CHEMICAL ENGINEERING TRANSACTIONS

VOL. 32, 2013

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at: www.aidic.it/cet

Chief Editors: Sauro Pierucci, Jiří J. Klemeš

ISBN 978-88-95608-23-5; **ISSN** 1974-9791

DOI: 10.3303/CET1332091

Sensitivity Analysis for the Thermal Stability Criteria of Hydrogen Peroxide

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Chemical reactors carrying on exothermic processes may undergo to runaway reactions. To prevent from this hazard, Early Warning Detection Systems (EWDSs) can be used in industry, because they allow the on-line detection at an early stage of the runaway. The stability criterion of Hub and Jones is frequently implemented in EWDSs. Despite its simplicity during the detection step (the criterion is based just on measurements of the temperatures inside the reactor and jacket), the effectiveness in distinguishing between dangerous and non-dangerous occurrence is strongly affected by the presence of noise in the monitored signals. Furthermore, the numerical methodology for the calculation of the derivative of the measured signals may be of great importance for the definition of alarm conditions. In this paper, the sensitivity analysis of the performances of Hub and Jones criterion with respect to the Savitzky and Golay smoothing filter degree is discussed. The analysis is applied to experimental data on the decomposition of hydrogen peroxide 35%wt carried out in a Thermal Screening Unit.

1. Runaway Reactions and Reactor Stability Criteria

Many industrial reactions are exothermic (polymerization, hydrogenation, neutralization, combustions …) so overheating of the system is likeable to occur. A runaway reaction (or thermal explosion) is the direct consequence of overheating in a chemical vessel. Different measures can be implemented to prevent the risk of a runaway reaction and to mitigate its possible consequences at different levels (HSE, 1998):

i. Reduction of the hazards by inherently safer design;
ii. Prevention of the risk by process control;
iii. Mitigation of the consequences by protective measures.

The use of EWDSs belongs to the second level. EWDSs consist in hardware and software parts that allow, by the direct on-line measurement of a variable of the reacting system, the early detection of the onset of a thermal explosion. In this process, three main steps can be sketched: monitoring the variable of the system through an interface with the process; Taking-over on the basis of a criterion which distinguishes the runaway from the normal operation; or Detecting and Assessing the anomalous conditions and starting the alarms and necessary measures. The Hub and Jones criterion (H&J, 1986) has been largely adopted and implemented in process industry due to its simplicity and cost effectiveness with respect to more detailed techniques (Westerterp & Molga, 2006). Indeed, the methodology does not imply neither the knowledge of the overall kinetic of the reaction process or in-depth process control, but only the data retrieved from thermocouples installed in the bulk reactor and the jacket temperature. To be specific, the method is based on the increase of heat evolution as the hazard identification criterion and implies the positive value of both the second derivative of the reactor temperature and the first derivative of the temperature difference between the reactor and the jacket:

$$\frac{d^2T_R}{dt^2} > 0 \tag{1}$$

Please cite this article as: Casson V., Salzano E., Maschio G., 2013, Sensitivity analysis for the thermal stability criteria of hydrogen peroxide, Chemical Engineering Transactions, 32, 541-546 DOI: 10.3303/CET1332091

$$\frac{d(T_R - T_J)}{dt} > 0 \tag{2}$$

Although its simplicity, the criterion is complicated by some factors which generally affect the temperature measurement and its derivative: even though this criterion is independent from the characteristics of the process, the method is largely affected by noise amplification. Furthermore the criterion does not work in some cases or for autocatalytic reactions and semi-batch reactors (Bosch et al., 2004). These conclusions are mainly related to the difficulty of calculating the divergence by using one dimension only (the temperature). The use of term divergence is not casual: the Hub and Jones criterion (based on differential) has been demonstrated to be equivalent to the numerical divergence criterion (div > 0, or the equivalent integral version $\Delta V(t)/V(t)$, where $V(t)$ is the volume phase, see Strozzi et al., 1999, for more details) if only one embedded variable (the temperature) is considered (Bosch et al., 2004). In the following sections, these issues and different options are analyzed for noise reduction. For the sake of the discussion, the experimental data obtained for the runaway decomposition of hydrogen peroxide 35 %wt in a Thermal Screening Unit (TSu) have been used. Two grams of hydrogen peroxide 35 %wt solutions have been then tested isothermally in stainless steel sample holders at namely 90°C, 95°C, 100°C and 110°C. The detected onset temperature for the runway reaction was found to be around 96°C. Details of the experimental system may be found in previous works (Casson and Maschio, 2012 and Casson et al. 2012).

2. Data Smoothing Technique and Sensitivity Analysis

Any signal related to the measurement of a variable of interest is affected by noise. Noise may be either observational (also called additive and, if identified, subtracted from the signal) or dynamic (that influences the dynamic of the system and not easy to account for). The two contributions are generally undistinguishable. The observational noise may be eliminated by filters which are based on the application of Fourier techniques (linear filters designed to eliminate some specific frequency from the signal) or non-linear noise reduction methods (Kostelich and Screiber, 1993). However, unless oscillating system, the Fourier techniques may be not efficient, as demonstrated by Lubansky et al. (2006), whereas the validity of the classic non-linear algorithm based on Savitzky–Golay (SG) method (Savitzky and Golay, 1964), which utilizes an array of weighted coefficients as a smoothing function to convolute uniformly-spaced m neighboring points, has been demonstrated. The SG method has the great advantage that the n-th derivative can be obtained from discrete data by the same algorithm. Details on the numerical methodology can be found elsewhere (Press et al., 1992). For the scope of divergence calculation, in this work we have used a quadratic function for smoothing and first derivative and a higher order function for the second derivative (Madden, 1979):

Smoothing Function: $$p_s^{(0)} = \frac{3\left(3m^2 + 3m - 1 - 5s^2\right)}{(2m+3)(2m+1)(2m-1)} \tag{3}$$

1st Derivative of reactor Temperature with respect to time: $$p_s^{(1)} = \frac{3s}{(2m+1)(m+1)(m)} \tag{4}$$

2nd Derivative of reactor Temperature with respect to time:

$$p_s^{(2)} = \left(-\frac{105}{2}\right)\cdot\frac{15\left(6m^2+6m-5\right)s^2 - 21\left(4m^4+8m^3-4m^2-8m+5\right)s^2 + 5m\left(2m^5+6m^4-m^3-12m^2-m+6\right)}{(2m+5)(2m+3)(2m+1)(2m-1)(2m-3)(m+2)(m+1)(m)(m-1)} \tag{5}$$

where *s* ranges in [-m, m] and is the number of data point. The sensitivity analysis on noise reduction has been performed by changing the value of m in the range 5-100.

3. Results of the Sensitivity Analysis on Hub and Jones criterion

For the aims of this work, we have considered the temperature histories for peroxide decomposition carried on at 100 °C as obtained experimentally in the thermal screening unit TSu. Figure 1 shows the results of the obtained temperature curve, the first derivative and the first derivative of the difference between the same temperature and the jacket temperature as in Eqs 1-2) by adopting two different values, namely m = 5 and m = 21 either for smoothing or for derivation. The constant, time step of the experiment is 0.01 s. With respect to smoothing, it is worth noting that the value of m = 21 is a typical value adopted for fast, deflagration tests. On the other hand, with respect to derivative, the use of 5 point differentiation is equivalent to the one-embedded parameter methodology for the divergence criterion performed on the basis of temperature data, at least in the case of isoperibolic reactor, as demonstrated by Bosch et al. (2005).

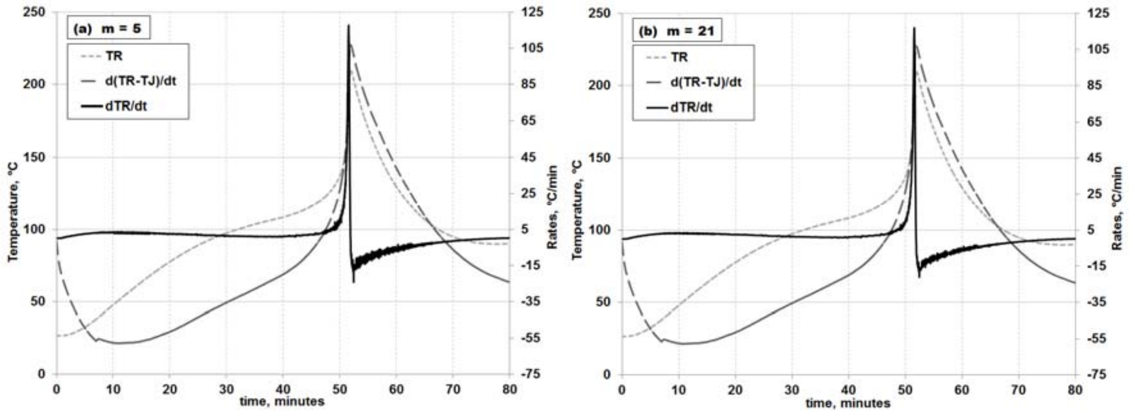

Figure 1: Temperature, first derivative of T_R and (T_R-T_J) with noise reduction obtained by using SG methodology with 5 points (a) and 21 points (b).

Results show clearly the substantial over-imposition of the temperature curve. The first derivative shows a near-constant value for almost the entire duration of the test, and a clear divergent behavior (the decomposition reaction), at about 80 °C, which represents the temperature limit for operation with hydrogen peroxide. Besides, if considering the difference between the temperature and the jacket temperature, it is clear that the correspondent first derivative of the difference is negative (thus the H&J criteria is not verified) unless in the proximity of the spike. Filtering the curves, even with large values of m does not modify the numerical significance of the three curves exposed in the figure. Similar behavior may be observed for pressure. To this regard, Figure 2 shows the pressure signal, for the same experiment at 100°C in the TSu, and with smoothing parameter m = 5 and m = 21.

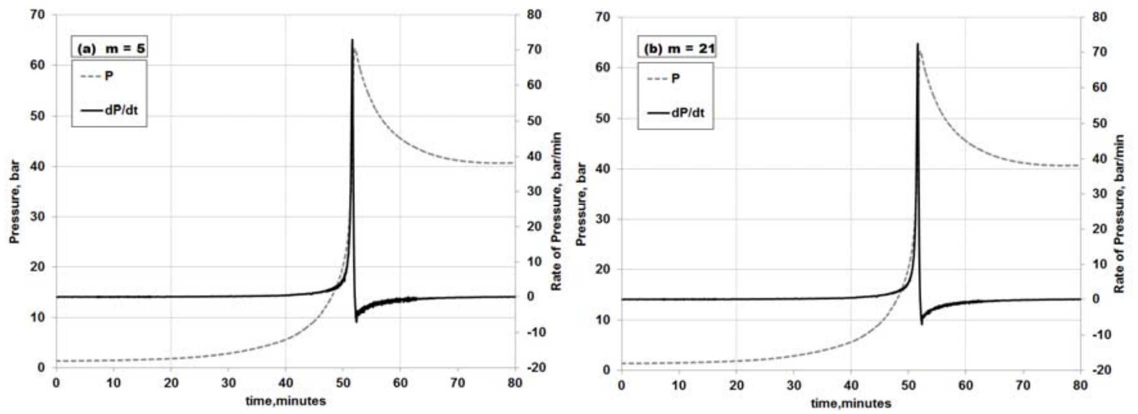

Figure 2: Pressure and its first derivative with noise reduction obtained by using SG methodology with 5 points (a) and 21 points (b). Test on 35 %wt hydrogen peroxide decomposition at 100°C.

Again, the pressure history overlaps exactly with the smoothed curves and does not modify the trends representing the divergent behaviour. However, for the sake of EWDS, it is worth noting that the trigger time for the pressure spike is almost coincident with the overpressurisation of the system. That further confirms that the jacket temperature is essential when non-isoperibolic reactors are adopted, and that using the pressure as secondary variable is confirmed to be less conservative than temperature in the H&J criterion (which has been however demonstrated to be often over-conservative by Bosch et al. (2004). For the application of H&J and for any high-order divergent criterion as the methodology of Strozzi and Zaldivar, the second derivative is however more sensitive to the noise issues. In Figure 3 the profiles of the second derivative of the reactor temperature with respect to time are reported for the data shown in Figure 1. The SG (as in Eq.5) has been adopted, by using m = 5 and m = 21 as for the previous analysis.

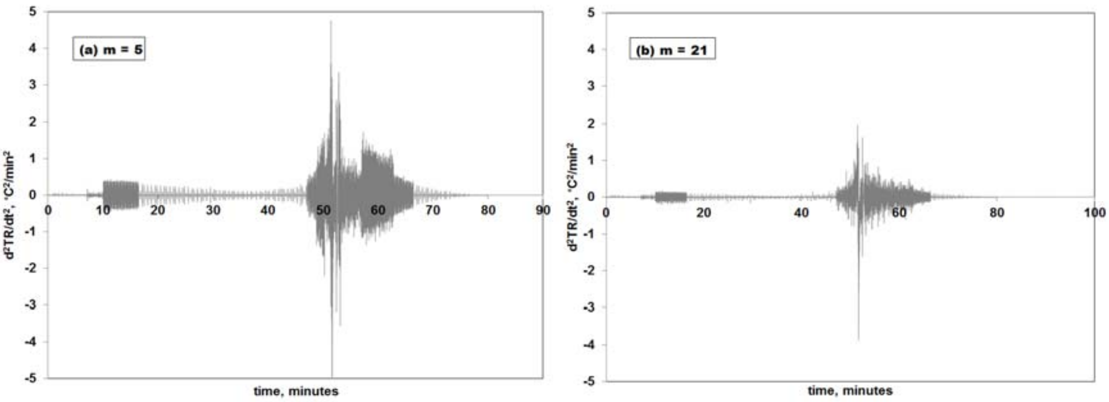

Figure 3: Second derivative for the temperature history reported in Figure 1 with noise reduction obtained by using SG methodology Derivative obtained by using m= 5 (a) and m = 21 points (b).

Figure 3 shows that large differences arise when passing from m = 5 and m = 21, and that a strong reduction of the noise is obtained by filtering over 21 points. On the other hand, it is quite obvious that a stronger filtering means a loss of information. This issue will be further analysed in future work but the obtained results can be however considered in the light of over-conservative results which are typically recognized in the application of H&J. For the specific case of the analyzed decomposition of hydrogen peroxide, the alarm is clearly possible by using H&J criterion. That is observable in the next Figure 4, where the two derivatives are only visible if both positive as binary value (0 – 1), for m = 21. Figure 4 shows clear that the prediction of the temperature spike may be observed at minute 46 (6 minutes before its occurrence which is at minute 52), thus partially confirming the effectiveness of H&J criteria for the sake of EWDS. High-order refinement for early warning detection system may be obtained by using a two parameters methodology (Bosch et al., 2004), which in differential form may be written as:

$$\mathrm{div} = \frac{\Delta V(t)}{V(t)} = \frac{d^2x}{dt^2} \Big/ \frac{dx}{dt} + \frac{d^2z}{dt^2} \Big/ \frac{dz}{dt} > 0 \qquad (6)$$

where V is the phase state volume, x is the temperature and z is any additional variable respect temperature which is measured in the reactor. This variable is typically the conversion. In this work, the pressure is available as secondary variable. Hence a further sensitivity analysis is needed.

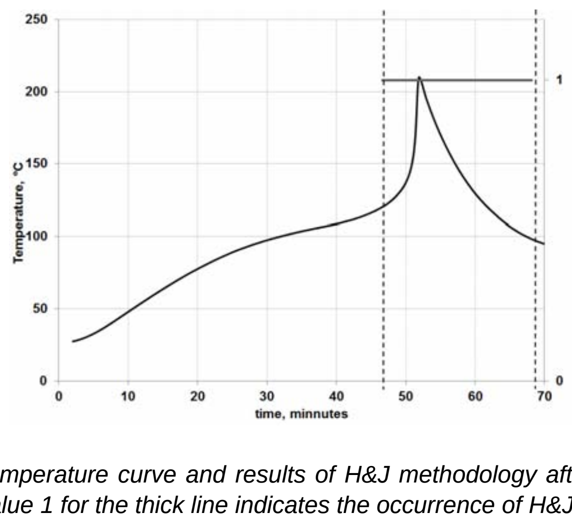

Figure 4: Experimental temperature curve and results of H&J methodology after filtration with SG (Eq.5) and m = 21 points. The value 1 for the thick line indicates the occurrence of H&J criterion.

Figure 5 shows the second derivative of pressure with time.

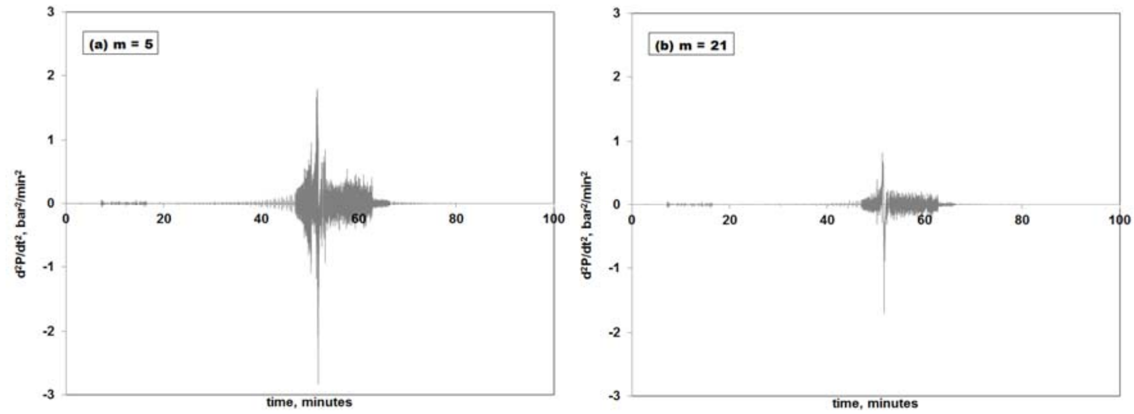

Figure 5: Second derivative for the pressure history reported in Figure 1 with noise reduction obtained by using SG methodology Derivative obtained by using m = 5 (a) and m = 21 points (b).

It is clear that the behavior of pressure second derivative follows that of temperature. The range of oscillation is shorter but however the time of alarm onset is very close either with respect the temperature or for both the filtration degrees. Finally, the calculation of the divergence based on Eq.6 is reported in Figure 6. The data reported in Figure 6 shows that if unfiltered or low-degree (m=5) is applied, the divergence shows large oscillation (due to the pressure curve) which may be only analysed by cut-off values. The onset of alarm is only visible at 52 minutes which essentially overlaps with the temperature spike. Hence, the H&J criterion, for this particular experimental system, is surely conservative, but however predicts the temperature rise with advance.

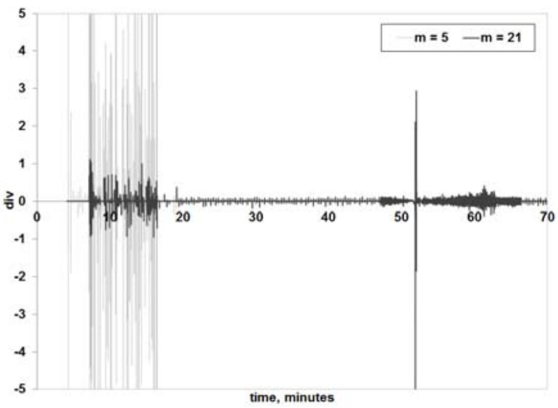

Figure 6: Calculation for the case at 100°C. The green curve is the divergence with filtration degree at m=5, the black curve represents m=21.

4. Conclusions

The sensitivity analysis of the performances of Hub and Jones criterion with respect to the Savitzky and Golay smoothing filter degree has been discussed. The analysis is applied to experimental data on the decomposition of hydrogen peroxide 35%wt carried out in a Thermal Screening Unit. The use of a pseudo adiabatic unit permits to analyze the performances of the thermal runaway criterion of an reacting system in conditions very close to a real runaway. The SG 21 points for either smoothing, as low-pass data filtering or for first or second derivative is a useful methodology. The obtained results can be easily applied to other higher-order methodology for the on-line control of divergent reactions.

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