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AWARE: Investigation of the early warning detection system through pilot and large-scale tests

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AWARE: Investigation of the early warning detection system through pilot and large-scale tests

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The chemical industry is increasingly expanding into the pharmaceuticals and speciality chemicals sectors. As a result, there is an increasing dependence in the sector on the existence of smaller, more flexible enterprises (SMEs) capable of providing specialised skills and products in niche markets. It is estimated that around 20% of these businesses carry out exothermic reactions or other chemical processing operations that require detailed investigations of the associated reactive hazards and the design and installation of safety venting systems. In the past, many criteria have been developed to determine whether a runaway - an excessive increase of the reaction temperatures, which cannot be kept within acceptable limits by the cooling system of the reactor - will occur. All these criteria have the disadvantage that the reactor dynamics cannot be taken into account. This project addressed the needs to detect runaway initiation in advance allowing countermeasures to be taken and to design emergency relief systems for chemical reaction hazards whilst still protecting the environment. The project produced an early warning detection system (EWDS) detection device as well as guidelines for use by SMEs.

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EXECUTIVE SUMMARY

Background

The chemical industry is increasingly expanding into the pharmaceuticals and speciality chemicals sectors. As a result, there is an increasing dependence in the sector on the existence of smaller, more flexible enterprises (SMEs) capable of providing specialised skills and products in niche markets. It is estimated that around 20% of these businesses carry out exothermic reactions or other chemical processing operations that require detailed investigations of the associated reactive hazards and the design and installation of safety venting systems. In the past, many criteria have been developed to determine whether a runaway – an excessive increase of the reaction temperatures, which cannot be kept within acceptable limits by the cooling system of the reactor – will occur. All these criteria have the disadvantage that the reactor dynamics cannot be taken into account. This project addressed the needs to detect runaway initiation in advance allowing countermeasures to be taken and to design emergency relief systems for chemical reaction hazards whilst still protecting the environment. The project produced an early warning detection system (EWDS) detection device as well as guidelines for use by SMEs.

Objectives

The primary objective of AWARE was:

“To develop, validate and verify, amongst end users in the chemical industries, a device for early detection of runaway events, by testing its validity in industrial conditions which are characterised by noise signals, frequent plant operators manipulations, and frequent change of process due to market demand.” HSL provided valuable information from pilot and large scale tests that enabled significant progress to be made.

Main Findings and Recommendations

The early warning system was improved as a result of the pilot scale tests at HSL. It identified practical problems such as noise and fluctuating jacket temperature that could be found in practice and trigger false alarms. Solutions were found that eliminated these false alarms by simplifying the data input and reducing the sensitivity to derivatives.

An algorithm was written at HSL to incorporate the early warning criteria into the large-scale facility data logging system and this was used successfully to demonstrate an early warning in a large scale runaway reaction.

1 INTRODUCTION

1.1 BACKGROUND

The maintenance of safe operation conditions for chemical reactors is of paramount importance to avoid personnel and installation damages and environmental pollution. Despite tremendous investments to improve the safety of chemical plants, the number of accidents and their consequences are still alarming. In the past many criteria have been developed to determine whether a runaway – an excessive increase of the reaction temperatures, which cannot be kept within acceptable limits by the cooling system of the reactor – will occur. All these criteria have the disadvantage that the reactor dynamics cannot be taken into account. So that, when the reactor temperature is increasing, no predictions can be made whether the reaction temperature goes to a new, higher and well balanced value, or whether the temperature will keep increasing and eventually lead to a runaway. Early warning devices are therefore indispensable irrespective of the detailed mechanisms of the reaction and irrespective of other safety measures installed in the plant. Whatever may be the reasons for the initiation of a runaway, if deviations from normal operation conditions are detected, it is still possible to avoid an incident.

These problems have been investigated recently by several partners of this project. Concerning early warning detection, non-linear dynamics systems theory (chaos theory) has been applied. This approach is the first one that takes into account the reactor dynamics. Some preliminary tests with very promising results have been published and a patent has been granted. This project intends to develop, validate and verify, amongst end users in the chemical industries, a device for early detection of runaway events, by testing its validity in industrial conditions that are characterized by noise signals, frequent plant operators manipulations, and frequent change of process due to market demand.

1.2 AWARD WORK PROGRAMME

The project, ***a***dvanced ***w***arning ***a***nd ***r***unaway ***d***isposal (AWARD), was selected to contribute to the Competitive and Sustainable Growth Programme. The project involves fourteen partners and an Associate Contractor from eight countries plus the European Commission Joint Research Centre. The partnership comprises the University of Manchester Institute of Science and Technology, UK (UMIST); the Health and Safety Laboratory of the Health and Safety Executive, UK (HSL); the European Commission (EC) Joint Research Centre, Italy (JRC) – Institute for Environment and Sustainability (IES) and Institute for the Protection and Security of the Citizen (IPSC); the Institut Químic de Sarrià (IQS), Spain; the Università Carlo Cattaneo (LIUC), Italy; the Università degli Studi di Messina (UM), Italy; Sanofi Chimie, France (Sanofi); Arran Chemical Company, Ireland (Arran); Rohm & Haas Italia (R&H), Italy; Esteve Química S.A. (EQ), Spain; Segibo Srl, Italy (SEGIBO); Investigacao e Desenvolvimento em Enegnharia e Ambiente Lda, Portugal (IrRADIARE); and Warsaw University of Technology Poland (WTU). Inburex have joined the consortium as an Associate Contractor to take over some of the responsibilities that were originally with JRC-IPSC.

The work plan comprised twelve work packages (WP's):

WP1: Project management: administration, financial and technical
WP2: Extension and theoretical development of the EWDS
WP3: Experimental validation of the EWDS in small scale reactors
WP4: Small-scale and pilot plant venting experiments
WP5: Industrial plant experiments for the EWDS
WP6: Large-scale venting experiments
WP7: Fundamental phenomena, Non-equilibrium effects
WP8: Level swell
WP9: Criteria for foaminess
WP10: EWDS prototype design and development
WP11: Sizing methods and guidelines on disposal system design
WP12. Project exploitation and dissemination

AWARD comprises two subprojects: AWARE relating to the early warning detection system and DISPOSE relating to hydrodynamic behaviour of venting and disposal systems.

An overview for the whole project is given in the final AWARD project report (Spagni et al 2005). Some of the work packages above relate to the DISPOSE part of the project. HSL's contribution to these in given elsewhere (Snee et al 2005 HSL report). The scope of this report is limited to HSL's contributions to AWARE.

1.3 OBJECTIVES OF AWARE

The objectives of the AWARE project were:

1. Theoretical development and improvements to the early warning detection system (EWDS), aiming at reducing the number of temperature measurements required inside the reactor and extending the range of applicability of the detection criteria.
2. Application of CFD techniques for supporting the development of the early detection system by predicting temperature profiles and indicating a number and location of temperature sensors inside the reactor.
3. Experimental validation of the EWDS in small-scale reactors with reactions of industrial interest.
4. Experimental validation of the EWDS in industrial sites under normal and abnormal operating conditions to assess its robustness and final verification using an industrial process by experimentally simulating plant malfunctions, i.e. loss of coolant, stirrer failure etc. leading to a runaway incident.
5. Design of the EWDS and improvements of the prototype after each experimental validation stage.
6. Dissemination of and exploitation of the research results so that they are available for use by European industry, including SMEs.

The primary contribution of HSL with regard to the AWARE early warning system, focused on:

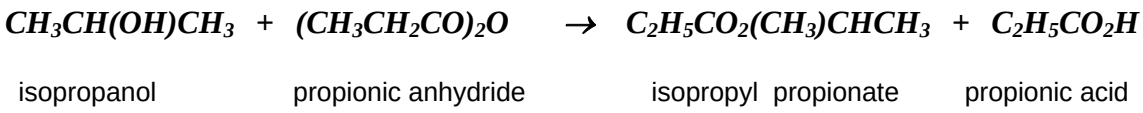
- providing pilot scale data for off site EWDS development early in the project
- on line pilot scale runaway and near runaway tests of the EWDS for troubleshooting, validation and input for further development
- on line large scale runaway reaction tests of the EWDS algorithm.

2 REACTION SYSTEMS

Two reaction systems were employed in the pilot and large scale runway reaction experiments that were used to evaluate and develop the EWDS. Both these systems had previously been studied at HSL on pilot scale and therefore were relatively well characterised. The safety of these reactions had been evaluated previously using adiabatic calorimetry, laboratory tests and heat transfer/kinetic modelling in addition to examination of literature data. Prior to the experiments HAZOPs and specific risk assessments were conducted to ensure the safety of personnel during the tests.

2.1 ESTERIFICATION OF PROPIONIC ANHYDRIDE

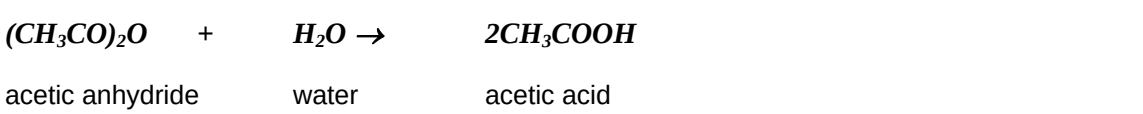
The uncatalysed esterification reaction between propionic anhydride and isopropanol was chosen as a vapour pressure system whose parameters could be selected to give the required control over the likelihood of a runaway reaction. This was used in the pilot scale (340 litre gross capacity) tests. The experimental system has been described fully in a previous HSL report (Snee et al 2000).



Previously obtained calorimetric data (Snee et al 2000) were used to determine the conditions for the pilot-scale runaway reaction experiments. The experimental parameters were chosen such that the test series covered the transition from non-runaway to runaway. This was achieved by altering the jacket temperature for the tests.

2.2 HYDROLYSIS OF ACETIC ANHYDRIDE

Acetic anhydride reacts with water to produce acetic acid:



Adiabatic and isothermal calorimetry had been previously performed (Snee et al 2000) to determine the temperature and concentration dependence of the rate of heat generation both with and without surfactant. The reaction is moderately exothermic and the kinetics are such that a runaway reaction can be initiated in the large-scale reactor at temperatures well within the operating range of the heat transfer system. The reaction was responsible for a severe explosion that occurred at an acetic anhydride plant in Australia (Leigh, 1992).

For three of the six large scale tests, small quantities of surfactant were added to the reagents in order to produce foaming behaviour during runaway reaction and venting. Such foamy behaviour was a crucial factor in studying the DISPOSE part of the project. These runaway reaction tests were also required to test the EWDS on planned large scale runway reactions.

The fill level in the reactor was varied in the test series to alter the maximum pressure, venting and level swell characteristics. This is discussed in detail elsewhere (Snee et al 2005).

3 EARLY WARNING DETECTION SYSTEM

The Early Warning Detection System (EWDS) utilises mathematical models to predict the onset of a runaway reaction. The theoretical basis is described extensively elsewhere (Strozzi et al 1999). An overview is given in Appendix 1.

3.1 ANALYSIS OF PREVIOUS HSL TEST DATA

In the early stages of the AWARE project, HSL provided other partners with detailed temperature and pressure data from numerous pilot scale runaway reaction tests that had been carried out previously. In particular HSL pilot plant data was used to compare methodologies that use temperature and pressure signals for activating the EWDS. This data was used to provide experimental information to develop the EWDS criteria and to evaluate which measurements could be used to provide early warning of a runaway reaction.

3.2 MODIFICATIONS TO EWDS

For the experimental work done at HSL as part of the AWARE project, two forms of EWDS were employed. For the pilot scale esterification experiments carried out in 2003, a prototype commercial system was connected to the temperature and pressure pilot plant data logging system. The prototype system comprised EWDS detection hardware and a separate computer system. Modifications were made by the development team during commissioning tests at HSL to improve reliability in a quasi-industrial environment.

An algorithm implementing the final version of the EWDS criteria was written at HSL. It was integrated into the data logging and video mimic software for the large-scale hydrolysis tests performed in 2005.

4 RESULTS

4.1 PILOT SCALE ESTERIFICATION TESTS

The results from these tests are presented more detail in Appendix 1. The full analysis of the performance of divergence criteria for the pilot scale tests is discussed in the related JRC report (Bosch et al 2004a).

The key findings of the evaluation of the EWDS in the pilot scale esterification reaction were:

- Sensitivity to noise from current switching devices such as inverter drives on agitator motors
- Sensitivity to change in jacket temperature during operational control of the reactor temperature caused false alarms to be activated.
- With modifications, runaway could be successfully detected without spurious false alarms.

The valuable lessons from operating in the quasi-industrial environment of the pilot plant facility led to modification of the EWDS criteria to produce a more robust detection system that was much less liable to false alarms.

4.2 LARGE SCALE HYDROLYSIS TESTS

To further evaluate the effectiveness, an algorithm was written at HSL to incorporate the modified EWDS criteria into the data logging and video monitoring systems of the new large scale high pressure runaway reaction test reactor. This 2 200 litre (gross volume) reactor is constructed of stainless steel and has an external heating loop. The experimental system is described in more detail in the HSL report for the DISPOSE part of the AWARD project (Snee et al 2005).

4.3 ALGORITHM FLOW SHEET

The flow sheet for the EWDS algorithm implemented in the large-scale hydrolysis tests is shown overleaf in Figure 1.

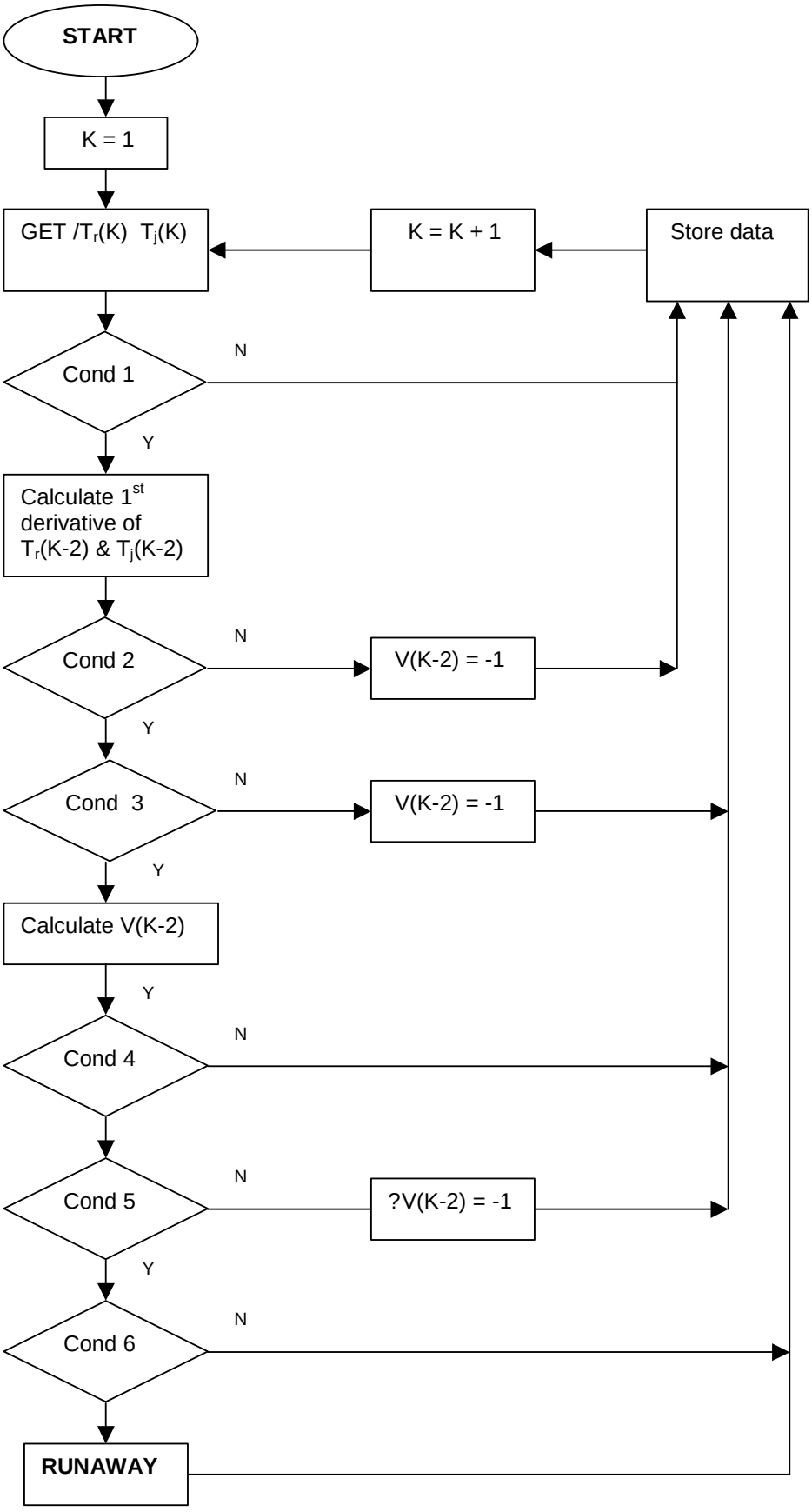


Figure 1 EWDS algorithm flow sheet

Table 1 Key to conditions and symbols in EWDS decision flow chart

	Definition
Cond 1	K>4
Cond 2	K>6 + 2 x delayA
Cond 3	$\frac{dT_R}{dt} > \lim 1$ and $\left(\frac{dT_r}{dt} - \frac{dT_j}{dt}\right) > \lim 2$ from {K-2 –(2 x delay A)} to {K-2}
Cond 4	*K*>6 + delayB + 2 x delayA
Cond 5	*V*(*K*-2-delayB) >0
Cond 6	$\Delta V(K-2) > \lim 3$
T_r	Jacket temperature
T_j	Reactor temperature
K	Counter (multiple of time step)
V	State space volume
DelayA	50
DelayB	50
lim1	-0.01
lim2	-0.01
lim3	8.4E-3

The decision flow chart, with appropriate conditions, was implemented into a remote data logging program that was used to produce a mimic to be superimposed onto live video images of the reactor contents. The software was written in Agilent Vee and linked to the data logging program.

The algorithm was successfully used on line to provide an early warning of runaway reaction in a large scale hydrolysis runaway reaction test (test number HP6).

4.4 DETECTION TIMES

The detection by the EWDS of a runaway is shown in Figure 2. It can be seen that operators or automatic systems would have just over 4 minutes from detection to vent opening to take whatever counter measures may be available.

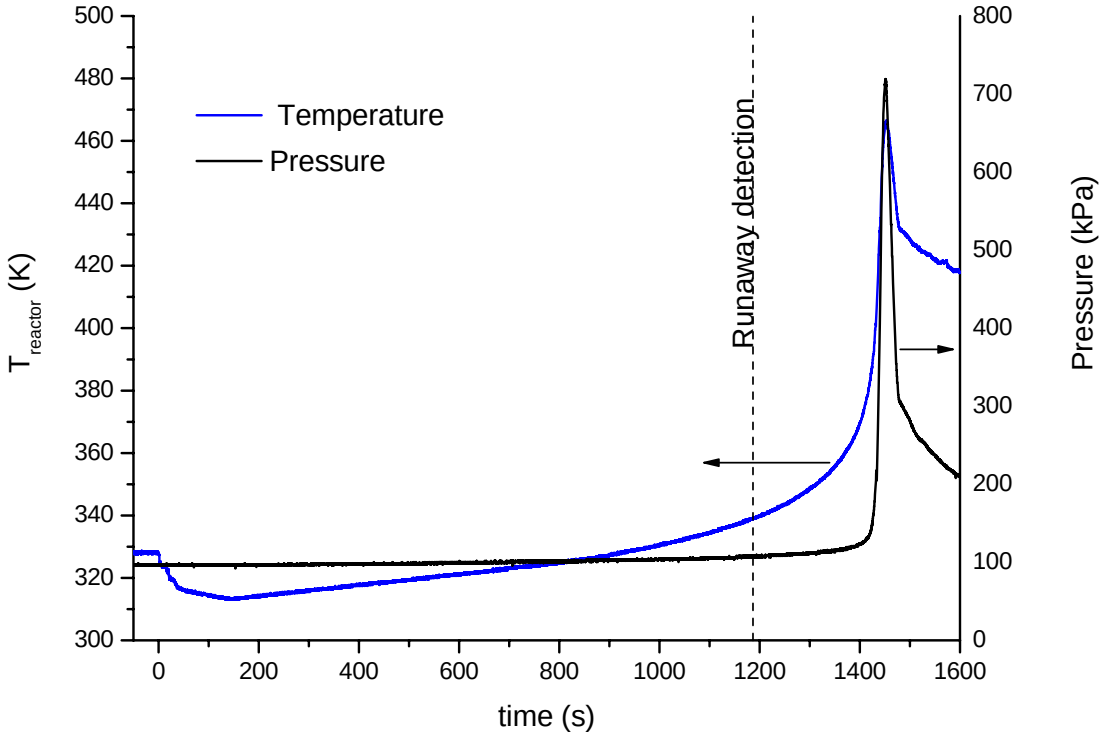


Figure 2 Detection of runaway during test HP6

Following this successful 'live' on-line test during a runaway reaction, the same criteria were applied to historical data from the other large-scale runaway reaction tests. The times for predicting runaway are shown in Table 2. Also shown for comparison are the times to vent opening, to T_{max} (maximum temperature during the runaway) and the time between the warning and vent opening.

Table 2 EWDS performance during large scale runaway reaction tests

HSL Expt No.	*Fill level (%)*	*Surfactant (%)*	*Times after end of reagent addition (s)*			*Time from detection until vent opening (s)*
			Detection time	*Vent opening*	T_{max}	
HP01	50	0	994.8	1582.2	1633.4	587.4
HP02	70	0	1036.4	1592.9	1617.3	556.5
HP03	60	0	987.9	1618.1	1640.9	630.2
HP04	50	2.5	1148.3	1496.8	1517.7	348.5
HP05	70	2.5	1022.6	1618.5	1640.6	595.9
HP06	60	2.5	1187.8	1433	1453	245.2

It can be seen that the warning times vary from 10½ minutes for HP03 to just over 4 minutes for HP06. In all case there were no false alarms during the addition, heating or cool down steps. The particular EWDS parameters used were: de1=de2=300s, sampling rate 2s, lim1=lim2=-0.1K/s, and lim3=1. No filter was applied to data.

5 CONCLUSIONS

The runaway esterification experiments showed that by including reactor jacket temperature dynamics, spurious signals in the state space reconstruction may be introduced by manipulation of valve positions and plant changes. An improved EWDS algorithm was subsequently produced that did not include jacket temperature in calculating state space volume. The inclusion of jacket dynamics had made sense during development of the prototype design when working with stand-alone reactors (such as the Mettler RC1) that were initially used in development. However, this was not suitable to a more industrial environment where other loads and fluctuations in utility systems could be present.

These pilot plant tests also identified problems of the prototype in dealing with noise that were traced to use of the derivative in state space reconstruction. Altering the algorithm so that derivative dependence was removed solved these problems.

Implementation of the EWDS algorithm into the remote data logging system for the large scale hydrolysis tests illustrated the effectiveness of predicting runaway at a batch industrial scale.

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7 APPENDIX 1: *INDUSTRIAL ENGINEERING CHEMISTRY RESEARCH* ARTICLE

The following article was written by members of the AWARD consortium, including HSL authors, and was published by Bosch et al (2004c) in the *Industrial Engineering Chemistry Research* in 2004. The analysis work was done by at the JRC, Ispra and at Castallanza. For ease of reference, the article is reproduced here in full.

RUNAWAY DETECTION IN A PILOT PLANT FACILITY

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Abstract

In order to assess the performances of an Early Waning Detection System (EWDS) recently developed a series of experiments were carried out in the pilot plant at Health and Safety Laboratory (Buxton, UK) for the esterification reaction between isopropanol and propionic anhydride. The main objective was to assess the performances of the EWDS algorithm and to study the changes necessary to improve it. The original algorithm that used {*Tr-Tj, dTr/dt*} as state space variables for the divergence reconstruction gave a false alarm during the experiments due to a sharp increase in the jacket temperature caused by a manipulation that decreased the jacket flow. After this false alarm, the algorithm was modified. First, it was decided to remove the jacket temperature from the reconstruction algorithm and use {*Tr(t), Tr(t-Δt)*} to improve the signal to noise ratio by eliminating the first derivative of the reactor temperature that has a considerable amount of noise. This has produced a noticeable improvement in the results obtained in the test phase in terms of time in advance of detection, independence of limits on temperature noise and decoupling the jacket characteristics from the runway detection and, hence, eliminating the analysis of heating/cooling circuits before the installation of the prototype. With these changes is now possible to calculate experimentally the divergence and compare with analytical values from simulation.

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 by the cooling system, there is a positive feedback mechanism, since the temperature of the reaction mass will rise, increasing in turn the heat generation rate. In this situation, 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. Apart from health and environmental considerations, an accident in a chemical reactor is extremely expensive (HSE, 1993). Furthermore, chemical industries experience 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 that these values are correlated (Petersen *et al*., 1980).

Methods for early warning detection can be divided into three main categories depending upon the quantities being used: Conventional limit check systems (Tufano, 1988; Marco *et al*., 1997), temperature derivatives (Hub and Jones, 1986), and model-based estimation techniques i.e. Kalman filtering or equivalent (Gilles and Schuller, 1982; King and Gilles, 1990). However, 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 in 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 consist in 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 it not economically feasible to develop 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*., 2003a) a criterion to delimit runaway boundaries was presented applying techniques from non-linear systems theory to characterise the sensitivity of chemical reactors. 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 -. Furthermore, this criterion was applied on-line to isoperibolic (jacket temperature constant), Bosch *et al*. 2004, and isothermal (Zaldívar *et al*., 2003b) batch and semibatch reactors. The results show that the method is able to distinguish between runaway and non-runaway situations and it does not produce false alarms for the cases studied, including quasi instantaneous semibatch reactions and controlled heating/cooling experiments, which normally are responsible for false alarms in the existing early detection devices.

In this work we have carried out an analysis on the EWDS results from a set of experiments carried out in the pilot plant of the HSL in Buxton (UK). The main objective was to assess the performances of the EWDS algorithm in a runaway situation in a pilot scale after satisfactory results in laboratory scale for both non-runaway and runaway scenarios (Bosch *et*

al., 2004 and Zaldívar *et al*., 2004), and industrial scale for non runaway scenario (Bosch et al., 2003 a,b). The selected reaction has been the esterification between isopropanol and propionic anhydride proposed by the HSL. This has been done since it is a well known reaction by HSL that has been extensively studied in the past (Snee and Hare, 1992) and for which an accurate kinetics exists. This fact has allowed us to calculate the analytical divergence, and therefore to compare it with the EWDS results.

In addition, we have also applied the EWDS algorithm offline to a set of experiments carried out in the same facility in the past, and finally, we have used pressure instead of temperature data to reconstruct the state space.

2. EXPERIMENTAL

2.1. Pilot plant installation

The pilot scale facility for investigating runaway reactions is based around a 250 litre (gross capacity - 340 litre), jacketed, glass lined reactor equipped with two glass feed vessels and connected, via a vent line, to a 2,500 litre stainless steel catch tank. Figure 1 is a schematic diagram of the pilot plant and catch tank, respectively. The reactor and the catch tank have a maximum working pressure of 6 barg. The vent line between the reactor and catch tank is fitted with either a restricting orifice plate or a short nozzle and an actuated valve. The valve is linked to a pressure controller and is opened automatically when the pressure reaches a pre-selected value. The catch tank is fitted with a 75 mm vent direct to atmosphere. Heat transfer fluid is circulated to the reactor jacket and to heating coils in the feed vessels. The temperature of each vessel can be independently controlled. Interconnecting chemical transfer pipe work is fitted with remotely operated actuated valves. The pilot plant can be controlled and monitored remotely from a control room 100 m from the reactor building.

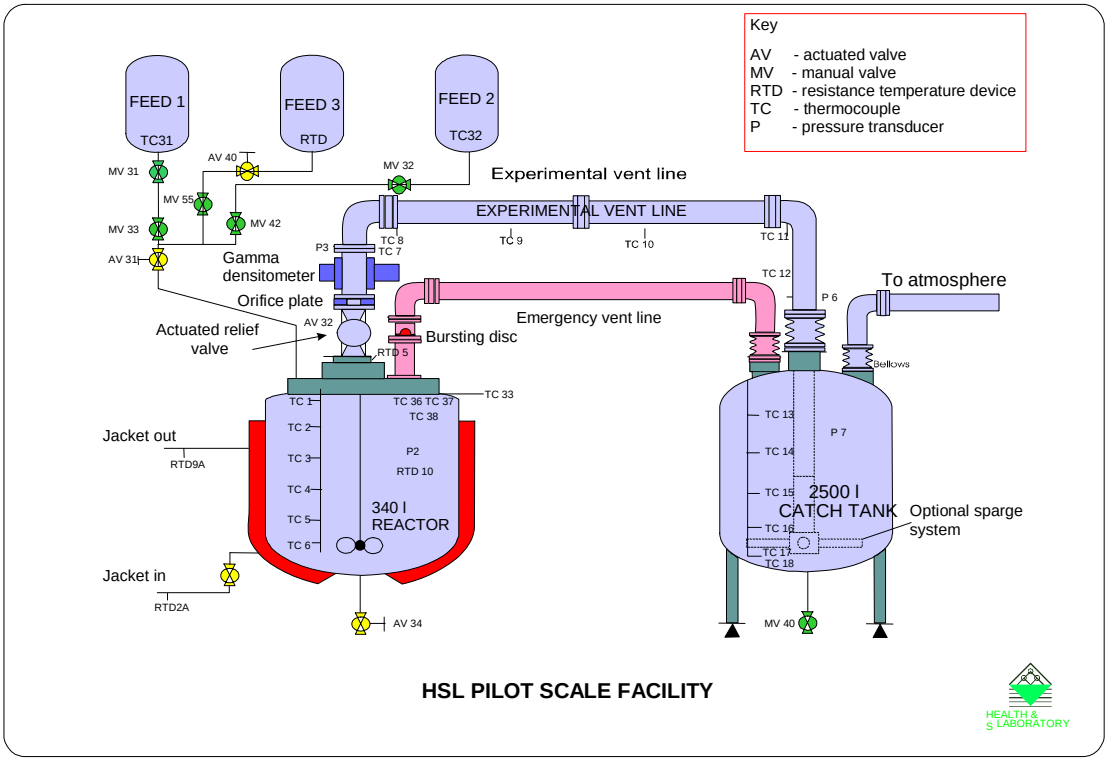

Figure 1. Pilot plant. Instrumentation diagram.

In addition to the normal instrumentation present in the pilot plant, an EWDS prototype assembled by SEGIBO srl has been installed to assess its performance during runaway experiments. The EWDS has been installed without placing new temperature sensors, its input is provided by the data acquisition system of the pilot plant after minor modifications done by SEGIBO technicians. The EWDS collects four temperature measurements, one from the jacket inlet and three from inside the reactor. Next table below contains the description of the EWDS inputs.

Table 1. EWDS measurements inputs description

Name	HSL signal	Description	Sensor type
TJ	RTD2a	Jacket inlet temperature	RTD
TT01	TC04	Reactor temperature	Thermocouple, type K
TT02	TC06	Reactor temperature	Thermocouple, type K
TT03	RTD10	Reactor temperature	RTD

2.2. Experiments design

A set of three experiments has been carried out on the pilot scale chemical plant in the Health and Safety Laboratory (HSL) in Buxton (UK) to evaluate the EWDS prototype performance. The selected reaction has been the uncatalyzed esterification between isopropanol and propionic anhydride whose kinetic scheme is given in Table 2. This reaction is interesting for our purposes because it is a highly exothermic reaction with no danger of side nor decomposition reactions. In addition, this reaction has been extensively studied in the past and an accurate kinetics has been developed. This fact has permitted to calculate the analytical divergence of the experiments, which has been very useful for the experimental design and for comparing the EWDS results, i.e. the reconstructed divergence, with the analytical divergence.

Table 2. Kinetic scheme for esterification reaction

$$(CH_3)_2CHOH + (CH_3CH_2CO)_2O \Rightarrow CH_3CH_2COOH + CH_3CH_2COOCH(CH_3)_2$$

It has been also decided to operate the reactor on isoperibolic conditions and to carry out the experiments batchwise using the parameters contained in Table 3 only changing the jacket temperature from one experiment to another.

Table 3. Experimental parameters.

Mass of isopropanol	58.7 kg
Mass of propionic anhydride	127.1 kg
Stirrer speed	25 rpm
Jacket flow	20 $Kg.min^{-1}$
Pressure vent set	1.5 bar

As previously stated, the experiments design has been done applying the divergence criterion using the kinetic expression provided by HSL. In order to apply the divergence criterion, the mass and energy balances of the system are necessary to calculate the divergence of the system. In this case, the energy and mass balances may be written as

$$\frac{dX}{dt} \quad A \cdot e^{\left(-\frac{E}{R}\cdot\frac{1}{T}\right)} \cdot (1-X)^n \qquad (1)$$

$$\frac{dT}{dt} \quad \frac{1}{\rho Cp V_0} \cdot \left(-\Delta H \cdot C_{A0} \cdot V_0 \cdot \frac{dX}{dt} - US \cdot \left(T - T_j \right) \right) \tag{2}$$

with initial conditions at t= 0 s, C_{A0}= C_{B0}= 4.81 mol·l^{-1}, V_0= 200 l and T= T_j – 15.

The values of the kinetic constants as well as the physico-chemical properties of the system are contained in Table 4.

Table 4. Kinetic constants and physico-chemical parameters of the esterification reaction	
A= 4.3·10^8 s^{-1}	E/R=9900 K
N= 2.1	ΔH= 66.641 KJ·mol
C_{A0}= 4.81 mol/l	US= 305.8 W·K^{-1}
V_0= 200 l	$\rho \cdot Cp$= 2432 J·l^{-1}·K^{-1}

Once the energy and mass balances are defined, it is possible to obtain the Jacobian, **J**, of the system, which is a 2x2 matrix defined as

$$\mathbf{J} \quad \begin{bmatrix} \frac{\partial \left(dX/dt \right)}{\partial X} & \frac{\partial \left(dX/dt \right)}{\partial T} \\ \frac{\partial \left(dT/dt \right)}{\partial X} & \frac{\partial \left(dT/dt \right)}{\partial T} \end{bmatrix} \tag{3}$$

Divergence is defined as the trace of the Jacobian matrix, which means the sum of the diagonal elements:

$$div \quad j_{11} + j_{22} \tag{4}$$

where

$$j_{11} \quad -n \cdot A \cdot e^{\left(-\frac{E}{R} \frac{1}{T} \right)} \cdot (1 - X)^{n-1} \tag{5}$$

$$j_{22} \quad \frac{1}{\rho Cp V_0} \cdot \left(-\Delta H \cdot C_{A0} \cdot V_0 \cdot \left(\frac{E}{R \cdot T^2} \right) A \cdot e^{\left(-\frac{E}{R} \frac{1}{T} \right)} \cdot (1 - X)^n - US \right) \tag{6}$$

and the criterion states that when divergence is grater than zero on a segment of the reaction path, the system is under runaway conditions.

Next figure below shows the maximum divergence value obtained in the first 12000 seconds for the parameters contained in tables 3 and 4 as a function of the jacket temperature. As can be seen the maximum divergence value increases as jacket temperature increases crossing the criterion boundary, i.e. when divergence is zero, in 331.59 K.

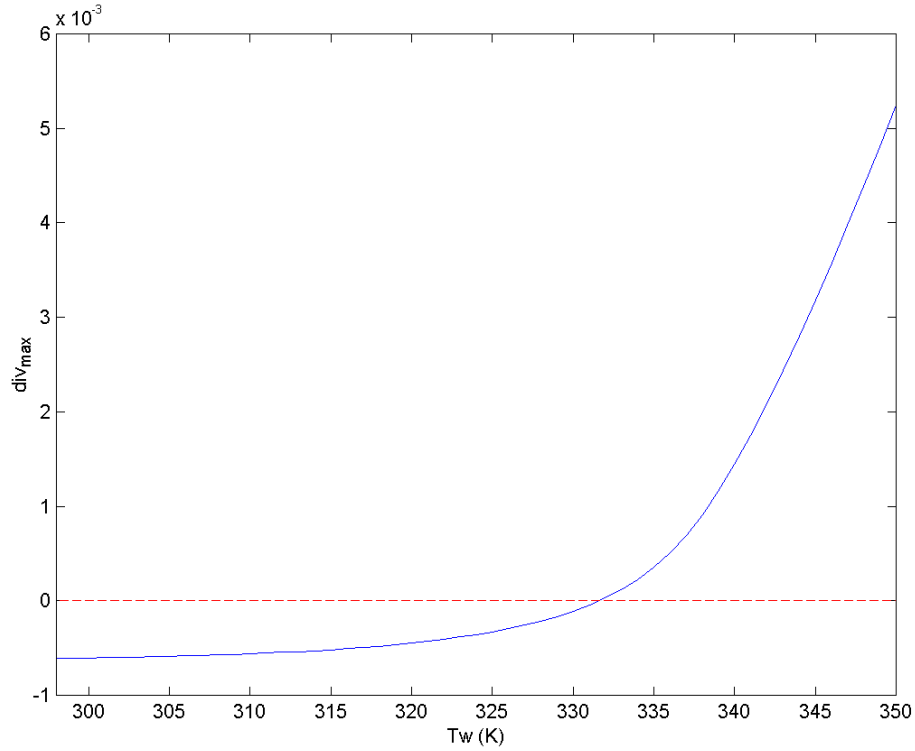

Figure 2. Maximum analytical divergence (blue) obtained in the first 12000 s for the studied system and divergence criterion runaway boundary (discontinuous red).

From the obtained results, it was decided to set the jacket temperature for Exp1, Exp2 and Exp3 on 348.16 K, 343.16 K and 333.16 K, respectively. These temperatures were selected in order to change the system characteristics from runaway to a non runaway scenario. Figures 3 and 4 show the simulated temperature profiles and the analytical divergence for the three selected cases, respectively. As can be seen in figure 3 higher layers, these cases correspond to runaway situation, whereas in the lower layer it corresponds to a non ignition case although the jacket temperature is above the limit established by the divergence criterion. This fact is produced because the boundaries of divergence criterion are conservative, as it has already been observed by Zaldívar *et al.* (2003a). Actually, when looking to figure 4 it is obvious that in the third proposed experiment divergence value s are clearly small, i.e. close to the criterion

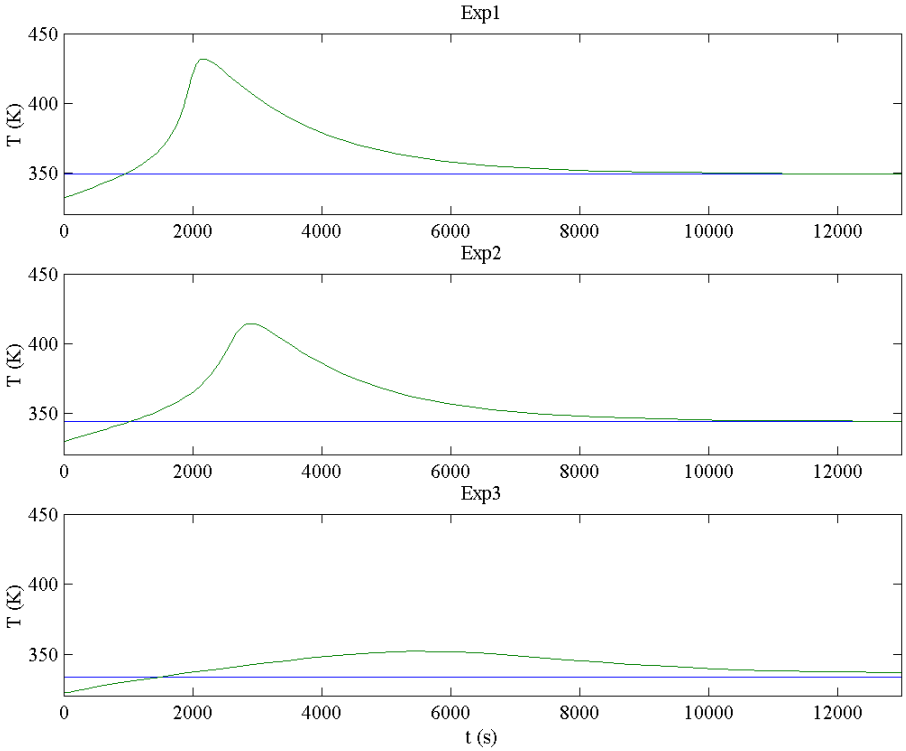

Figure 3. Jacket (blue) and reactor (green) simulated temperatures for Exp1, Exp2 and Exp3

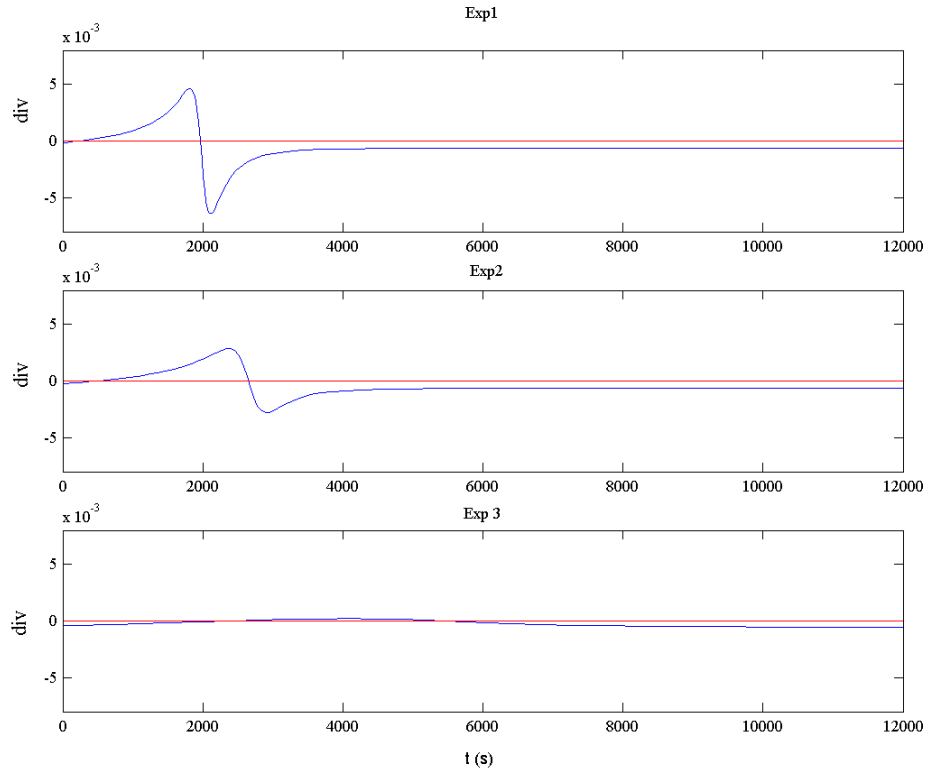

Figure 4. Divergence (blue) and divergence criterion limit (red) obtained from simulation of Exp1, Exp 2 and Exp 3.

boundary. Nevertheless, the jacket temperature of the third proposed experiment is less than two Kelvin above the boundary limit and its the maximum divergence value is more than forty times smaller than in the first one.

2.3. Experimental procedure

The esterification experiments have been carried out following the procedure bellow summarised:

- Isopropanol was weighed and loaded into a feed vessel.

- Propionic anhydride was weighed and loaded into the reactor.

- Reactor and fed vessel temperatures were set at the desired temperature.

- Once feed vessel and reactor had reached the set point temperature, isopropanol was added to the reactor from the fed vessel.

- When reaction had finished the reactor contents, and the catch tank if the reactor had been vented, were discharged.

2.4. Additional experiments

As stated before, the EWDS algorithm has been applied offline to a set of experiments carried out in the HSL pilot plant facility in the past in order to extend its validation to other chemical systems. The experiments analysed correspond to two different reactive systems: the acetic anhydride hydrolysis and the tert-butyl peroxy-2-ethylhexanoate decomposition. These systems are a vapour and a gassy system, respectively. A brief description of the experimental conditions and procedures is given bellow.

- Acetic anhydride hydrolysis, Exp4, Exp5, Exp6 and Exp7:

Stoichiometric quantities of acetic anhydride and water were charged to the reactor in the two first experiments with a batch volume of 100L and 150L, respectively. The jacket temperature was maintained constant, 323K, during the experiments and when a pressure relief set pressure, 2 bar, was reached the venting valve was automatically opened. Exp6 and Exp7 were carried out maintaining the same conditions as in Exp4 and Exp5, respectively, but with the addition of 0.25% of surfactant. The temperature and pressure profiles of acetic anhydride hydrolysis experiments are given in figures 5 and 6, respectively.

- Tert-butyl peroxy-2-ethylhexanoate decomposition, Exp8, Exp9, Exp10 and Exp11.

The Shellsol T and a cobalt catalyst were charged into the reactor and time was left for temperature stabilisation to the required initial temperature of 368K.Then the tert-butyl peroxy-2-ethylhexanoate was charged into the reactor from a feed vessel. When the pre-selected pressure relief, 2 bar, was reached the venting valve was automatically opened. All experiments were carried out at constant jacket temperature at 368K. Exp8, Exp9 and Exp10 were carried out with a 1% of catalyst and initial batch volume of 150L, 200L and 250L, respectively,

whereas Exp11 was carried out with 2% of catalyst and initial batch volume of 150L. The temperature and pressure profiles of acetic anhydride hydrolysis experiments are given in figures 7 and 8, respectively.

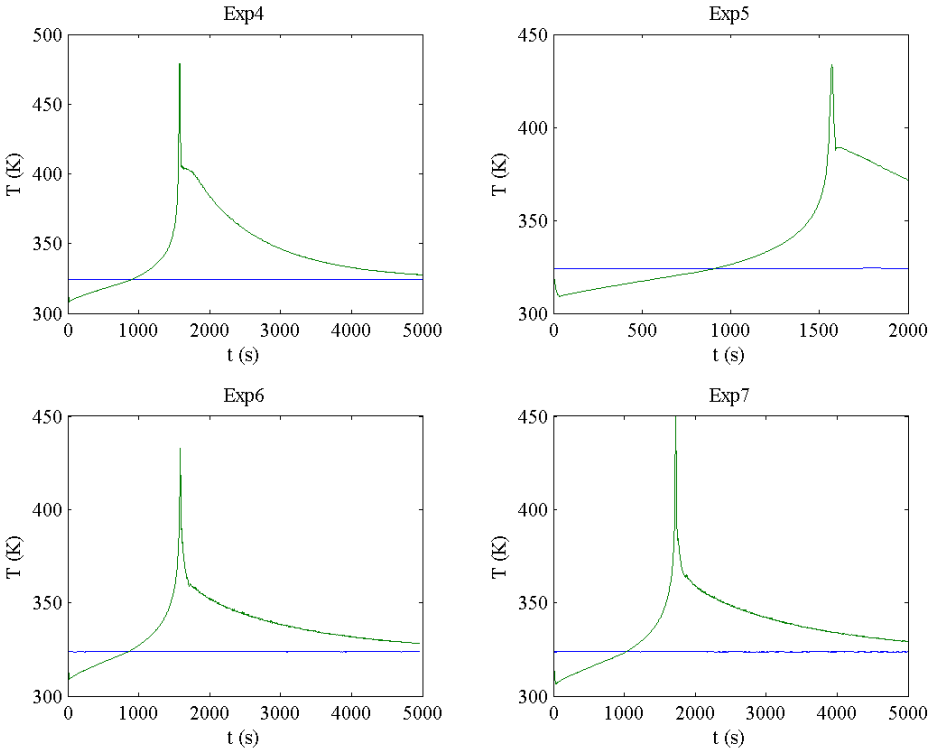

Figure 5. Jacket (blue) and reactor (green) temperatures profiles for Exp4, Exp5, Exp6 and Exp7.

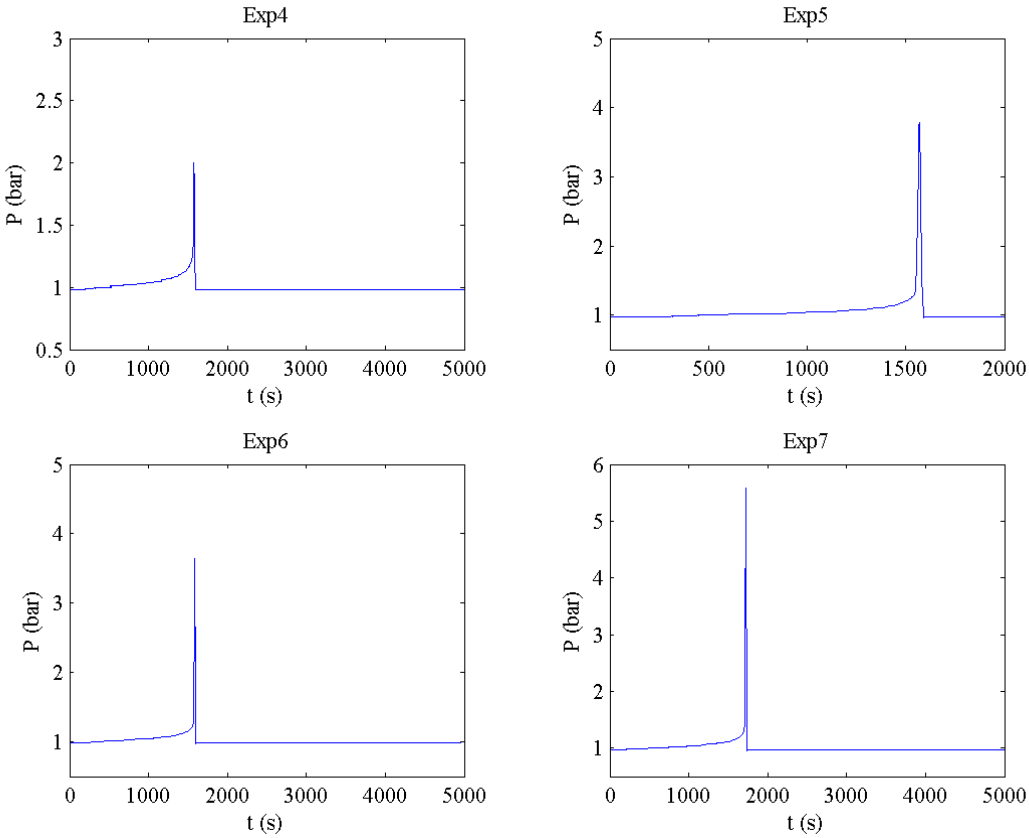

Figure 6. Experimental pressure profile for Exp4, Exp5, Exp6 and Exp7.

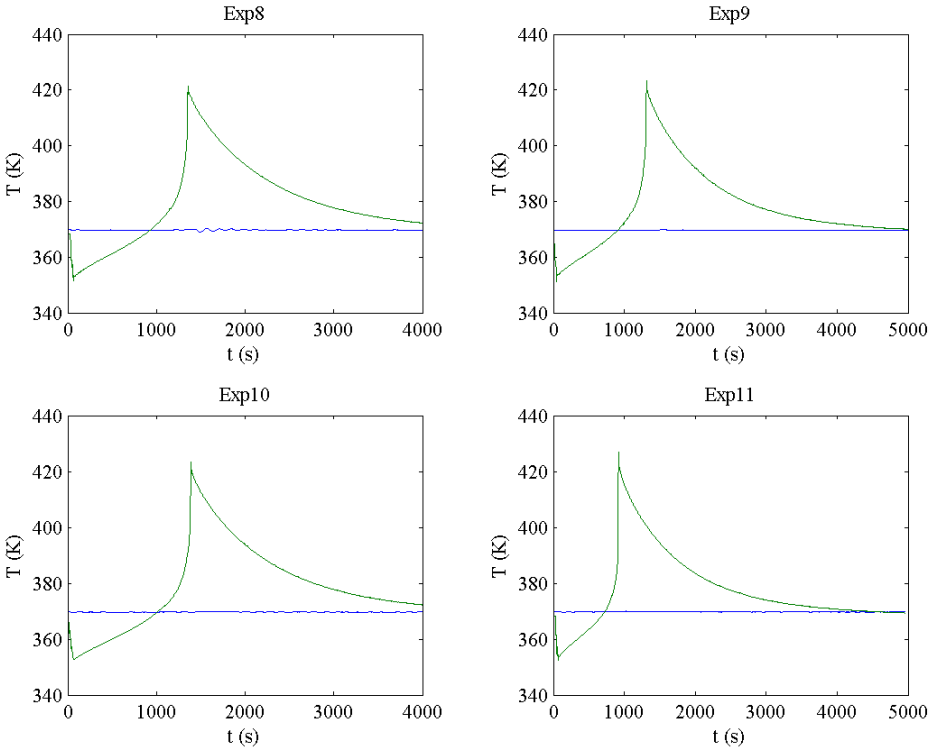

Figure 7. Jacket (blue) and reactor (green) temperatures profiles for Exp8, Exp9, Exp10 and Exp11

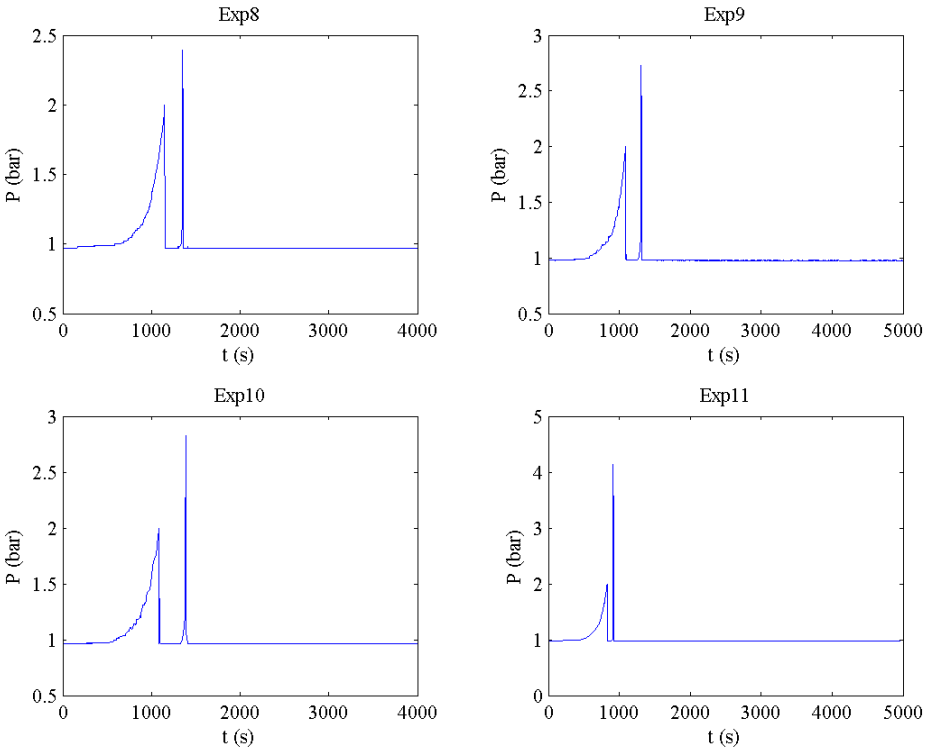

Figure 8. Experimental pressure profile for Exp8, Exp9, Exp10 and Exp11.

3. 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 by Takens (1981), who showed 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,

$$s(t) = h(\mathbf{x}(t)) \tag{7}$$

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 best (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 non-stationarity of our system.

In a former work (Bosch *et al*., 2004), we 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.

As previously mentioned, derivative coordinates disadvantage is their sensitivity to noise and this has been clear on the results obtained from laboratory and industrial experiments (Strozzi *et al*., 2003; Bosch *et al*., 2003a,b,c). Because the last mentioned fact, we have decided in this work to introduce a new state space reconstruction based on delayed vectors to maximise the signal noise ratio, and hence obtain a better divergence reconstruction. One of the reasons we used derivatives in the past was to avoid the need to estimate not only the embedding dimension but also the time delay, Δt, or the lag between data when reconstructing the state space. This, at that time seemed an additional effort on the EWDS tuning. However, this approach may be reasonable if the obtained results are significantly better.

Divergence calculation

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 (Arnold, 1973). There are several methods to calculate the divergence which give the rate of expansion or contraction of the phase space (ps). Liouville's theorem (Arnold, 1973) states that:

$$V_{ps}(t) \quad V_{ps}(0)\cdot\exp\left[\int_0^t div\{\mathbf{F}[\mathbf{x}(\tau)]\}d\tau\right] \tag{8}$$

where

$$div\{\mathbf{F}[\mathbf{x}(t)]\} \quad \frac{\partial F_1[\mathbf{x}(t)]}{\partial x_1}+\frac{\partial F_2[\mathbf{x}(t)]}{\partial x_2}+\ldots+\frac{\partial F_d[\mathbf{x}(t)]}{\partial x_d} \tag{9}$$

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

$$div \quad \frac{\dot{V}_{ps}(t)}{V_{ps}(t)} \tag{10}$$

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 as the denominator in Eq. (10). However, by definition the volume is always positive and hence, $div>0$ is equivalent to checking if:

$$\Delta V_{ps}(t) > 0 \tag{11}$$

where $\Delta V_{ps}(t)$ is an infinitesimal state space volume variation. This eliminates the need to divide the two small numbers that produces an increase in the numerical errors. Even though the values of $\Delta V_{ps}(t)$ are, in principle, not preserved under state space reconstruction, its sign, which is the sign of the divergence and, hence, it identification criteria, is preserved.

Several methods to calculate the divergence using one or more temperature trajectories have been developed (Bosch *et al*., 2004). In the present work we have applied one reconstructions that use one trajectory in the state space.

Figure 9 shows how to calculate the volume evolution of the system using one temperature sensor in two dimensions state space. As can be seen, two points are used for the volume calculation. The time between two volume calculations is defined as Δt_1, whereas the time between two state space points, Q_0 and Q_1, is defined as Δt_2. The volume V_{ps} (d_E=2) is using the following equation

$$V_{ps}(t) \quad \left| \det \begin{bmatrix} Q_1^x - Q_0^x & 0 \\ 0 & Q_1^y - Q_0^y \end{bmatrix} \right| \tag{12}$$

where |..| stands for absolute value and *det* refers to the determinant of the matrix; and (Q_i^x, Q_i^y) are the x and y component of the vector $\vec{Q}_i$. Once V_{ps} has been calculated, ΔV_{ps} is obtained as

$$\Delta V_{ps} \quad \frac{V_{ps}(t) - V_{ps}(t - \Delta t_1)}{\Delta t_2} \tag{13}$$

Note that the difference of volumes is divided by Δt_2 since the points used to calculate the volume are not synchronised.

When $\Delta V_{ps}(\tau) > \Delta V_{ps}^{\lim} > 0$ a runaway alarm is triggered off.

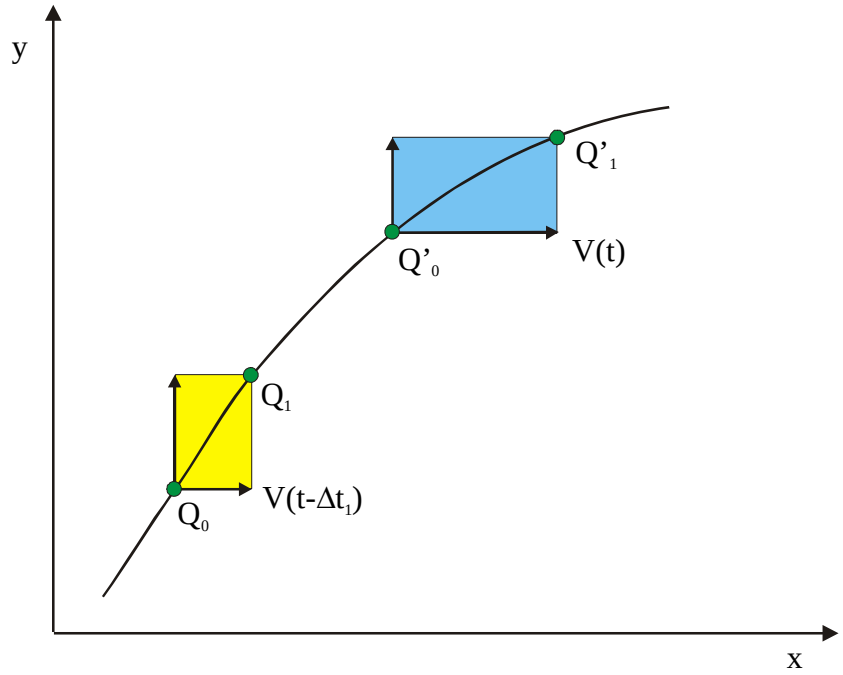

Figure 9. Representation of the evolution of the volume (surface) for a reconstructed space in two dimensions using two points on one reactor temperature trajectory.

4. RESULTS AND DISCUSSION

A set of three experiments of the esterification between isopropanol and propionic anhydride has been carried out in the pilot scale plant facility of the HSL in Buxton (UK) in order to verify that the reconstructed divergence is in accordance with the analytical divergence. The experiments have been designed using the kinetic model furnished by HSL combined with the divergence criterion as described preciously. The experiments have been conducted keeping the same experimental conditions contained in table 2. The only difference among the three experiment conditions is the jacket temperature that it has been set on 348.16 K, 343.16 K and 333.16 K, respectively, in order to change from runaway to non runaway conditions. Figures 6

and 7 show the collected temperature and pressure data, respectively. In the first two experiments, the reactor pressure has reached the pressure vent set, which was 1.5 bar, causing the vent valve aperture which is noticeable by the reactor temperature sudden decrease in figure 6 at 1810s and 2504s, respectively, and by the corresponding pressure drop in Exp1 in figure 7. Due to problems with the pressure transducer, no pressure data is available for Exp2. On the contrary, the third experiment presents a clear, but slower, exothermic effect without auto-acceleration behaviour or venting of the reactor contents.

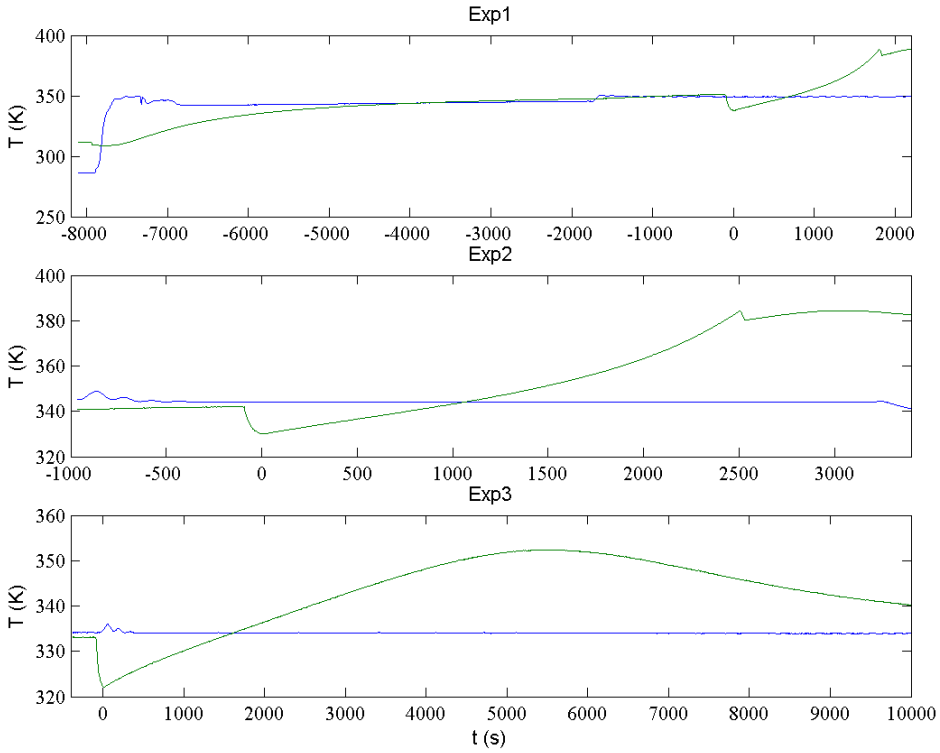

Figure 10. Experimental reactor (green) and jacket (blue) temperatures of 200 litres batch experiments Exp1, Exp2 and Exp3.

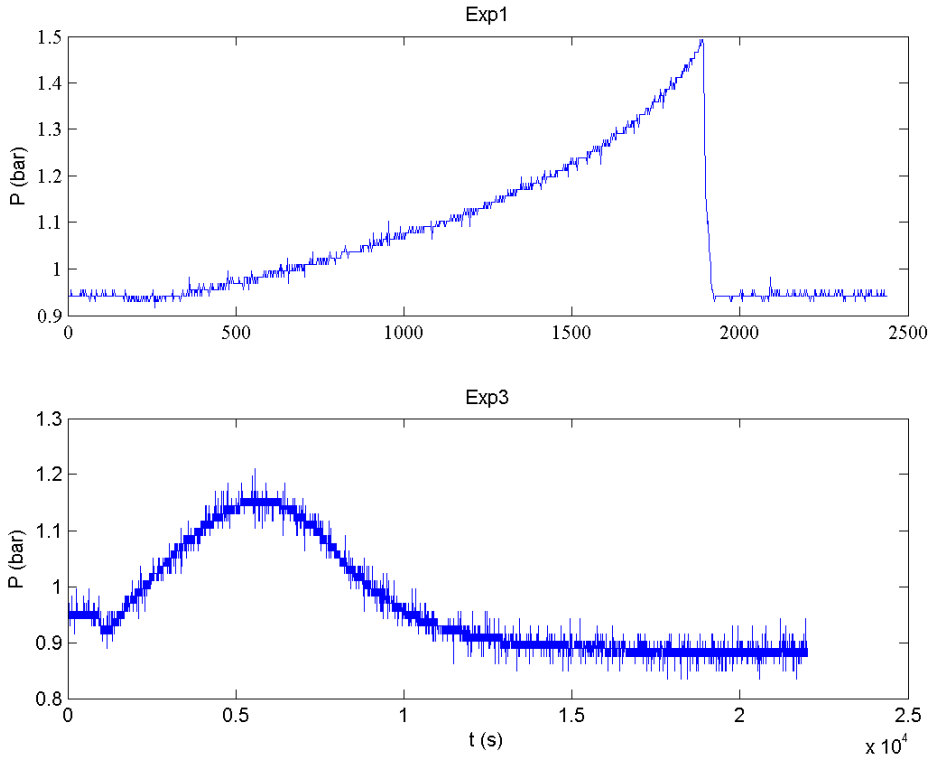

Figure 11. Pressure data recorded in Exp1 (upper layer) and Exp3 (lower layer)

Next figure bellow displays the experimental reactor temperature and their corresponding simulations during the reaction path data for Exp1, Exp2 and Exp3. As shown in this figure, simulations are in good agreement with the experimental results during the reaction path while vent valve is closed presenting slight differences on the profile in the ignition region in Exp1 and Exp2 where the simulated experiments present a higher heating rate. This fact is due the characteristic high sensitivity of the system in this segment of the reaction path. Regarding the reactor contents venting, the performed simulations do not take into account this scenario and therefore the simulated results differ from the experimental results after the venting valve is opened. For this reason, the comparison between reconstructed divergence and analytical divergence is only carried out from the addition of isopropanol to the venting of reactor contents in Exp1 and Exp2 or the end of reaction in Exp3.

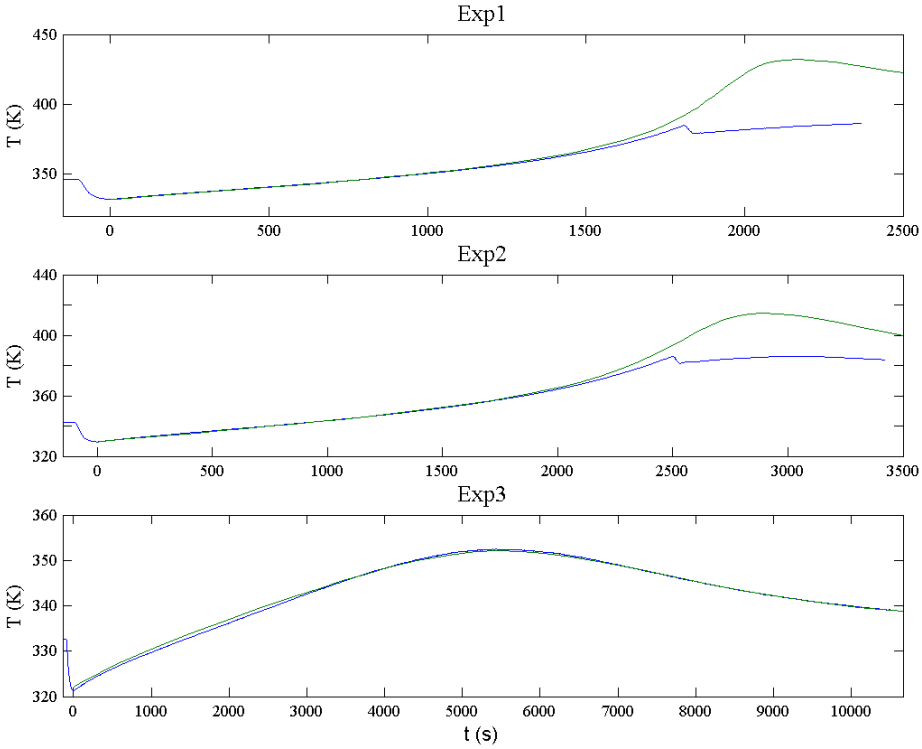

Figure 12. Experimental (blue) and simulated (green) reactor temperature in Exp1, Exp2 and Exp3

4.1. State space reconstruction using reactor temperature data

The reconstructed divergences using reactor temperature data in Exp1, Exp2 and Exp3 and their corresponding analytical divergences are displayed in figures 13, 14 and 15 for three different time delays. Analytical and reconstructed divergences have been calculated using Eq.4 and Eq.10, respectively. To avoid numerical errors due to division by a small number in Eq.10, reconstructed divergence has only been calculated when volume values were bigger than a limit value. As can be seen, the reconstructed divergence presents a good agreement with analytical divergence, especially in the first two experiments. However in the third experiment, reconstructed divergence oscillates close to analytical divergence that improves as time delay increases. This behaviour is produced because of the volume contraction in the state space typical of dissipative systems as chemical reactors. This means that V_{PS} tends to zero and hence when introduced as denominator in equation 10 produces numerical errors and simultaneously amplifies the noise level. This fact is confirmed by the results at different time delays that show improved results as time delay among points increases for Exp3 since volume increases and therefore numerical errors decrease, and by the comparison of the volumes values of the three experiments displayed in figure 16. As shown in this figure, in the two first experiments the values are clearly bigger

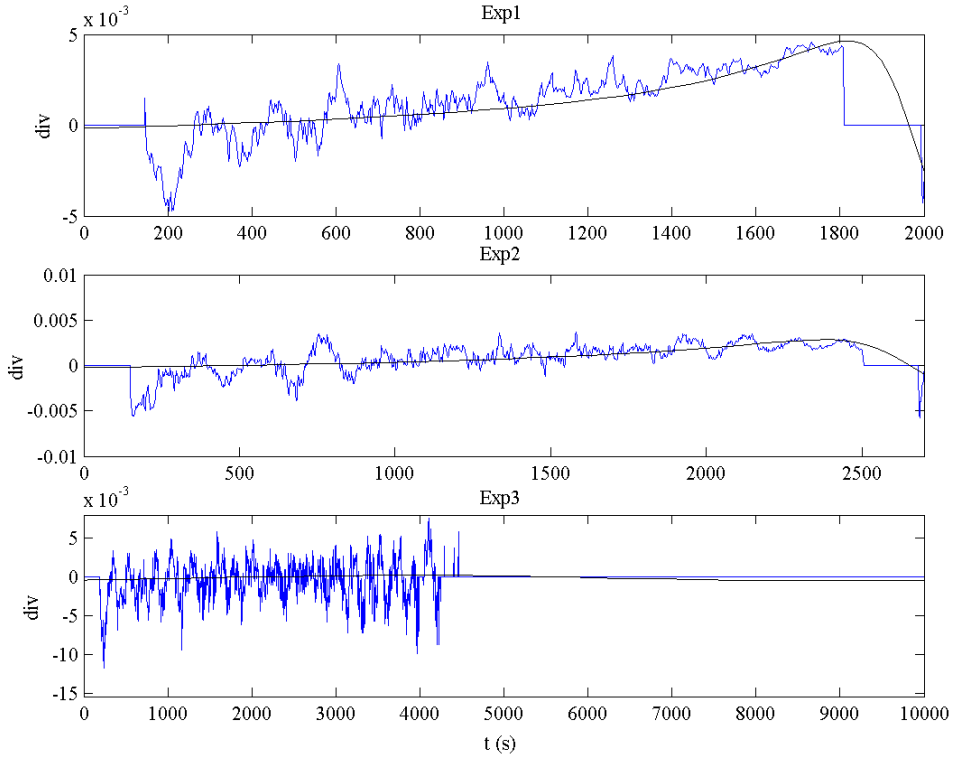

Figure 13. Reconstructed (blue) and analytical (black) divergence using $\{T_r(t),T_r(t-\Delta t_2)\}$ state space on TT02 on HSL1, HSL2 and HSL3 (Δt_1 Δt_2= 50s).

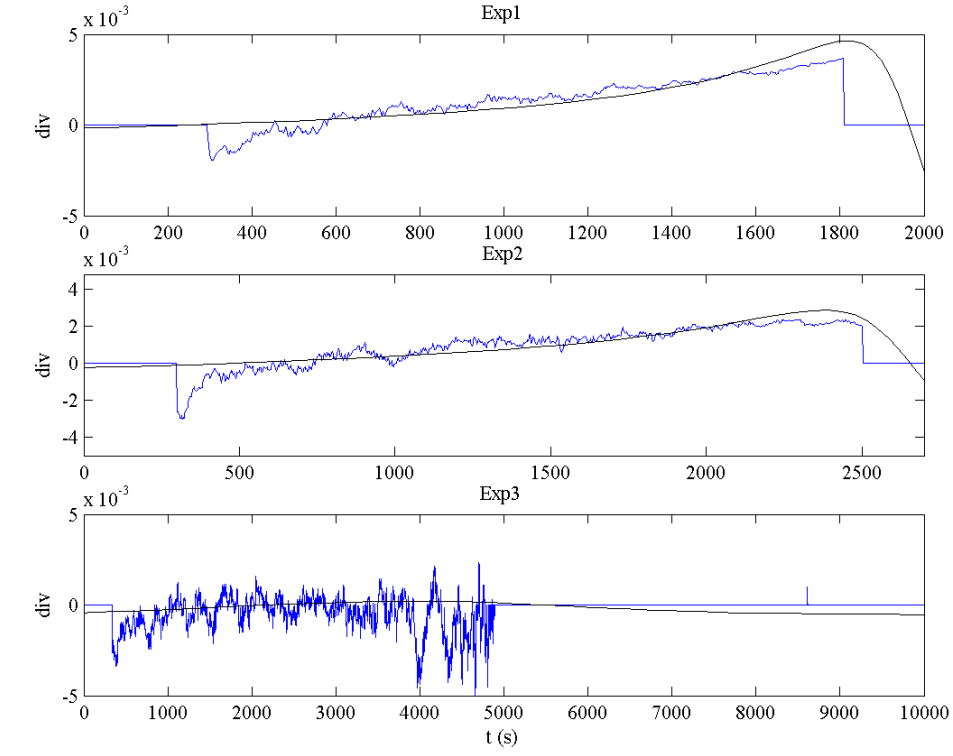

Figure 14. Reconstructed (blue) and analytical (black) divergence using $\{T_r(t),T_r(t-\Delta t_2)\}$ state space on TT02 on HSL1, HSL2 and HSL3 (Δt_1 Δt_2= 100s)

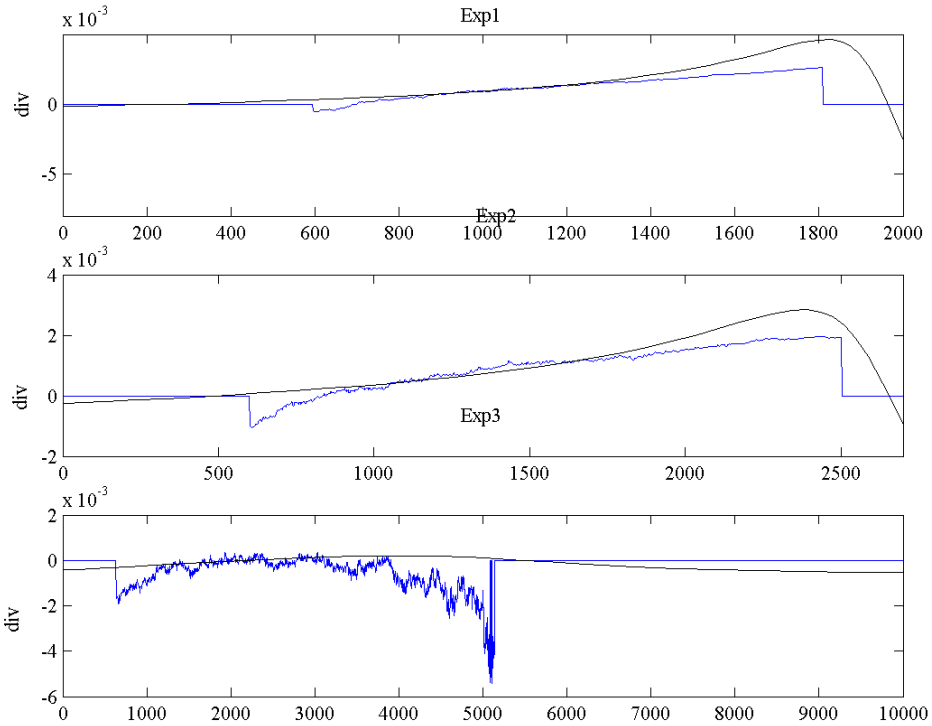

Figure 15. Reconstructed (blue) and analytical (black) divergence using $\{T_r(t),T_r(t-\Delta t_2)\}$ state space on TT02 on HSL1, HSL2 and HSL3 (Δt_1 Δt_2= 200s).

On the other hand, the presented results show that it is possible to calculate the divergence satisfactorily using reconstructed state space on a wide range of time delays.

To avoid the numerical errors and noise increase when volume tends to zero, we may just evaluate ΔV_{PS} as stated previously. As can be seen in figure 16 from Exp1, Exp2 and Exp3, ΔV_{PS} values exceed the alarm limit in the two first cases presenting and increasing profile, whereas in the third case, i.e. the non runaway case, ΔV_{PS} values remain oscillating around zero. In particular, alarms are triggered off at 584s in Exp1 and at 797s in Exp2, i.e. 1226s and 1707s before the reactor venting, respectively. The detection and the maximum temperature times for the previously stated and others analysed experiments are summarised in the table 5.

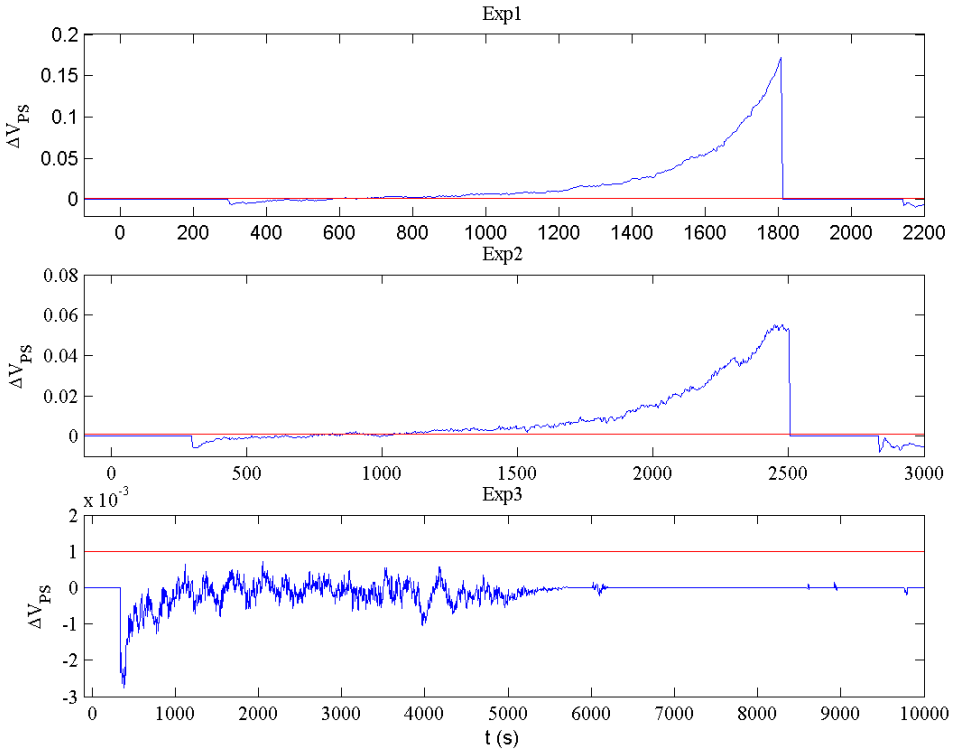

Figure 16. ΔV_{PS} values (blue) obtained using $\{T_r(t), T_r(t-\Delta t_2)\}$ state space on TT02 during HSL1, HSL2 and HSL3. ($\Delta t_1 = \Delta t_2 = 100$s and $\Delta V_{PS}^{\lim} = 1 \cdot 10^{-3}$)

Furthermore, ΔV_{PS} produces a larger segregation among non runaway and runaway conditions than the reconstructed divergence which is an important feature to avoid false alarms. For the last mentioned facts, ΔV_{PS} is more convenient than calculating the reconstructed divergence for early detection of runaway reactions.

4.2. State space reconstruction using pressure data

One of the usually considered properties in closed vessels is pressure. Pressure may be a direct measure of a state variable in gassy systems or related to the state variables in vapour systems. In any case, the theory of embedding ensures that the state space reconstruction is possible in these conditions and hence divergence may be calculated as well.

Following the procedure analogously as in the temperature reconstruction, reconstructed V_{PS}, ΔV_{PS} and divergence reconstructed divergence has been calculated for experiments 1 and 3 to compare the analytical and the reconstructed divergences. Because of the high levels of noise contained as can be seen in figure 11, pressure data has been filtered using a eleven points centred moving window before the reconstruction of the state space. As shown in figure 17, the reconstructed divergence in Exp1 firstly oscillates around the analytical divergence to finally present a good agreement with the analytical divergence. This fact is due the initial low values of V_{PS} that amplify the remaining noise as it has already been observed in the former reconstructions. On the other hand, reconstructed divergence is not possible to calculate for Exp 3 since the V_{PS} values are below the limit value fixed to avoid numerical errors due to division by a small number when calculating the reconstructed divergence.

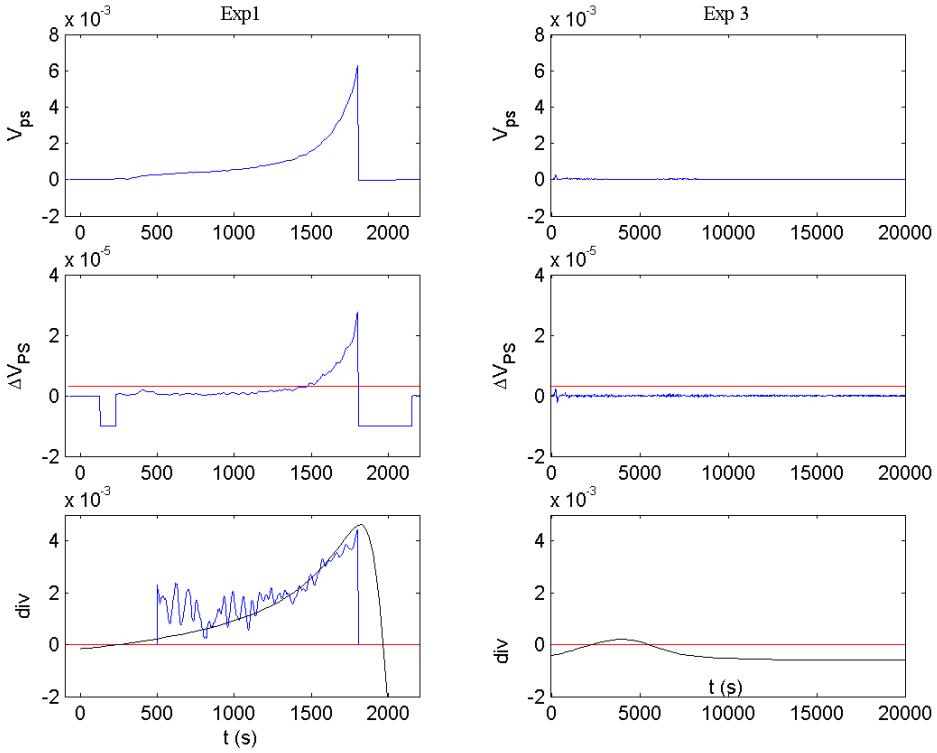

Figure 17. Reconstructed (blue) V_{PS}, ΔV_{PS} and divergence values obtained using {*P(t), P(t-Δt$_2$)*} state space on TT02 and its analytical divergence (black) on Exp1 and Exp3 . (Δt_1=Δt_2= 100s and ΔV_{PS}^{lim} = 3·10^{-6}, $V_{PS,min}$ 2·10^{-4}),

However, it is still possible to evaluate ΔV_{PS} in this case as shown in figure 17. The ΔV_{PS} remains below the alarm limit in Exp3, whereas in Exp1 the alarm limit is exceeded at 1546s.

Table 5. Summary of detection times using reactor temperature

Experiment	**Runaway detection using {*T$_R$(t), T$_R$(t-Δt$_2$)*}$^{(1)}$ (s)**	**Maximum temperature time (s)**	**Runaway detection using {*P(t),P(t-Δt$_2$)*}$^{(2)}$ (s)**	**Maximum pressure time (s)**
Exp 1	584	1810	1471	1815
Exp 2	797	2504	NA	NA
Exp 3	-	5433	-	5430
Exp 4	773	1579	1413	1575
Exp 5	767	1569	1338	1569
Exp 6	815	1590	1423	1586
Exp 7	580	1727	1496	1723
Exp 8	605	1359	733	1353
Exp 9	558	1316	647	1310
Exp 10	589	1393	642	1387
Exp 11	494	924	530	916

1- Δt_1=Δt_2= 100s and ΔV_{PS}^{lim} = 1·10^{-3} 2- Δt_1=Δt_2= 100s and ΔV_{PS}^{lim} = 3·10^{-6}

5. CONCLUSIONS

The EWDS performance has been evaluated online and offline on a set of esterification reaction between isopropanol and propionic anhydride experiments carried out on the HSL pilot plant

facility. The set of experiments contains runaway and non runaway experiments. The experiments have been carried out batchwise on isoperibolic conditions using the same quantities of reactants at different jacket temperatures. Experimental conditions have been set previously applying the divergence criterion on kinetic data furnished by the HSL. We have tested two different state space reconstructions, the originally implemented on the EWDS prototype based on temperature derivative coordinates online and a new one that uses embedded delayed vectors offline. This second reconstruction in addition to avoid using derivatives does not use the jacket temperature either.

Results have shown that the temperature derivative reconstruction detects that the system is in runway conditions late and produces false alarms because of changes in the jacket. On the other hand, results obtained with the second reconstruction show that is able to detect runaway situations earlier without producing false alarms. In addition, the reconstructed divergence is in good agreement with the analytical divergence, which confirms the accuracy of the reconstruction. However, numerical errors produced during reconstructed divergence calculation confirm theoretical statements and point to ΔV_{PS} as the best parameter for early warning of runaway initiation. Finally, we have applied the two reconstructions and a third one based on pressure measurements on a set of experiments carried out in the same reactor to confirm the validity of the embedded delayed reconstruction.

We are now applying the same reconstruction scheme to previous experimental data and to date this modified reconstruction scheme clearly improves the results obtained previously, and, hence, the new prototype will include this algorithm.

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AWARE: Investigation of the early warning detection system through pilot and large-scale tests

The chemical industry is increasingly expanding into the pharmaceuticals and speciality chemicals sectors. As a result, there is an increasing dependence in the sector on the existence of smaller, more flexible enterprises (SMEs) capable of providing specialised skills and products in niche markets. It is estimated that around 20% of these businesses carry out exothermic reactions or other chemical processing operations that require detailed investigations of the associated reactive hazards and the design and installation of safety venting systems. In the past, many criteria have been developed to determine whether a runaway - an excessive increase of the reaction temperatures, which cannot be kept within acceptable limits by the cooling system of the reactor - will occur. All these criteria have the disadvantage that the reactor dynamics cannot be taken into account. This project addressed the needs to detect runaway initiation in advance allowing countermeasures to be taken and to design emergency relief systems for chemical reaction hazards whilst still protecting the environment. The project produced an early warning detection system (EWDS) detection device as well as guidelines for use by SMEs.

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