

Use Of Screening Analysis Calorimetry In The Study Of Peroxides Decomposition

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In this study the analysis of di-tert-butyl peroxide decomposition in different organic solvents by screening calorimetry is proposed. Organic peroxides are liable to decompose exothermically at normal or high temperatures. The type of solvent changes the effects in the runaway behavior.

Screening calorimetry data allow us to define the conditions and ranges of temperature and pressure involved. In the experimental apparatus used, the experiments are carried out safely even when there is a rapid and large increase in temperature and pressure.

Screening calorimetry represents in this sense a first step in risk analysis studies and also a key in scaling up of processes.

Screening calorimetry data have to be validated by experiments carried out in more complex calorimeters, similar to industrial reactors (adiabatic and reaction calorimeters), but the use of the TSu makes it possible to save time and reduce the number of experiments with laboratory scale calorimeters. In this paper a comparison between screening and adiabatic data for hydrogen peroxide decomposition is shown.

1. Runaway reactions and thermal screening

According to Semenov theory if, during a chemical process, the heat evolved by the reaction exceeds that removed by the cooling system, the reagent mass accumulates heat until a point is reached in which the temperature increases uncontrollably and so does the reaction rate (self heating); this phenomenon is known as a runaway reaction or thermal explosion, which means the loss of thermal control of the reacting system.

According to Barton and Nolan (1987), most causes of this dysfunctional behavior are due to errors in the kinetics or heat balance of the system (in the design and scale up stages), or due to cooling or agitation system failure, the presence of impurities in the reaction mass in the case of organic peroxides (during the process). Runaway reactions may cause toxic or flammable releases or more simply a pressure increase in the reactor (due to vapour pressure of products or to the formation of gaseous decomposition products) leading to the rupture of the reactor.

Thermal screening of components and reaction mixtures is useful to identify conditions under which a thermal explosion can occur and the temperature and pressure ranges developed. With this approach a preliminary risk analysis of the process can be made: onset temperature, Self Accelerating Decomposition Temperature (SADT), maximum rate of self heating, heat of reaction, kinetics parameters and other parameters can be evaluated.

The advantages are: short time for analysis and small quantities required (suitable for analyzing unstable substances, reaction intermediates, new compounds or contaminants).

The experimental runs are carried out in a Thermal Screening Unit (TSu), a pseudo-adiabatic and Non Differential Thermal Analysis instrument: a spherical sample holder is placed in the oven. During the tests the temperature and pressure profile of the sample is observed. Scanning or isothermal test can be run.

2. Solvent effect on peroxide decomposition

As already shown by Saraf, Rogers and Mannan, the type of interaction between the solvent and the peroxide causes the variation of the most relevant parameters in screening tests, such as the maximum temperature, the increasing rate of temperature and pressure and also the kinetics and thermodynamics of the reaction.

In this work the decomposition of di-tert-butyl peroxide (DTBP, $C_8H_{18}O_2$) in different organic solvents (methylbenzene, dimethyl ketone and n-butanol) is analyzed: 5 g of solution of peroxide in solvent (30%wt) have been subjected to ramped heating tests ($2^\circ C/min$). Hastelloy sample holders have been used. In table 1 the onset temperatures, the maximum temperatures and pressures and the maximum increasing rates of these two parameters are reported for the three tests.

Table 1: Main experimental data (and corresponding times) for the solutions of DTBP 30%wt in different organic solvents.

	T_{onset} $^\circ C$	t min	T_{max} $^\circ C$	t min	dT/dt_{max} $^\circ C/min$	P_{max} bar	t min	dP/dt_{max} bar/min
methyl benzene	136	83	245	94	90	84	94	978
dimethyl ketone *	136	82	229	93	53	136	93	1156
n-butanol	136	84	221	96	45	60	96	122

*tests stopped automatically: pressure value exceeded instrumental safety value (120 bar).

The onset temperatures hold steady and so does the time to maximum rate. The largest variations are in the peak values of temperature, pressure and their increasing rates.

In figure 1, sample temperature, pressure and increasing rate of temperature are showed for the three different peroxides.

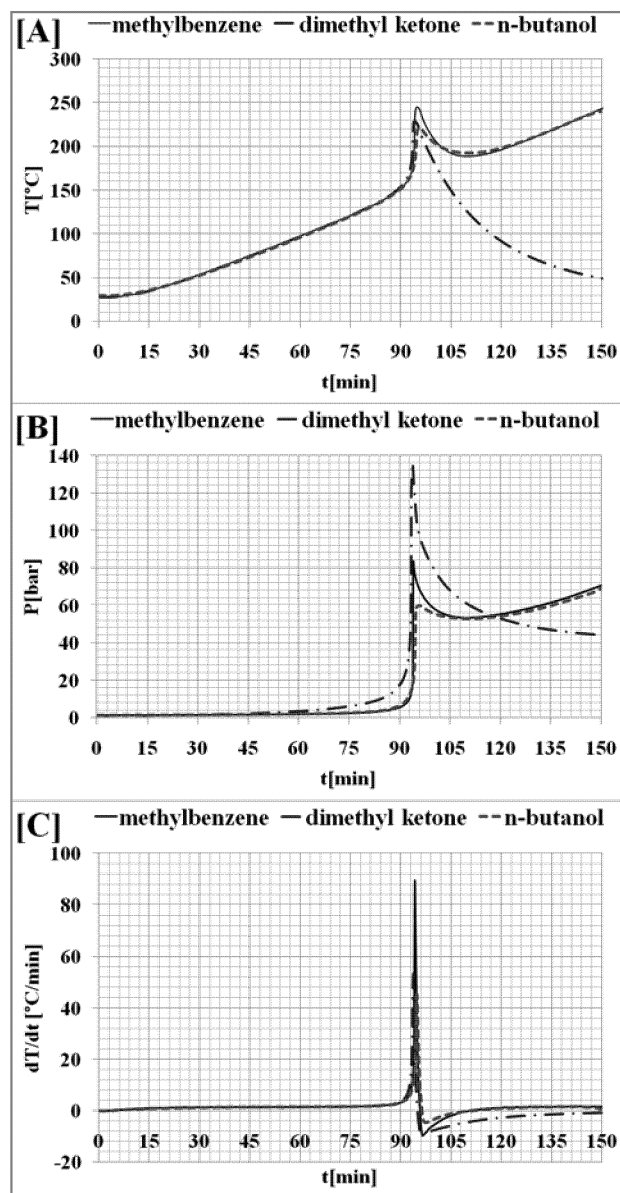


Figure 1: Effect of the solvent in DTBP decomposition reaction: experimental on-line profiles of (a) T , (b) P , (c) dT/dt . Samples: 5g, 30%wt DTBP. Scanning: $2^{\circ}\text{C}/\text{min}$. Hastelloy cells.

Experimental data show that n-butanol is the most solvating: temperature and pressure peaks and the increasing rate of temperature are lower than in the other two cases (dT/dt_{max} is almost 50% reduced respect to methylbenzene). The effect on maximum increasing rate of pressure is remarkable: in methylbenzene test it is 978 bar/min and it decreases to 122 bar/min in the case of n-butanol. Although the two solvents boiling

points are similar but their enthalpies of evaporation at the boiling temperature are different and the vapour pressure of n-butanol increases more slowly with temperature than that of methylbenzene). On the other hand dimethyl ketone interacts with DTBP in a way that the runaway behaviour of the decomposition is amplified: the pressure increase reached is such that the experimental apparatus stops automatically the test because of safety (default safety pressure value: 120 bar). The maximum increasing rate of pressure for dimethyl ketone test is of 1156 bar/min. This result is also due to the major volatility of this solvent (normal boiling point 56°C versus 110°C for methylbenzene and 118°C for n-butanol).

This screening tests prove that changes in solvent is a very important aspect in risk analysis of chemical processes. In fact it is statistically a cause of severe accident due to runaway reactions in chemical plants (Cardillo, 1998).

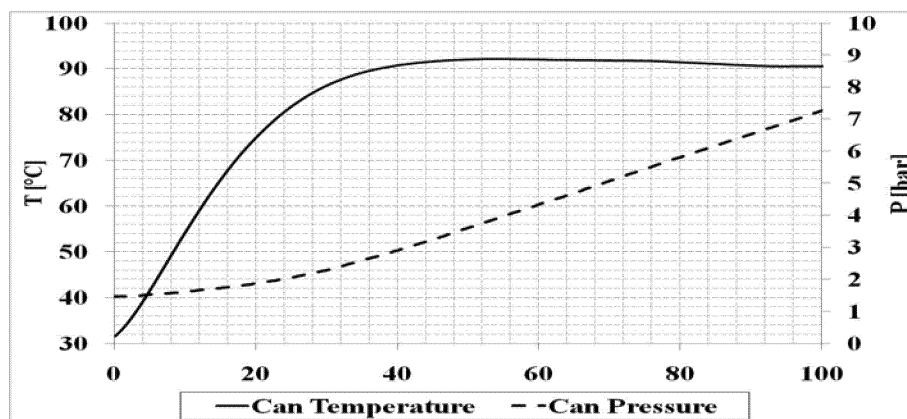
3. Screening and adiabatic test data

When a runaway occurs in a chemical reactor, the system behaves as an adiabatic one, because the heat evolved is much more than the one removed by the cooling system, so there is an increasing build up of heat. Because of this, in risk analysis it's important to study a process in adiabatic instruments, in order to monitor the process behaviour in the worse accident case.

Adiabaticity is an intrinsic characteristic of experimental devices; in this section the comparison between a pseudo-adiabatic instrument (TSu) and an adiabatic one (PhiTec II) is shown, in order to underline advantages and disadvantages of screening calorimetry techniques. Both two are Non Differential Thermal Analysis instruments in which temperature and pressure are monitored. The decomposition of a solution of hydrogen peroxide 35%wt is proposed. In TSu an isothermal test (90 °C) is run, while in PhiTec II a more accurate kind of test (heat-wait and search) is carried out. In both instruments stainless steel cells are used. The isothermal value for the TSu test has been chosen after a scanning test of the solution, that showed an onset temperature for the solution of 96°C.

Figure 2 shows experimental profiles obtained in TSu and figure 3 in the adiabatic test.

Figure 2: Experimental TSu profiles for 2g of 35%wt H_2O_2 solution.



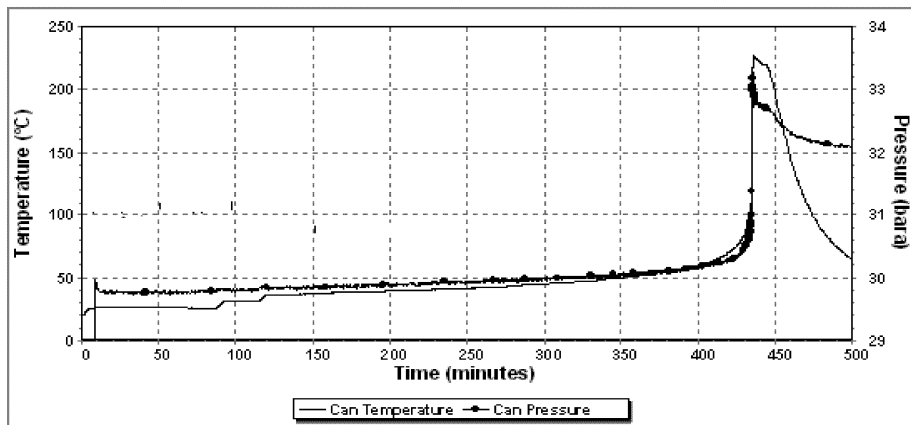


Figure 3: Experimental PhiTecII profiles for 50g of 35%wt H_2O_2 solution.

In table 2 a comparison between the main experimental data of both tests is reported.

Table 2: Main experimental data (and corresponding times) of TSu and PhiTecII tests.

	Φ	T_{onset} °C	t min	T_{max} °C	t min	dT/dt_{max} °C/min
TSu	1.6	-	-	92	53	0.036*
PhiTec	1.06	41.5	126	228	311	469

* evaluated after reaching setting temperature of 90°C ($t > 37$ minutes).

The first thing to point out is the different kind of decomposition developed by the peroxide: in the TSu the reaction does not follow a runaway path, even if the sample is subjected to higher temperature than in the adiabatic instrument. This can be attributed to the characteristics of different heat exchange between oven-sample and also instrument-ambient, that is: the value of the Φ Factor (which indicates the degree of adiabaticity of the system, ideally 1) is 1.06 for the PhiTecII, whereas it is 1.6 for TSu. In TSu part of the heat is lost to external ambient. A consequence is the major precision of the adiabatic instrument in the determination of the onset temperature (thanks to heat-wait and search technique that allows to determine the self heating accurately), adiabatic ΔT and so T_{max} . Pressure values are not comparable for these tests because of the different can volume: the adiabatic instrument was connected to an expansion vessel, in order not to damage the experimental device in case of explosion. The adiabatic instrument simulates a runaway process at lower temperature and so a worse case of accident. On the other hand times and costs of experiments are very high for PhiTec tests and are not always justified: a more simple instrument (like TSu) allows to define ranges of temperature and pressure with good precision, saving times and costs.

4. Conclusions

This study is focused on runaway decompositions as they're more interesting in plant safety and risk analysis, because in the past they have been the cause of severe

accidents. In particular solvent influence has been analyzed, proving that a solvent change has always to be tested before applied in reactor scale in order to avoid an anomalous runaway behaviour of the reaction.

Screening calorimetry allowed us to analyze these processes in safety and to gain useful results such as onset temperatures, ranges of temperature and pressure evolved by reactions and others. Remember that screening equipments are not adiabatic: data have to be validated by tests run in adiabatic and reaction calorimeters, where real operational conditions (such as agitation and heat transfer) can be simulated; the use of the TSu makes it possible to save time and reduce the number of experiments with laboratory scale calorimeters.

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