# Investigation of Thermal Runaway in Semibatch Chemical Reactors by an Early Warning Detection Device

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Notwithstanding the numerous studies in the last decades to prevent runaway reactions, the maintenance of stability in chemical reactors is still a current issue in industrial chemical plants. There is an urgent need to implement an efficient and robust algorithm capable of detecting in advance anomalous behaviours of the reactor temperature during exothermic processes, in order to take appropriate countermeasures and avoid accidents occurring.

In this work we have investigated the behaviour of an early warning detection device, based on the divergence calculation, to control the temperature within a laboratory-scale jacketed reactor, during the methyl methacrylate emulsion polymerization process carried out under semibatch conditions.

In order to test the reliability of the detection system, some failures or malfunctions were simulated, such as the rupture of the agitator or feeding pumps. Results showed that the divergence criterion was able to detect dangerous situations, by distinguishing in advance runaway phenomena from situations under normal operating control. In particular during the simulation of the agitator breakage, the presence of three thermo-resistance sensors located at different positions inside the reactor, allowed to identify the formation of hot-spots due to the missing of stirring. In that case the stability of the emulsion was lost and polymerization occurred with a higher chemical heat flow, with potential dangerous consequences such as the explosion of the reactor.

## 1. Introduction

In the last decades many efforts of chemical engineers have been focused on the development of preventive and safety systems for maintaining the stability in chemical reactors in which runaway phenomena may occur. Notwithstanding this, literature data well demonstrate that runaway events are unfortunately of frequent occurrence in batch and semibatch reactors, even if almost the totality of these phenomena lead only to production loss with some damage to the equipment (Westerterp and Molga, 2004). In chemical reactors the major problem is the loss of temperature control (Badrtamam et al., 2011): when the rate of heat generation by chemical reaction overtakes the rate of heat removal by the cooling system, there is a positive feedback mechanism, resulting in an auto-acceleration behaviour of the heat generation rate. Under this circumstance, if no countermeasures are taken, the large amount of heat generated in a very short time is accumulated in the system and can generate a strong increase in temperature and pressure; on the other hand this phenomenon may activate side and chain reactions with the possibility to destroy the reactor and make the plant inoperable (Russo et al., 2007). There are several methods in literature to detect early a runaway phenomenon, based on

the calculation of different quantities: the technique by Hub and Jones (1986) considers measurements from the system, that in case of chemical reactors come to be temperature measurements or its derivatives, or a combination of them; the method by Gilles and Schuler (1982) instead refers to model-based estimation techniques (i.e. Kalman filtering or equivalent). Nevertheless the different approaches, the issue to detect in advance hazardous states in an industrial chemical reactor is still open because of the wide range of processes and difficulty related to the solution of strongly non-linear equation systems and complex evaluation of parameters which are often time-varying.

In the frame of an European Project, an efficient and robust runaway detection system (EWDS: Early Warning Detection System) was developed and successfully tested both in small-scale and pilot plant chemical reactors, as well as in an industrial chemical reactor (Ampelli et al., 2004). The EWDS, based on the on-line calculation of reactor divergence, was able to detect in advance runaway phenomena without producing false alarms. The promising results obtained within the project, together with the current safety issues in chemical reactors, have encouraged us to study more in depth the applicability of the EWDS to highly exothermic reaction systems under different operating conditions. In this work we have investigated the thermal runaway occurring in semibatch chemical reactors during the emulsion polymerization process of methyl-methacrylate (MMA). In order to evaluate the response given by the EWDS during a possible anomalous behaviour of the reactor temperature, we have simulated some failures and malfunctions, such as the breakdown of feeding pumps or rupture of agitator. We have also carried out some batch experiments under isothermal control (at temperatures ranging from 60 to 90 °C) to simulate the extreme case of monomer accumulation.

Emulsion polymerization is a complex heterogeneous process used for the production of acrylic paints and adhesives, which presents some safety issues, related to the difficulty of maintaining a stable emulsion over the period of reaction and avoiding the separation of the mixture into two phases with the formation of dangerous hot spots. The stability of the emulsion is strongly dependent on the operating conditions (nature of emulsifying agent, reactor temperature, mixing pattern and stirring rate). For that reason the control of emulsion polymerization processes is of paramount importance and safety considerations are necessary to prevent runaway reactions (Maschio et al., 2004).

## 2. Theoretical analysis

The detection criterion used in this work is based on the reactor divergence (*div*) calculation. The method has been derived from non-linear dynamical system theory to characterize the sensitivity of chemical reactors (Bosch et al., 2004). By evaluating the divergence of the reactor it is possible to distinguish between runaway and non-runaway situations without producing false alarms.

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). The algorithm of the early warning detection system (EWDS) is able to calculate the divergence not by the resolution of the differential equations, but by using phase space reconstruction techniques from only temperature measurements (Zaldívar et al., 2003). This 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 systems we are interested in analysing. Once the state space has been reconstructed, in our case from only temperature measurements, the reactor divergence can be evaluated.

The divergence measures the rate of change of a phase-space volume $V_{ps}(t)$, following an orbit $\mathbf{x}(t)$. In this case Liouville's theorem (Arnold, 1973) states that:

$$V_{PS}(t) = V_{PS}(0) \cdot \exp\left[\int_0^t div\{\mathbf{F}[\mathbf{x}(t)]\} dt\right]$$

(1)

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

(2)

For chemical reactors, $\mathbf{F}[\mathbf{x}(t)]$ is given by the mass and energy balance equations, so the knowledge of the differential equations of the system would be fundamental to calculate the divergence. However, after several manipulations starting from Eq.(1), it is possible to arrive at the following expression:

$$div = \frac{\dot{V}_{PS}(t)}{V_{PS}(t)}$$

(3)

As $V_{PS}(t)$ is correlated to the total energy of the system, also its change, described by the phase-space volume flow rate $\dot{V}_{PS}(t)$, can be related with the total energy variation. In non-conservative systems, such as chemical reactors, if $div > 0$ $V_{PS}(t)$ also increases, while if $div = 0$ there is no change in the total energy. Since by definition the volume is always positive, $div > 0$ is equivalent to verify if:

$$\Delta V_{PS} > \Delta V_{PS}^{\lim} > 0$$

(4)

where $\Delta V_{ps}$ is the phase-space volume change between two time instants. A threshold value ($\Delta V_{PS}^{lim}$) has been 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. The methodology using the $V_{PS}(t)$ evaluation was recently presented and applied successfully for controlling semibatch reactors by Zaldívar and Strozzi (2010).

## 3. Experimental

Emulsion polymerization lab-scale experiments have been carried out under semibatch conditions with the aim to reproduce the same procedure usually adopted in the industrial production of acrylic paints. The reaction vessel is initially charged with an aqueous solution of MMA in the form of an emulsion (by using sodium dodecylsulphate as emulsifying agent) and then both the MMA and initiator solution (potassium peroxodisulphate in water) are continuously fed into the reactor, allowing the reaction to self-sustain by keeping the temperature within an established range, depending on the desired final properties. The rate of addition of the reactants has been determined by the rate of heat transfer. The presence of water in the reacting mass (~50 % vol.), which acts as means of heat dissipation, and the reaction mechanism through water-to-monomer micellar diffusion, allow to limit the chemical heat generation rate.
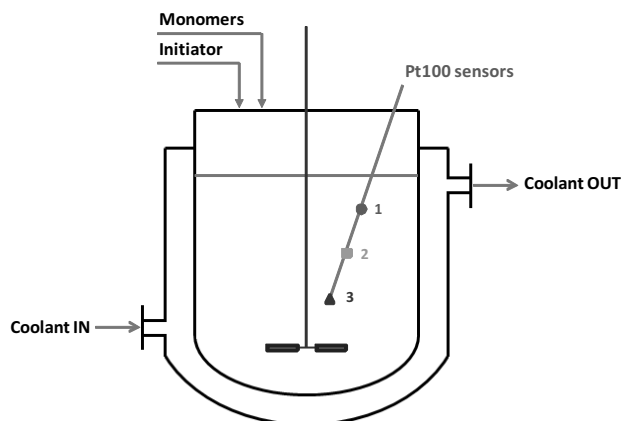


Figure 1: Scheme of the laboratory-scale reactor.

Figure 1 shows a scheme of the semi-continuous lab-scale chemical reactor. It is a stainless steel jacketed and stirred autoclave (supplied by Büchi Glas Uster) with a capacity of 2 L. Three Pt100 thermo-resistance sensors allow to measure the reactor temperature at different positions inside the reactor. The inlet jacket temperature is continuously adjusted by using a thermostat (Unistat Tango, supplied by Huber) through a proportional-integral (PI) controller, while the coolant flow rate is keeping as constant. However in industrial chemical reactors, the coolant (usually service water) is available at room temperature and control of temperature within the reactor is performed adjusting the water flow rate by opening or closing manually a valve by an operator.

The energy balance equation for the semibatch reactor is as follows (Ampelli et al., 2006):

$$\rho V c_P \frac{dT_R}{dt} = UA(T_J - T_R) + \dot{Q}_{chem} + \dot{Q}_{loss} + P_{stirrer} + \sum c_{Pi} \rho_i \left( \frac{dV_i}{dt} \right)(T_i - T_R)$$

(5)

## 4. Results and discussion

In order to test the reliability of EWDS, some failures or malfunctions were simulated and responses from the divergence-based algorithm were evaluated in terms of $\Delta V_{PS}$. From a historical analysis of accidents occurred in discontinuous or semi-continuous reactors, problems related to mixing and errors in reactor loading are some of the main causes of runaway reactions (Barton and Nolan, 1991). In order to create an accumulation of monomer within the reactor, we choose to simulate the breakdown of feeding pumps (monomer or initiator solution) and failure of the stirring system. Batch experiments were also carried out to simulate the extreme case of monomer accumulation. Figure 2a shows the temperature profiles for a typical semibatch experiment. The flow rates of monomer and initiator solution were chosen to keep the reaction temperature within the range 80-85 °C, reproducing as much as possible the industrial process to produce acrylic paints. Starting from the instant t=0 until ~55 min, the jacket provided heat to sustain the reaction ($T_J > T_R$), since the reaction rate was initially lower. Afterwards (t>55 min) the chemical heat flow increased and $T_J < T_R$. A gradual feeding of both the monomer and initiator allowed to broaden the total chemical heat production during the process and limit uncontrolled temperature increments. But If there was a strong accumulation of monomer, such as in the batch experiment, the reaction started very rapidly producing a temperature increment of ~30 °C, in spite of the strong decrement of the jacket temperature (until to 58 °C), as Figure 2b shows.
Figure 3a shows the maximum values of $\Delta V_{PS}$ obtained in each of the laboratory-scale experiments, calculated separately from the temperature measurements by the three thermo-resistances.
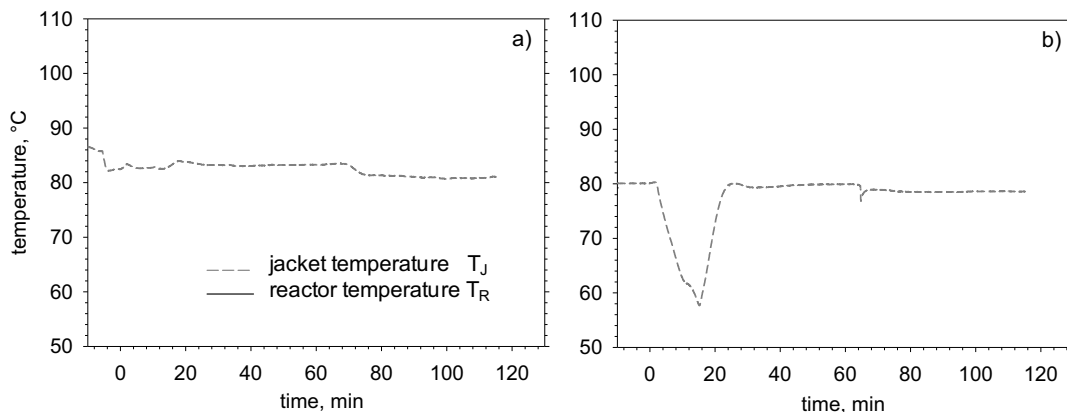


*Figure 2: Temperature profiles for a) semibatch experiment and b) batch experiment at 80 °C.*

The horizontal segment (dashed line) indicates the threshold value to be overcome for producing an alarm by EWDS, which depends mainly on the reactor size. In all the batch experiments (n. 1-4) the anomalous behaviours of the reactor temperature were well signalled by EWDS, with the higher value of $\Delta V_{PS}$ obtained by the bottom thermo-resistance sensor (n. 3), showing that hot spots were created in the region in proximity of the disc-turbine, where turbulence is higher due to the mixing pattern. In emulsion polymerization processes, a deep mixing is needed to enhance the diffusion rate of the radical initiator from the aqueous to organic (monomer) phase. Therefore mixing maintenance plays a fundamental role for a good performance of the process. In experiment n. 9 an accidental failure of the stirring system was simulated, in order to evaluate the behaviour of EWDS in such a potential situation. The stirrer was stopped for 15 min from t = 55 min, when the chemical heat flow was rather high. The reaction was temporarily quenched by the lack of mixing, but once the stirring system was restored

(after 15 min) it started again with a higher rate with respect to the standard conditions. The anomalous behaviour was immediately detected by EWDS with an alarm signal and in this case the top thermo-resistance sensor (n. 1) gave the higher value of $\Delta V_{PS}$. A possible explanation is that monomer, which was usually fed into the reactor from the head, was accumulated on the surface of the reacting mixture, producing a higher local chemical heat flow at the top with respect to the reactor core when mixing was re-established.
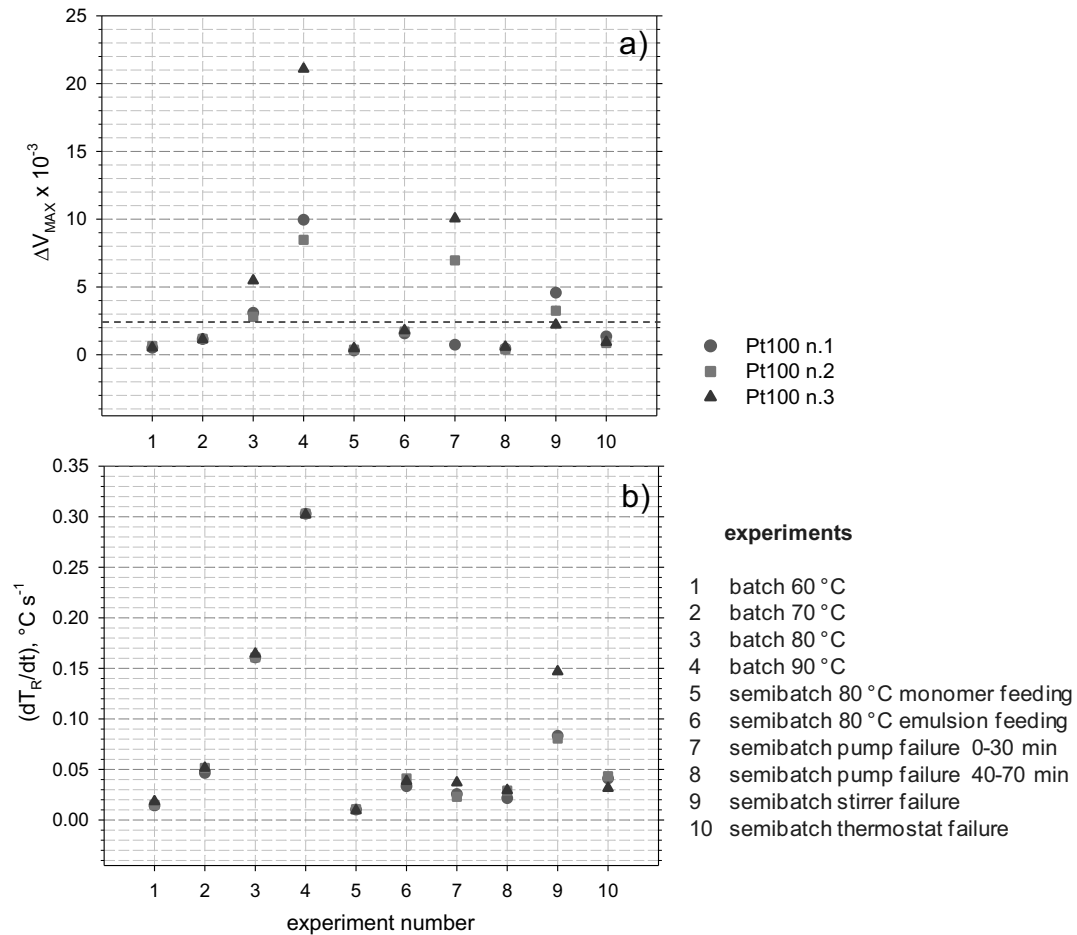


Figure 3: a) Maximum values of $\Delta V_{PS}$ and b) maximum values of the reactor temperature first derivates obtained in the laboratory-scale experiments from the three thermo-resistance sensors.

Another explanation is that the lack of homogeneity within the reactor led to different temperature profiles by the three Pt100 sensors which interacted differently with the jacket dynamics in the $\Delta V_{PS}$ calculation.

In order to understand better the superiority of the divergence-based algorithm, the maximum values of $\Delta V_{PS}$ can be compared with the maximum values of the reactor temperature first derivatives shown in Figure 3b. As it can be observed, both Figures 3a and b have a similar profile, but the algorithm amplifies the difference between low and high values. This enhances the segregation between safe and unsafe conditions, i.e. the detection of runaway.

## 5. Conclusion

In this work we presented results obtained by using an early runaway detection device based on the reactor divergence calculation. The EWDS was tested on a laboratory-scale jacketed reactor, during the MMA emulsion polymerization process under semibatch conditions. Experiments allowed to evaluate the reliability of the implemented algorithm through some failure simulations which caused local accumulations of monomer within the reactor.

Results showed that EWDS was able to detect dangerous situations, by distinguishing in advance runway phenomena from situations under normal operating control. In particular during the simulation of the agitator breakage, the presence of three thermo-resistance sensors located at different positions inside the reactor, allowed to identify in advance the formation of hot spots due to the lack of mixing. In that case the stability of the emulsion is lost and polymerization occurs with a higher chemical heat flow, with potential dangerous consequences such as the explosion of the reactor, if no countermeasures are adopted.

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