

An Integrated Approach for the Early Detection of Runaway Reactions by Using UV-Visible and Temperature Sensors

Claudio Ampelli^{a,*}, Valeria Casson^b, Giuseppe Maschio^c

^aDepartment of Electronic Engineering, Industrial Chemistry and Engineering, University of Messina, V.le F. Stagno d'Alcontres, 31 - 98166 Messina, Italy

^bTexas A&M University at Qatar, 217 Texas A&M Engineering Building, Education City, 23874, Doha, Qatar

^cDepartment of Industrial Engineering, University of Padua, Via F. Marzolo, 9 - 35131 Padua, Italy
ampellic@unime.it

We report here on a novel approach for the early runaway detection in chemical reactors, based on the integration of two kinds of sensors: i) a set of three Pt thermo-resistances for measuring the temperatures both within the reactor and in the cooling jacket and ii) an UV-visible probe for the indirect evaluation of the conversion through measurements of light absorbance. The measured variables (temperature and conversion) were used as input to our model based on the divergence calculation. The early warning detection system (EWDS) was tested for the sulphuric acid catalyzed esterification of acetic anhydride and methanol, a very simple reaction but releasing ~ 70 kJ per mole of anhydride consumed. The responses given by EWDS were examined during the simulation of runaway reactions in a lab-scale reactor working under batch isoperibolic conditions. Different chemical heat flows were generated by varying the concentration of the sulphuric acid and adding at once the acetic anhydride into the reactor. The behaviour of the detection criterion was evaluated comparing the EWDS signals using both temperature and conversion as input variables, with the responses obtained from only temperature measurements. A detailed kinetic model was also developed to solve the differential energy and mass balance equations and define the runaway boundaries. Results showed the importance of an input variable indirectly related to conversion in such kinds of processes where other enthalpy variations (i.e. due to an endothermic mixing of the reagents) may hide a runaway reaction occurring.

1. Introduction

The maintenance of safe operation in industrial plants is of great importance to avoid damage to personnel, environment and equipment. Despite significant efforts in research, design and management dedicated in the last decade by chemical engineers in the field of reactor safety, thermal runaway accidents are still quite frequent in chemical reactors and vessels (Molga et al., 2007). There is the need to intensify the studies to i) prevent a runaway reaction, i.e. by choosing properly the operating conditions and adopting a safety criterion to detect in advance anomalous temperature behaviours (Zaldívar and Strozzi, 2010), and ii) minimize the consequences, by the application of a suitable system to handle or quench reactions running away (Russo et al., 2007).

In the frame of the AWARD European Project, an early warning detection system (EWDS) was developed and successfully tested both in small-scale and pilot plant chemical reactors, as well as in an industrial chemical reactor under batch and semibatch conditions (Ampelli and Maschio, 2012). The EWDS, based on the on-line calculation of the reactor divergence, is able to detect beforehand runaway phenomena without producing false alarms. The EWDS has the peculiarity to be independent of the actual process and this aspect is very important from an economical point of view. The high number of processes carried out batchwise, in fact, does not make economically feasible to develop a detailed kinetic model for each process. The EWDS works by using only temperature measurements (in the reactor and in the cooling system) as input values to the model for the divergence calculation. However, sometimes having on-line information about the concentrations of either the reagents or products may help to distinguish a potential

runaway reaction. Unfortunately, one of the main issues in the field of reactor control is the lack of reliable sensors to measure on-line variables related to conversion. Alternatively measurements of concentration may be performed off-line, but the responses are characterized by a delay not compatible with the rapid development of a runaway reaction.

In this work we report on a novel approach for the early runaway detection based on the integration of two kinds of sensors: i) a set of three Pt-thermistances for measuring the temperatures both within the reactor and in the cooling jacket (in and out) and ii) an UV-visible probe for the evaluation of conversion through measurements of light absorbance. The measured variables (temperature and conversion) were used as input to our model based on the divergence calculation, for the process of esterification of acetic anhydride and methanol, catalysed by sulphuric acid. The process was performed by using a lab-scale calorimeter working under isoperibolic conditions. The dependence of the kinetic constant on the concentration of sulphuric acid and temperature was also evaluated in order to develop a kinetic model, useful to solve the mass and energy balances, and define the runaway boundaries for this process.

Finally, the behaviour of the detection criterion was evaluated comparing the EWDS signals using both temperature and conversion (obtained from measurements of light absorbance) as input variables, with the responses obtained from only temperature measurements.

2. Theoretical analysis

2.1 Divergence criterion

The criterion to define runaway limits was developed by Zaldívar et al. (2003): in particular when the divergence of the reactor becomes positive on a segment of the reaction path, a warning alarm is given by the EWDS. 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 (conversion and temperature, respectively). However, the EWDS does not calculate the divergence solving those differential equations, but using phase space reconstruction techniques (Arnold, 1978). This method is a way to move, in a topological sense, from a temporal time series of measurements to a phase-space, whose volume defines the system at each point of time. This allows to describe the reaction course by the evolution of the phase-space volume (V_{ps}) through trajectories which should converge to a final point (since a chemical process is an energy dissipative system) but may strongly diverge if a runaway reaction occurs. Figure 1 shows an example of reconstruction of V_{ps} in a three-dimensional topological representation. The equations used to calculate $V_{ps}(t)$ and ΔV_{ps} are also reported. In this case 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 phase-space volume variation (ΔV_{ps}) is related to the reactor divergence and it can be adopted as parameter to define a runaway reaction, when $\Delta V_{ps}(t) > 0$.

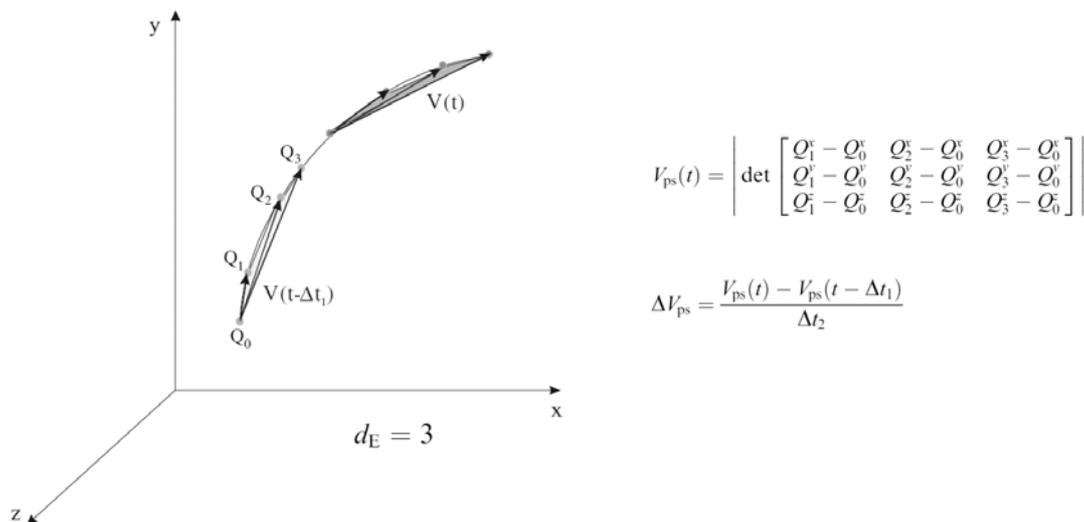


Figure 1: Representation of the evolution of the volume for a reconstructed space in three dimensions using one reactor temperature trajectory. Adapted from Zaldívar et al. (2005).

2.2 Model of reaction

The reaction studied is the esterification of acetic anhydride (OAc_2) and methanol (MeOH), catalysed by sulphuric acid (H_2SO_4) to give methyl acetate (MeOAc) and acetic acid (HOAc):



This is a relatively safe reaction for studying thermal runaway in the laboratory and because of the modest reaction enthalpy ($\Delta H_R = \sim 70 \text{ kJmol}^{-1}$) and low activation energy, it provides a severe test of the divergence criterion by EWDS. The model is based on the simultaneous integration of the differential mass and energy balances:

$$dX/dt = k(1 - X) \quad (\text{mass balance}) \quad (2)$$

$$dT/dt = (n_{\text{Ac}_2\text{O}}^0 \Delta H_R dX/dt + UA(T^0 - T))/C_p \quad (\text{energy balance}) \quad (3)$$

where X is the conversion, k is the kinetic rate constant, T is the reactor temperature, T^0 is the reactor temperature before starting the reaction, $n_{\text{Ac}_2\text{O}}^0$ is the initial number of moles of acetic anhydride, ΔH_R is the enthalpy of reaction, UA is the global heat transfer coefficient and C_p the overall heat capacity of the system. Once defined all the thermodynamic and kinetic parameters, the two balance equations can be simultaneously integrated by using a fourth order Runge-Kutta procedure (Casson et al., 2012).

3. Experimental

The experiments were carried out using a jacketed, stirred glass reactor with a capacity of 0.5 L, working under batch isoperibolic conditions (Ampelli et al., 2001). The apparatus was assembled from readily available components: three resistance thermometers (Pt-100) to measure the reactor temperature and the inlet and outlet jacket temperatures; a 25 Ω resistance heater for the determination of UA and C_p ; a thermostat (Haake F3) used to circulate the heating/cooling fluid and maintain the jacket temperature as constant (ranging from 10 to 40 $^\circ\text{C}$). The operating mode for the temperature control was previously reported by Ampelli et al. (2005). In addition, an UV visible probe was fitted with the reactor to monitor the light absorbance variation during the process. The UV-visible system (USB 2000 Ocean Optics) consists of i) a light source, ii) a compact housing including the diffraction grating and the multi-channel detector and iii) an immersion probe working in transmission-reflection mode. The light radiation is transmitted between the different components through fiber-optic cables. The assembling of the probe to the reactor and its operating mode were discussed elsewhere (Ampelli et al., 2003).

The experiments were performed by adding OAc_2 very quickly to a solution of H_2SO_4 in MeOH , thus avoiding the influence of the not-catalyzed esterification during the calibration. The reaction was carried out in excess of MeOH with gradually increasing amounts of H_2SO_4 in order to obtain different increment of the reactor temperature. In a first series of experiments the maximum increment of the reactor temperature was limited to 1 $^\circ\text{C}$, thus operating under quasi-isothermally conditions and reducing the influence of temperature on the kinetic data; in this case the maximum concentration of H_2SO_4 used was $\sim 14 \text{ mmol L}^{-1}$. In a second series of experiments higher concentrations of sulphuric acid were used (until $\sim 80 \text{ mmol L}^{-1}$) in order to simulate thermal runaway phenomena.

4. Results and discussion

In the general idea to develop a safety criterion to delimit runaway boundaries that could be applied on-line, the divergence calculation by EWDS may be a good opportunity for industrial companies to obtain information about the parametric sensitivity of the chemical reactor, thus preventing from thermal runaway accidents. The possibility to calculate the divergence (or ΔV_{ps} , which is directly correlated with the divergence) without solving the differential balance equations, is very attractive. In principle, all the measurable variables, which may describe the state of the system at each time, are potential inputs for the EWDS model. Depending on the kind of process, the on-line evaluation of the concentration of one of the reagents and/or products, may give complementary information about the course of reaction, increasing the sensitivity of the detection criterion.

Firstly, we developed a kinetic model for the esterification of OAc_2 with MeOH , to determine the dependence of the kinetic constant k on the H_2SO_4 concentration and temperature. Then, we simultaneously solved the differential balances as described in the theoretical part.

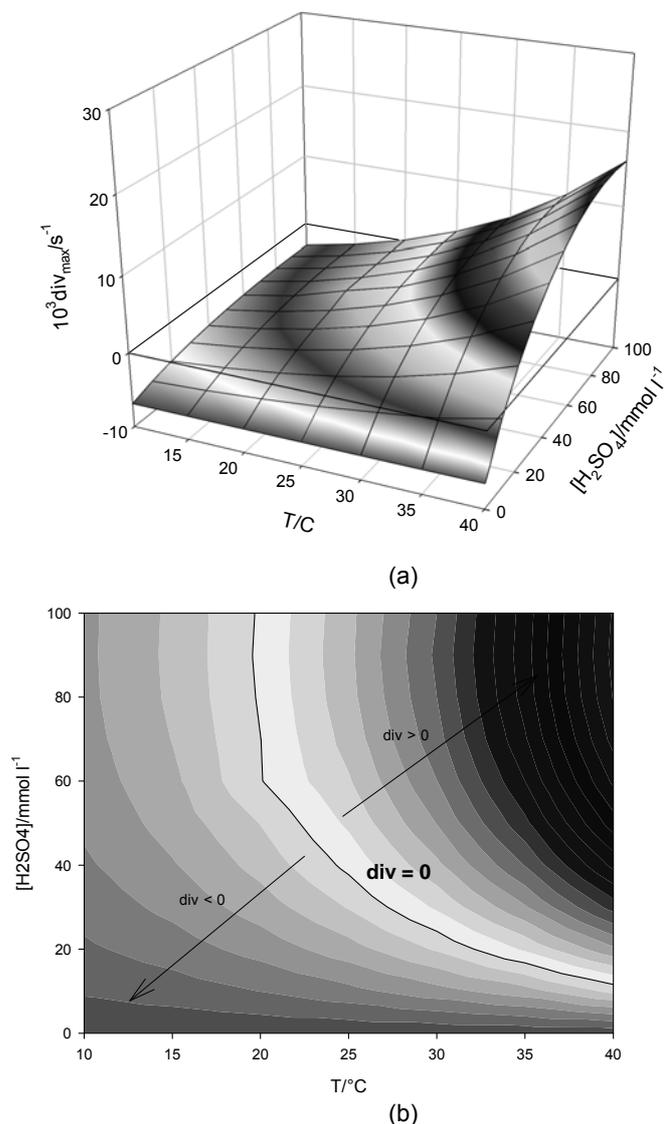


Figure 2: Three (a) and two (b) dimensional representation of the theoretical maximum values of the divergence (div) with respect to H_2SO_4 concentration and reactor temperature (OAc_2 concentration is 1.25 mol L^{-1}).

Figures 2a and b show the representation of the maximum values of the divergence with respect to H_2SO_4 concentration and reactor temperature in a three- and two-dimensional graph respectively, obtained by the application of the theoretical model. The graphs refer to an initial OAc_2 concentration of 1.25 mol L^{-1} . In these conditions, from the theoretical model it is not to be expected a runaway phenomenon ($\text{div} > 0$) at temperatures below $20 \text{ }^\circ\text{C}$, whatever the value of H_2SO_4 concentration. This depends on the saturation value of H_2SO_4 concentration, which was considered as 100 mol L^{-1} in the theoretical model. The runaway boundary strongly changes by increasing the OAc_2 concentration and, at a value of 2 mol L^{-1} , a runaway behaviour is possible also at $10 \text{ }^\circ\text{C}$. However, the amount of H_2SO_4 needed to have a runaway reaction diminishes with the temperature.

The EWDS criterion, instead, does not use the resolution of the differential mass and energy balance equations, but is based on the application of techniques of phase-space reconstruction. The continuous on-line evaluation of the volume change in the phase-space (ΔV_{ps}) allowed to individuate the onset of a runaway phenomena in advance, without producing false alarms. The upper part of the Figure 3 shows the response of the EWDS i) when only temperature measurements were used as input variables (solid line)

and ii) when also conversion, obtained by measurements of light absorbance, was used together with temperatures (dashed line). The conversion was indirectly determined from the UV light absorbance of OAc_2 showing an absorption band in the range 220 - 280 nm. The measures were performed at 275 nm to avoid the influence of absorption of the other species. The graphs refer to an experiment of esterification carried out at 10 °C with 2 mol L⁻¹ of OAc_2 and 40 mmol L⁻¹ of H_2SO_4 . In the lower part of the Figure 3 the profiles of temperature and conversion are also reported. A high positive value of ΔV_{ps} means that the reaction is running away from the normal operating conditions. A threshold value of ΔV_{ps} is usually introduced in the detection criterion to avoid false alarms due to i) the presence of noise in the signal and ii) heating and cooling ramps carried out by the operator that are not related to chemical heat flow (Ampelli et al., 2006). The signal of ΔV_{ps} obtained from only temperature measurements gave a first warning after ~ 25 s from the start of the reaction (time = 0) initiated by the quick addition of OAc_2 into the reactor. The signal-to-noise ratio is rather good and the values of ΔV_{ps} are relatively high.

In comparison, the profile of ΔV_{ps} obtained from temperature and conversion is quite similar, but with some differences: i) the first warning (high positive value of ΔV_{ps}) is anticipated, occurring after ~10 s from the start of the reaction; ii) the signal is very noisy.

The reactor temperature profile shows a little decrement of ~ 3 °C immediately after the introduction of the OAc_2 into the reactor. As the OAc_2 was maintained at the same temperature with respect the steady-state conditions existing within the reactor before the start of the reaction, the decrease of the temperature was the result of an endothermic effect of mixing between the reagents (OAc_2 and MeOH). The endothermic enthalpy of mixing was determined as ~ 6 kJ mol⁻¹.

Despite of this temperature decrement, the reaction started very rapidly, as evidenced by the conversion profile, with a kinetics of pseudo-first order, reaching a maximum temperature value of almost 50 °C ($\Delta T = \sim 38.5$ °C). The ΔV_{ps} profile obtained with temperature and conversion signalled earlier this rapid development of the reaction heat. In this case the EWDS was more efficient and reliable in the early detection of the runaway phenomenon. Unfortunately, its profile is characterized by a high noise due mainly to mathematical issues (the conversion has an absolute value lower than temperature, ranging from 0 to 1). Work is in progress to improve the quality of the signal using a smoothing filter based on the classic non-linear algorithm of Savitzky and Golay (1964).

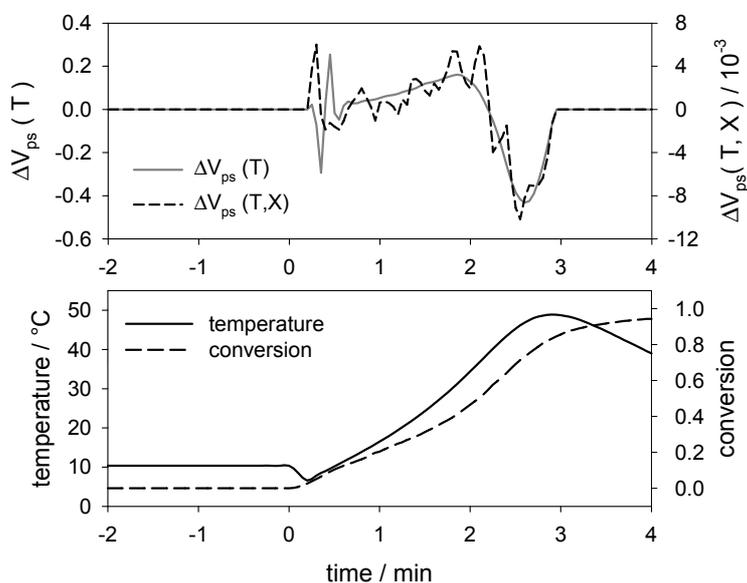


Figure 3: Upper part: profiles of ΔV_{ps} obtained both from only temperature measurements (solid line) and also using conversion (dashed line); lower part: temperature and conversion profiles ($T=10$ °C, $[\text{OAc}_2]=2$ mol L⁻¹, $[\text{H}_2\text{SO}_4]=40$ mmol L⁻¹).

5. Conclusions

In this work a novel approach of the early detection of runaway phenomena in chemical reactors has been presented. The detection criterion is based on the on-line evaluation of the phase-space volume change

(ΔV_{ps}) through techniques of phase-space reconstruction. The idea is to use as input variables to the model not only temperature measurements, but also the conversion values obtained indirectly through measurements of light absorbance.

The hardware part of the early warning detection system (EWDS) consists of i) a set of three Pt thermoresistances for measuring the temperatures both within the reactor and in the cooling jacket and ii) an UV-visible probe to measure the light absorbance. The EWDS was tested in the process of esterification of acetic anhydride and methanol, catalysed by sulphuric acid. A detailed kinetic model has also been presented, showing the mathematical issues related to the simultaneous resolution of the energy and mass balance equations. The EWDS has the advantage to calculate the reactor divergence (or ΔV_{ps}) without solving those balances by using phase-space reconstruction techniques. The quick addition of OAc_2 into the reactor led to a little decrement of the reactor temperature, due to an endothermic effect of mixing between the reagents. This phenomenon would hide or delay the detection of the onset of a runaway reaction if only temperature measurements were used as input variables to EWDS. The use of a measurable variable (such as the light absorbance) indirectly correlated to the conversion may improve the efficiency and reliability of the divergence criterion diminishing the detection time of the onset of the runaway, which is fundamental to take appropriate countermeasures and avoid potential accidents.

The EWDS is a versatile system which is in principle independent of the nature of the process, but the choice of the input variables is crucial for a correct operation of the detection criterion, as well as the determination of the threshold limit to give a warning alarm. Other variables can be used to describe the phase-space at each point (pressure, flow of the cooling fluid within the jacket, etc.) but there are very few sensors for the conversion evaluation which can operate on-line. The UV-visible probe is a good attempt to determine on-line the conversion, but several issues have to be overcome before its actual industrial implementation. In particular light scattering phenomena due to the possible presence of particles do not recommend its use for such kinds of process carried out in suspension and in emulsion, or when the solution is not very clear.

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