



# Hydrogen Peroxide Decomposition Analysis by Screening Calorimetry Technique

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In a study of Nolan and Barton in 1987 it was already underlined that process safety is primarily based on an accurate and detailed knowledge of the thermo-chemistry of the reaction and afterwards on a correct scale up and management.

In this work the experimental analysis of hydrogen peroxide decomposition is proposed by the use of a modified pseudo-adiabatic and non differential thermal analysis screening calorimeter.

The objective of the work is to study the decomposition of this peroxide and its effects in different operating conditions, particularly when a runaway reaction occurs and may be the cause of incidents leading to fires and explosions and losses of chemicals in general. Runaway reactions have the potential to inflict considerable damage if appropriate emergency measures are not in place.

Hydrogen peroxide is liable to decompose exothermically at also at ambient temperature. According to the Major Accident Reporting System (MARS) data bank, in the last 30 years there have been several major accidents involving peroxides and in particular almost 70 % of these accidents were caused by hydrogen peroxide. This is the main reason for which we focused our study on this substance.

The Thermal Screening unit (TS<sup>u</sup>) used to carry out the experiments permitted us to find easily useful results such as onset temperature (the temperature at which the decomposition starts), time to maximum rate (the time at which the rate of temperature is maximum) and maximum pressure reached during the reaction. Adding an expansion vessel to the instrument made possible to study the reaction in different initial conditions of pressure (up to 12 bar), and so to evaluate the consequences of it on some critical parameters used to identify runaway reactions. The experimental data obtained by this simple and cost efficient technique have to be validated by experiments run in more complex calorimeters, such as adiabatic and reaction calorimeters, but the use of the TS<sup>u</sup> makes it possible to reduce the number of experiments and to have a first step in risk analysis studies as key in scaling up of processes.

An Early Warning Detection System (EWDS) based on divergence criterion is finally applied off-line to the data regarding the decomposition. Both temperature and pressure profiles have been evaluated in order to compare the efficiency of the method to these parameters in terms of advance in detecting the runaway reaction.

## 1. Introduction

In chemical reactors may happen that the heat generated by the reaction is greater than the heat removed by the cooling system, leading the system to an increase of the heat accumulated with a consequent acceleration of the kinetics. According to Semenov theory, the reagent mass goes toward a

self heating until a particular point is reached; this phenomenon is known as *runaway reaction* or *thermal explosion*, which represents the loss of thermal control of the reacting system (Cardillo, 1998). In a study of Nolan and Barton (1987) it is underlined that process safety is primarily based on an accurate and detailed knowledge of the thermo-chemistry of the reaction and then on a correct scale up and management:

- 21 % for lack of understanding in the chemistry and thermodynamics of the process or inadequate reactor design (during the design and scale up steps);
- 40 % for inadequate of control and safety devices and of procedures/operator training;
- 17 % for mischarging of reactants;
- 22 % for other factors (including equipment leaks).

Runaway reactions may cause considerable damage like toxic and/or flammable releases or even a pressure increase in the reactor leading to the collapse of the vessel; hydrogen peroxide is an unstable substance because of its chemical bonds: it is liable to decompose exothermically also at ambient temperature (AIChE, 1995).

In order to prevent the thermal explosion an on line Early Warning Detection System (EWDS) could be developed to identify warning situations, which should be supported by theoretical criteria for the prediction of the onset of runaway reactions; in literature it is possible to find many different stability criteria for chemical reactors (Varma and Morbidelli, 1999) that can be implemented in an EWDS system.

Different studies proved that temperature is a more sensitive parameter in runaway detection, but in case of formation of non-condensable gases pressure increase can be very high and so pressure monitoring can be used as a parameter for early detection of anomalous behaviour of the system (Bosch et al., 2004).

## 2. Thermal Runaway Criteria

Historically the first on-line criterion was the Hub and Jones one. It is sensitivity based and independent from a model for the process (Hub and Jones, 1986), so it has been widely used in industrial applications for its simplicity. This criterion states that the runaway reaction starts when both the first and second derivatives of the reactor temperature with respect to time become positive; these two terms are originated by the expression of the energy balance derived with respect to time:

$$Q_{\text{chem}} = \rho \cdot V \cdot c_p \cdot \frac{dT_R}{dt} + U \cdot S \cdot (T_R - T_J) \quad (1)$$

Equation (1) shows that the heat accumulation term is always increasing when the following conditions are verified:

$$\frac{d(T_R - T_J)}{dt} > 0 \quad \text{and} \quad \frac{d^2 T_R}{dt^2} > 0 \quad (2)$$

where  $T_R$  is the temperature inside the reactor and  $T_J$  is the jacket one; equation (2) represents that the reaction produces more heat than the one loss by the system, which is the cause leading to thermal explosions.

The EWDS used in this work is based on the divergence criterion by Strozzi and Zaldivar, which uses the Lyapunov exponents to define sensitivity (Strozzi and Zaldivar, 1994). This criterion states that if the mass and energy balances equation exhibit positive divergence at some point on the temperature or pressure vs. time trajectory, the process operates in runaway conditions. After the reconstruction of the space phase via temperature and pressure data (Strozzi et al., 1999), the successive passage is to calculate the divergence of the system as:

$$\text{div}F(\mathbf{x}) = \frac{V^o(\mathbf{t})}{V(\mathbf{t})} \quad (3)$$

where  $V^\circ(t)$  is the volume change with respect to time of the space phase. To avoid numerical errors due to the ratio of two small numbers as  $V^\circ(t)$  and  $V(t)$  are, the criterion can be modified considering that the volume can be evaluated by Equation 4:

$$\Delta V(t) = \frac{V(t) - V(t - \Delta t_2)}{\Delta t_2} \quad (4)$$

that is the infinitive variation of the phase-space volume; when

$$\Delta V(t) > \Delta V_{LIM} \quad (5)$$

the divergence becomes positive and so the process can undergo a runaway reaction. In the practice the application of the criterion consists in stating that when the variation of the phase space volume  $\Delta V(t)$  is greater than a threshold value the system is to be considered in the runaway field (Maschio et al., 2010). The results obtained showed that the method is able to distinguish between runaway and non-runaway situations and did not produce false alarms for the cases studied, so they can be easily applied (Casson, 2007).

### 3. Experimental

The advantages of thermal screening of reaction mixtures are wide: short time for analysis and small quantities of sample to be used. The disadvantages in the utilization of this instrument are the non adiabaticity of the obtained experimental data, the difficulty in mixing the sample and the impossibility of simulating the heat transfer through a jacket.

The experimental runs here described are carried out in a Thermal Screening Unit (TS<sup>u</sup>) modified with an expansion vessel which allows the studies of the reactions in a physical and chemical controlled atmosphere. The complete apparatus used in this work can be seen in Figure 1.

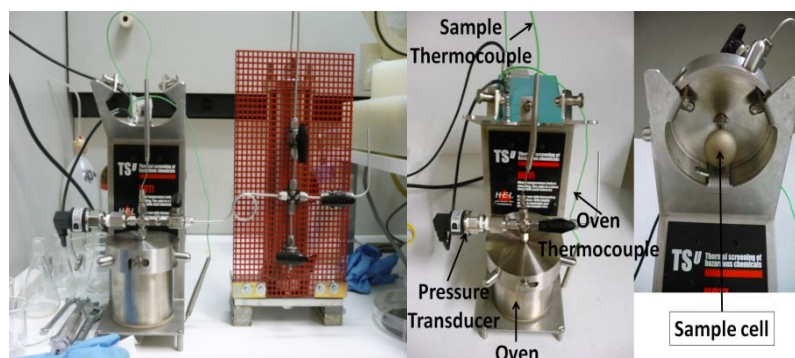


Figure 1: Experimental apparatus TS<sup>u</sup> with the expansion vessel.

The sample is contained in a pressure tight metal (stainless steel SS) test cell. The expansion vessel has a volume of 170 cm<sup>3</sup>, about thirty times the volume of the cells.

The TS<sup>u</sup> has been designed to work until 500 °C e 250 bar (HEL, 2008). When an exothermic or endothermic process is detected the sample temperature will be deviated from the background-heating rate identifying the detected onset temperature ( $T_{ONSET}$ ). The rate of rise in sample temperature ( $dT/dt$ ) and the maximum value reached ( $T_{MAX}$ ) reflects important characteristics of the thermal event. The pressure data enables very mild exothermic decomposition reactions which result in the production of non-condensable gas to be detected (Singh and Simms, 2001).

#### 4. Results Of The Isothermal Tests On Hydrogen Peroxide

Samples of 3 g of solution of hydrogen peroxide (HP) 35 %wt have been analyzed in four different isothermal tests (90 °C, 100 °C, 110 °C and 120 °C) and in three different pressure conditions (1, 6.5 and 12 bar) in order to evaluate the differences in the decomposition reaction depending on the conditions in the reactor. The temperatures have been chosen on the basis of three different scanning tests performed on the same type of sample aimed at the detection of the onset temperature for the peroxide in the TSu derived from previous experiments (Casson, 2007). All the experiment here reported have been repeated at least three times in order to make the experimental data reliable. In Figure 2a and 2b respectively the trend of temperature maximum and maximum pressure are reported as a function of the temperature set for the test and the initial pressure. The values are mainly dependant on the set temperature.

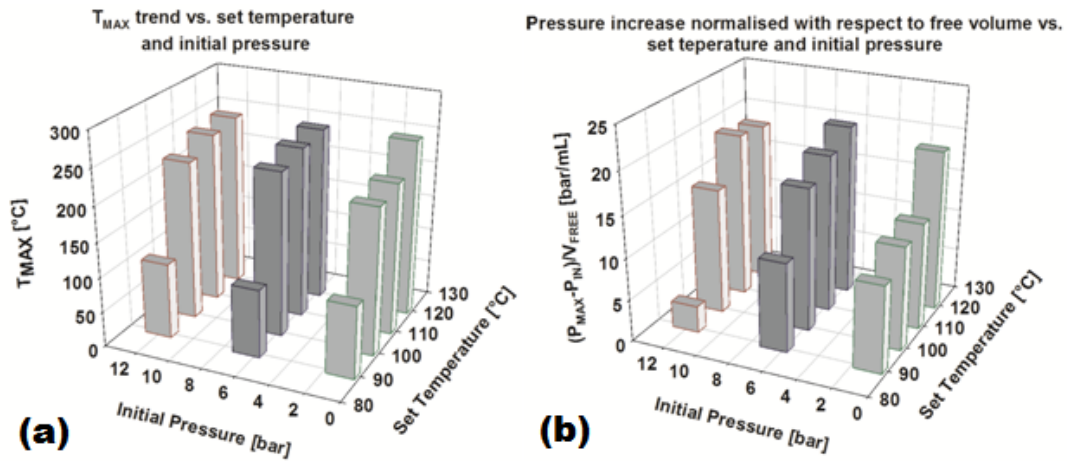


Figure 2: Trend of temperature maximum (a) and maximum pressure (b) as a function of the temperature set for the test and the initial pressure.

The conversion has been calculated by the experimental values of the final pressure (and temperature) on the basis of the stoichiometry of the decomposition reaction and of the Van der Waals equation of state:

$$X = \frac{n_{O_2}^{dec}}{n_{O_2}^{stoichiometric}} \quad (6)$$

In Table 1 the values of conversion are summarized.

Table 1: Conversion of the experimental tests.

$T_{SET}$ [°C]	1 bar	6.5 bar	12 bar
90	54 %	54 %	34 %
100	55 %	57 %	34 %
110	55 %	63 %	51 %
120	65 %	67 %	73 %

The application of the EWDS can be well represented by the tests carried on at 12 bar. When the variation of phase space volume  $\Delta V(t)$  is greater than a limit value (chosen when the variation of volume profile starts to destabilize,  $\Delta V_{LIM}$ ) the system can undergo a runaway reaction (Zaldívar et al., 2003). The values of  $\Delta V_{LIM}$  are reported in Table 2 in which is also shown a comparison of the

application of the test to temperature and pressure decomposition profiles. In Figure 3 the profiles are shown for temperature (a) and pressure (b) application.

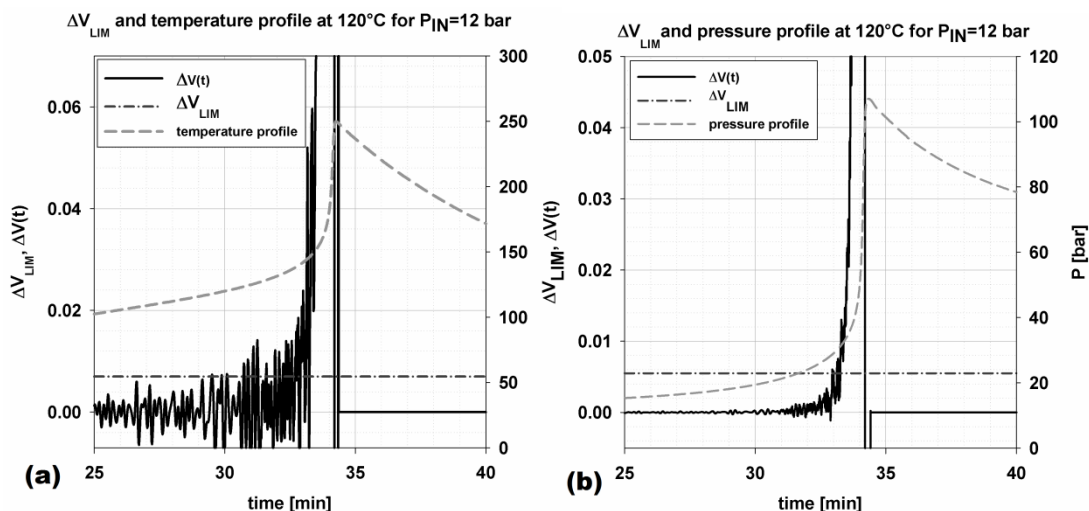


Figure 3: EWDS application to temperature (a) and pressure (b) experimental profiles of HP decomposition carried on at 120 °C and 12 bar.

Table 2: Results of the application of the EWDS to isothermal tests at 120 °C.

Test pressure [bar]	Parameter	t peak [min]	$\Delta V_{LIM}$	t $\Delta V_{LIM}$ [min]	$T_{ONSET}$ [°C]	$\Delta$ (t peak-t $\Delta V_{LIM}$ ) [min]
$P_{IN}=1$ bar	T [°C]	35	0.0070	26	116	9
	P [bar]	35	0.0055	29	-	6
$P_{IN}=12$ bar	T [°C]	34	0.0070	29	117	5
	P [bar]	34	0.0055	33	-	1

The value was found for the first test, the one at 1 bar of initial pressure, and was then applied to the test carried on at 12 bar of initial pressure. The main result is the advance (with respect to the peak of the parameter) in the detection of the onset which is shown in the last column of Table 2: this is the time in which it is possible to operate some corrective measure on the system to prevent the full development of the runaway reaction (i. e. quenching, chemical inhibition, ...). The advance is greater for the case of the application to temperature data.

## 5. Conclusions

This study is focused on runaway decompositions of hydrogen peroxide because in the past peroxides have been the cause of many severe accidents; the aim of the study was to find the characteristics parameters of the reactions in order to define a method to prevent thermal explosion and to avoid the loss of control of the system. From the experimental results we can conclude that the detected onset temperature does not change increasing the set temperature and pressure. The maximum temperature increases by increasing the set temperature but not pressure; the same trend was found for the pressure peak. The value of final conversion is mainly dependant on the set temperature but an effect due to higher initial pressure is visible for the tests run at higher pressure, in which the conversion is lower for the test run at 90 and 100 °C.

An Early Warning Detection System has been then applied off-line to the experimental data; this method requires only temperature or pressure experimental measurements to detect a runaway reaction in the system. Because of this, it can be applied also on line, after an appropriate calibration, to industrial reactors and large storage tanks. The results of the application show that EWDS works

better with temperature compared to pressure data, because the advance is greater than the one obtain with the pressure and so it can be easily to intervene to the process.

## SYMBOLS

$\Delta V_{LIM}$ phase-space volume threshold value, [-]	$P_{IN}$ initial pressure, [bar]
$\Delta V(t)$ variation of phase-space volume with time, [-]	$P_{MAX}$ maximum pressure, [bar]
$n_{O_2}$ moles of oxygen decomposed, [mol]	$P_{FIN}$ final pressure, [bar]
$n_{O_2}^{stoich}$ stoichiometric moles of oxygen, [mol]	$Q_{chem}$ heat of reaction, [J]
$c_P$ specific heat, [J/kg·K]	$t$ time, [min]
<i>EWDS</i> Early Warning Detection System	$T_J$ jacket temperature, [K]
<i>HP</i> Hydrogen Peroxide	$T_{MAX}$ maximum temperature, [°C]
$S$ external surface area per unit of volume, [m <sup>2</sup> /m <sup>3</sup> ]	$P_{IN}$ initial pressure, [bar]
$T_{onset}$ temperature (or decomposition temperature), [°C]	$T_R$ temperature inside the reactor, [K]
$T_{SET}$ set temperature for the test, [°C]	$U$ overall heat transfer coefficient, [J/m <sup>2</sup> ·s·K]
$V$ reactant volume, [m <sup>3</sup> ]	$X$ conversion, [-]
$V^\circ(t)$ volume change with respect to time of the space phase, [-]	$\rho$ reactant density, [kg/m <sup>3</sup> ]

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