence we try to reconstruct a phase space using only time-delay measurements of θ, that is, $\{\theta(\tau),\ \theta(\tau - \Delta\tau),\ \ldots\}$, or θ and the derivatives of successively higher orders, that is, $\{\theta(\tau),\ \dot{\theta}(\tau),\ \ldots\}$. To accomplish this for the case of delay coordinates, we have to find the optimum time delay, $\Delta\tau$, and the embedding dimension, d_E. For the derivative coordinates finding the optimum time delay is not necessary. In this case study, because the system has two ordinary differential equations $d = 2$, it would be enough to have $d_E = 5$.

Choosing the Time Delay. A description of the most common techniques for choosing the time delay, $\Delta\tau$, can be found in Abarbanel (1996). Most of these techniques are based on the implicit assumption that the time-series lies on the attractor and that the transient part has been removed from the data. However, we are interested only in the transient part, since our attractor is a fixed point and our process is not as steady state as the chaotic ones. For this reason, it is evident that care must be taken when applying the standard algorithms, since most of them are not suitable for our purposes. We have found that the first passes through zero of the autocorrelation function (see Mees et al., 1987 and Albano et al., 1988), calculated using only data preceding the temperature maximum, give a reasonable estimate of the time delay. Table 1 shows the time delays found for the simulation runs of Figure 1 when using this criterion and the calculated time-delay optimum, which was defined as the one that gives the minimum error when reconstructing the divergence.

Choosing the Embedding Dimension. A description of the techniques for choosing the embedding dimension, d_E, can be found in Kantz and Schreiber (1997). As for the time delay, the same basic assumptions were used to develop the algorithm. In this case, the false nearest-neighbor algorithm (Kennel et al., 1992) is based on the existence of a chaotic attractor and hence a densely populated object in phase space. In the case of the isoperibolic batch reactor in which an nth-order reaction takes place, whatever the time delay $\Delta\tau$, $d_E = 2$ is always obtained, which is a reasonable function value of the phase-space trajectories produced by the system, that is, there is no self-crossing of the orbits to eliminate even at dimension two.

Table 1. Calculated Time Delays, $\Delta\tau$, for Phase-Space Reconstruction from Simulated Temperature Profiles for a First-Order Reaction Carried Out Batchwise in an Isoperibolic Reactor*

α	$\Delta\tau_{\text{correl}}$	$\Delta\tau_{\text{optim}}$
6	0.01	0.01
10	0.08	0.05
16	0.08	0.155
26	0.05	0.1

*$B = 10,\ \epsilon = 0.05$.

Figures 7 and 8 show two phase spaces reconstructed just from temperature measurements using the derivatives and the time-delay coordinates, respectively. As can be seen when we compare these figures with the original phase space $\theta - z$ from Figure 1, phase-space reconstruction techniques do not provide us with the real phase space but, as we shall see, with one in which the divergence is the preserved. The embedding theorem is important because it gives a rigorous justification for the state-space reconstruction. However, the measurements in the proof of the theorem are assumed to be of infinite precision (Casdagli et al., 1991), which makes the specific value of the time delay $\Delta\tau$ arbitrary, so that any one reconstruction is as good as any other. In practice, with noisy data and a finite number of points, it is a problem to find an appropriate $\Delta\tau$.

If we assume that we have found an appropriate $\Delta\tau$ and the embedding dimension d_E, then the divergence of the system in the real state space and the reconstruction one, using $\Delta\tau$ and d_E, is preserved, that is, the divergence is an invariant characteristic of the dynamics. For the mathematical proof, see Strozzi (1997).

Calculation of the reconstructed divergence from simulated temperature data

To better understand the procedure, let us describe the numerical calculation of the divergence for the system given by Eqs. 12–13 in the real space $(\theta,\ z)$. In this case, the divergence is given by the trace of its Jacobian, Eq. 3, which is the sum of the diagonal elements of the Jacobian matrix, and the nth-order exothermic reaction is given by Eq. 27. On the other hand, the Jacobian gives the evolution law of a set of perturbations near a fiducial point x_0:

$$\delta\dot{x}_0(\tau) = J(\tau)\,\delta\dot{x}_0(\tau). \tag{44}$$

Liouville's formula (see Arnold, 1973) states that the solutions of the system given by Eq. 44 multiply the volume of any infinitesimal region in the state space by a factor equal to $\exp[\tau \cdot \mathrm{tr}(J(\tau)]$. If we consider a region in the state space in which $J(\tau)$ is constant, using Liouville's formula we can calculate the divergence at time τ as follows:

$$\operatorname{div} F(\tau) = \frac{1}{\Delta\tau} \ln \frac{\text{Area}[\mathbf{P1}(\tau+\Delta\tau), \mathbf{P2}(\tau+\Delta\tau), \mathbf{P3}(\tau+\Delta\tau)]}{\text{Area}[\mathbf{P1}(\tau), \mathbf{P2}(\tau), \mathbf{P3}(\tau)]}, \tag{45}$$

where Area $(\mathbf{P1}(\tau),\ \mathbf{P2}(\tau),\ \mathbf{P3}(\tau))$ is the area of the parallelogram given by points $\mathbf{P1}(\tau)$, $\mathbf{P2}(\tau)$, $\mathbf{P3}(\tau)$ in Figure 9. Assuming that we have calculated the appropriate time delay, $\Delta\tau$, and that the embedding dimension has a value of two, in order to calculate the divergence in the reconstructed space we have to consider the points in a space whose coordinates are only temperature-delayed measurements. Let $T1(\tau)$, $T2(\tau)$, $T3(\tau)$ be three temperature measurements suffi-

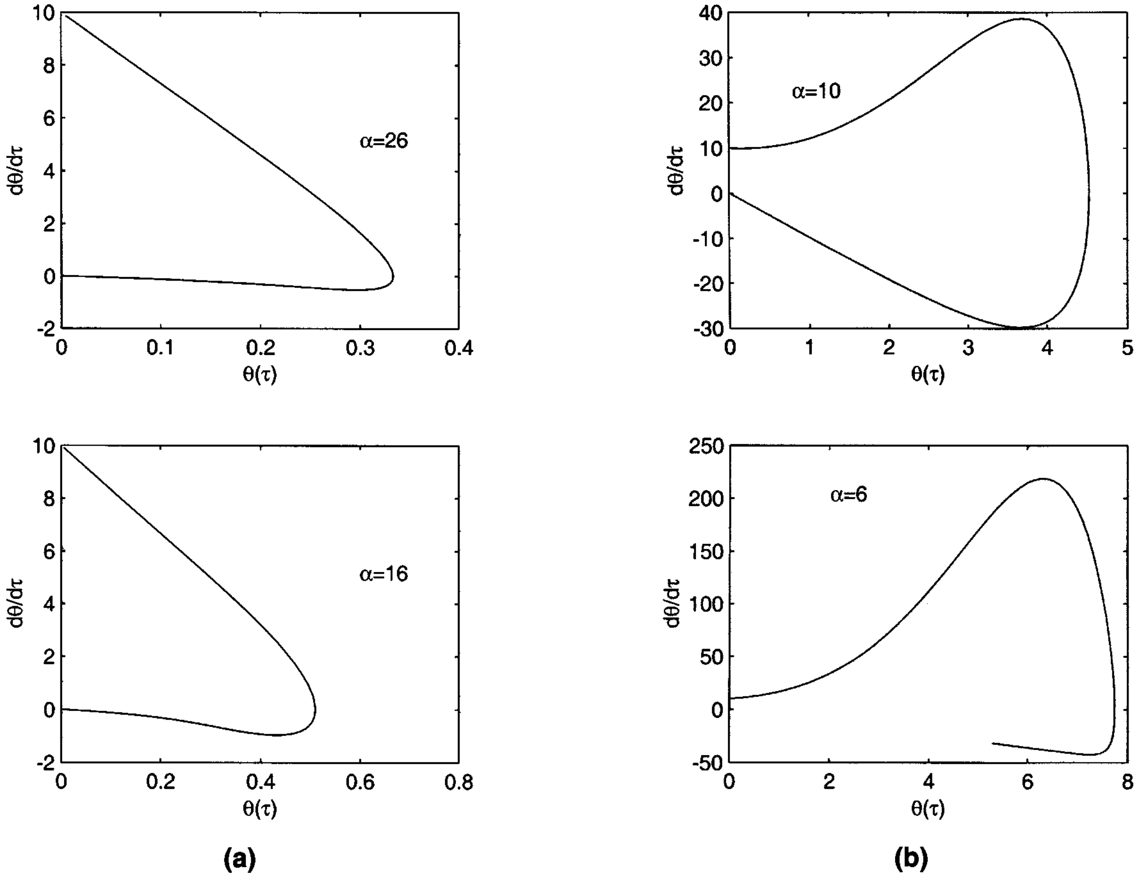


Figure 7. Reconstructed space using the method of derivatives, $\{\theta, d\theta/d\tau\}$.

ciently close, then

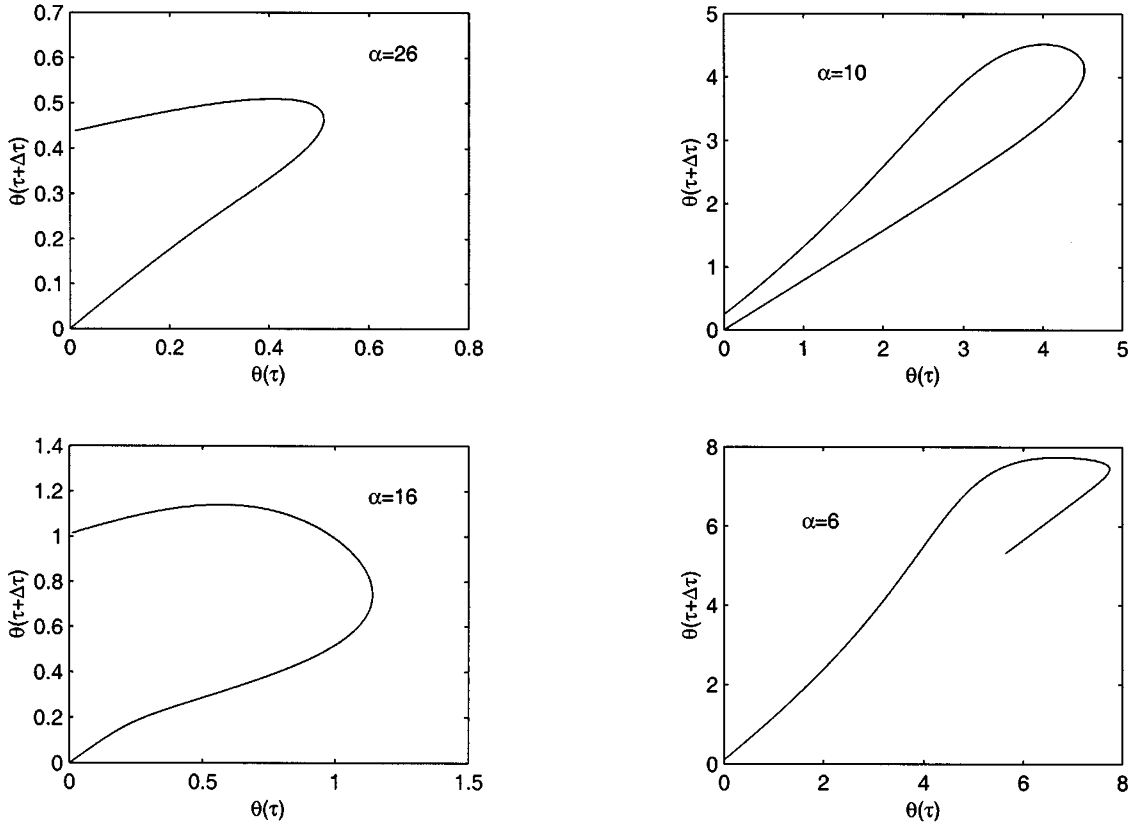
$$P\mathbf{1}(\tau) = \{T1(\tau), T1(\tau+\Delta\tau)\};$$
$$P\mathbf{2}(\tau) = \{T2(\tau), T2(\tau+\Delta\tau)\};$$
$$P\mathbf{3}(\tau) = \{T3(\tau), T3(\tau+\Delta\tau)\} \quad (46)$$

will be considered points. For phase-space reconstruction using the derivatives, we have used $dTi/d\tau$ instead of $Ti(\tau+\Delta\tau)$. Figures 10–12 show the calculated divergence, using dimensionless temperature and conversion points, and reconstructed divergence, using only temperature-delayed measurements or temperature derivates, for the batch isoperibolic reactor, and $B = 10$, $\epsilon = 0.05$ change the dimensionless heat-transfer coefficient, α. The reconstructed divergences from Figures 10 and 11 were calculated using the time delays from Table 1, respectively, whereas Figure 12 shows the reconstructed divergences using the method of derivatives for phase-space reconstruction. Since optimum time delays were defined as those that reproduce the theoretical divergence better, optimum reconstructed divergences are obtained with those time delays. The other two reconstructions—using the time delays provided by the first cross through zero of the autocorrelation function and using the derivatives—will give positive divergence for the case where $\alpha = 16$, while the calculated divergence is negative during all the reaction, even though it is really close to crossing the zero. It seems that when the first cross through zero of the autocorrelation function is taken, the divergence becomes positive, giving a false alarm for the case of $\alpha = 16$, but when the system shows runaway, $\alpha = 6$ and $\alpha = 10$, it gives a good approximation of the real divergence.

Discussion and Conclusions

Safe operation of chemical reactors in which strongly exothermic reactions take place requires that measurement devices that can detect the early stages of hazardous states be available, so plant operators can adopt the necessary countermeasures to return to safe conditions. The principal bottleneck for an on-line detection system is the criterion that distinguishes between dangerous and nondangerous situations. Especially for batch reactors, because of the variety processes, the on-line safety criteria must be as independent as possible of the actual process being carried out in the plant.

A first step in this direction was the safety criterion developed by Hub (1977) and Hub and Jones (1984). This criterion, which has been used industrially, considers that the state of the reactor is dangerous when both the first derivative of the temperature difference between the reactor and the jacket and the second derivative of the reactor temperature with respect to time are positive (see Eq. 32). The difficulty with using a double differentiation of the measured temperature with respect to time is that the noisy parts in the signal are



(a) **(b)**

Figure 8. Reconstructed space using embedding time-delay techniques, $\{\theta(\tau), \theta(\tau + \Delta\tau)\}$.

greatly amplified and have a major effect on the result of the evaluation, with false alarms being the principal problem. Furthermore, when an autocatalytic reaction is taking place in the reactor, because of the autoacceleration of the reaction rate, and hence the rate of heat generation, this criterion will always give an alarm no matter how hazardous the process, if no sufficiently positive limits are defined for the values of the first and second derivatives.

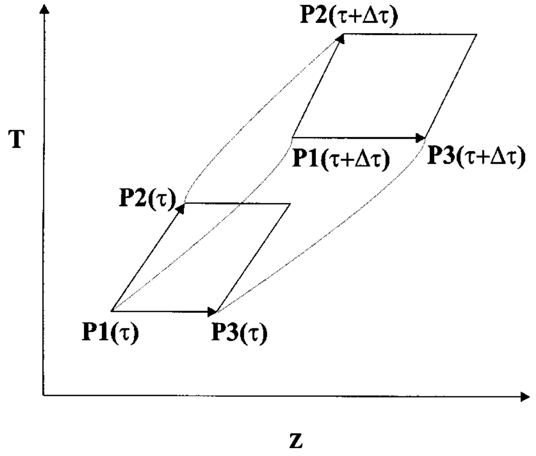
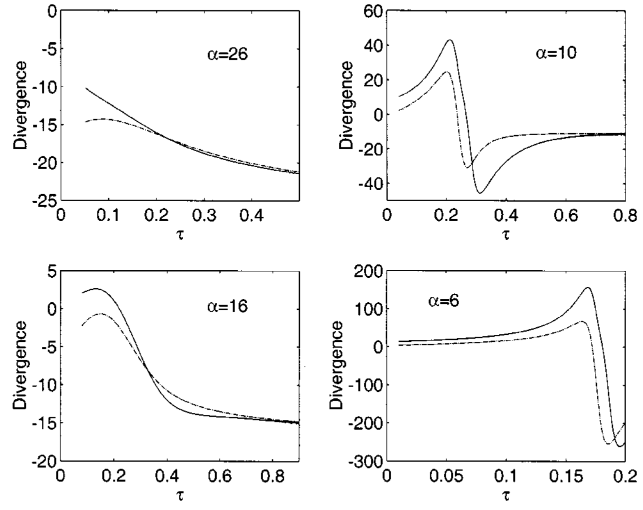


Figure 9. Evolution of three nearby trajectories in the real phase space.

On the other side, a considerable amount of study has been done on the parametric sensitivity of chemical reactors. These studies focused on finding simple criteria that allowed it to



(a) **(b)**

Figure 10. Calculated (· — · —) and reconstructed divergence profiles for the simulations (Figure 1), using the time delay obtained from the autocorrelation function (Table 1).

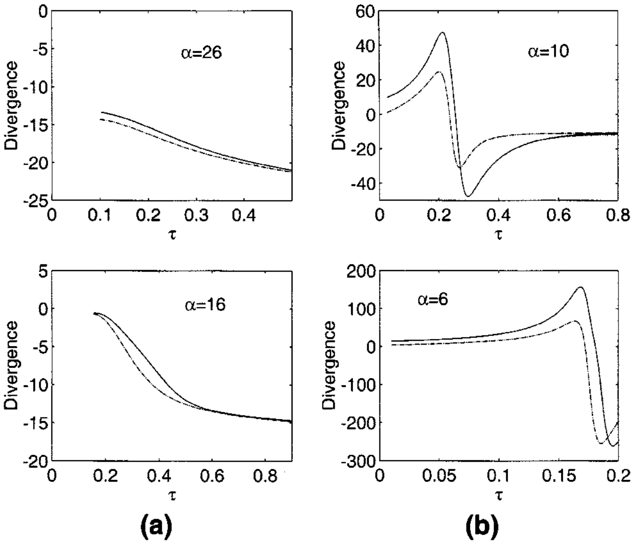


Figure 11. **Calculated (·—·—) and reconstructed divergence profiles for the simulations (Figure 1), using the optimum time delay (Table 1).**

be established in which regions of the parameters—that characterize the algebraic-differential equations describing the mass and energy balances of these reactors—the operation would be safe. The question arising at this point is if it is possible from these studies to extract a safety criterion that can be used on-line as an early-warning detection criterion.

A first attempt in this direction was carried out by Gilles and Schuler (1982), who used the criterion previously developed by Adler and Enig (1964) to distinguish between safe and runaway situations. To use such a criterion, the conversion must be estimated on-line from the temperature measurements, so a mathematical model of the reaction rate, as well as of the reactor, is necessary. Unfortunately, because of the low production levels, time constraints, and the large variety of processes, the development of reaction-rate models for batch processes usually is not economically justified, and therefore the application of model-based techniques is not always possible, being reserved for special cases.

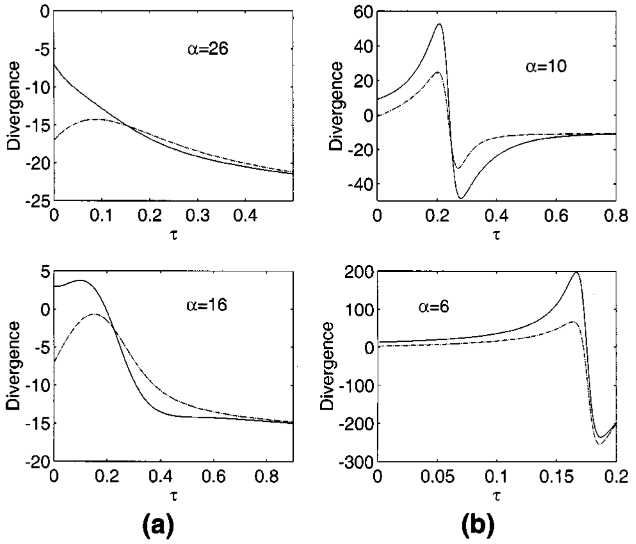


Figure 12. **Calculated (·—·—) and reconstructed divergence profiles for the simulations in Figure 1, using the derivatives for the phase-space reconstruction.**

Apart from that and related criteria, computation of the parametric sensitivity region requires the calculation of the local temperature sensitivity, defined as $dT_{\max}/d\phi$, where ϕ is one of the independent parameters that characterize the behavior of the model being considered (Morbidelli and Varma, 1988; Vajda and Rabitz, 1992; Strozzi and Zaldívar, 1994). Hence, these criteria are not directly applicable to on-line detection in which we want to know, with sufficient advance warning, if our specific process is approaching a dangerous situation.

Strozzi and Zaldívar (1994) developed a new method for calculating the parametric sensitivity or thermal runaway. In this work, the physical interpretation of such a criterion in terms of the contraction or expansion of the flow in phase space is carried out. From the physical interpretation, it is possible to compare with previous criteria and to study the limits of such a criterion based on the concept of local Lyapunov exponents. For the case of autocatalytic reactions in particular, this criterion is not able to predict accurately, in some part of the parameter space, the boundary between runaway and safe operation. This is because the sum of the Lyapunov exponents is an average over time of the divergence of the system: if the divergence is negative at the beginning of the process and then suddenly changes sign, as in the case of autocatalytic reactions, the average will respond only slowly to this effect. To correct these results, the value of the divergence is considered to be the safety criterion instead of its mean. This criterion, which for certain types of reaction systems is equivalent to earlier parametric sensitivity criteria, has the advantage, as in the calculation of Lyapunov exponents, that it can be applied on-line because the divergence can be computed from the measurement of only one system variable—for example, the temperature—using phase-space reconstruction techniques (Takens, 1981). It should be noted that in phase-space reconstruction the conversion is not estimated as in model-based estimation techniques. Instead, a phase space, which has some invariant properties, is reconstructed.

This new criterion is compared with the previous early-warning detection criteria and off-line parametric sensitivity studies. From the comparisons, it is possible to observe that, for an *n*th-order reaction, the criterion is slightly more conservative than previous on-line criteria, but still not as conservative as Barkelew's criterion. This means that an earlier detection of hazardous situations is expected. In the case of autocatalytic reactions, the criterion lies between Barkelew's criterion and the maximum of the parametric sensitivity criterion (see Figure 5). On the other hand, the Adler and Enig (1964) criterion, which was used by Gilles and Schuler (1982), would be too conservative, producing unnecessary false alarms.

Where once time-series analysis was shaped by linear systems theory, it is now possible to recognize when an apparently complicated time series has been produced by a low-dimensional nonlinear system, and to characterize its essential properties (Abarbanel, 1996). The phase-space methods used in the analysis of signals from nonlinear sources have been applied to the analysis of temperature data from discontinuous reactors, with the goal of developing an early-warning detection system.

The techniques required to perform these analyses depend on a coherent use of the time-series data and should not be treated using a black-box approach, but by considering the nature of the data and how they were obtained. Specifically, it is always possible to define a time-delayed vector from a time series, but this certainly does not mean that it is always possible to identify a meaningful structure in the embedded data. Because the mapping between a delay vector and the system's underlying state is not known, the precise value of an embedded data point is not significant. However, because the reconstruction is a diffeomorphism on the real state space, a number of important properties of the system will be preserved by the mapping. These include local features such as the number of degrees of freedom and global topological features (see Melvin and Tufillaro, 1991). Furthermore, as has been demonstrated (Strozzi, 1997), the divergence is preserved under phase-space reconstruction, and hence early-warning runaway detection based on the sign of the divergence can, in principle, be accomplished.

It is clear that a number of practical problems remain unsolved: for example, the selection of the optimal time-delay, which should be done on-line as the experimental data arrive, and the necessary embedding dimension, which in this article has been thought to be two, like the dimension of the system. What is the influence of the chemical kinetics on such a value? Furthermore, it would be necessary to carry out a complete experimental validation in different reactors and with different reactions to compare them with previous criteria. Our work is currently continuing along these lines.

Despite all these open questions, we have demonstrated the validity of such an approach in dealing with the problem of an early-warning detection of runaway first steps. A new route, between the simple use of measured variables and the complex model-based state reconstruction techniques, has been opened to assess in advance hazardous situations in chemical reactors so as to allow for the necessary countermeasures to be taken.

Acknowledgments

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Notation

A = frequency factor
B = dimensionless adiabatic temperature rise
C = concentration, $\mathrm{kmol \cdot m^{-3}}$
Cp = mean specific heat capacity, $\mathrm{kJ \cdot kg^{-1} \cdot K^{-1}}$
E = activation energy, $\mathrm{kJ \cdot kmol^{-1}}$
k = reaction rate constant
n = reaction order
R = universal gas constant
r = reaction rate, $\mathrm{kmol \cdot m^{-3} \cdot s^{-1}}$
S = heat transfer area, $\mathrm{m^2}$
t_{co} = characteristic time for cooling, s
t_g = characteristic time for heat generation, s
t_R = characteristic time for reaction, s
U = overall heat-transfer coefficient, $\mathrm{kJ \cdot m^{-2} \cdot K^{-1} \cdot s^{-1}}$
x = state vector
z = reactant conversion
α = dimensionless heat-transfer coefficient
ΔH = enthalpy of reaction, $\mathrm{kJ \cdot kmol^{-1}}$
$\epsilon = R \cdot T_e / E$, dimensionless jacket temperature parameter
λ_i = ith Lyapunov exponent
θ = dimensionless temperature
ρ = mixture density, $\mathrm{kg \cdot m^{-3}}$
τ = dimensionless time

Subscript

ad = adiabatic

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