

Modeling of properties of energetic materials: influence of surrounding temperature and container properties on the time to self-ignition

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The critical temperature-time regime of the self-ignition of energetic ammunition systems is usually investigated by elaborated experimental setups, e.g. in the EIDS slow cook-off the sample is heated with a rate of 3.3°C/h in a steel container. The results collected in such experimental setups can be successfully simulated by applying kinetic parameters obtained from non-isothermal isochoric experiments (closed crucibles) performed on any commercial Differential Scanning Calorimetry (DSC) system. During modeling two important factors have to be considered: (i) the application of advanced kinetics, which properly describes the complicated, multistage course of the decomposition process and (ii) the effect of heat balance in the energetic ammunition system, as the sample mass is increased by a few order of magnitude compared to the thermoanalytical DSC experiments. The correct accumulation of heat for large sample masses can be calculated by applying Finite Element Analysis (FEA) methods as described by us in [1-2].

The results of modeling have been verified by the comparison with the experimentally determined values of the time to ignition for single base propellant being used in 5.56 mm small caliber system and a new 155 mm artillery charge for the Swiss army under isothermal conditions. For the artillery charge the simulations have been done for the sample being in the form of cylinder containing three layers of the materials possessing significantly different thermal properties, namely single-base propellant, combustible cartridge case and steel container. The very good prediction of the experimental results indicates the high accuracy of the applied method.

Evaluation of kinetics

The evaluation of the kinetics of the decomposition of energetic materials is one of the main prerequisites necessary for the correct modelling of their properties. Generally, the kinetic parameters are calculated from the experimental data obtained either from thermogravimetry (change of the mass, TG) or differential thermal analysis (monitoring thermal effects, DSC or DTA). Independent of the experimental technique applied, the kinetic calculations require the dependence of the reaction extent α on the time or temperature. Calculations of the reaction progress are much easier from TG data and require only the correction of the signal due to the buoyancy phenomena. More complicated is the determination of the relationship α - T from DSC (DTA) traces because it requires the integration of the signals influenced by the construction of the baseline.

Often applied the straight-line form of the baseline is incorrect [3]. The recorded signal depends not only on the heat of the reaction but is additionally affected by the change of the specific heat of the mixture reactant-products during the progress of the reaction.

With:

$B(t)$ the baseline,

$S(t)$ the differential signal (DSC or DTA)

the reaction rate $\frac{d\alpha}{dt}$ and progress $\alpha(t)$ can be expressed as

$$\frac{d\alpha}{dt} = \frac{(S(t) - B(t))}{\int_{t_0}^{t_{end}} (S(t) - B(t)) dt} = \left[\frac{1}{s} \right] \quad (1)$$

$$\alpha(t) = \frac{\int_{t_0}^t (S(t) - B(t)) dt}{\int_{t_0}^{t_{end}} (S(t) - B(t)) dt} \quad (0 < \alpha < 1) \quad (2)$$

with

$$B(t) = (1 - \alpha(t)) \cdot (a_1 + b_1 \cdot t) + \alpha(t) \cdot (a_2 + b_2 \cdot t) \quad (3)$$

where:

$(a_1 + b_1 \cdot t)$ is a tangent at the beginning and $(a_2 + b_2 \cdot t)$ a tangent at the end of the signal $S(t)$. The construction of the baseline for the DSC signal obtained during decomposition of the single base propellant with a heating rate of 1 K/min is depicted in the Fig.1.

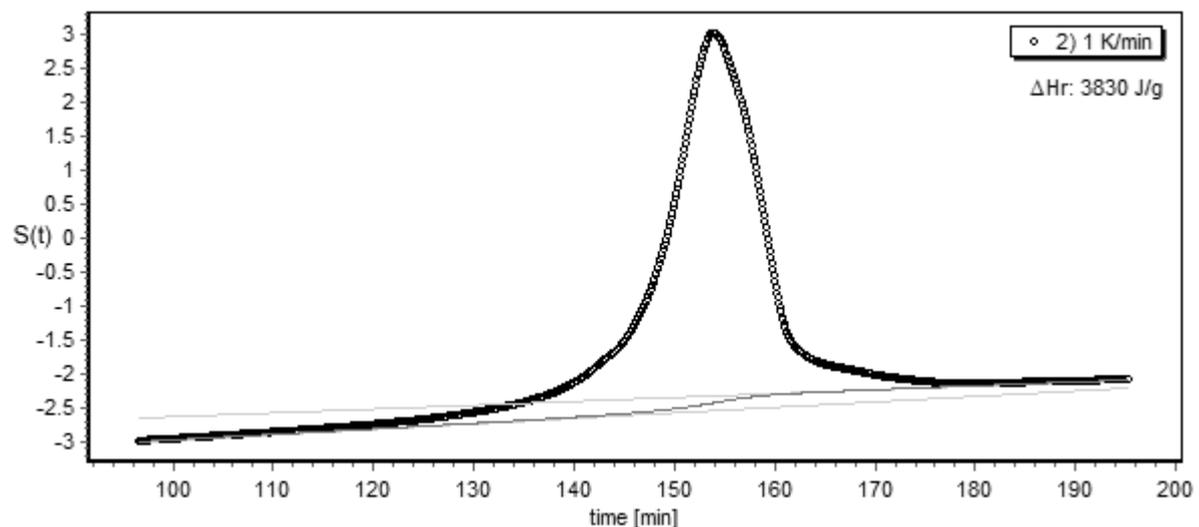


Fig.1. Single base propellant: the construction of the baseline for DSC heat flow signal recorded with the heating rate of 1 K/min. (units of $S(t) = [mW/mg]$).

After correct determination of the α and da/dt values the next step of modelling consists of determination of the kinetic parameters which are necessary

for the prediction of the properties of the investigated materials under conditions different than those at which the experiments have been carried out. If the decomposition follows a single kinetic model then the reaction can be described in terms of a single pair of Arrhenius parameters and the commonly used set of functions $f(\alpha)$ reflecting the mechanism of the process. In such a case the dependence of the logarithm of the reaction rate over $1/T$ is linear with the constant slope $m = E/R$ in full range of conversion degree α . The reaction rate can be described by only one value of the activation energy E and one value of the pre-exponential factor A by the following expression:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT(t)}\right) f(\alpha) \quad (4)$$

where t is time, T - temperature, E - the activation energy, A - the pre-exponential factor and $f(\alpha)$ is the differential form of the conversion function.

However, the decomposition reactions are sometimes too complex to be described in terms of a single pair of Arrhenius parameters (A and E) and the commonly applied set of reaction models $f(\alpha)$. In general, solid state reactions demonstrate profound multi-step characteristics. The assumption that the decomposition of an energetic material will obey a simple rate law is not often true. Moreover, the determination of the kinetic parameters from single run recorded with one heating rate only (so called 'single curve' method) leads to erroneous results and according to the recent opinions should not be applied anymore [4].

As concluded in the International ICTAC Kinetics project [5], the proper calculation of the kinetics requires the series of non-isothermal measurements carried out at different heating rates. This procedure allows supplying the data set that generally contains the necessary amount of information required for full identification of the complexity of a process.

In the present paper the kinetic parameters have been calculated by an isoconversional method based on the calculation of E and A values at different degrees of conversion α without assuming the form of $f(\alpha)$ function, i.e. applying logarithmic form of the following reaction rate expression :

$$\frac{d\alpha}{dt} = (A(\alpha) f(\alpha)) \exp\left(-\frac{E(\alpha)}{RT(t)}\right) = (A^*(\alpha)) \exp\left(-\frac{E(\alpha)}{RT(t)}\right) \quad (5)$$

according to the isoconversional method of Friedman [6]

$$\ln \left. \frac{d\alpha_i}{dt} \right|_{\alpha_i} = \ln(A(\alpha_i) f(\alpha_i)) - \frac{E(\alpha_i)}{RT_{i,j}} = \ln \left. \frac{d\alpha_i}{dt} \right|_{\alpha_i} = \ln(A^*(\alpha_i)) - \frac{E(\alpha_i)}{RT_{i,j}} \quad (6)$$

with i : index of conversion, j : index of heating rate.

The illustration of the Friedman isoconversional method for the determination of the kinetic parameters for small calibre propellant is depicted in Fig.2A. The Fig.2B presents the dependence of E and A on the reaction progress and Fig.2C shows the comparison of the experimental (dots) and calculated, applying the

determined E and A values, courses of the reactions for different heating rates (lines). Note the very good fit of calculated and experimental relationships.

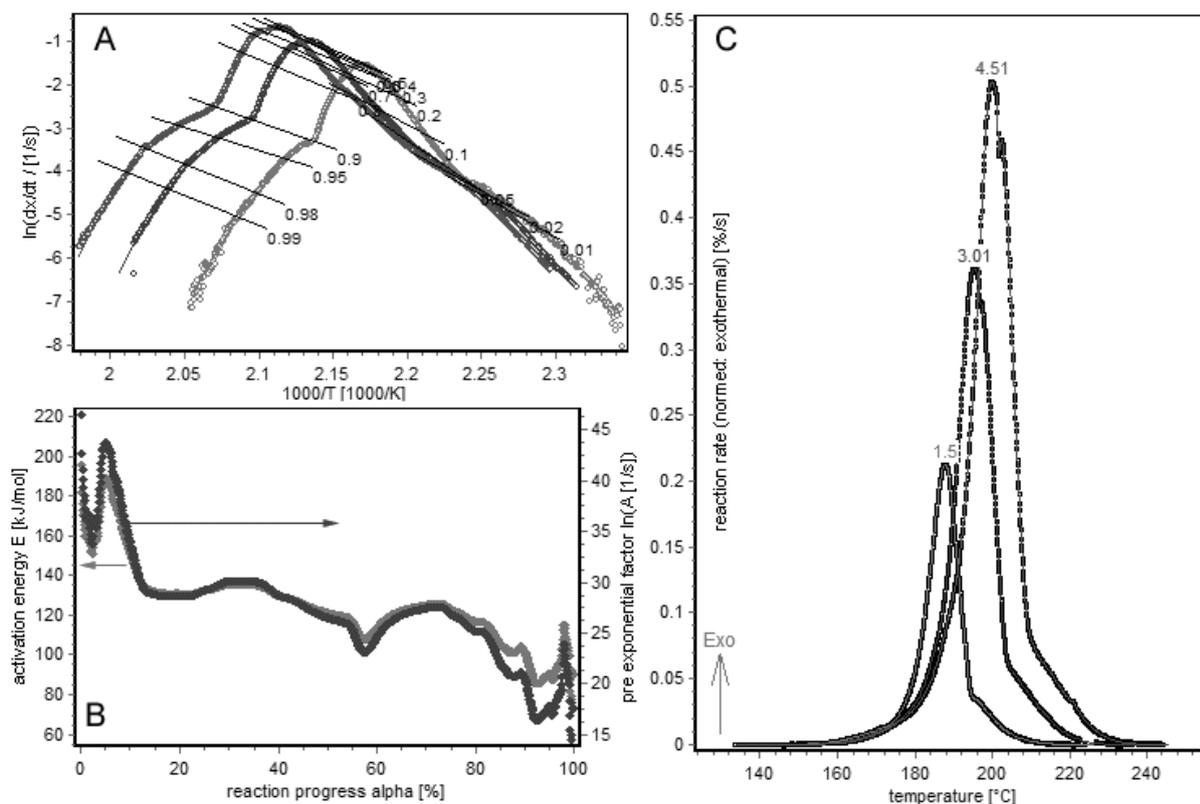


Fig.2: Kinetic analysis of small caliber propellant:

(A) Friedman analysis carried out with DSC data obtained under isochoric conditions (after baseline optimization). (B) Activation energy E and pre-exponential factor A as a function of the reaction progress. (C) Normalized DSC-signals as a function of the temperature and heating rate (marked in $^{\circ}C/min$ on the curves). Experimental data are depicted as symbols, solid lines represent the signals calculated on the basis of kinetic parameters determined by the method presented in Figs. 2A and B.

Determination of the heat accumulation under adiabatic and non-adiabatic conditions

Determined kinetic parameters can be subsequently applied for predicting reaction progress of the investigated samples under any given temperature mode. However, it has to be taken into account that during investigating and predicting properties of the real energetic ammunition system the sample mass increases by few orders of magnitude comparing to thermoanalytical DSC experiments. For the proper modelling the heat balance has to be taken into considerations.

The concept of the Time to Maximum Rate under adiabatic conditions (TMR_{ad}) is very often used for describing the safety of chemical processes. TMR_{ad} can be estimated by combining the advanced kinetic description of the investigated process with the following heat balance when $U=0$ for the adiabatic conditions:

$$\begin{cases} \frac{d\alpha}{dt} = \text{reaction rate expression} \\ M_R c_p \frac{dT}{dt} = V(-\Delta H_R) C_o \frac{d\alpha}{dt} + UA(T_c - T) \end{cases} \Rightarrow \begin{cases} \frac{d\alpha}{dt} = \text{reaction rate expression} \\ \frac{dT}{dt} = \frac{UA}{M_R c_p} (T_c - T) + \Delta T_{ad} \frac{d\alpha}{dt} \end{cases} \quad (7)$$

where:

M_r - sample mass, C_p - specific heat, V - volume, ΔH_r - heat of the reaction, U - heat transfer coefficient, A - heat exchange area, T_c - surface temperature of the container, T - surrounding temperature.

The value of the heat of reaction is one of the key data required for correct evaluation of the potential risk. It gives a direct measure of the consequences which result from a runaway scenario. Commonly, instead of the heat of the reaction, the adiabatic temperature rise $\Delta T_{ad} = \Delta H_r / c_p$ is taken into considerations.

The numerical simulation technique can be applied also in determination of the process safety carried out under non-adiabatic conditions i.e. when $U \neq 0$. This option requires the solution of partial differential equations as they are encountered in the heat conduction problem, especially when analyzing the heat accumulation conditions. In order to consider the change of the temperature inside the layer a heat balance over a volume element (see Fig. 3) can be made as follows:

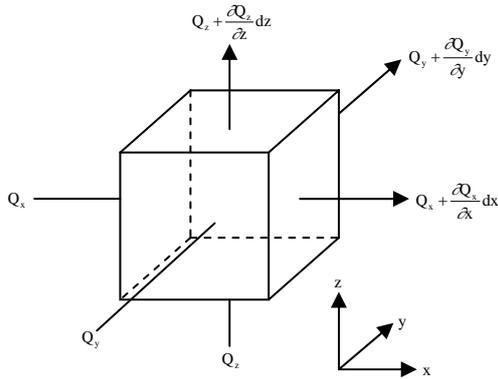


Fig. 3: Heat balance over a volume element.

Assuming the relationship:

Input = Output + Accumulation + Reaction

we get:

$$Q_x + Q_y + Q_z = \left(Q_x + \frac{\partial Q_x}{\partial x} dx \right) + \left(Q_y + \frac{\partial Q_y}{\partial y} dy \right) + \left(Q_z + \frac{\partial Q_z}{\partial z} dz \right) + \frac{d(\rho c_v T)}{dt} dV + Q_r dV \quad (8)$$

where Q , ρ , c , V , T mean: heat flow, density, specific heat, volume and temperature, respectively. With $dV = dx dy dz$

$$Q_x = -\lambda dy dz \frac{\partial T}{\partial x}, Q_y = -\lambda dx dz \frac{\partial T}{\partial y}, Q_z = -\lambda dx dy \frac{\partial T}{\partial z} \quad (9)$$

and considering different cylindrical pre-defined geometries of the reactors applied in the cook-off experiments, we can write:

$$\frac{\partial T}{\partial x} \gg \frac{\partial T}{\partial z} \Rightarrow \frac{\partial^2 T}{\partial x^2} \gg \frac{\partial^2 T}{\partial z^2} \quad \text{and} \quad \frac{\partial T}{\partial y} \gg \frac{\partial T}{\partial z} \Rightarrow \frac{\partial^2 T}{\partial y^2} \gg \frac{\partial^2 T}{\partial z^2} \quad (10)$$

The heat balance (eq. 8) after further mathematical treatment can now, after simplification, be expressed as

$$\frac{dT}{dt} = \frac{\lambda}{c_v \rho} \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right) - Q_r \quad (\text{cartesian coordinates}) \quad (11)$$

or
$$\frac{dT}{dt} = \frac{\lambda}{c_v \rho} \left(\frac{\partial^2 T}{\partial r^2} + \frac{J}{r} \frac{\partial T}{\partial r} \right) - Q_r \quad (\text{cylindrical coordinates}) \quad (12)$$

where J is a geometry factor which is dependent on the type of the container: J=0 for the infinite plate, J=1 for the infinite cylinder and J=2 for the sphere.

$$Q_r = \frac{\Delta H_r}{c_p} \frac{d\alpha}{dt} = \Delta T_{ad} \frac{d\alpha}{dt} \quad (13)$$

The rate of the heat production in eq. (13) can be expressed by the Arrhenius type equation as those applied in Friedman analysis (eq.5).

Simulation of the properties of small caliber ammunition

Applications of Finite Element Methods and accurate kinetic description of the single-base propellant applied in small caliber ammunition enabled the determination of the effect of scale, geometry, heat transfer, thermal conductivity and ambient temperature on the heat accumulation conditions. 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.

The goal of the simulations was the prediction of the time to self-ignition of the ammunition systems due to the accumulation of the heat when kept at constant temperature as during e.g. the cook-off experiments in a hot loading chamber. The results of modeling have been verified by the comparison with the experimentally determined values of the time to ignition for 5.56 mm small caliber system. Figure 4 depicts the comparison of the predicted time to ignition as function of the temperature for non-adiabatic and adiabatic conditions (lines) and presents the experimental results (open circles) which fit very well calculated non-adiabatic dependence.

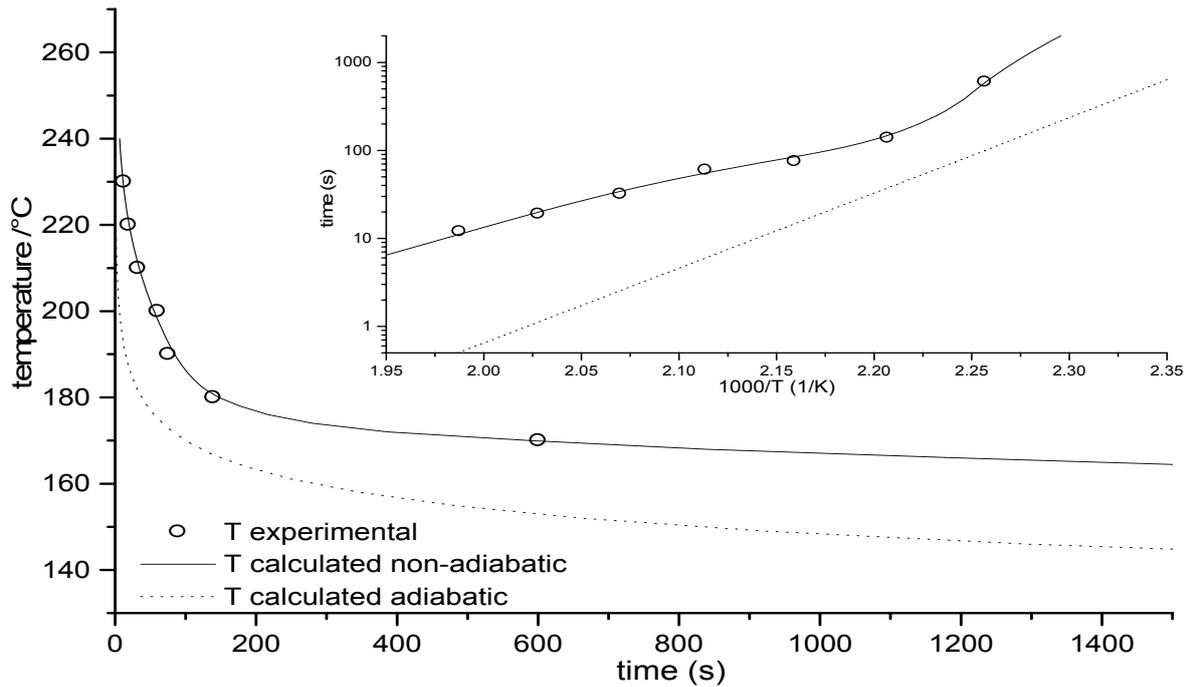


Fig. 4: Single-base propellant for small caliber applications: the dependence of the calculated time to ignition on the temperature under non-adiabatic and adiabatic conditions (with $\Delta T_{ad} = \Delta H_r / c_p = 3496 \pm 464 \text{ J/g} / 1.5 \text{ J/g}^\circ\text{C} = 2330.7^\circ\text{C} \pm 309^\circ\text{C}$). The experimental results are marked by open circles, the inset presents the time to ignitions vs. reciprocal temperature.

Simulation of properties of 155 mm artillery charge of Swiss army

Here we extend the simulations under isothermal conditions to the prediction of the time to self-ignition of a 155mm artillery charge used in Swiss army. During modeling the geometry, dimension of the ammunitions container and, additionally, the amount, properties and thickness of the layers of different materials used for the construction of the ammunition container have been taken into account. Application of FEA and the appropriate decomposition kinetics (calculation results presented in Fig.5) enabled the determination of the effect of scale and geometry of the container as well as the heat transfer, thermal conductivity and surrounding temperature on the heat accumulation in the sample.

The simulations (simulation results together with the experimental data are depicted in Fig.6) have been done for the sample in the form of cylinder containing four layers of the following materials possessing significantly different thermal properties: single-base propellant, combustible cartridge case, protection material and steel container. The properties of these materials, required for the modeling, are summarized in Tab. 1.

	container wall	protection material	combustible cartridge case	single-base propellant
Layer thickness [mm]	0.7	9	3	64.5
$\lambda / (\rho C_p)$ [cm^2/s]	0.15	0.13	0.005	0.001
Heat of reaction [J/g]	-	-	2768 +/- 255.8	3579 +/- 350.6

Table1. The properties of the components of 155 mm artillery charge.

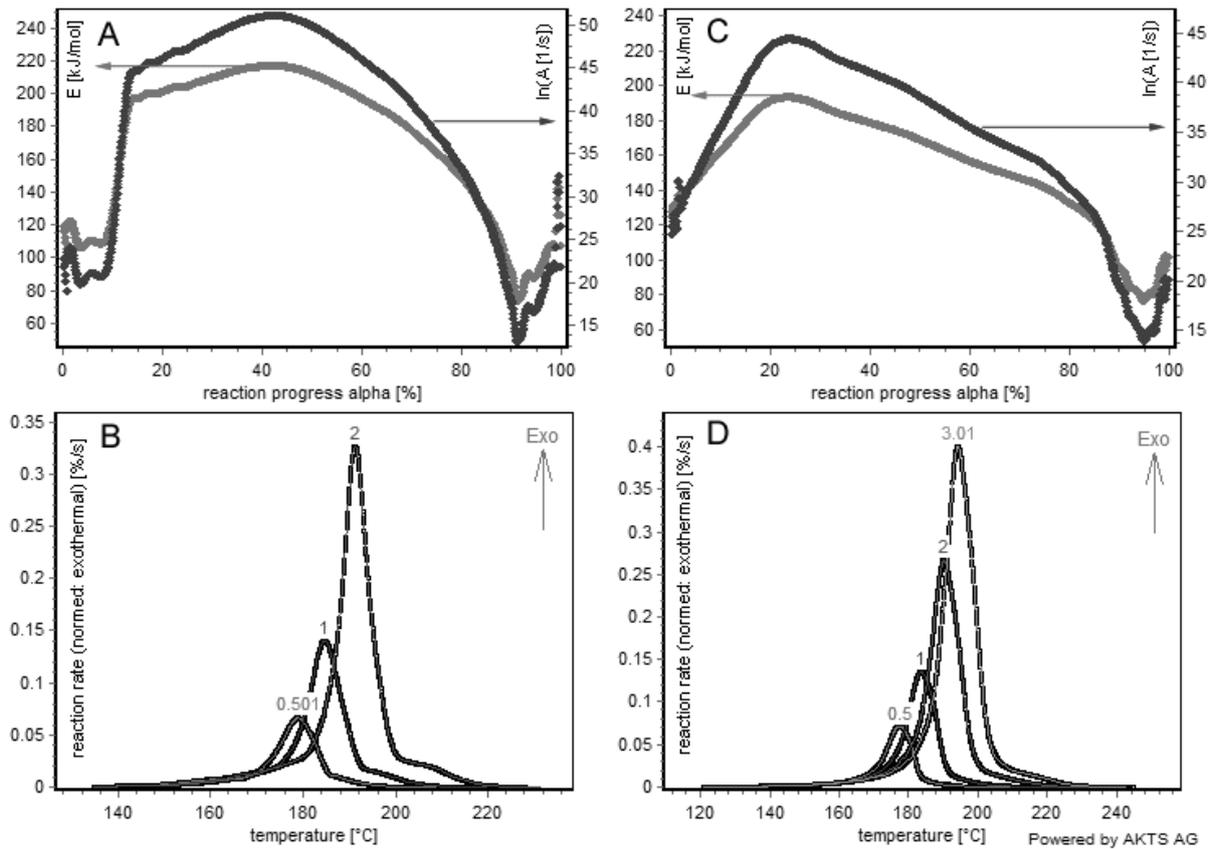


Fig.5: Kinetic analysis of 155 mm artillery charge of Swiss army: A, B: combustible cartridge, C, D: single-base propellant. (A, C) Activation energy E and pre-exponential factor A as a function of the reaction progress. (B, D) Normalized DSC-signals as a function of the temperature and heating rate (marked in $^{\circ}\text{C}/\text{min}$ on the curves). Experimental data are depicted as symbols, solid lines represent the signals calculated on the basis of kinetic parameters determined by the Friedman analysis method.

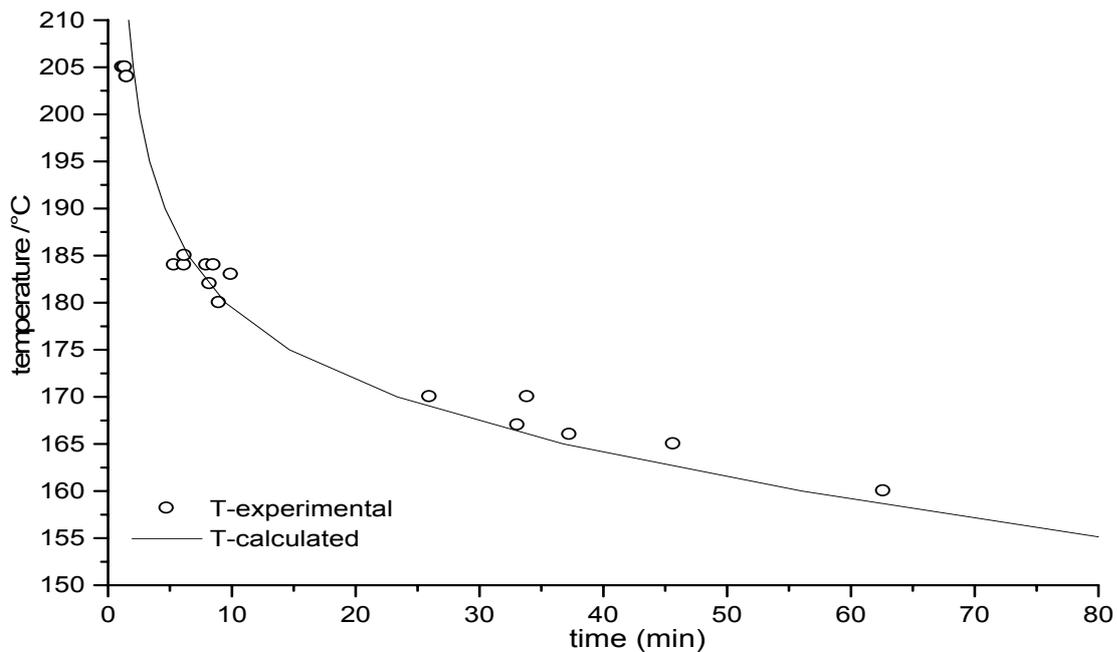


Fig. 6 Single-base propellant for a 155 mm artillery charge applied in Swiss army: the dependence of the calculated time to ignition on the temperature under non-adiabatic conditions. The experimental results are marked by open circles, the line presents the simulated relationship.

Additionally to the isothermal investigations of the properties of the energetic materials also the commonly applied non-isothermal cook-off experiment (heating rate 3.3 °C/h, initial temperature of the charge 40°C, 6h) has been carried out with the 4.5 kg artillery charge. The experimental data and results of the simulation of the slow cook-off investigation are presented in the Fig. 7. For the simulation of the experimental results the heat balance calculated by the Finite Element Analysis (FEA) was applied together with the advanced kinetic description of the reaction. The experimentally determined ignition temperature of artillery charge amounted to 137°C (Fig. 7-A). The predicted ignition temperature of 138°C (Fig. 7-B) was in a very good agreement with the experimental value.

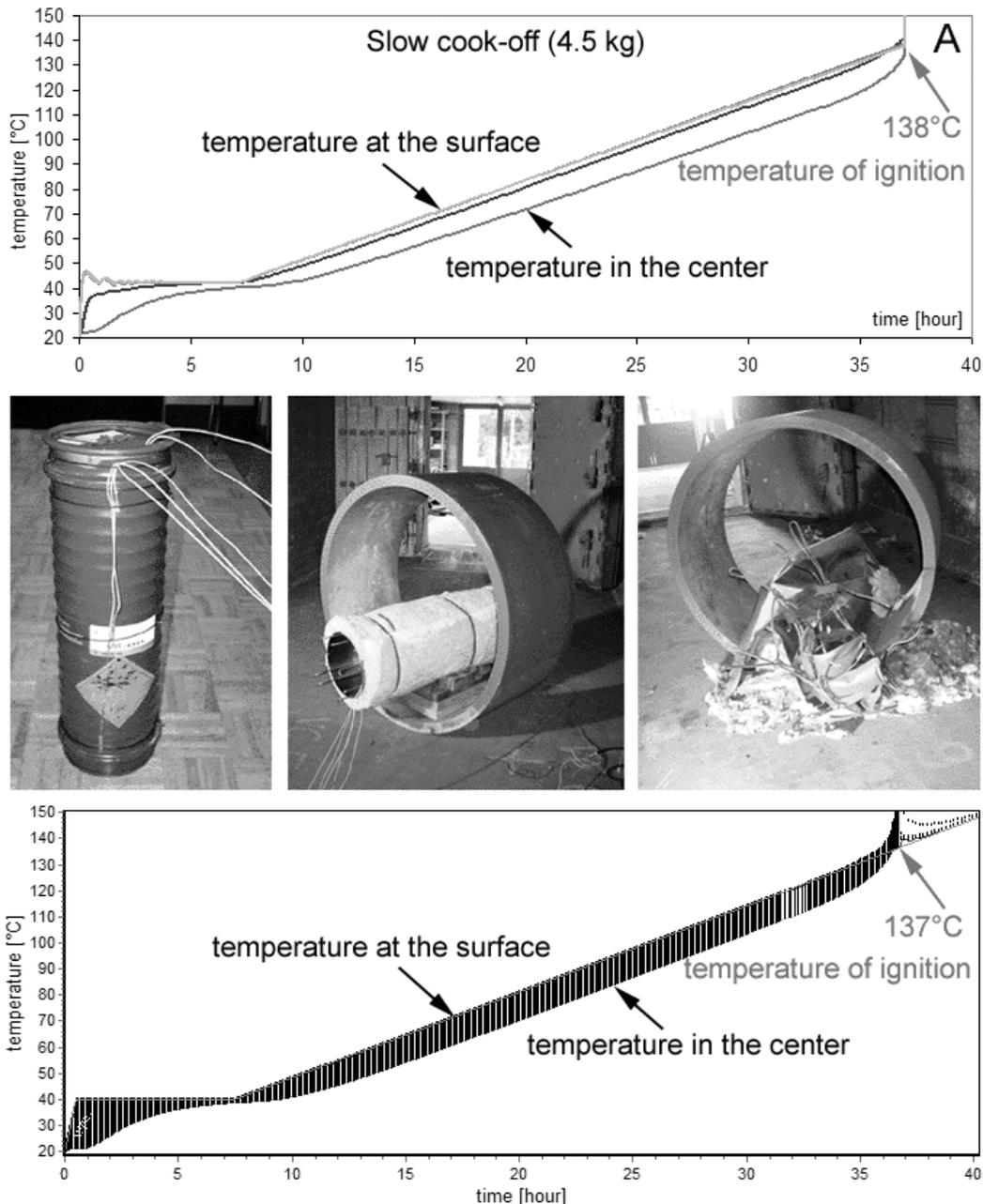


Fig.7. Slow cook-off of the 155 mm artillery charge (A) experiment and (B) simulation. The predicted temperature of explosion 137°C was in good agreement with the slow cook-off experiment (138°C).

Conclusions

Application of FEA and the appropriate decomposition kinetics enabled the determination of the effect of scale and geometry of the container as well as the heat transfer, thermal conductivity and surrounding temperature on the heat accumulation in the sample. The results of the simulation of the properties of both, small-caliber and 155 mm charge under isothermal conditions and during non-isothermal slow cook-off agreed very well with the experimentally determined values. Applied modeling procedure allows the optimal choice of the design parameters of the containers such as critical radius and the kind and thickness of the insulation. The simulation can be done for any profile of the surrounding temperature, starting from the isothermal through stepwise, modulated or temperature shock resulting e.g. from an external fire. Additionally, the temperature profiles, reflecting the real daily minimal-maximal fluctuations for different localizations, can be taken into account. The software enables simulating time to the ignition due to an unexpected incident during transportation as well.

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