AKTS-Thermokinetics & AKTS-Thermal Safety Software: An advanced solution for thermal stability determination and safety analysis

Introduction

Generally, all energetic materials evolve heat during decomposition. Processing, design, quality control, and operational applications all require an understanding of thermal hazards and an ability to predict safety limits and decomposition process in extended temperature ranges [1-4]. Several methods have been presented for predictions of the reaction progress of exothermic reactions under heat accumulation conditions. However, because decomposition reactions usually have a multi-step nature, the accurate determination of the kinetic characteristics strongly influences the ability to correctly describe the progress of the reaction. The use of simplified and conservative kinetic models for the assessment of runaway reactions leads to economic drawbacks, since they result in unnecessary large safety margins.

Applying the results obtained by:

- DTA (Differential Thermal Analysis)
- DSC (Differential Scanning Calorimetry)
- TG (Thermogravimetry)
- EGA (Evolved Gas Analysis MS or FTIR)

advanced numerical techniques such as AKTS-Thermokinetics and AKTS-Thermal Safety Software enable prediction of the reaction progress of materials in broad temperature range. In fact, numerical simulations are used to replace experiments in situations, which are not directly accessible to the experiment for timing or safety reasons.

Experimental and analysis process

Providing accurate input data thanks to DSC and C80 calorimeters of SETARAM Instruments

Upstream the kinetic evaluation is the accurate measurement of thermal effects. State of the art thermal analysers and calorimeters are required to provide valuable input data. Such data can be easily imported from our SETSYS Evolution (coupled with MS), Standard DSC, MicroDSC, Calvet DSC, Calvet Calorimeters.

Among those instruments, DSC and C80 are certainly the best fitted for the study of thermal decompositions followed by kinetic evaluation and safety analysis.

Heat measurement in a C80 Tian-Calvet type microcalorimeter is done by two fluximeters, each of which measures the thermal power exchanged constantly between the experimental vessel and the calorimetric unit. The main difference in comparison to the DSC plate transducer technique is that fluximetric transducer envelopes the sample and is therefore capable of measuring almost all the exchanges between the vessel and the unit, a characteristics that gives this device a clear metrological advantage in terms of both the qualification of the measurements and the capacity to measure very weak effects.

Also, because large C80 cells allow to set up experiments with 1-10mL of products, upscale predictions are finer than with a usual DSC 100µ crucible.

Two types of cells (so-called pressure measurement cells and safety cells) allow simultaneous measurement of the internal pressure. In case of gas releasing decomposition study, gas evolution can be quantified. AKTS software applied to the derivative of the pressure signals can also be used for vent sizing application [5].

Figure 1: Calvet C80 Calorimeter

Providing accurate kinetic description thanks to AKTS-Thermokinetics

As a general rule, solid state reactions demonstrate profound multi-step characteristics as presented in figure 2. The assumption that the decomposition of an energetic material will obey a simple rate law is not often true. Using for example DSC data, the analysis process requires determination of the kinetic characteristics of the reaction. The noticeable weakness of the ‘single curve’ methods (determination of the kinetic parameters from single run recorded with one heating rate only) has led to the introduction of the ‘multi curve’ methods over the past few years, as discussed in the International ICTAG Kinetics project [6-9]. Only series of non-isothermal measurements carried out at different heating rates can give an insight which generally contains the necessary amount of information required for full identification of the complexity of a process. This data set usually contains:

- the relationship between specific conversion, \( \alpha \), and temperatures for different heating rates (non-isothermal mode).
- the relationship between specific conversion, \( \alpha \), and time for different temperatures (isothermal mode).

\[
\ln \left( \frac{dt}{d\alpha} \right) = \ln \left( A(\alpha) f(\alpha) \right) - \frac{E(\alpha)}{RT(\alpha)}
\]

with \( \alpha \) index of conversion, \( j \) index of heating rate, \( f(\alpha) \) the function dependent on the decomposition mechanism. As \( f(\alpha) \) is constant at each conversion degree \( \alpha \), the method is so-called ‘isocoversion’ [10-12].

\[\begin{align*}
\Delta H_j & = U(T_j - T_s) \\
\Delta T & = \frac{U(T_j - T_s)}{C_p}
\end{align*}\]

Figure 2: Analysis process. (A) Friedman analysis of a nitrocellulose based compound with baseline optimization. (B) Activation energy as a function of the reaction progress for decomposition of the high energetic material (DSC closed crucibles / isochoric conditions). (C) Normalized DSC-signals of a nitrocellulose based compound as a function of the temperature for a reaction involving at least two exothermal events. Experimental data are represented as symbols, solid lines represent the calculated signals. The values of the heating rate in °C/min are marked on the curves.

The accurate determination of the kinetic parameters and optimization of the baseline which enable the correct fit of the experimental data is a prerequisite for prediction of the reaction progress under any new temperature profile (see figure 3). The comparison can be achieved by performing additional DSC runs or microcalorimetry experiments.

Figure 3: Prediction of the reaction extent (DSC, normalized signals) and confidence interval of a nitrocellulose based substance as a function of time under isothermal conditions (T = 120°C). These values indicate that there is a 95% probability that the reaction progress after 10 days exposure at 120°C is greater than 77 and lower than 95%. These values are in good agreement with a subsequent measurement under isothermal conditions (92% decomposition at 120°C after 10 days).

**TMR** & safety margins (adiabatic conditions)

Prediction of the reaction progress \( \alpha(t) \), development of the temperatures \( T(t) \) and adiabatic induction times for selected starting temperatures and conditions (adiabatic (\( \Delta T \)) with \( \Delta H_j/c_p \), heat of reaction and \( c_p \) : heat capacity).

The calculated kinetic parameters can be subsequently employed to predict the reaction progress of the investigated samples under any given temperature mode. The heat accumulation is the result of the difference between the production of heat and the dissipation of heat depending on the system parameters in the reaction’s environment. When the dissipation ability of the system does not exactly compensate the produced heat, it results in a variation of temperature that can lead to an explosion. The heat transfer from the solid surface to the fluid can be described by Newton’s law. It states that the heat transfer, \( dQ/dt \), from a solid surface of area \( A \), at a temperature \( T_a \), to a fluid of temperature \( T_f \), is

\[
\lambda \frac{d\alpha}{dt} = U(T_f - T_a)
\]

where \( U \) is the heat transfer coefficient and \( \lambda \) the thermal conductivity. For chemical process safety adiabatic conditions are used for the prediction of the
Time to Maximum Rate under adiabatic conditions (TMR\text{ad}). This TMR\text{ad} can be estimated by applying a heat balance with \( U = 0 \) for the adiabatic conditions.

Figure 5 illustrate a slow cook-off experiments (Up-scaling of DSC data to 4.5 kg) of a nitro-cellulose based compound carried out with the rate 3.3°C/h. For the simulation of the experimental results the heat balance based on the Finite Element Analysis (FEA) was applied together with the advanced kinetic description of the reaction. The comparison of the experimental and simulated data indicates that applied procedure resulted in a very good prediction of the temperature of the ignition. Application of commonly used simplified assumptions concerning the mechanism of the decomposition (such as first- or n-th order mechanisms) led to significantly worse prediction of the cook-off temperatures.

Conclusions

Advanced kinetic analysis enables the calculations of the progress of decomposition reactions under temperature conditions different from those at which the original examinations are carried out. The proper kinetic description of the process of the thermal decomposition of energetic materials using the advanced kinetic software of AKTS and applying detailed heat balance calculations with the Finite Element Analysis (FEA) allow very good simulation of cook-off experiments and lead to the similarity of the predicted and experimentally found temperatures of the ignition. The use of simplified kinetics, being the procedure commonly reported in the literature, leads to much worse prediction of the cook-off temperatures. Applications of Finite Element Methods and accurate kinetic description enable determination of the effect of scale, geometry, heat transfer, thermal conductivity and ambient temperature on the heat accumulation conditions.

References