

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 fluxmeters, 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 fluxmetric 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 quantification 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 100µL 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 ICTAC Kinetics project [6-9]. Only series of non-isothermal measurements carried out at different heating rates can give a data set that 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, α_i , and temperatures for different heating rates (non-isothermal mode).
- the relationship between specific conversion, α_i , and time for different temperatures (isothermal mode).

$$\ln \frac{d\alpha_i}{dt} \bigg|_{\alpha_i} = \ln(A(\alpha_i) f(\alpha_i)) - \frac{E(\alpha_i)}{RT_{i,j}}$$

with i : index of conversion, j : index of heating rate, $f(\alpha_i)$ the function dependent on the decomposition mechanism. As $f(\alpha_i)$ is constant at each conversion degree α_i , the method is so-called 'isoconversional' [10-12].

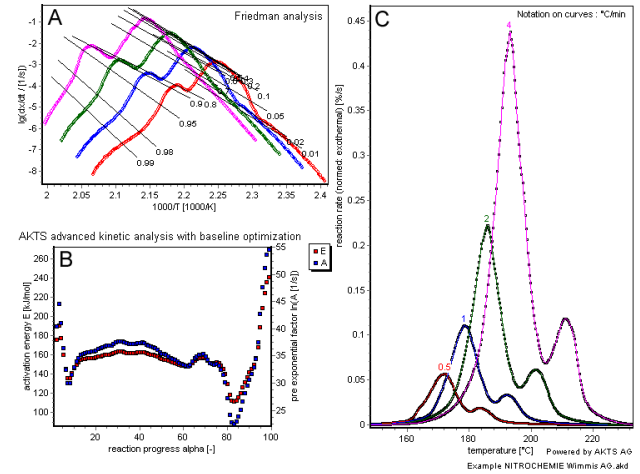


Figure 2: Analysis process. (A) Friedman analysis of a nitrocellulose based compound with baseline optimization. (B) Activation energy as a function of the reaction progress for decomposition of the high energetic material (DSC closed crucibles / isochoric conditions). (C) Normalized DSC-signals of a nitrocellulose based compound as a function of the temperature for a reaction involving at least two exothermic 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 run or microcalorimetry experiments.

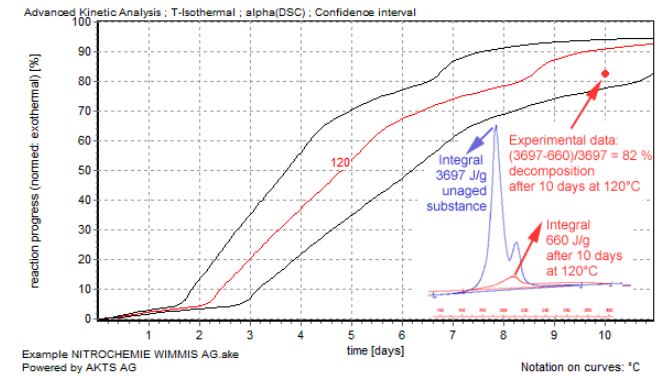


Figure 3: Prediction of the reaction extent (DSC, normalized signals) and confidence interval of a nitrocellulose based substance as a function of time under isothermal conditions ($T = 120^\circ\text{C}$). These values indicate that there is a 95% probability that the reaction progress after 10 days exposure at 120°C is greater than 77 and lower than 93%. These values are in good agreement with a subsequent measurement under isothermal conditions (82% decomposition at 120°C after 10 days).

TMR_{ad} & safety margins (adiabatic conditions)

Prediction of the reaction progress $\alpha(-)$, development of the temperatures $T(t)$ and adiabatic induction times for selected starting temperatures and ΔT -adiabatic ($\Delta H_r/c_p$ with ΔH_r : 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_s , to a fluid of temperature T_∞ is

$$\lambda \frac{\partial T}{\partial x} \bigg|_s = U(T_s - T_\infty)$$

where U is the heat transfer coefficient and λ the thermal conductivity. For chemical process safety adiabatic conditions are used for the prediction of the

Time to Maximum Rate under adiabatic conditions (TMR_{ad}). This TMR_{ad} can be estimated by applying a heat balance with $U=0$ for the adiabatic conditions.

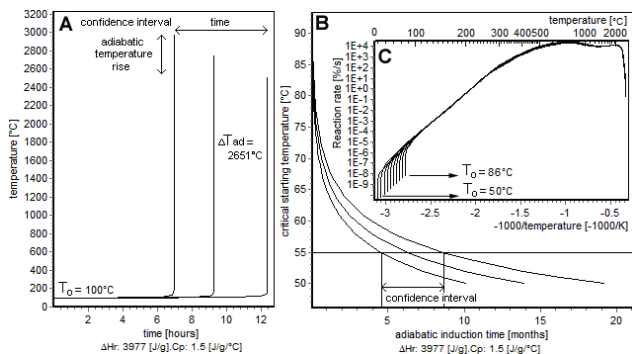


Figure 4 (A) Adiabatic runaway curves for a boost propellant (isochoric conditions) showing the confidence interval for the prediction ($T_{begin}=100^\circ\text{C}$ and $\Delta T_{ad}=\Delta H_f/C_p=2651\pm 233^\circ\text{C}$). The confidence interval was determined for 95% probability. (B) Starting temperature and corresponding adiabatic induction time TMR_{ad} relationship of the boost propellant under isochoric conditions. The choice of the starting temperatures strongly influences the adiabatic induction time (confidence interval: 95% probability). (C) Heat rate curves versus temperature for the boost propellant under isochoric conditions.

Heat accumulation conditions (non-adiabatic conditions)

The second field of application for numerical simulation techniques in process safety is the solution of partial differential equations as they are encountered in heat conduction problems. These problems arise when heat accumulation situations are to be analyzed [13-14].

$$\frac{dT}{dt} = \frac{\lambda}{c_v \rho} \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right) \text{ (cartesian)} \quad \frac{dT}{dt} = \frac{\lambda}{c_v \rho} \left(\frac{\partial^2 T}{\partial x^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right) \text{ (cylindrical)}$$

Applications of Finite Element Methods (FEM) and accurate kinetic description enable the determination of the effect of scale, geometry, heat transfer (insulation), thermal conductivity and ambient temperature on the heat accumulation conditions. In fact, the assumption that it is safe to handle an energetic material at any temperature below the first appearance of an exothermic signal on the DSC curve can be often false. The highest safe temperature for handling any energetic material depends on several factors such as its size, shape, and previous thermal history. Due to insufficient thermal convection and limited thermal conductivity, a progressive temperature increase in the sample can easily take place, resulting in a thermal explosion. Safe operating conditions with tailored safety margins can be defined using numerical simulation.

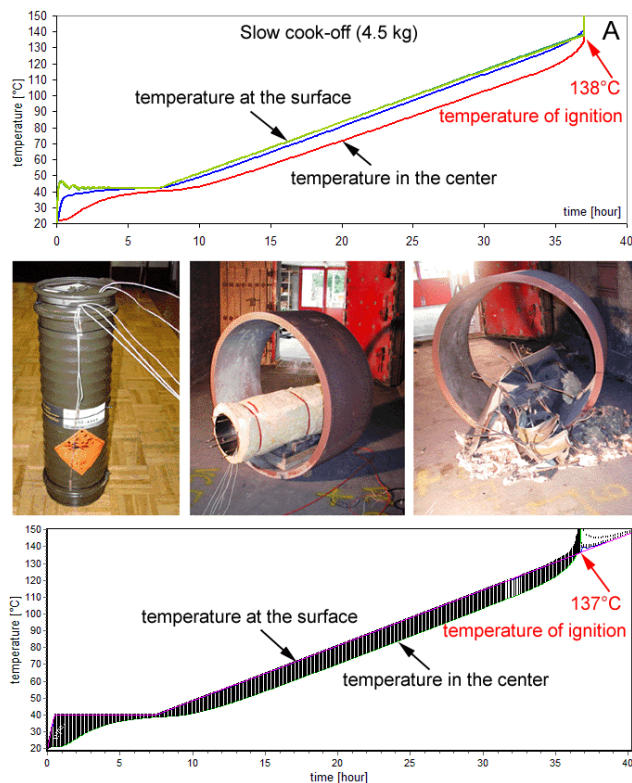


Figure 5: Slow cook-off experiments of a nitrocellulose based substance (A) and simulation (B). As presented in the figure, the predicted temperature of explosion was 137°C . It is in good agreement with the slow cook-off experiments (138°C).

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.

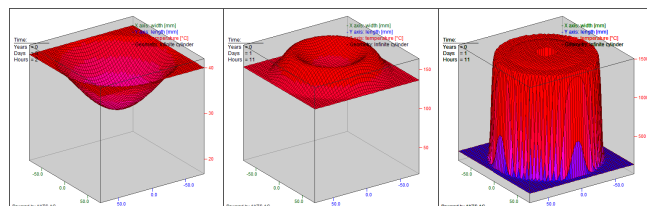


Figure 6: 3D calculations representing the different stages of the slow cook-off performed on the nitro-cellulose based compound.

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 calculated 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.

<http://www.akts.com> & <http://www.setaram.com>

AKTS-Thermokinetics and AKTS-Thermal Safety Software

References

- [1] Stoessel F, Steinbach J, Eberz A: Plant and process safety, exothermic and pressure inducing chemical reactions, In: Ullmann's encyclopedia of industrial chemistry. Weise E (Eds), VCH, Weinheim (1995):343-354.
- [2] Roduit B, Borgeat Ch, Berger B, Folly P, Alonso B, Aebischer JN and Stoessel F Advanced kinetic tools for the evaluation of decomposition reactions, J. Therm. Anal. Cal., ICTAC special issue, 80 (2005), 229-236
- [3] Keller A, Stark D, Fierz H, Heinzele E, Hungerbuehler K: Estimation of the TMR using dynamic DSC experiments. Journal of Loss Prevention in the Process Industries (1997) 10(1):31-41.
- [4] B. Roduit, Prediction of the progress of solid state reaction under different temperature modes, Thermochim. Acta, 388 (2002) 377.
- [5] Reuse P, Fierz H, Characterisation of pressure and temperature rise of run-away reactions using temperature-programmed measurements, CHISA 2004 Proceedings [510].
- [6] M.E. Brown et al. Computational aspects of kinetic analysis. Part A: The ICTAC Kinetics project data, methods and results. Thermochim. Acta, 355 (2000) 125.
- [7] M. Maciejewski, Computational aspects of kinetic analysis. Part B: The ICTAC Kinetics Project - The decomposition kinetics of calcium carbonate revisited, or some tips on survival in the kinetic minefield. Thermochim. Acta, 355 (2000) 145.
- [8] Burnham A K, Computational aspects of kinetic analysis. Part D: The ICTAC kinetics project - multi-thermal-history model-fitting methods and their relation to isoconversional methods. Thermochimica Acta 355 (2000) 165-170
- [9] B. Roduit, Computational aspects of kinetic analysis. Part E: The ICTAC Kinetics Project - Numerical techniques and kinetics of solid state processes, Thermochim. Acta 355, 171-180, 2000.
- [10] Friedman H L: J. Polymer Lett., 4 (1966) 323.
- [11] Ozawa T: Bull. Chem. Soc. Japan, 38 (1965) 1881.
- [12] Flynn J H, Wall L A, J. Res. Nat. Bur. Standards, 70A (1966) 487.
- [13] Gygax, R., Thermal Process Safety, Data Assessment, criteria, measures, ed. ESCIS. Vol. 8. 1993, Lucerne: ESCIS.
- [14] Roduit B, Borgeat Ch, Berger B, Folly P, Alonso P, Aebischer JN, The prediction of thermal stability of self-reactive chemicals: From milligrams to tons, J. Therm. Anal. Cal., ICTAC special issue, 80 (2005), 91-102

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