EUROPEAN COMMISSION
JOINT RESEARCH CENTRE
Institute for Environment and Sustainability
Inland and Marine Waters Unit
I-21020 Ispra (VA) Italy

On-Line Application of the Divergence Criterion for Runaway Detection in Isothermal Batch Reactors: Simulated and Experimental Results

AWARD Project (Advanced Warning And Runaway Disposal)
(Growth Project G1RD-CT-2000-00499)

J.M. Zaldivar,

J. Bosch and F. Strozzi
Carlo Cattaneo University
Quantitative Methods Institute
Castellanza (VA) Italy

2002

EUR 20414 EN

Mission:

The mission of the Institute for Environment and Sustainability is to provide scientific and technical support to EU strategies for the protection of the environment and sustainable development. Employing an integrated approach to the investigation of air, water and soil contaminants, its goals are sustainable management of water resources, protection and maintenance of drinking waters, good functioning of aquatic ecosystems, and good ecological quality of surface waters.

EUR 20414 EN

Printed in Italy

CONTENTS

AWARD (Advanced Warning And Runaway Disposal) Project
(Growth Project G1RD-CT-2000-00499)

Deliverable: Advancement report on the improvement and testing of state space reconstruction numerical schemes (**WP2.Extension and theoretical development of the EWDS**. *Task 2.2,* Second Part: Batch and Semibatch reactors working on isothermal operating conditions)

Objective: The objective of *Task 2.2* is to implement and test several reconstruction algorithms to be used for the on-line reconstruction of the divergence of the system, using simulation results from *Task 2.1* and experimental results from **WP 4** (*Task 4.1*) and existing experimental data sets.

Summary

In this work, we have extended the application on-line of the divergence criterion for the early warning detection of runaway in isothermal reactors. In this case, it is necessary to take into account the temperature dynamics inside the jacket that depends on the heating/cooling system installed in the plant as well as on its control devices. For this reason, the jacket temperature has been included in the state space reconstruction for the calculation of the divergence of the system.

Divergence reconstruction has been validated beforehand using simulation results. This has allowed analysing the most suitable reconstruction strategy. Furthermore, the experimental validation has been carried out using experimental data from a bench-scale 2 L reactor and from a 100 L pilot plant reactor. The results show that the system is able to distinguish between runaway and non-runaway situations and it does not produce false alarms during heating/cooling due to changes in the temperature set-point.

In order to develop a robust early warning detection system it is now necessary to show its feasibility in "realistic" situations, i.e. in industrial plants under normal and abnormal operating conditions. Our experimental research is continuing along these lines.

1. INTRODUCTION

The reliability of a chemical reactor installed in a plant depends on the capability of the control/supervision system to estimate its state and to identify, in time, its operation malfunctions or failure modes. Specifically for chemical reactors carrying out exothermic reactions, the major problem is the loss of temperature control. In this situation, when the rate of heat generation by chemical reaction exceeds the rate of heat removal of the cooling system, there is a positive feedback mechanism, since the temperature of the reaction mass will raise increasing in turn the heat generation rate. In this situations, if no countermeasures are taken, a runaway or thermal excursion may occur.

There are several reasons for which the early detection of dangerous states is important for the correct operation of chemical reactors. A part from health and environmental considerations, an accident in a chemical reactor is extremely expensive (HSE, 1993). Furthermore, chemical industries experiment a number of near-misses, which could be reduced by the use of an early warning detection system (EWDS). This reduction would also contribute to the reduction of minor and major accidents, since as it has been shown by Petersen *et al.* (1980) that these values are correlated.

Methods for early warning detection can be divided into three main categories depending upon the quantities being used: Conventional limit check systems, temperature derivatives, and model-based estimation techniques (Kalman filtering). The first methods use only measurements from the system, which in the case of chemical reactors turns out to be mainly temperature, but also pressure (Tufano, 1988) and concentration measurements (Marco *et al.*, 1997) have been proposed. The second type of methods use the reactor temperature derivatives. Specifically, the method proposed by Hub and Jones (1986) based on the increase of heat evolution as the hazard identification criterion uses the second derivative of the reactor temperature, i.e. $d^2T/dt^2>0$, and the first derivative of the temperature difference between the reactor and the jacket, i.e. $d(T-T_w)/dt>0$. Finally, the third type of methods use a model of the system, the available measurements and, normally, a Kalman filter (or equivalent) to estimate the non-measurable variables (Gilles and Schuler 1982; King and Gilles 1990).

Despite all the different approaches, the early on-line detection of hazardous states in batch and semibatch processes is still an open problem because of the wide range of processes that are carried out on such equipment: their complexity; strong non-linearities; and time-varying parameters. In this context, the bottlenecks for the development of an effective on-line detection system are the definition of criteria, which distinguish between dangerous and non-dangerous situations; the

avoidance of false alarms, since countermeasures may consists on dumping the reactor contents or injecting an inhibitor with the loss of the batch, which means that in practice a trade-off exists between early detection (sensitivity) and number of false alarms (reliability); and the use of few measurements since the number of process carried out batchwise makes not economically feasible the development of a detailed kinetic model for each process, i.e. the EWDS has to be as independent as possible of the actual process carried out in the plant.

In a series of recent works (Strozzi *et al.*, 1999; Zaldívar *et al.*, 2002) a new criterion to delimit runaway boundaries was developed using techniques from chaos theory and the fact that the sensitivity to initial and operating conditions is a well-known characteristic of chemical reactors (Varma *et al.*, 1999). The runaway detection criterion was defined as when the divergence of the reactor becomes positive on a segment of the reaction path, i.e. *div>0*. 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 conversions-, i.e., $\partial(dT/dt)/\partial T + \sum_i \partial(dz_i/dt)/\partial z_i$. It was then shown, from a theoretical analysis using simulated data, that the divergence of the system could be reconstructed from only temperature measurements (Strozzi *et al.*, 1999). Furthermore, the criterion was calculated on-line an applied to isoperibolic (constant jacket temperature) batch reactors (2L and 100L), using simulated as well as experimental temperatures (Bosch *et al.*, 2002). The results shown that the application on-line of the divergence criterion for the early warning detection of runaway initiation is feasible. Furthermore, we had shown the equivalence, considering an embedding dimension of one, between Hub and Jones (1986) and *div>0* criteria. The use of an embedding dimension of two as suggested by theoretical and experimental results could be seen as a way to solve the problem of false alarms that the Hub and Jones criterion produces, for example for the case of autocatalytic reactions and for the case of semibatch processes (Nomen *et al.*, 2002).

In this work, we have extended the divergence criterion to the on-line detection of runaway in isothermal reactors. In this case, it is necessary to take into account not only the reactor temperature but also the jacket (or cooling coils) temperature that changes as a function on the heating/cooling system operating in the plant as well as its control system.

The work has been divided as follows, in Section 2 we introduce the isothermal batch reactor model, whereas in Section 3 the theoretical background needed to carry out the state space reconstruction of the divergence as well as non-linear noise reduction techniques are briefly discussed. In Section 4 the procedure is applied to simulated data for heating/cooling ramps,

runaway and non-runaway cases. Section 5 is devoted to the experimental results obtained using data from isothermal batch and semibatch experiments carried out in a bench-scale reactor (2 L) and in a pilot plant reactor (100 L) as well as data on heating/cooling experiments where no reaction occurs inside the reactor. In parallel, non-linear noise reduction techniques developed from chaos theory discussed in Section 3 are applied to improve the performance of the early warning detection algorithm. Finally, in Section 6, we made some conclusions and describe future work.

2. THE ISOTHERMAL BATCH REACTOR

An important aspect in the definition of runaway boundaries in chemical reactors, that has received little attention, is the influence of the control system. Normally, all the studies have been carried out assuming isoperibolic behaviour, i.e. constant jacket temperature.

In this work we are interested in studying the applicability of the divergence criterion to a batch reactor controlled with a master/slave proportional controller which is typical for these types of installations (Zaldívar *et al.*, 1993).

In this case, the control configuration may be summarised as follows, when the process is carried out in isothermal conditions, the reactor temperature is maintained at its desired value, set-point, by adjusting the temperature set-point for the heat transfer fluid recirculating through the reactor jacket. This is accomplished by the master controller. The temperature of the heat transfer fluid, which circulates through the reactor jacket, is controlled using a slave controller. Hence, the controller of the outer loop corrects deviations of the reactor temperature, θ, from the set value, θ^{sp}, following a proportional criterion:

$$\theta_w^{sp} = \theta^{sp} + Kp_1(\theta^{sp} - \theta) \tag{1}$$

providing the set value for the heat transfer fluid temperature, θ_w^{sp}, which is adjusted by the inner loop controller by means of another proportional controller. Expressing this in terms of heat balance, it is possible to write:

$$Q_R = Kp_2(\theta_w^{sp} - \theta_w) \tag{2}$$

By substituting Eq. (1) into Eq. (2) we obtain the heat flux necessary to keep the temperature of the reactor close to the pre-defined set-point.

Then the differential equations, that describe the dynamic behaviour of a controlled batch reactor with an exothermic first-order reaction $A \xrightarrow{r_1} B$, can be written, in dimensionless form, as:

$$\frac{dz}{d\tau} = Da \cdot R_1 \tag{3}$$

$$\frac{d\theta}{d\tau} = B \cdot Da \cdot R_1 - St \cdot (\theta - \theta_w) \tag{4}$$

$$\frac{d\theta_w}{d\tau} = \delta \cdot St \cdot (\theta - \theta_w) + Q_R \tag{5}$$

where Da , B, St and δ are the Damköhler number, the dimensionless heat of reaction parameter, the Stanton number and the cooling dimensionless time of the heat transfer fluid system, respectively. The dimensionless reaction rate is given by the following expression:

$$R_1 = \exp\left(\frac{\gamma \cdot \theta}{\gamma + \theta}\right) \cdot (1 - z)^n \tag{6}$$

In order to consider control saturation during transients, the manipulated variable, Q_R, is constrained as follows: if the required Q_R is higher than the maximum heating/cooling capacity of the system, $Q_R^{\max}$, this parameter takes this maximum value and if Q_R is lower than the minimum heating/cooling capacity then the parameter is equal to $Q_R^{\min}$.

The divergence, $div(z, \theta, \theta_w) = j_{11} + j_{22} + j_{33}$, is calculated as:

$$j_{11} = -Da \cdot \exp\left(\frac{\gamma \cdot \theta}{\gamma + \theta}\right) \cdot n \cdot (1 - z)^{n-1} \tag{7}$$

$$j_{22} = \frac{B \cdot Da \cdot R_1 \cdot \gamma^2}{(\gamma + \theta)^2} - St \tag{8}$$

$$j_{33} = -\delta \cdot St - Kp_2 \tag{9}$$

When the controller works in saturation the term j_{33} is modified as follows:

$$j_{33} = -\delta \cdot St \tag{10}$$

The criterion states that when $div>0$ on a segment of the reaction path, the system is in the runaway (sensitive) region.

2.1. Heating/cooling dynamics

Let first study the case in which there is no reaction in the reactor, i.e. $Da=R_1=0$, and we change the temperature set-point. This is a typical reactor manipulation that posses several problems to existing runaway detection criteria. Figure 1 shows a heating/cooling temperature profile in the reactor as well as in the jacket. As can be seen the divergence is in this case always negative indicating that we are not in a runaway situation.

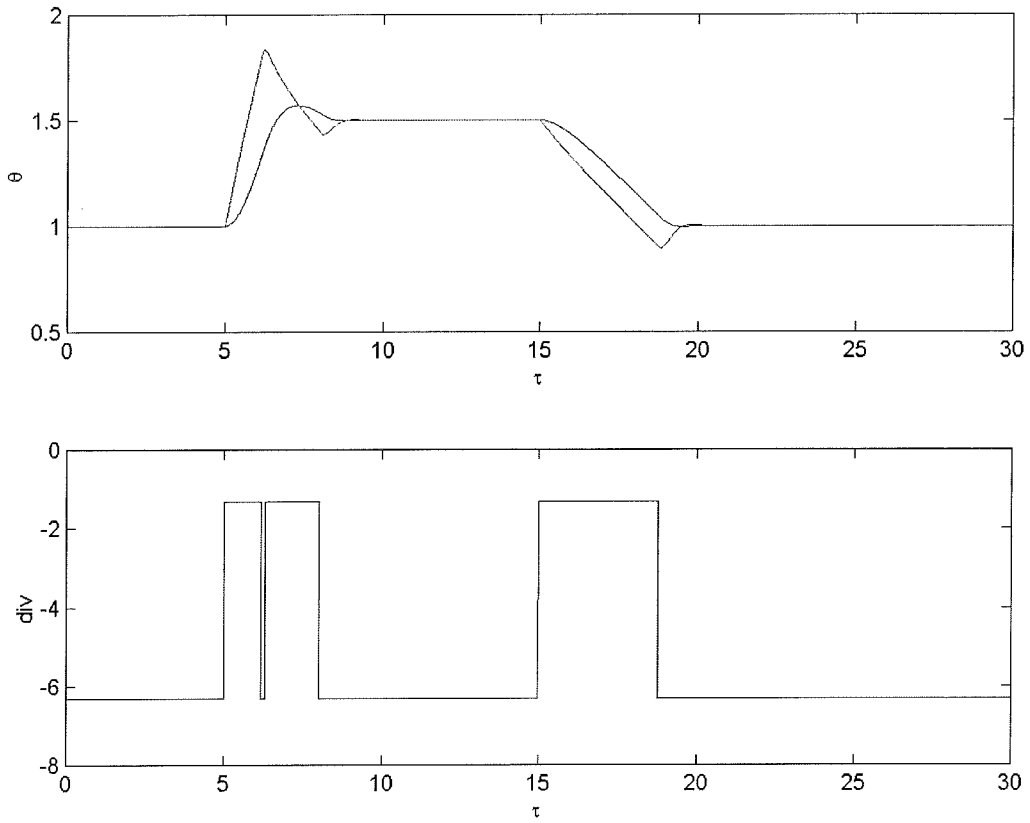

Figure 1. a/ Dimensionless reactor and jacket temperature during a heating/cooling simulation. $\theta^{sp} = 1 \rightarrow 1.5 \rightarrow 1$ at $\tau = 0$, $\tau = 5$ and $\tau = 15$. b/ Calculated divergence (steps are due to the constraints in Q_R). Parameters during the simulation: St = 1; δ=0.33; Kp_1 = 3; Kp_2 = 5; $Q_R^{\max}$ = 0.8; $Q_R^{\min}$ =-0.2.

2.2. Non-runaway and runaway in isothermal reactors

In a previous work Zaldívar *et al.* (2002) have calculated off-line the critical set of parameters that distinguishes between safe and runaway regions using the divergence criterion. This boundary surface is defined as the first at which the divergence of the system becomes positive. In general terms the introduction of a control system reduces the runaway region. It is clear that if the control system had infinite power supply and no time delay, there will not be a runaway in the reactor, and hence, the runaway boundaries depend on the maximum cooling capacity of the system and on its time constant to respond to a change in the reactor temperature. Zaldívar *et al.* (2002) found that for slow reaction rates (low values of Damköhler number) the determination of adequate control parameters, in this case the proportional gains in the inner and outer loops, is essential to keep the reaction temperature under control. For fast reaction rates the power capacity is the principal factor, since in this case we are going to reach saturation in the control system. In this situation, the

appropriate solution would be to change the type of process from batch to semibatch since the temperature control system is not enough to maintain safe operating conditions.

Figure 2 shows two typical examples of non-runaway and runaway conditions for the isothermal batch reactor. As can be seen, in the later case the divergence becomes positive during the reactor operation. Of course, as batch and semibatch processes are dissipative systems, the state space volume will at the end contract and, hence, the divergence will be negative. These examples will be used afterwards to show how the divergence can be calculated using only temperature measurements.

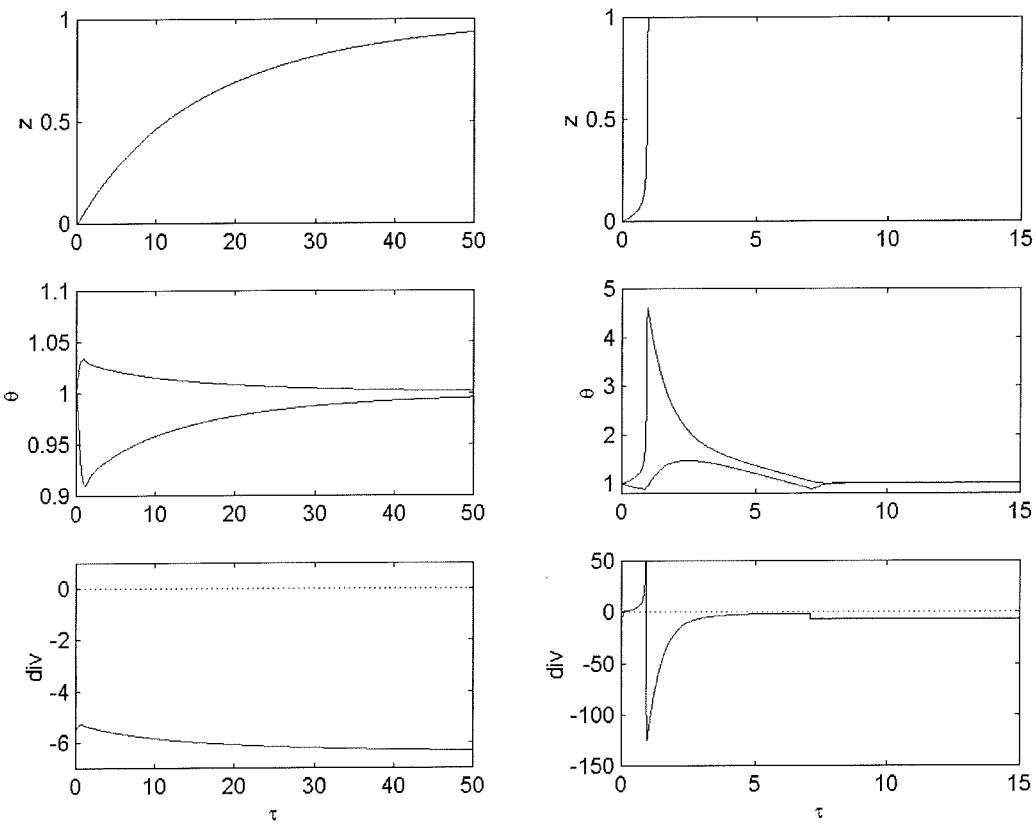

Figure 2. Conversion, dimensionless reactor and jacket temperature and divergence during a non-runaway (Bo = 1.8) and a runaway (Bo = 4.0) simulations. Parameters: Da=0.05; St = 1; γ = 0.1; δ=0.33; $Kp_1 = 3$; $Kp_2 = 5$; $Q_R^{\max} = 0.8$; $Q_R^{\min}$ =-0.2.

3. NON-LINEAR TECHNIQUES

3.1. State space reconstruction and divergence calculation

In order to calculate on-line the divergence without the need of knowing the differential equations of the system we have used the theory of embedding. The theory of embedding is a way to move from a temporal time series of measurements to a state space "similar" -in a topological sense- to

that of the underlying dynamical system we are interested in analysing. Techniques of state space reconstruction were introduced by Packard *et al.* (1980) and Takens (1981), which showed -under certain generic assumptions- it is possible to address this problem using measurements of a time series of the dynamical system of interest.

In a general case, let $s(t)$ be the measure of some variable of our system, which is related to the state variables by an unknown function h,

$$s(t) = h(\mathbf{x}(t)) \tag{11}$$

Takens (1981) proved that, under certain conditions, the dynamics on the attractor of the underlying original system has a one-to-one correspondence with measurements of a limited number of variables. Even though, theoretically, all the methods of reconstruction should produce the same result, there is no *a priori* method to decide which is the more adequate (Casdagli *et al.*, 1991) and there is a considerable difference in the quality of the resulting reconstructed state space coordinates and hence in the calculated quantities from these coordinates. 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 (Breeden and Packard, 1994). Furthermore, in our case the situation is complicated by the nonstationarity of our system.

In a previous work (Bosch *et al.*, 2002) we have tested several methods: time delay embedding vectors $\{s(t),\ s(t-\Delta t),\ s(t-2\Delta t),\ldots,\ s(t-(d_E-1)\Delta t)\}$; derivative coordinates $\{s(t), ds(t)/dt,\ldots,d^{(d_E-1)}s(t)/dt^{(d_E-1)}\}$and integral coordinates $\{s(t),\ I_1[s(t)],\ldots,I_{d_E-1}[s(t)]\}$. As the results were similar we decided to use derivative coordinates. The advantage of derivative coordinates is their clear physical meaning; their drawback lies in their sensitivity to noise. In this case we need to establish only one embedding parameter, i.e. the embedding dimension, d_E. The embedding dimension is the dimension of the state space required to unfold the system from the observation of scalar signals. When using time delayed vectors the time delay, Δt, or the lag between data points to consider when reconstructing should also be estimated.

Once the state space has been reconstructed, in our case from temperature measurements, it is possible to calculate the divergence, *div*, of the system, that should be preserved (Strozzi, 1997). There are several methods to calculate the divergence which are related to the volume of the system in phase space by the Liouville's theorem (Arnold, 1973) which states that:

$$V_{ps}(t) = V_{ps}(0) \cdot \exp\left[\int_0^t div\{\mathbf{F}[\mathbf{x}(\tau)]\}d\tau\right] \tag{12}$$

where

$$div\{\mathbf{F}[\mathbf{x}(t)]\} = \frac{\partial F_1[\mathbf{x}(t)]}{\partial x_1} + \frac{\partial F_2[\mathbf{x}(t)]}{\partial x_2} + \ldots + \frac{\partial F_d[\mathbf{x}(t)]}{\partial x_d} \tag{13}$$

After several manipulations it is possible to arrive to the following expression:

$$div = \frac{\dot{V}_{ps}(t)}{V_{ps}(t)} \tag{14}$$

Due to the volume contraction in state space, characteristic of dissipative systems, $V_{ps}(t)$ will rapidly tend to zero and produce artefacts when introduced dividing in Eq. (14). However, by definition the volume is always positive and hence, $div>0$ is equivalent to check:

$$\Delta V_{ps}(t) > 0 \tag{15}$$

where $\Delta V_{ps}(t)$ is an infinitesimal state space volume variation. This eliminates the need to calculate the division of two small numbers that produces an increase in the numerical errors of the calculation (Bosch *et al.*, 2002). Even though the absolute values of $\Delta V_{ps}(t)$ are not preserved under state space reconstruction, its sign, which is the identification criteria, will be preserved.

3.2. Non-linear noise reduction

In order to remove the observational noise, different possibilities are available which can be broadly divided into two categories: linear filters which are based on the application of Fourier techniques, and non-linear noise reduction methods that make use of the deterministic origin of the signal we are interested in.

Linear digital filters have been developed to eliminate noise at high, low or specific frequencies (notch filters, for example to take out the 50 Hz AC contamination in signals recorded with electronic circuits), respectively, and there is a vast amount of literature and algorithms developed for such a purpose (Oppenheim and Schafer, 1975; Goodwin and Sin, 1984; Press *et al.*, 1986; amongst others).

If the nonlinearity tests are positive and hence, one may assume that the data originated from a deterministic non-linear system, then methods for non-linear noise reduction may be applied. The basic idea of all these methods is to exploit the underlying determinism by correcting the states and the time series values using a model that is previously fitted to the raw data - for a recent survey see Kostelich and Schreiber (1993), and Davies (1994). The main objective as opposite to linear filtering techniques resides in the fact that one tries to maintain the general characteristic that dissipative motion tends to occupy smooth submanifolds of the total available state space. This implies that the reconstructed state vectors are constrained to fall onto geometrical locally linear objects.

Both, linear and non-linear filtering techniques assume we are dealing with a stationary signal and there is only observational noise. Normally this is not our case, since batch and semibatch reactors are non-stationary by definition and we cannot exclude the existence of dynamical noise, but the situation is the same in a larger number of real applications, and hence, caution should be taken when applying these techniques that have been developed and tested for system with fundamental different characteristics.

In this work we have applied the modified (Schreiber and Richter, 1999) non-linear local projective noise reduction algorithm developed by Grassberger *et al.* (1993). This method assumes that the deterministic part of the time series lies on a low-dimensional manifold, d_q, in a high-dimensional reconstructed state space, d_E, while the effect of the noise is to distribute the data randomly in the surroundings of the manifold. Interested readers are referred to Kantz and Schreiber (1998) and references therein for a detailed description of the method and relevant discussions. This noise reduction scheme has been implemented in the TISEAN software package (Hegger *et al.*, 1999) by the routine *noise*, and it has been tested in different application with considerable improvements over traditional filtering (Hegger *et al.*, 2002).

4. RUNAWAY DETECTION USING SIMULATED DATA

In order to avoid problems related to noise in the temperature measurements, we decided, as a first step, to use the simulated temperature data obtained for isothermal batch reactor in which no reaction (heating/cooling profiles) or a first order reaction take place. This will allow us to choose, by comparing theoretical and calculated divergence, the most appropriate, i.e. best fit and/or less false alarms, reconstruction scheme in absence of noise.

For the case of isoperibolic reactors (Bosch *et al.*, 2002), we found that an embedding dimension of two was enough and, hence, we used the reactor temperature and its first derivative, i.e. $\{T(t), dT(t)/dt\}$. This low dimension is due to the fact that our dynamical system describes a simple trajectory in the phase space before reaching the attractor -a fixed point at the end of the reaction-. Furthermore, even though theoretically best results were obtained using three temperature measurements (trajectories), experimentally there was no difference between using three temperature sensors or one temperature measurement only.

In the case of isothermal reactors we have to consider the dynamics of the heating/cooling system and, hence, we have to include the jacket temperature. The isothermal reactor shows a similar behaviour as the isoperibolic reactor in terms of trajectory "complexity" and, hence, we expect that a low embedding dimension will be sufficient to unfold the dynamics of the system from

temperature measurements. As there is no method to know a priori which is the best embedding (Breeden and Packard, 1994), several alternatives have been tested using two and three as embedding dimension and a combination of the following state variables: $\theta(\tau)$, $\theta_w(\tau)$, $\theta(\tau)-\theta_w(\tau)$, $d\theta(\tau)/d\tau$, $d\theta_w(\tau)/d\tau$, $d[\theta(\tau)-\theta_w(\tau)]/d\tau$. We report here only the most relevant results.

Figure 3 shows the analytical and reconstructed state space volume variations, $\Delta V_{ps}(\tau)$, for the heating/cooling dynamics described in Fig. 1, using an embedding dimension of 2 and three temperature trajectories generated changing slightly the initial conditions. As can be seen the four reconstruction schemes give similar results and it is not possible to distinguish between analytical and reconstructed $\Delta V_{ps}(\tau)$. The error is one order of magnitude inferior to the values of $\Delta V_{ps}(\tau)$. $\Delta V_{ps}(\tau)<0$ means according to our criterion, Eq. (15), that the divergence is always negative and, hence, we are in a safe condition.

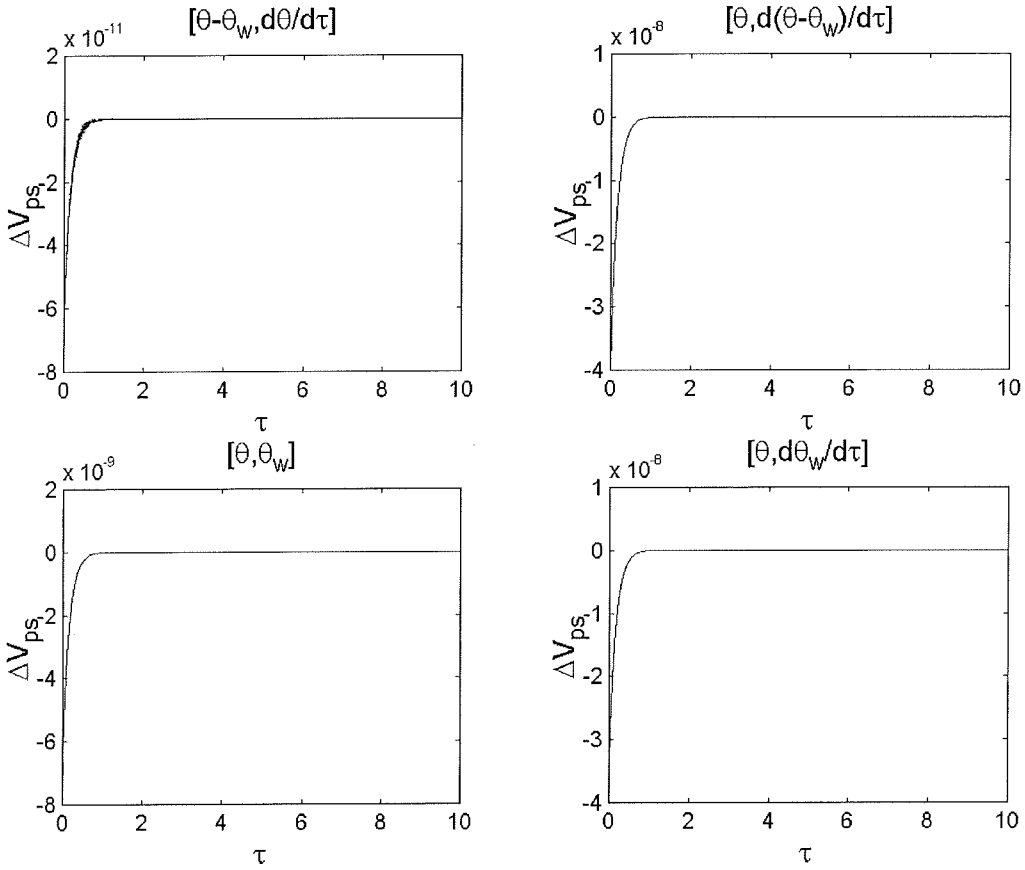

Figure 3. Analytical (continuous line) and reconstructed (discontinuous line) $\Delta V_{ps}(\tau)$ for the heating/cooling simulation (fig. 1) using different state space variables.

Figure 4 shows the analytical and calculated divergences for the simulations described in Fig. 2, i.e. non-runaway (Fig. 4a and 4b) and runaway (Fig. 4c and 4d) simulations using an embedding dimension of three and four temperature trajectories generated changing slightly the initial

conditions. As can be seen, it is possible to distinguish between non-runaway, i.e. $\Delta V_{ps}(\tau)<0$ and runaway, i.e. $\Delta V_{ps}(\tau)>0$. Furthermore, there is a good agreement between $\Delta V_{ps}(\tau)$ calculated analytically and reconstructed using only temperature data. Other reconstruction schemes give similar results.

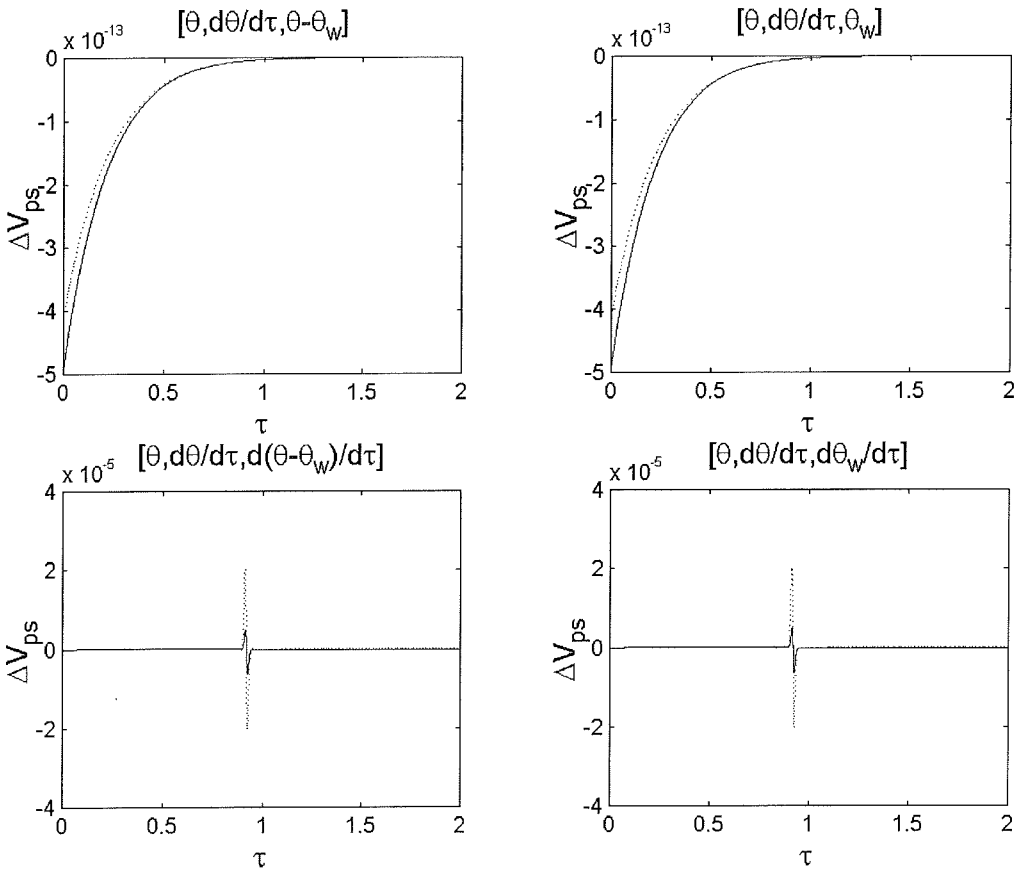

Figure 4. Analytical (continuous line) and reconstructed (discontinuous line) $\Delta V_{ps}(\tau)$ for the non-runaway (a and b) and for the runaway (c and d) simulations (fig. 2) using different state space variables.

In practice, we are interested in using only one temperature trajectory, i.e. one temperature measurement. This can be achieved instead of using several trajectories by using close state space points along the same trajectory assuming that the Jacobian between close points has not changed (Bosch *et al.*, 2002). Of course, this is an approximation and one should expect results $\Delta V_{ps}(\tau)$ will show more differences between analytical and reconstructed. Figure 5 shows the results obtained calculating the increase in state space volume for the runaway and non-runaway simulations using only one temperature trajectory (i.e. reactor and jacket temperatures), with embedding dimensions of two and three respectively. Several state space variables has been also checked. As can be seen,

the results in these cases are less accurate than before, but still the method works properly by defining suitable limits in the check of $\Delta V_{ps}(\tau)$.

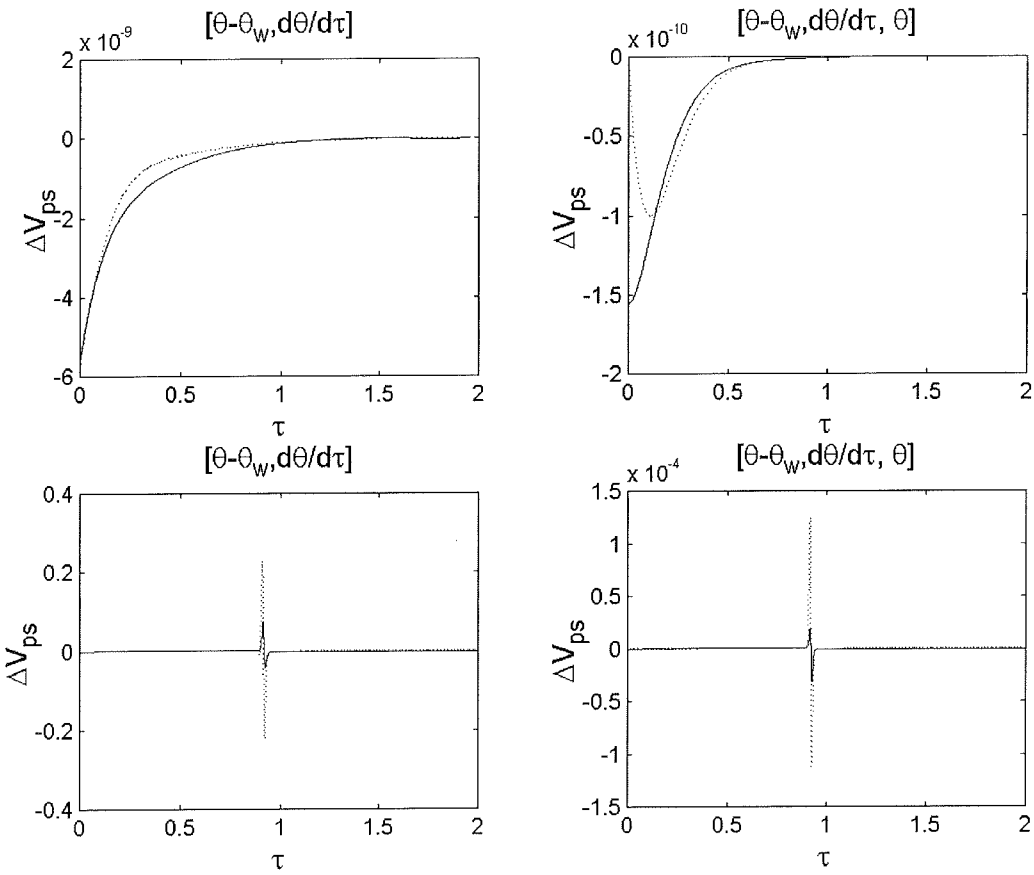

Figure 5. Analytical (continuous line) and reconstructed (discontinuous line) $\Delta V_{ps}(\tau)$ for the non-runaway (a/d_E=2 and b/d_E=3) and for the runaway (c/d_E=2 and d/d_E=3) simulations (fig. 2) using only one temperature trajectory.

From this theoretical analysis it is not possible to conclude which are the best reconstruction state variables nor the embedding dimension (2 or 3) using only one temperature sensor, since all of them -$\theta(\tau)$, $\theta_w(\tau)$, $\theta(\tau)-\theta_w(\tau)$, $d\theta(\tau)/d\tau$, $d\theta_w(\tau)/d\tau$, $d[\theta(\tau)-\theta_w(\tau)]/d\tau$ - produce similar results. Of course, taking into account an appropriate number of temperature trajectories, i.e. 3 for heating/cooling simulations, 4 for the case of reaction inside the reactor, differences between analytical and reconstructed $\Delta V_{ps}(\tau)$ are reduced. However, the possibility of using only one temperature measurement in the reactor and one in the jacket to perform the same calculation, is important from the point of view of the practical application of the algorithm. In this case there is the possibility of false alarms and a limit should be defined when checking the positiveness of $\Delta V_{ps}(\tau)$, i.e. $\Delta V_{ps}(\tau) > \Delta V_{ps}^{\lim} > 0$.

5. RUNAWAY DETECTION USING EXPERIMENTAL DATA

In order to test the influence of noise and fluctuations, present in real temperature measurements, on the sensitivity and reliability of the different algorithms for early detection of runaway initiation based on the divergence criterion, several experimental data sets have been analysed. Observational noise have been reduced applying non-linear filters to reactor as well as jacket temperature-recorded measurements.

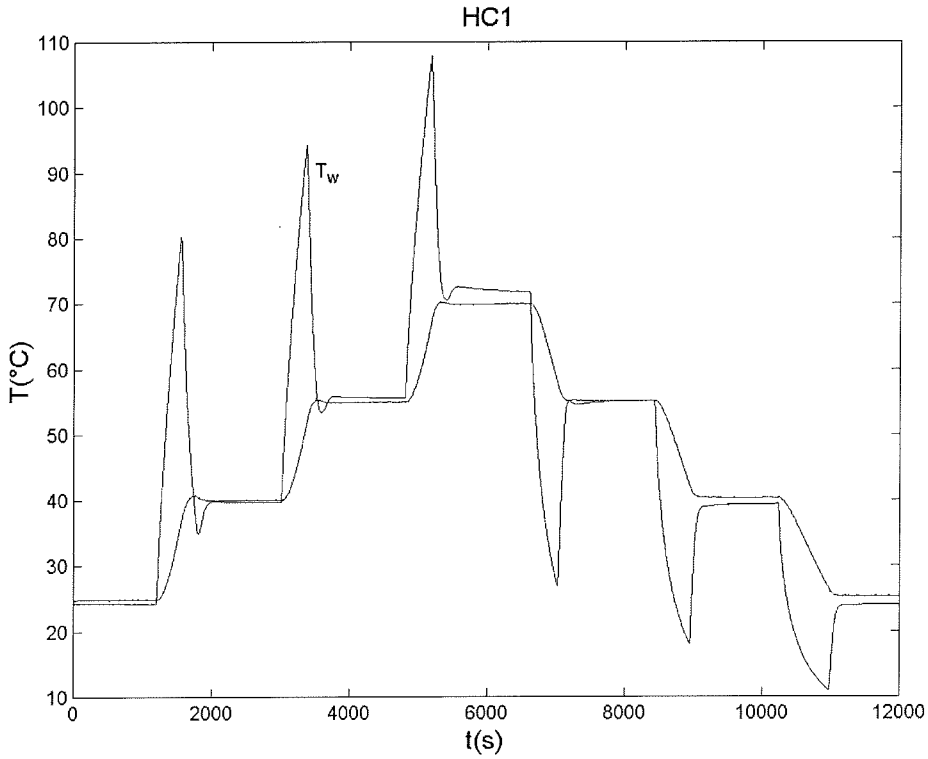

Figure 6. Reactor and Jacket temperature measurements recorded by the bench scale reactor (2 L) data acquisition system during a heating/cooling experiment. Set-points: 25 → 40 → 55 → 70 → 55 → 40 → 25 °C.

5.1. Heating/cooling experiments

The first experiment, *HC1*, was carried out in the bench scale reactor (2 L) filled with water, 400 rpm of stirrer speed, and changing the reactor temperature set-point as follows: 25-40-55-70-55-40-25 °C. Sufficient time was allowed for temperature stabilisation. In this case the system should not give any alarm since these can be considered as operator manipulations in the plant and there is no reaction taking place inside the reactor.

The second heating/cooling experiment, *HC2*, analysed was carried out in a 100 L pilot plant reactor (Zaldívar *et al.*, 1993). Also in this case the reactor was charged with water (80 L) and constant stirred speed (300 rpm) was maintained during all the experiment. The dynamics of the

heating/cooling behaviour was tested changing directly the output of the controller. In this case, no time was allowed for temperature stabilisation.

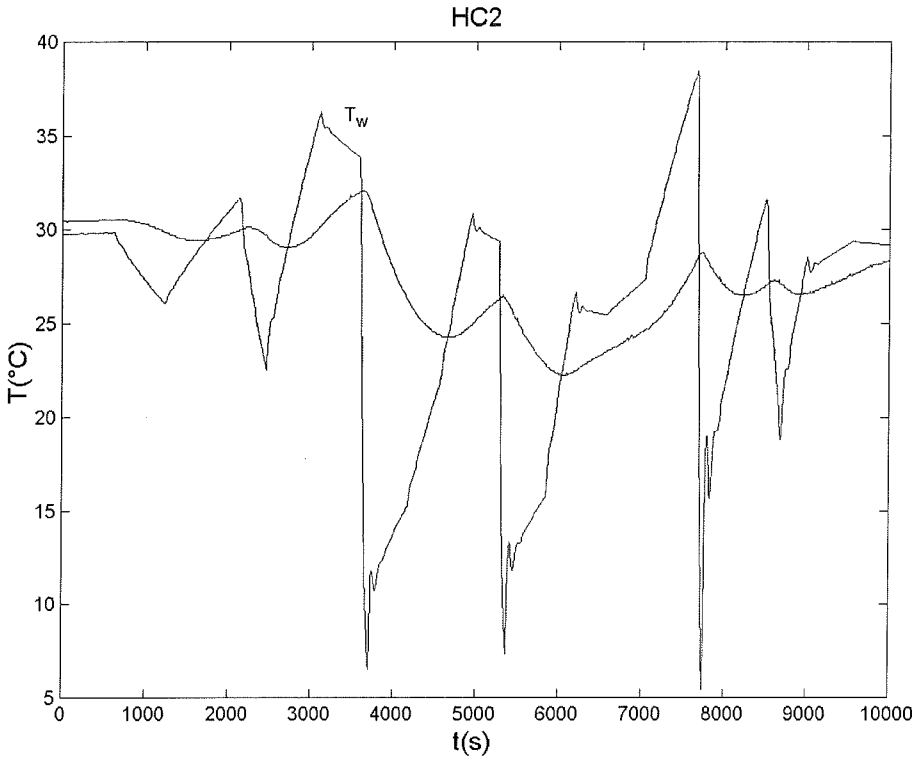

Figure 7. Experimental reactor and jacket temperature profiles for the pilot scale (100 L) batch reactor heating/cooling experiments.

5.2. Non-runaway and runaway experiments

The data sets are part of several experimental campaigns carried out in different reactors, i.e. a 2 L bench-scale reactor (Zaldívar *et al.*, 1996) and 100 L pilot plant reactor (Zaldívar *et al.*, 1993). The reaction studied in the 2 L reactor was the esterification reaction between 2-butanol and propionic anhydride catalyzed by sulphuric acid carried out batchwise. This reactions that has been extensively analysed elsewhere (Snee *et al.*, 1992; Galván *et al.*, 1996). In the 100 L pilot plant we report the results on the semibatch toluene nitration by mixed acid in which a stirrer failure accident was experimentally simulated. Toluene nitration has also been analysed in Zaldívar *et al.* (1995).

- Bench-scale experiments (2L)

Exp1 and *Exp2* are two typical runaway experiments under slightly changed sulphuric acid concentrations (0.85 and 0.8 wt %). The temperature set-point , T^{sp}, for both experiments was 40 °C and the stirrer speed 400 rpm. As can be seen, Fig. 8, the heating/cooling system tries to maintain a constant temperature by changing the jacket temperature. However, the reaction rate is so fast that the rate of heat generation exceeds the rate of heat removal of the cooling system. This makes the temperature of the reacting mass to rise and a thermal runaway occurs. The first peak in jacket

temperature is due to the endothermic heat of dilution, whereas the second is due to an internal safety interlock that tries to avoid more than 50 °C difference between reactor and jacket temperatures to protect the glass reactor against breakage. In *Exp1* there was a venting of the reaction mass and, hence, part of the liquid went out of the reactor. One should notice that the duration of the overall experiment, from the introduction of the reagent to the temperature peak is 7.9 minutes. In *Exp2*, the maximum reactor temperature parameter was set at 100 °C. When the reactor temperature reached this value an emergency cooling programme was triggered off and a safety valve was opened to increase the cooling power. However the effects of this action are practically negligible. *Exp3* and *Exp4* where performed under similar sulphuric acid concentration than *Exp2* but the temperature set-point was decreased to 31 and 23 °C respectively. As can be seen the initial jacket temperature increase is also associated to the endothermic mixing of the reagents. Furthermore, there is some autocatalytic effect in the esterification reaction as can be seen from the jacket temperature behaviour that shows an increase in heat released as the reaction proceeds (Galván *et al.*, 1996).

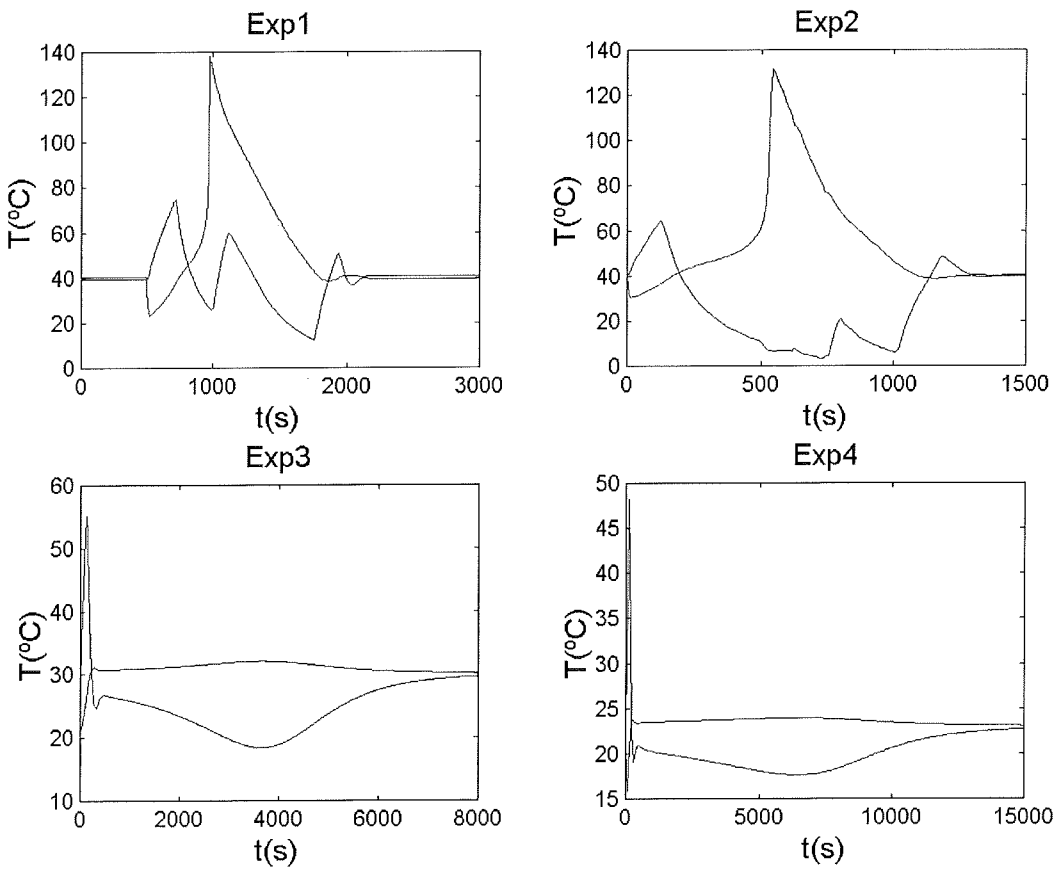

Figure 8. Experimental reactor and jacket temperature profiles for the bench scale (2L) batch reactor experiments. The reaction was the equimolar esterification between propionic anhydride and 2-butanol. A runaway occurred in the first two experiments (*Exp1* and *Exp2*), whereas the heating/cooling system was able to control the last two (*Exp3* and *Exp4*).

- Pilot Plant experiments (100L)

These experiments, Fig. 9, were carried out to experimentally simulate the stirring problems for homogenizing the reacting mass below a certain volume (Zaldivar *et al.*, 1993). In the first experiment, *Exp5*, 40 L of toluene were introduced in the reactor and, after temperature stabilization at 35 °C, mixed acid (80% sulphuric acid strength) was added at 2.44 $g \cdot s^{-1}$ during two hours. In the second experiment all the operating conditions were equivalent, but only 32 L of toluene where initially present in the reactor. Under these conditions the mixing was not effective and mixed acid started to accumulate in the bottom of the reactor until the reactor volume reached the critical volume. At this point all the mixed acid started to react producing a thermal runaway. At 50 °C maximum cooling was triggered off and at 60 °C the fast injection system was brought into operation injecting 18 L of water that stopped the reaction.

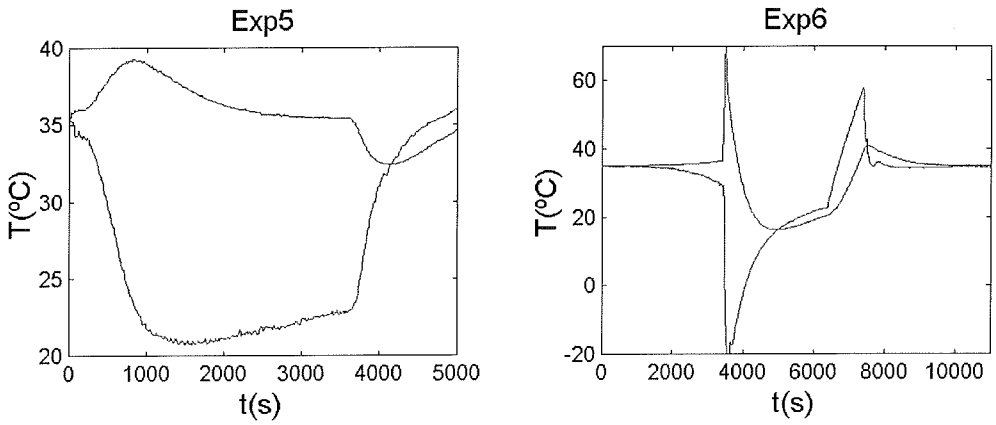

Figure 9. Reactor and jacket temperature profiles for the pilot plant (100 L) semibatch nitration experiment. Two different initial volumes (40 and 32 L) of toluene where introduced in the reactor and mixed acid was dosed during two hours (*Exp5*). T^{sp} = 35 °C. A runaway due to poor mixing occurred in *Exp6*, whereas the heating/cooling system was able to control *Exp5*.

5.3. Runaway detection

In order to improve the sensitivity and the reliability of the EWDS which in practice means to increase the time in advance and to reduce the number of false alarms, several linear (moving average, exponential, Savitzky-Golay, etc.) and non-linear filters have been tested. Due to the non-stationary nature of our system and the transients that the reactor and jacket temperatures experiment during the processes, it was shown (Bosch *et al.*, 2002) that linear filters were not suitable since they tend to smooth excessively those transients. Furthermore, in some cases the linear filtering process introduced false alarms (Bosch *et al.*, 2002). For these reasons we decided to apply non-linear filters. One advantage of these filters is that when there are no neighbours in state space, the filter does not perform any action, and, hence, fast transients are not filtered. On the

contrary, if the filter has an adequate neighbourhood of points in the state space then the points are projected into a lower dimension and the trajectory is smoothed. This means that the sensitivity of filtered compared with non-filtered data practically does not change, since when approaching runaway as the temperature differences increase the number of neighbour points in state space decreases and the algorithm stops filtering, whereas the reliability increases due to the fact that the filter smooth fluctuations when the temperature of reactor and the jacket is not changing appreciably.

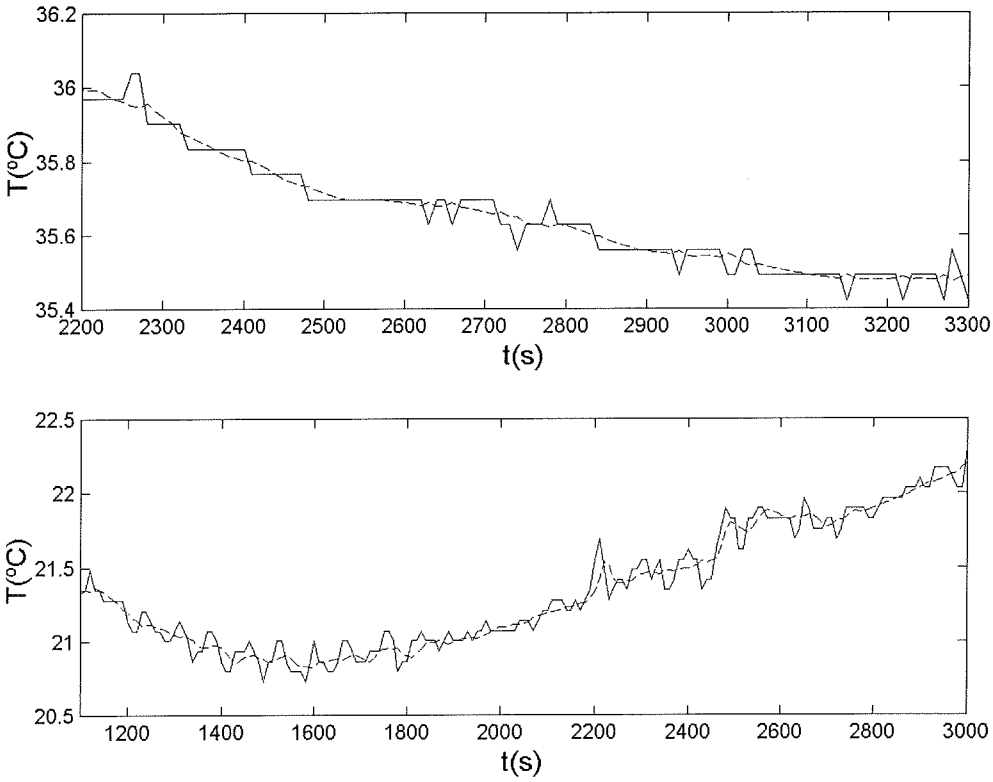

Figure 10. Experimental and filtered reactor (a) and jacket (b) temperature data for *Exp5* in the 100 L pilot plant reactor. Filter parameters: d_E=8, d_q=3, Δt=1, ε=0.5, t_p =100.

In order to apply the on-line projective noise reduction algorithm to reactor temperature data it is necessary to define a number of parameters, between them the embedding dimension, d_E, and the time delay, Δt, which are the reconstruction parameters, the dimension of the manifold to project onto, d_q, the minimal diameter, ε, the desired maximal number of neighbourhoods, and the maximal time in the past considered as neighbours, t_p (Hegger *et al.*, 1999). The filter parameters are the same than the used for isoperibolic reactors (Bosch *et al.*, 2002). Figure 10 shows a window of experimental and filtered reactor and jacket temperatures for the 100 L semibatch nitration experiment, *Exp5*. As can be seen, non-linear filtering is able to reduce the small fluctuations

present in the temperature measurements. By comparing non-filtered with filtered measurements, we have observed a reduction approximately of 10 % in the limits one has to impose to $\Delta V_{sp}(t)$, this reduction increases the margin between non-runaway and runaway limits decreasing in practice the number of false alarms due to temperature fluctuations.

Once the experimental data has been filtered then the divergence of the system is reconstructed. As the results from theoretical reconstruction were equivalent for several schemes, we have tested these in order to assess which is the most suitable from the experimental point of view.

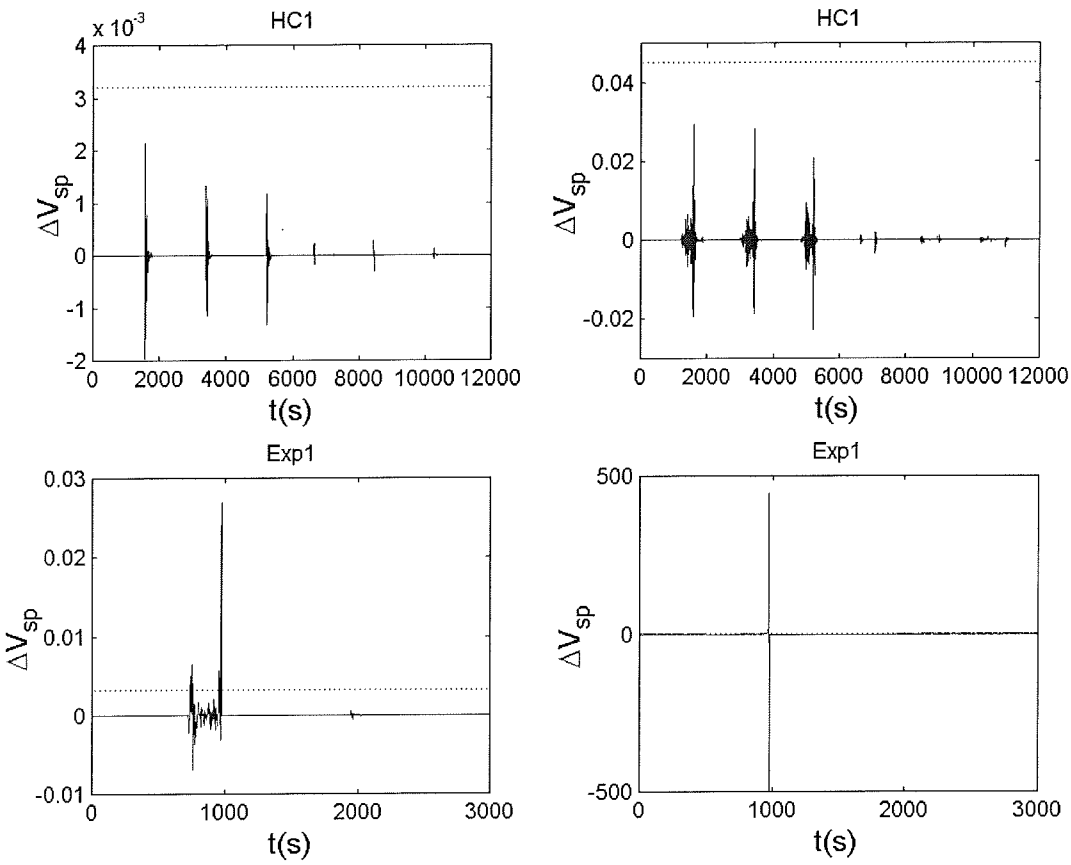

Figure 11. Reconstructed $\Delta V_{ps}(t)$ for the non-runaway experiment *HC1* and for the runaway experiment *Exp1* using: a/*HC1* with three temperature measurements inside the reactor and d_E=2; b/*HC1* with one temperature measurement inside the reactor and d_E=3; c/ *Exp1* with three temperature measurements inside the reactor and d_E=2; and d/*Exp1* with one temperature measurement inside the reactor. $\Delta V_{ps}^{\lim}$ (discontinuous line). State variables: $\{T\text{-}T_w, dT/dt\}$ with d_E=2 and $\{T, dT/dt, d(T\text{-}T_w)/dt\}$ with d_E=3.

First we have compared the results obtained considering only one temperature sensor and several temperature measurements inside the reactor for the experiments *HC1* and *Exp1*, for which several data was available. As can be seen in Fig. 11, even though theoretically more temperature trajectories produce better results, experimentally the presence of noise and fluctuations in

temperature measurements decrease the improvement in sensitivity and reliability, and, in practice, there is no appreciable difference between the use of one or several temperature measurements. Concerning the runaway experiment, with three temperature sensors the runaway initiation is detected earlier at 740 s whereas with only one temperature sensor the detection occurs at 764 s or 768 s depending on which embedding dimension we are using (maximum temperature time 974 s). However, even though the runaway detection occurs earlier, the difference between the maximum reconstructed $\Delta V_{ps}(t)$ is higher in the second case and, hence, there is more margin between non-runaway and runaway, which will probably reduce the false alarms.

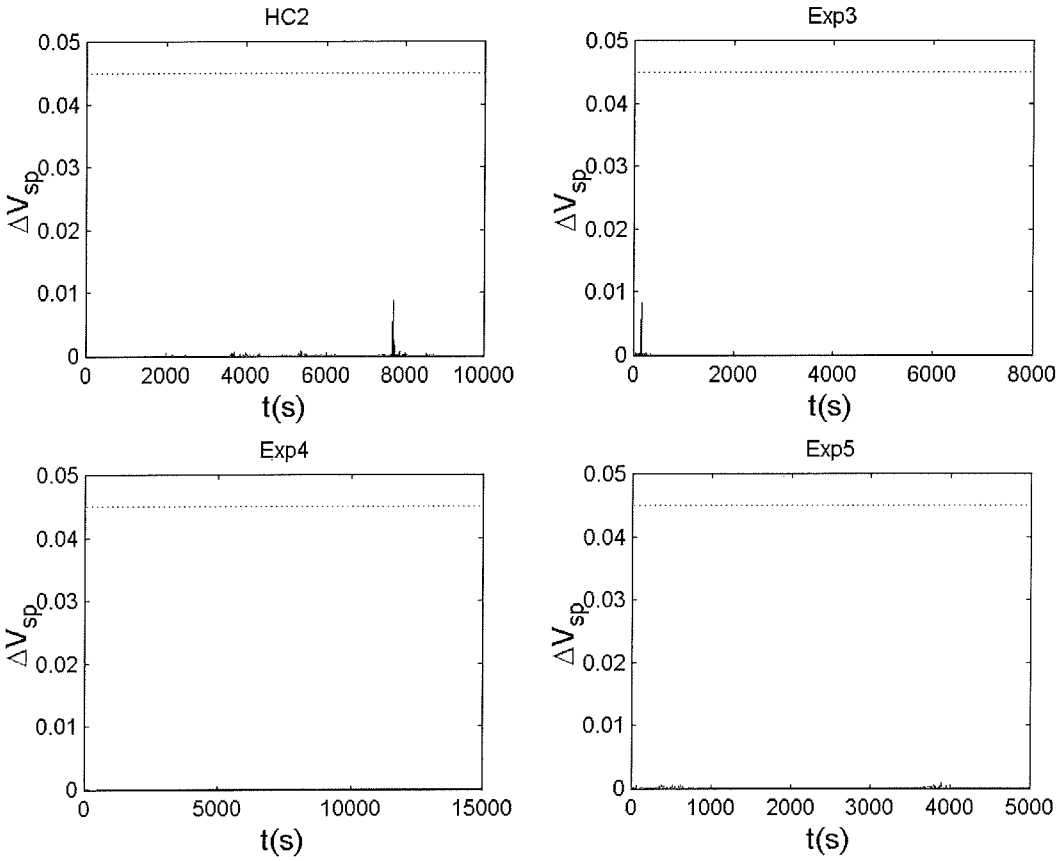

Figure 12. Reconstructed $\Delta V_{ps}(\tau)$ for the non-runaway experiments *HC2*, *Exp3*, *Exp4* and *Exp5* using one temperature measurement inside the reactor and d_E=2. State variables:$\{T\text{-}T_w,\ dT/dt\}$. $\Delta V_{ps}^{\lim}$ =4.5·10-2 (discontinuous line).

As with simulated data, different combinations of state variables -$T(t)$, $T_w(t)$, $T(t)\text{-}T_w(t)$, $dT(t)/dt$, $dT_w(t)/dt$, $d[T(t)\text{-}T_w(t)]/dt$ - and two and three of embedding dimensions have been tested. For example the following combinations did not produce adequate results: $\{T,T_w\}$,$\{T,T\text{-}T_w\}$, $\{T\text{-}T_w,d(T\text{-}T_w)/dt\}$, $\{T,T_w,dT/dt\}$. However, similar results were obtained with other variables using two and three embedding dimensions. The fact that a low embedding dimension is able to work properly is

related to the nature of our dynamical system. In principle, the dimension in which we can unfold the dynamics of our system will be dictated by the number of state variables of the system. Due to the dissipative nature of batch and semibatch chemical reactors and the fact that the final attractor is a fixed point (dimension zero), the real dimension of our system is rapidly decreasing with time as we approach to infinity. This dimension reduction implies that, in practice, we need few dimensions to unfold the dynamics, even though initially our system had a higher dimension.

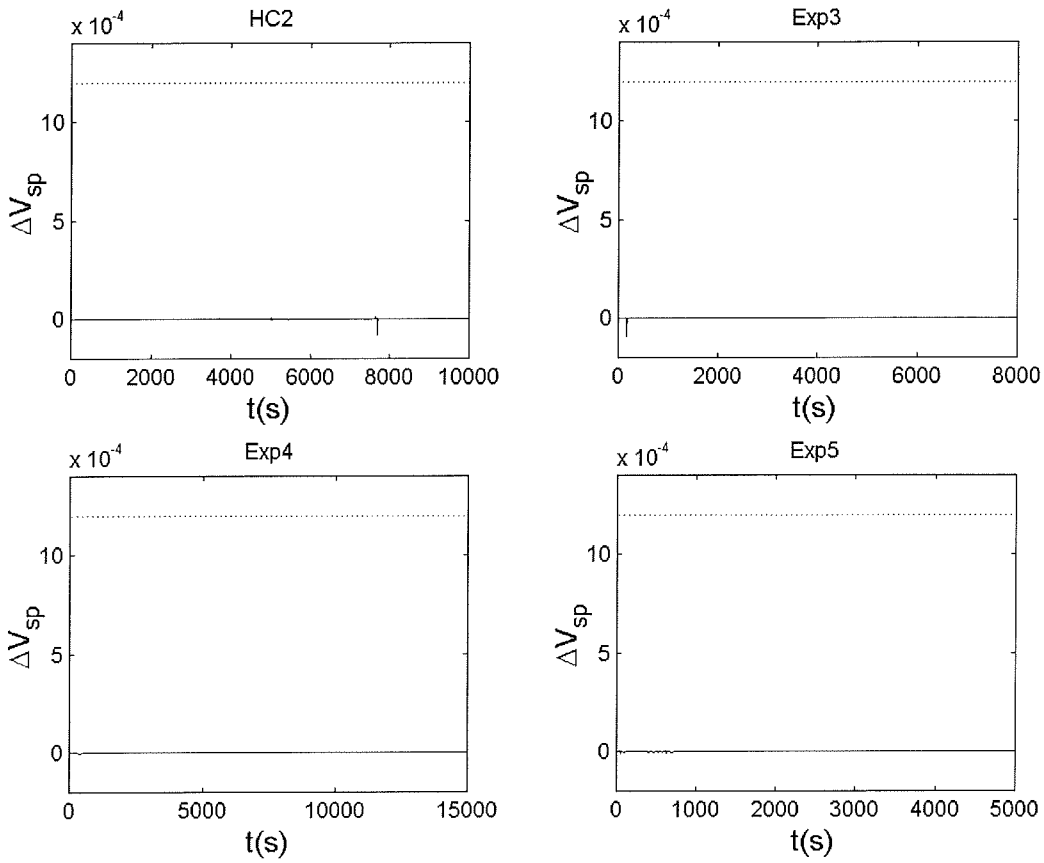

Figure 13. Reconstructed $\Delta V_{ps}(\tau)$ for the non-runaway experiments *HC2*, *Exp3*, *Exp4* and *Exp5* using one temperature measurement inside the reactor, one temperature measurement in the jacket and d_E=3. State variables: $\{T, dT/dt, d(T-T_w)/dt\}$. $\Delta V_{ps}^{\lim}$ =1.2·10-3 (discontinuous line).

Figures 12 and 13 show the reconstructed state space volume variation reconstructed in two and three embedding dimensions. The experiments in these figures are non-runaway experiments and, hence, no alarms should be triggered off. In this case, instead to $\Delta V_{sp}>0$, we have established an upper limit, i.e. $\Delta V_{sp}>\Delta V_{ps}^{\lim}$, which depends on the embedding dimension and the number of state variables we are using. We have taken as limit 1.5 times the upper limit of ΔV_{sp} found for all the heating/cooling experiments. As can be seen there are no false alarms during these experiments.

Concerning runaway experiments, Figures 14 and 15 show the results obtained with two and three embedding dimensions. Using an embedding dimension of two the runaway detection occurred for *Exp2* at 520 s (maximum temperature time 544 s) and for Exp6 at 3440 (maximum temperature time 3510 s), similar results were found for the case of embedding dimension of three (Fig. 15). The low time in advance for *Exp2* when compared with a similar experiment, i.e. *Exp1*, is mainly due to the high sampling time that in the former case in 10 s when compared with 2 s for the latter experiment. This sampling time for a 2 L bench scale reactor were the runaway occurs in 9.5 minutes is not adequate. The same sampling time gives adequate results for the 100 L experiments since in this case the time constant of the reactor is higher.

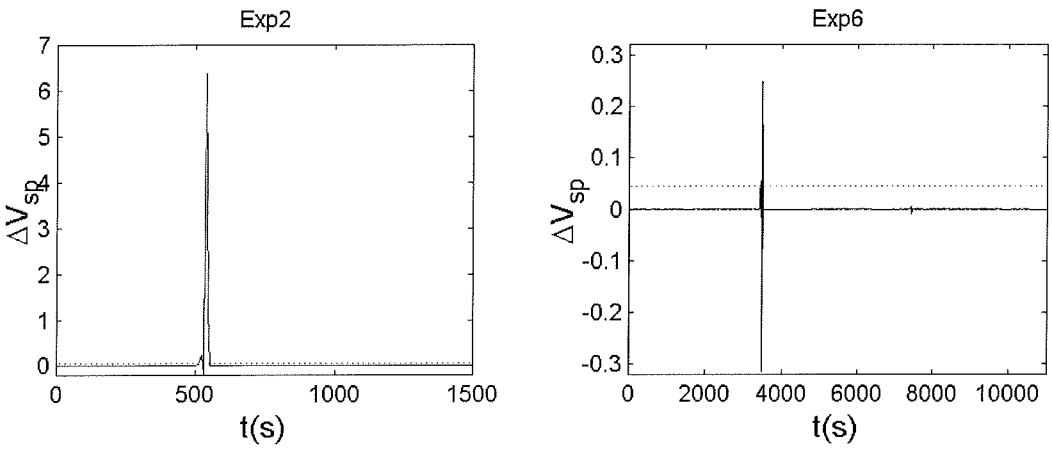

Figure 14. Reconstructed $\Delta V_{ps}(\tau)$ for the runaway experiments *Exp2* and *Exp6* using one temperature measurement inside the reactor and d_E=2. State variables:$\{T\text{-}T_w, dT/dt\}$.

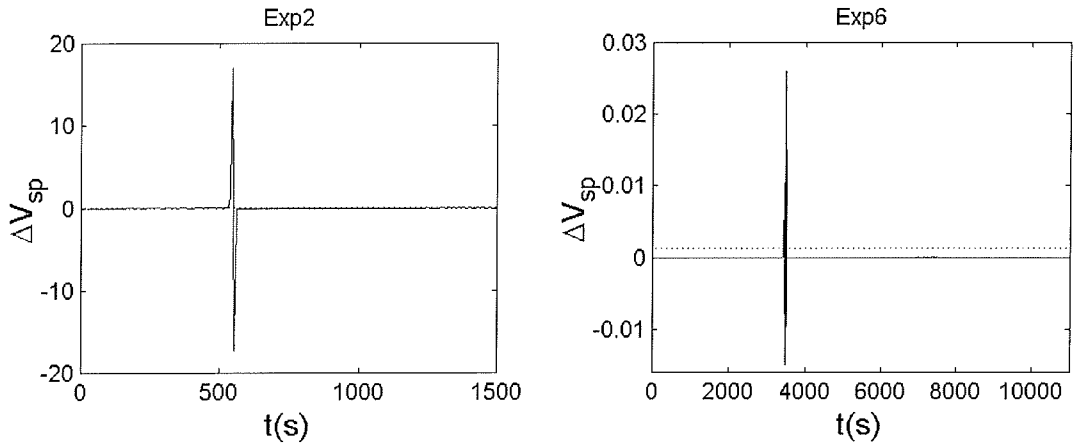

Figure 15. Reconstructed $\Delta V_{ps}(\tau)$ for the runaway experiments *Exp2* and *Exp6* using one temperature measurement inside the reactor and d_E=3. State variables:$\{T, dT/dt, d(T\text{-}T_w)/dt\}$.

6. CONCLUSIONS

This study shows that it is possible to carry out on-line state space reconstruction, to evaluate the divergence of the reactor and to use this value to decide if we are approaching a dangerous situation. From the theoretical point of view, it is important to notice that we are using a criterion that has shown its validity off-line for a considerable number of chemical kinetics schemes, types of reactors and types of operating conditions (Zaldívar *et al.*, 2002). From the practical point of view, the fact that its calculation is based on only two temperature measurements (reactor and jacket) increases its possibilities of real industrial application.

When comparing isothermal versus isoperibolic reactors (Bosch *et al.*, 2002), not only the temperature inside of the reactor is necessary but also the jacket temperature. Otherwise, we are not able to capture the dynamics in the system, our state space reconstruction will be not correct and, hence, the criterion will produce wrong results.

Even though using simulated data the reconstruction is more accurate when increasing the number of temperature trajectories we are using, experimentally, due to noise and fluctuations in the temperature measurements, it seems that similar results in terms of sensitivity and reliability are obtained.

In order to develop a robust early warning detection system it is now necessary to show its feasibility in "realistic" situations, i.e. in industrial plants under normal and abnormal operating conditions. Our experimental research is continuing along these lines.

NOTATION

B	Dimensionless heat of reaction parameter, $B = \dfrac{(-\Delta H)C^i\gamma}{\rho \cdot Cp \cdot T^i}$
Cp	Mean specific heat of reaction mixture kJ/(K·kg)
C	Concentration of reactant, kmol/m^3
Da	Damköhler number, $Da = k(T^i)(C^i)^{(n-1)}t_{ref}$
E	activation energy, kJ/mol
k	reaction rate constant, (kmol/m^3)$^{(1-n)}$/s
Kp	proportional controller constant
n	reaction order
r	reaction rate, kmol/(m^3·s)
R	universal gas constant
R_1	dimensionless reaction rate
St	Stanton number, $St = \dfrac{U \cdot S \cdot t_{ref}}{\rho \cdot V \cdot Cp}$
S	heat exchange surface area, m^{-2}
t	time, s
t_{ref}	Reference time = residence time, $t_{ref} = \dfrac{V}{q_d}$
T	temperature, K
T_w	Jacket temperature, K
u_A	dimensionless concentration of A, C_A/C_A^i
U	heat transfer coefficient, kJ/(m^2·K·s)
V	volume
z	conversion, $z = 1-u$

Greek symbols

δ	cooling dimensionless time. $\delta = (V \cdot \rho \cdot Cp)_w/(V \cdot \rho \cdot Cp)$
ΔH	heat of the reaction, kJ/kmol
γ	dimensionless activation energy, $\dfrac{E}{RT^i}$
θ	dimensionless temperature in the reactor, $\theta = \left(\dfrac{T}{T^i} - 1\right)\gamma$
τ	dimensionless time, t/t_{ref}

Superscripts

i	initial condition
sp	set-point

Subscripts

d	dosing
ps	state-space
w	jacket

REFERENCES

Arnold, V. I., 1973, Ordinary differential equations, MIT Press, Cambridge.

Bosch, J., Strozzi, F., Zbilut, J.P. and Zaldívar, J.M., 2002, Application of the divergence criterion to isothermal batch reactors: Simulated and experimental results. *Chem. Eng. Sci.* (Submitted)

Breeden, J. L. and Packard, N. H., 1994, A learning algorithm for optimal representation of experimental data. *Int. J. Bifurcations and Chaos* **4**, 311-

Casdagli, M., Eubank, S., Farmer, J. D., Gibson, J., 1991, State space reconstruction in the presence of noise. *Physica D* **51**, 52-

Davies, M., 1994, Noise reduction schemes for chaotic time series. *Physica D* **79**, 174-192

Galván, I. M. , Zaldívar, J. M., Hernández, H. and Molga, E., 1996, The use of neural networks for fitting complex kinetic data, *Computers Chem. Engng* **20**, 1451-1465.

Gilles, E. D. and Schuler, H., 1982, Early detection of hazardous states in chemical reactors. *Ger. Chem. Eng.* **5**, 69-78.

Goodwin, G. C. and Sin, K. S., *Adaptive filtering prediction and control.* Prentice-Hall, Englewood Cliffs, 1984.

Grassberger, P., Hegger, R., Kantz, H., Schaffrath, C and Schreiber, T., 1993, On noise reduction methods for chaotic data, *CHAOS* **3**, 127-141.

Health and Safety Executive, 1993, The costs of accidents at work, HMSO, London.

Hegger, R., Kantz, H. and Schreiber, 1999, Practical implementation of nonlinear time series methods: the TISEAN package, *CHAOS* **9**, 413-.

Hegger, R., Kantz, H. and Schreiber, T., 2002, Nonlinear noise reduction, *in Modelling and Forecasting financial data: Techniques of nonlinear dynamics*, Soofi, A. S. and Cao, L. (eds.), Kluwer, Boston, pp 401-416.

Hub, L. and Jones, J. D., 1986, Early On-line Detection of Exothermic Reactions, *Plant/Operation Progress,* **5**, 221.

Kantz, H. and Schreiber, T., *Nonlinear Time Series Analysis*, Cambridge, Cambridge University Press, 1997.

King, R. and Gilles, E.D., 1990, Multiple filter methods for detection of hazardous states in an industrial plant. *A.I.Ch.E. J.* **36**, 1697.

Kostelich, E. J. and Schreiber, T., 1993, Noise reduction in chaotic time-series data: A survey of common methods. *Phys. Rev. E* **48**, 1752-1763.

Marco, E., Peña, J. A., and Santamaría, J., 1997, Early detection of runaway reactions in systems with gas evolution using on-line spectrometry. *Chem. Engng. Sci.* **52**, 3107-3115.

Nomén, R., Sempere, J., Cano, J., 2002, Implementation of OLIWA criterion and comparative analysis against the divergence criterion. IQS Report, 19pp.

Oppenheim A. V. and Schafer, R. W., *Digital signal processing*, Prentice-Hall, London.1975.

Packard, N., Crutchfield, J., Farmer, D. and Shaw, R., 1980, Geometry from a time series. *Phys. Rev. Lett.* **45**, 712-715.

Petersen , D.C., Heinrich, H. W., and Roos, N. R., 1980, Industrial accident prevention: a safety management approach.

Press, W. H., Flannery, B. P., Teukolsky, S. A., Vetterling, W. T., *Numerical recipes*, Cambridge University Press, Cambridge, 1986.

Schreiber, T. and Richter M., 1999, Fast nonlinear projective filtering in a data stream, *Int. J. Bifur. Chaos* **9**, 2039-2045.

Snee, T. J., Barcons, C., Hernández, H. and Zaldívar J.M., 1992, Characterisation of an exothermic reaction using adiabatic and isothermal calorimetry, *J. of Thermal Analysis* **38**, 2729-2747.

Strozzi, F., 1997, Runaway prevention in chemical reactors using chaos theory techniques. PhD Thesis, Twente University, Twente, The Netherlands.

Strozzi, F., Zaldívar, J. M., Kronberg, A. and Westerterp, K. R., 1999, On-line runaway prevention in chemical reactors using chaos theory techniques. *AIChE J.* **45**, 2429-2443.

Takens, F., 1981, in *Dynamical Systems and Turbulence*, Warwick 1980, vol 898 of Lecture Notes in Mathematics, edited by A. Rand and L.S. Young, Springer, Berlin, pp 366-381.

Tufano, V., 1988, Modeling runaway reactions in reactors protected with suppression systems. J. of Hazardous Materials 19, 225-

Varma, A., Morbidelli, M. and Wu, H., *Parametric Sensitivity in Chemical Systems*, Cambridge, Cambridge University Press, 1999.

Zaldívar J.M., Hernández H., Nieman H., Molga E. and Bassani C., 1993, The FIRES project: experimental study of thermal runaway due to agitation problems during toluene nitration, *J. Loss Prev. Process Ind.* **6**, 319-326.

Zaldívar, J. M., Cano, J., Alós, M. A., Sempere, J., Nomen, R., Lister, D., Maschio, G., Obertopp, T., Gilles, E. D., Bosch, J., and Strozzi, F., 2002, A general criterion to define runaway limits in chemical reactors. *Chemical Engineering Science* (submitted).

The mission of the JRC is to provide customer-driven scientific and technical support for the conception, development, implementation and monitoring of EU policies. As a service of the European Commission, the JRC functions as a reference centre of science and technology for the Union. Close to the policy-making process, it serves the common interest of the Member States, while being independent of special interests, whether private or national.

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE