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Runaway Reaction Hazard Assessment for Chemical Processes Safety

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INERIS, as part of its missions for accident prevention, has been developing its expertise for several years on chemical processes safety to help industries avoid accident caused by runaway reactions, using theoretical knowledge on thermal hazards and experimentation.

1. Introduction

Thermal runaway is the loss of temperature control of a chemical substance or of a reaction mixture due to an exothermic reaction, which can cause the thermal explosion of a reactor characterized by a sudden release of a large amount of energy, often accompanied by high gas emissions potentially flammable and toxic.

Thermal runaway is a dreaded phenomenon in chemical industries, as it can lead to catastrophic events when it occurs in an industrial facility. INERIS, as part of its missions for accident prevention, has been developing its expertise on chemical processes safety to help industries avoid such hazardous events for several years.

This expertise is based on a rigorous methodological approach to assess hazards linked to substances and reactions carried out in processes to prevent possible deviations, using theoretical knowledge concerning thermal runaway and efficient calorimetric tools which make it possible to characterize these phenomena experimentally.

The chemical processes safety laboratory of INERIS gathers several experimental devices, enabling studies at different scales and giving complementary information. Screening tests are firstly carried out in micro-calorimetry device on samples of milligrams size to study their thermal stability. With a greater sensitivity and larger quantities of products, the isothermal calorimeter offers a range of test cells enabling to quantify the thermal fluxes released according to different configurations: mixing of reactants, gas circulation, high pressure. After obtaining preliminary data, the overall operation of a process can be tested using a reaction calorimeter. This pilot makes it possible to reproduce the operating conditions of an industrial reactor on a liter scale, its instrumentation measuring numerous physico-chemical parameters over time. Then, thermal and kinetics parameters of runaway phases are accessible by tests in pseudo-adiabatic calorimeters at lab scale and at medium scale in a 10 Liter reactor and can be used to size emergency relief systems.

2. Thermal runaway phenomenon

2.1 Description

Thermal runaway is the loss of temperature control of a chemical substance or reaction mixture in an enclosure.

The temperature rise is due to exothermic phenomena such as chemical or physical transformations. It might be the thermal decomposition of a substance. The loss of control occurs when the heat generated by these phenomena is insufficiently dissipated and therefore accumulates in the considered system.

The consequences of the loss of temperature control are:

- The increase in the rate of chemical reactions,
- The occurrence of undesired reactions that do not occur under normal process conditions. Most often, these are reactions of decomposition of the mixture,

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- The increase in the total pressure due to the vaporization of the mixture resulting from the rise in temperature and/or the chemical production of incondensable gases.

This last consequence can lead to the bursting of the enclosure, which is referred to as “thermal explosion”. The loss of containment may be associated with the emission of toxic and / or flammable products, and cause blast effects as well as mechanical and thermal effects (Laurent, 2003).

The major accidents of Bhopal and Seveso were caused by such phenomena.

The accidents resulting from a thermal runaway concern more particularly the sector of the fine chemistry, where the chemical reactions are often implemented in batch reactors, for reasons of polyvalence. These processes are more critical because their heat transfer performances are more limited.

Moreover, some reactions are more sensitive to the risk of thermal runaway. Polymerisation, nitrations, sulfonations, halogenations, aminations and esterifications reactions are among the most represented in runaway accidents, as they are highly exothermic and likely to produce significant amounts of gaseous products.

Among the means of protecting reactors and enclosures against thermal runaway, safety vents represent the most commonly used solution in the industry. A safety vent is a device which evacuates the pressure generated in the reactor during a runaway, releasing material (liquid, gas and / or vapor). There are two types of safety vents: valves and rupture discs. Downstream of the safety vent, the collection of emitted effluents can be performed in a catch-tank.

2.2 Causes

The causes of thermal runaways correspond generally to process drifts leading to an imbalance between heat production and dissipation, resulting from human error or technical malfunction (Laurent, 2003).

The most common causes are:

- Excessive temperature: for example, an excessive temperature of the heating fluid, the presence of a fire,
- Excessive residence time: in some cases, thermal runaway occurs when the duration of operations is abnormally long, in the presence of autocatalytic reactions. Autocatalytic reactions are reactions whose products formed act as catalysts of the reaction. In this case, the reaction can accelerate even If the temperature is kept constant,
- Error of introduction of reactant: for example, adding a reactant at higher flow than expected may increase the amount of heat released by the reaction,
- Introduction of an incompatible product, presence of impurities: the introduction of an incompatible substance or impurity in the reactant mass can trigger undesired exothermic reactions,
- Accumulation of reactant: this may happen when the temperature is abnormally low or when the catalyst is not or insufficiently added in semi-continuous processes. In that case, the consumption of reactant may be slower than the introduction of reactant, which accumulates in the reactor. Subsequently, a slight increase in temperature or the adding of the catalyst can trigger the sudden reaction of all the accumulated reactant mass.

3. Parameters of interest for reactive chemical hazards assessment

The assessment of reactive chemical hazards related to a process is a complicated task which requires the deep knowledge of the chemical reactions, notably their thermal and kinetics characteristics, in normal but also in degraded operating conditions (Stoessel, 2011). The main parameters used to estimate thermal risk are presented below.

3.1 Reaction relating to the process and decomposition reactions

To assess the safety of a chemical process, it is important, firstly, to distinguish the reaction that is implemented to obtain, from given reactants, the desired products, from secondary reactions, mainly decomposition reactions, that triggers at high temperature.

Thus, for example, the desired reaction can be:

$A + B \rightarrow C + D + Heat$

Followed by a decomposition reaction of one of the products:

$C \rightarrow E + Heat$

A good knowledge of the reaction processes relative to the mixture considered in a wide range of operating conditions is essential when collecting quantitative information of a chemical process.

3.2 Thermodynamic parameters

Reaction enthalpy

Reaction enthalpy ΔH_r (J.mol^{-1} or J.g^{-1}) corresponds to the amount of energy generated or absorbed during a reaction. It is a parameter which allows to know if the reactions are endothermic $\Delta H_r > 0$ or exothermic $\Delta H_r < 0$. Exothermic chemical reactions are those that present a potential hazard of reaction runaway. The measurement of the heat of reactions (desired and secondary reactions) is therefore a first indication of the criticality of a process.

Temperature elevation in adiabatic conditions

Accidental circumstances generally result from a significant reduction in heat exchange capacity, for example due to the loss of cooling capacity of the jacket or the loss of agitation. Therefore, the risk assessment is done considering the most severe case, corresponding to the adiabatic conditions. In such conditions, the total energy potential of the reaction is accumulated in the reaction mass.
In practice, the potential temperature increase under adiabatic conditions (ΔT_{ad}) is given by the expression:

$$\Delta T_{ad} = \frac{\Delta H_r}{C_p}$$

With ΔH_r the reaction enthalpy (J.g^{-1}) and C_p the specific heat of the mixture (J.g^{-1}.K^{-1}).

3.3 Kinetic parameters

Reaction kinetics

Three types of kinetics behavior can be distinguished:

- Reactions following the Arrhenius equation,
- Autocatalytic reactions,
- Radical polymerizations.

Most of the reactions obey the law of Arrhenius. In that case, the reaction rate is an exponential function of the temperature.
For a chemical reaction whose equation is:
$A + B \rightarrow C + D$
The rate of reaction r is:

$$r = k_0 * e^{-E_a/RT} * C_A^n * C_B^m$$

With T, temperature; R, gas constant (R = 8.31431 J.mol^{-1}.K^{-1}); E_a, activation energy; k_0, preexponential factor; C_A, C_B, reactants concentration; n, m reaction order with respect to A and B.

The heat flow generated by the reaction ($^{dq}/_{dt}$) is linked to its rate by:

$$^{dq}/_{dt} = r * \Delta Hr$$

The kinetics data give information on the criticality of a reaction with respect to thermal risk. The faster an exothermic reaction is, the faster the heat will be released, and the reaction runaway will be violent.

Induction time

Another commonly used indicator is the "time required to reach maximum rate under adiabatic conditions", TMR_{Ad} or "induction time", which permits to assess the probability of obtaining the conditions of a thermal runaway. This indicator can be estimated by the following formula:

$$TMR_{Ad} = \frac{C_p * R * T_0^2}{\left(\frac{dq_0}{dt}\right) * E_a}$$

With R, gas constant (J.mol^{-1}.K^{-1}); T_0, initial temperature (K); dq_0/dt, heat flux produced by the reaction at T_0 (W.kg^{-1}); Ea, activation energy (J.mol^{-1}); C_p, specific heat of the mixture (J.kg^{-1}.K^{-1}).

4. Experimental methods for the evaluation of reactive chemical hazards

Knowledge of the thermodynamic and kinetics parameters of reactions used to assess thermal runaway risks of processes generally requires experimental studies. The chemical processes safety laboratory of INERIS gathers several experimental devices, enabling studies at different scales and giving complementary information (Demissy, 2005).

4.1 Differential scanning calorimetry (DSC)

Screening tests are firstly carried out in a Differential Scanning Calorimeter on samples of products of milligrams size to study their thermal stability, in normal or in degraded conditions of storage or process. Degraded conditions may include the presence of impurities in the product for example.

The sample is contained in a crucible placed into a temperature-controlled oven. Since it is a differential method, a second crucible is used as a reference. The apparatus records heat flow generated or absorbed by the sample when heated from room temperature to about 400-500°C. The temperature of beginning of a reaction corresponding to a thermal event highlighted can be deduced, and the enthalpy of the reaction. Since the DSC uses only small sample sizes, very exothermal phenomena may be studied. The thermogram obtained shows the energetic potential of a sample (see Figure 1). The corresponding adiabatic temperature rise allowing the assessment of the severity of a runaway reaction can be calculated.

DSC is best suited for the determination of heat of decomposition. Overall heats of reaction may also be determined if the reactants are mixed at low temperature in order to slow down the reaction before starting the temperature scan.

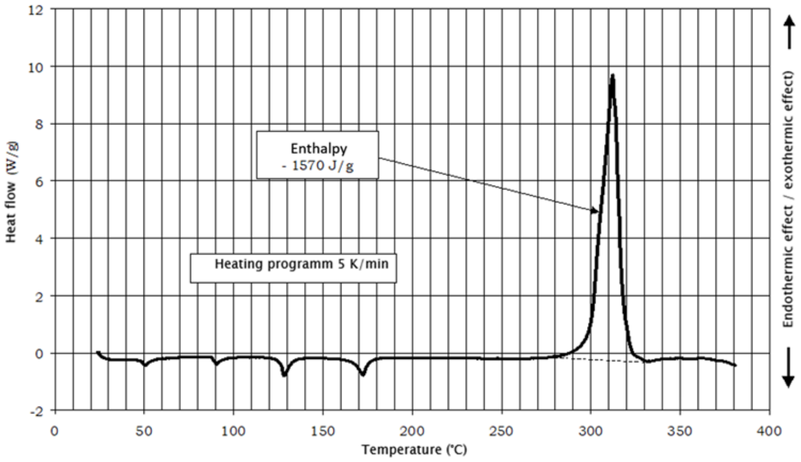

Figure 1. Example of a thermogram obtained from a DSC test.

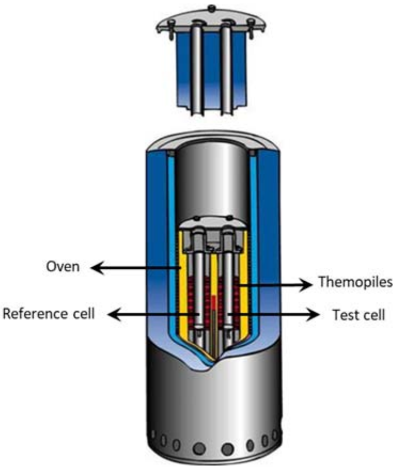

Figure 2. Schematic diagram of Calvet Calorimeter C80.

4.2 Calvet calorimeter

This calorimeter type is commercialized by Setaram (C80). It is a differential calorimeter that may be operated isothermally or in the scanning mode as a DSC in the temperature range from room temperature to 300°C. The Calvet calorimeter has a high sensitivity, thanks to its measurement principles, based on a pile of thermocouples surrounding the cell containing the sample (see Figure 2). Also, it is possible to test samples of up to several grams.

Like a DSC test, the Calvet calorimeter used in the scanning mode gives information on reaction temperature and enthalpy. The isothermal mode can be used to determine the induction time and kinetics parameters of the reaction, by conducting several tests at different temperatures. Moreover, mixing cells can be used to study instantaneous reactions between two solids, liquids or gaseous reactants.

4.3 Reaction calorimeter

After obtaining preliminary data, the overall operation of a process can be tested using a reaction calorimeter. INERIS uses the reaction calorimeter RC1 of Mettler Toledo (see picture 1). This pilot makes it possible to reproduce the operating conditions of an industrial reactor on a liter scale. The reaction mass is mechanically stirred, its temperature is controlled by a cooling/heating jacket, and the calorimeter allows adding reactants, distillation or refluxing. The variations of power required to maintain the temperature of the reaction mass are recorded, which makes it possible to acquire thermal data (reaction temperature, heat of reaction, diagrams of the heat flows as a function of time), kinetics (reaction rate versus reactant concentrations, maximum heat production rates), and information on reaction mass (reaction mass specific heat, solubility data, phase equilibrium, transfer coefficients). Such tests allow optimizing processes in terms of safety, giving useful information on critical and safe operating conditions.

Picture 1. Picture of reaction calorimeter RC1.

4.4 Adiabatic calorimeters

Adiabatic calorimetry is a technique which consists in keeping the temperature around the test cell containing the sample equal to the temperature of the sample, by a heating device. The thermal flow produced by an exothermic reaction is therefore used to rise the temperature of the sample. As it is unavoidable that a part of the heat released by the sample serves to heat the test cell, a correction for the thermal inertia of cell is required.

During a test in an adiabatic calorimeter, the temperature of the sample and the pressure in the test cell (or containment if an open test cell is used) is measured as a function of time.

Several types of adiabatic calorimeters are used at INERIS (see picture 2):

- The Advanced Reactive System Screening Tool (ARSST, Fauske),
- The Vent Sizing Package II (VSP II, Fauske),
- The Phi-Tec I (HEL).

These devices differ by the type of test cell (open or closed), the sample size (about 10g for ARSST and Phi-Tec I, 70g for VSP II) and the method to reach adiabatic conditions.

Tests in adiabatic calorimeters provide rate of temperature and pressure rise, as well as adiabatic temperature rise, which are parameters used for emergency relief systems sizing.

Picture 2. *Pictures of Phi-Tech I (a), ARSST (left) and VSP II (right) (b).*

4.5 Medium scale reactor (10 Liter)

INERIS has a 10-liter test reactor which permits to study runaway phases at a medium scale (see picture 3). The reactor is equipped with a heating resistor and several thermocouples and pressure sensors. This device can be used to size emergency relief systems for vessels containing self-reactive materials, according to the United Nation Manual of Test and Criteria for the transportation of dangerous goods (UN, 2015).

Picture 3. Picture of 10-liter test reactor.

5. Conclusions

Thermal runaway can occur when heat generated by exothermic reactions in a chemical process or storage is not sufficiently dissipated outside the system, leading to an uncontrolled temperature rise, often accompanied by a pressure increase. The causes are process drifts resulting from human error or technical malfunction. Such reactive hazards concern particularly the fine chemical sector operating with batch processes.

The assessment of reactive chemical hazards related to a process is a complicated task which require the deep knowledge of the chemical reactions, notably their thermal and kinetics characteristics, in normal but also in degraded operating conditions. Experimentation is an essential way to obtain such information. The chemical processes safety laboratory of INERIS gathers several experimental calorimeters which provide data allowing the quantification of reactive hazard.

References

Demissy M., 2005, La sécurité des procédés chimiques, Oméga 17, INERIS, France.
Laurent A., 2003, Sécurité des procédés chimiques, Editions Tec&Doc, France.
Stoessel F., 2011, Thermal Safety of Chemical Processes, Wiley-VCH.
UN, 2015, UN Recommendations on the Transport of Dangerous Goods - Manual of Tests and Criteria, 6th revised edition, United Nations, Geneva.