Reaction Calorimetry and UV-Vis Spectrophotometry Integration aimed at Runaway Reaction Early Detection

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The use of different calorimetric techniques for process design and scale up is well consolidated, allowing the definition of the kinetic and thermodynamic of the process and the evaluation of several parameters useful to optimization and process safety. During a calorimetric analysis temperature (or a temperature difference) is measured; from experimental data it is for example possible to calculate the heat flow and the heat evolved by the reaction and consequently the conversion and the reaction rate constant just if kinetics of the reaction is known. To overcome these limitations and to obtain additional information about the reaction, it is possible to couple to a calorimeter different type of sensors such as densitometers, refractometers, electrochemical, chromatographic and spectrophotometric probes (Schwedt, 1997). Some of these sensors are able to log data on line during the process and so to monitor the reaction at the same time of the calorimetric analysis. For safety aims, it is important to choose a sensor whose time for the analysis is comparable to the reaction time in order to have an accurate profile of the monitored parameter during the reaction (Moritz, 1989).

In a previous study (Parisi, 2002; Ampelli et al. 2003) an Ultra Violet - Visible spectrophotometer was integrated to a reaction calorimeter to analyse the kinetic of a specific reaction. In this work a similar UV - Vis probe has been coupled to an isoperibolic reaction calorimeter in order to study the feasibility of the application of an Early Warning Detection System (EDWS) to a spectrophotometric signal. The innovation of this integration of techniques is the analysis of the spectrophotometric signals with a reactor stability criterion based on divergence theory in order to check if this method of monitoring allows detecting runaway reactions at an early stage of the process, when it is still possible to take protective measures.

1. Experimental

The reaction under study was the esterification of acetic anhydride and methanol catalysed by sulfuric acid, because its kinetics and thermodynamic are well-known and suitable to be monitored in the UV-Vis range: the distinctive feature of the process is the difference between the spectra of the reagent and the products (Figure 1-a): the Absorbance of the acetic anhydride has a maximum at about 265 nm (where the value of Absorbance is greater than 1) and the acetic acid and methyl acetate spectrum has a maximum at 235nm (where the Absorbance is lower than 1). This esterification is a relatively safe reaction for studying thermal runaway in the laboratory and, because of the modest reaction enthalpy and low activation energy, it provided a severe test for the runaway criterion implemented in the EWDS (Strozzi, Zaldívar, Kronberg, Westerterp, 1999) as already shown by Casson, Maschio, Milazzo and Lister (2012).

The experiments were carried out in a 250 ml stainless steel stirred and jacketed calorimeter in isoperibolic conditions. The reactor was equipped with three Pt100 thermoresistances (to measure reactor temperature and the inlet and outlet jacket temperatures) connected to a multimeter scanner card and to a PC by a GPIB-USB interface; inside the reactor was also placed the UV-Vis spectrophotometric probe, which was connected to the UV light source and the spectrophotometer. In Figure 2 a schematic diagram of the experimental set up and pictures of it are reported.

In order to test the effectiveness of the EDWS when using different signals, it is necessary to run an experiment that undergoes runaway conditions: the concentration of catalyst was 100 mol/m^3, 0.4 moles of acetic anhydride were used, and 180 ml of MeOH and the temperature was set at 23 °C. The experiments

was performed by adding pure acetic anhydride (99%, Sigma Aldrich) to pure methanol (100%, Sigma Aldrich) and when the system went to thermal equilibrium (after the effect of the enthalpy of mixing of acetic anhydride), the catalyst was added to the reactor. All the reagents were added at the set temperature for the test (they were kept in the same thermostatic bath containing the jacket fluid). The speed of the stirrer was set at 400 rpm. This value is enough to have a good mixing in the system (which is important specially when adding the catalyst, whose viscosity is very different from the one of the solvent) and it is enough to break bubbles that could form: this aspect is important when working with an immersion probe, as the UV-Vis used in this work, because if bubbles enter the probe, the transmission of the spectrophotometric signal becomes too noisy or null and not suitable for calculations.

As shown in Figure 1-b, applying Hub and Jones criterion to the temperature data of the reaction it is possible to identify the onset for the runaway at 270 s (T_{onset} = 24.31 °C), immediately after the addition of sulfuric acid. The maximum of temperature for the test was 50.16 °C (ΔT=27 °C) at 324 s.
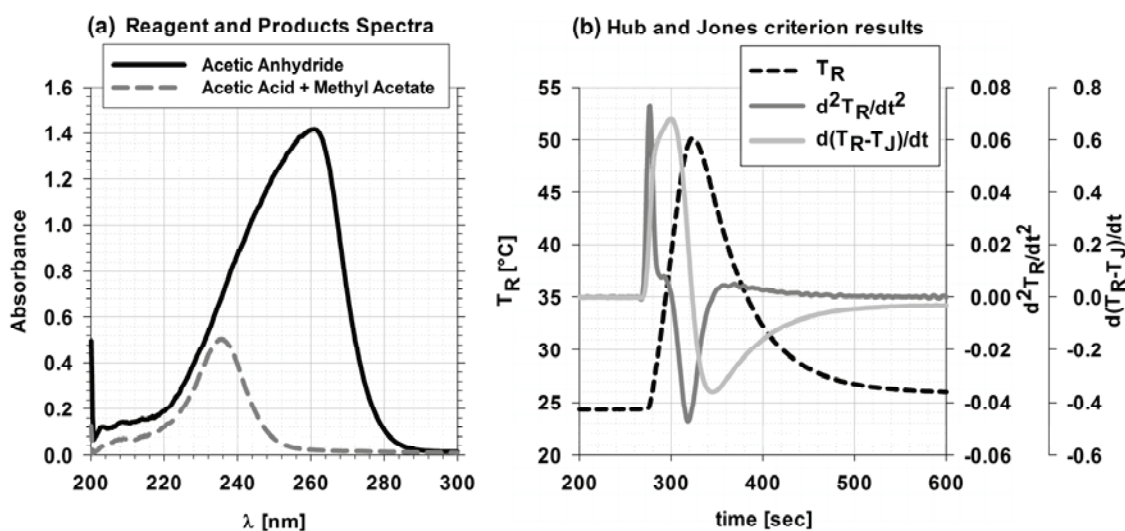

Figure 1: a) UV spectra of acetic anhydride and products of the esterification. b) Hub and Jones criterion applied to the experimental temperature profile.
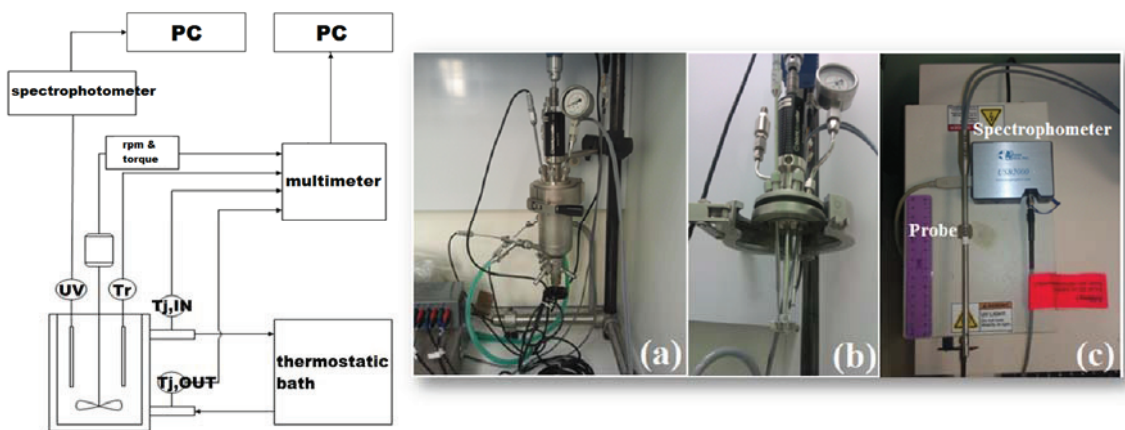

Figure 2: Schematic diagram of the experimental set-up: a) reaction calorimeter, b) probes inside the reactor, c) UV-Vis spectrophotometer.

2. Early Warning Detection System application

Generally, a EWDS consist in a hardware and software sensor that permits, by the direct measurement of temperature in the reacting system, the early detection of the onset of a runaway situation (Casson & Maschio, 2012; Ampelli et al., 2006; Bosch et al., 2004). It is composed by:

1. An interface with the process for the acquisition of the tests data (monitoring);
2. A criteria which distinguishes the thermal explosion by the isothermal reactions (takeover);
3. A procedure to start the alarms (detection and assessment).

At step 2, the EWDS uses the monitored data of temperature or the signals logged by spectrophotomer and calculate the phase space volume:

$$V(t) = \frac{V(t) - V(t - \Delta t_1)}{\Delta t_2} \qquad (1)$$

where $V(t)$ is

$$V(t) = \left| \det \begin{bmatrix} s(t) - s(t - \Delta t) & 0 \\ 0 & s(t) - s(t - 2\Delta t) \end{bmatrix} \right| \qquad (2)$$

In which $s(t)$ is the signal of the monitored parameter. According to Strozzi and Zaldívar criterion, the system undergoes a runaway reaction when the variation of the phase space volume is greater than zero, but in the practice (to avoid false alarms due to the presence of noise in the signals, Bosch et. al. 2004), the alarm is emitted when the variation of the phase space volume is greater than a threshold value (chosen depending on the system under study):

$$\Delta V(t) > \Delta V_{LIM} \qquad (3)$$

3. Results

In this section the results of the application of the EWDS to temperature and spectrophotometric signals will be shown.

3.1 Application to Temperature signal
The application of the EWDS to temperature data gave the results shown in Figure 3: the detected onset for the reaction was at 271 s, similarly to the Hub and Jones application, so the runaway was detected 53 seconds before the maximum of temperature (the ΔV_{LIM} was 10^{-4}, on the basis of the analysis of the signal when there is no reaction).
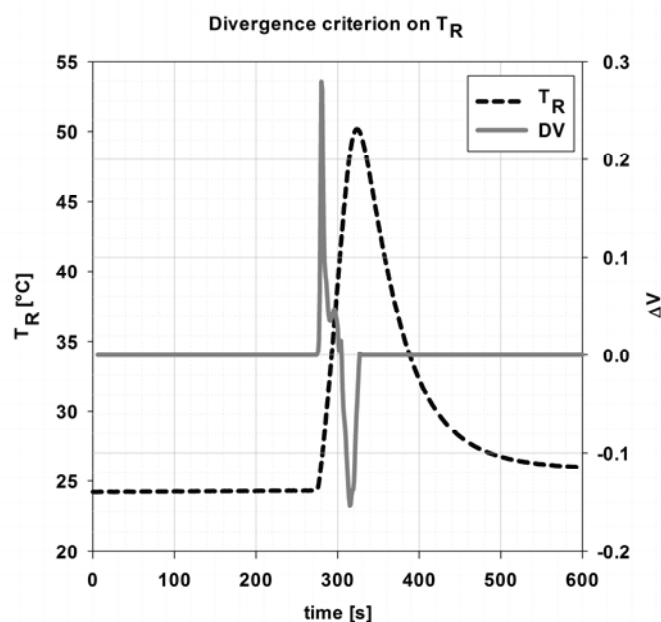

Figure 3: EWDS applied to temperature data (esterification of 0.4 moles of acetic anhydride, $[H_2SO_4] = 100$ mol/m^3)

3.2 Application to Spectrophotometric signals
The software for the acquisition of the spectrophotometer allowed us to monitor 8 different wave-lengths on line during the process (Figure 4), chosen in the range before and after the characteristic Absorbance

peak of acetic anhydride. The time-scaling in the x-axis of the Graphs is different from the previous figures because it refers to the acquisition time of the spectrophotometer. The EWDS was applied to signal of Absorbance (monitored during the experiment) and Intensity, calculated according to Beer-Lambert law:

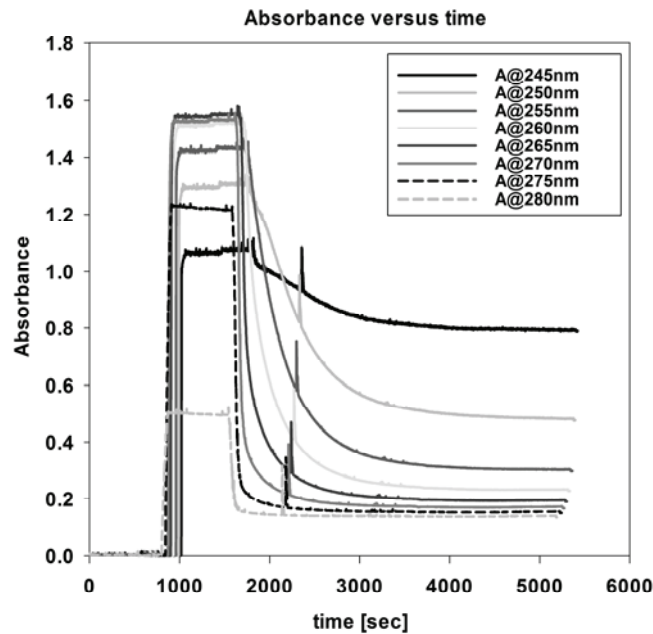$$A_\lambda = -\log_{10}\left(I_\lambda / I_{0,\lambda}\right) \qquad (4)$$

Figure 4: Absorbance vs. time (esterification of 0.4 moles of acetic anhydride, $[H_2SO_4] = 100$ mol/m^3)

Figure 5-a shows the results of the application of the EWDS to the Absorbance monitored at 275nm, which is a wave-length near to the peak of the acetic anhydride spectrum (Figure 1-a). It is possible to notice that the EWDS does not give a good result in the detection of the onset when applied to Absorbance: it is not possible to define a ΔV_{LIM}, and the profile of $\Delta V(t)$ does not show a peak when adding catalyst. There is a signal when adding acetic anhydride and also for some noise in the transmission of the signal. This makes the analysis not reliable and subject to false alarm. This monitoring cannot be used for process safety purpose.
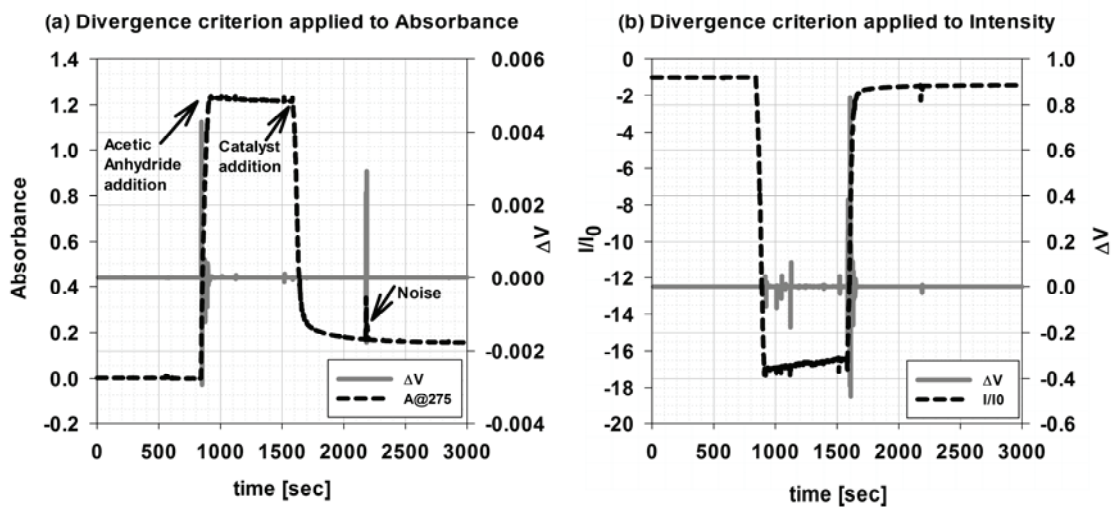

Figure 5: EWDS applied to Absorbance (a) and Intensity (b) signals at 275 nm

The application of the method to the Intensity signal gave different results. The algorithm is able to detect the runaway onset 59 s before the maximum of temperature is developed (Figure 5-b, ΔV_{LIM} = 0.1) and the noise is more smoothed than in the previous case.

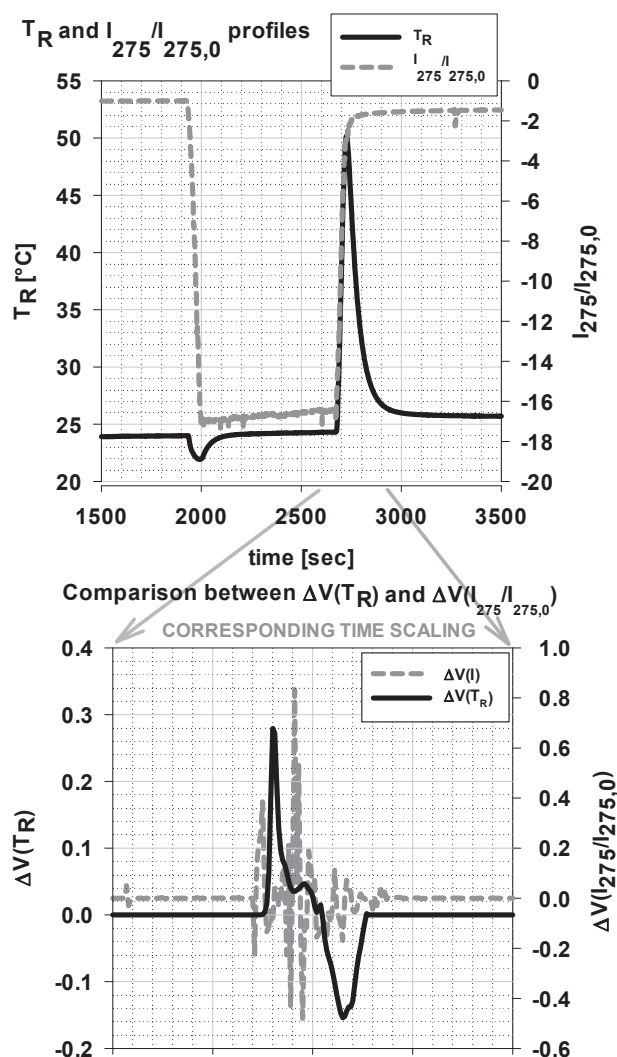The comparison between the temperature and intensity signals application is reported in Figure 6.

Figure 6: Comparison between EWDS applied to temperature and Intensity signals

4. Conclusions

The innovation of the integration between the calorimetric and the spectrophotometric techniques is the application of an Early Warning Detection System based on divergence criterion to spectrophotometric signals in order to check if this method of monitoring high reactive processes could lead to a greater advance in the detection of the thermal explosion with respect to temperature monitoring.

The results are that EWDS does not give a good result in the detection of the onset when applied to Absorbance signal: it is not possible to define a ΔV_{LIM}, and the profile of ΔV does not show a peak when adding catalyst. This makes the analysis not reliable and subject to false alarm. This monitoring cannot be used for process safety purpose.

The application of the method to the Intensity signal gives different results. There is the detection of the onset 1 second before the profile of Intensity starts to decrease and the noise is more smoothed than in the previous case. The algorithm is able to detect the runaway start 59 seconds before the maximum of temperature is developed (6 seconds before the application to temperature signal). This monitoring could be used at the same time than temperature monitoring, in order to improve the efficiency of the system in

detecting runaway reaction decreasing the possibilities of false alarms. The method could be very useful if applied to those processes in which the accumulation of a reaction intermediate, that develops no temperature increase in the system, could lead to thermal explosion by starting a secondary reaction: in this case the EWDS working on Intensity signal (that can be monitored on line, during the process) could detect the runaway at a very early stage, when the temperature in the system could still be kept under control by some protective measure activated after the alarm.

The integration of calorimetry and spectrophotometry gave good results: spectrophotometry is able to supply useful data for process modelling and also for safety purpose. This methodology could be easily implemented in a plant-scale reactor providing a valid process safety monitoring against runaway reactions.

The divergence criterion account reasonably well for the thermal runaway in the considered reaction. An advantage of the Strozzi and Zaldívar criterion over existing criteria is that it is possible to reconstruct, using non-linear time series analysis techniques, the divergence of the system from a monitored signal without the necessity to have a model for the process. Hence, all the results and conclusions obtained from an off-line analysis may be extended and applied on-line to develop a general early warning detection device, based on a robust criterion.

Symbols

ΔV_{LIM} phase-space volume threshold value, [-]

$\Delta V(t)$ variation of phase-space volume with time, [-]

$[H_2SO_4]$ catalyst concentration, [mol/m3]

A_λ absorbance of the transmitted light, [-]

$I_{0,\lambda}$ intensity of the incident light, [-]

I_λ intensity of the transmitted light, [-]

t time, [s] [min]

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