

Thermal Characterization Of Naturally Aged Gun And Rocket Propellants

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Abstract

In this work, seven different, naturally aged gun propellants and four rocket propellants have been investigated by heat flow calorimetry, ARC, mass loss and stabilizer consumption. The investigated gun propellants are A 5020, K 503, GK 5030, Feldgeschütz Rottweil 1909 (FG 1909), K 6210, US M5 and US M26, the rocket propellants are D 714, HV 5, DBE 40, DBE 470 each with ageing time ranging up to several decades of natural ageing. From heat flow calorimetry data, activation energies for stabilizer consumption, NC decomposition and autocatalytic reaction are determined as well as time of reaction change depending on temperature of 70 °C, 80 °C and 90 °C. Conversion-dependent activation energy is calculated using an iso-conversional method for the three temperatures. The results are compared to the mass loss results obtained at 90 °C. Based on these results, the overall stability of the propellants is assessed.

Introduction

Nitrocellulose based propellants suffer from thermal degradation. The reason is a scission of nitrated cellulose strains resulting in nitrous gases (NO_x) as reaction products. The gases themselves react with nitrocellulose which leads to accelerated decomposition of NC. Stabilizer is added to NC-containing propellants as a scavenger. The capability of the stabilizer to react with NO_x defines the quality of the stabilizer and therefore determines the service life of the NC. The stabilizer consumption can be monitored by different means, e.g. ageing with subsequent chromatographic analysis of stabilizer content, heat flow calorimetry with kinetic modelling of the recorded heat flow according to stabilizer consumption, mass loss with modelling of the proportion of gaseous compounds or vacuum stability. All eleven propellants aged several decades under ambient conditions. To assess them, all propellants have been investigated using 90 °C mass loss and heat flow calorimetry at 70 °C, 80 °C and 90 °C under argon. The actual heat of explosion for each propellant has also been measured to allow iso-conversional analysis of the heat flow curves.

Results and Discussion

Heat of explosion

Heat of explosion was determined in a bomb calorimeter with each propellant determined threefold. The results are shown in Figure 1.

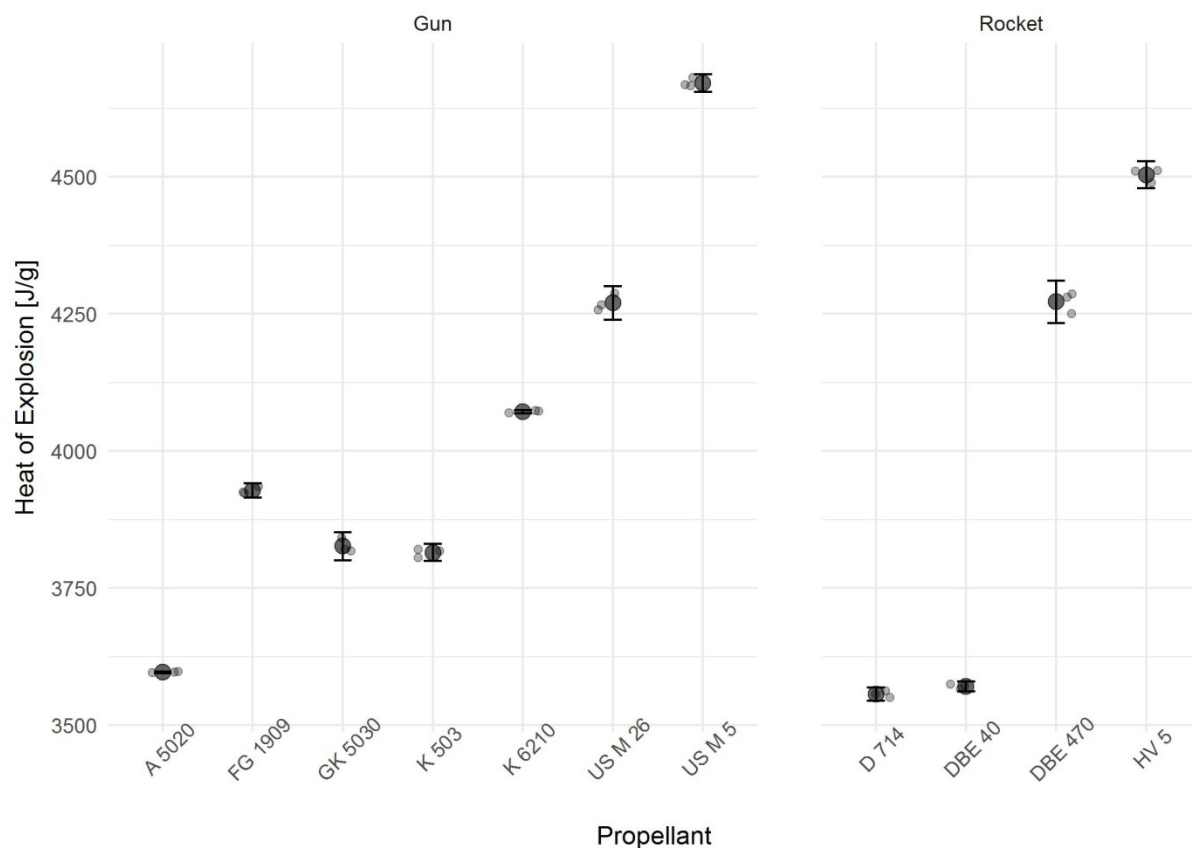


Figure 1: Heat of explosion for investigated propellants. For each propellant, the three values as well as mean and standard deviation are given.

Heat flow calorimetry

All propellants are isothermally measured at 70 °C, 80 °C and 90 °C. The samples were placed in stainless steel vials with inserted glass tubes. During the measurement, the samples were kept under Argon atmosphere. An exemplary plot is shown in Figure 2. The heat flow curves are investigated using different methods: integral iso-conversional method, differential iso-conversional model (Friedman model) and kinetic modelling of the heat flow curves using a combined first and zero order reaction mechanism for the first part and a first order autocatalytic reaction mechanism afterwards. From these approaches, activation energies for the different propellants are calculated. Additionally, a simple approach to estimate activation energy and pre-exponential factor is compared.

Iso-conversional method is a model-free kinetic that assumes that the same reaction progress leads to the same amount of reaction heat independent of the temperature of the sample. The reaction progress or conversion is named α and is defined as $\alpha = \frac{Q(t)}{Q_{max}}$. Q_{max} can be defined in different ways, e.g. the lowest amount of heat measured at the end of different heat flow measurements, .i.e. $Q_{max} = \min(\max(\{Q_1, \dots, Q_n\}))$. In this work, Q_{max} is the total heat of explosion as shown in Figure 1. This also means that α is the total conversion. Here, the samples were measured for 35 days at 70 °C, (standard STANAG time) as well as 80 °C and 90 °C. For the integral method shown in Equation 1, the time elapsed to reach a given conversion at a given temperature is used to calculate kinetic parameters:

$$\ln k(\alpha) = \ln \frac{1}{t(\alpha)} = \ln A(\alpha) - \frac{E_a(\alpha)}{R} \cdot \frac{1}{T}$$

Equation 1: Iso-conversional method, integral form. This form is directly derived from the Arrhenius equation.

The differential method is based of Friedman's model [1]. This model uses the actual heat flow as shown in Equation 2.

$$\ln \frac{dQ(\alpha)}{Q_{max}} = \ln A(\alpha) - \frac{E_a(\alpha)}{R} \cdot \frac{1}{T}$$

Equation 2: Iso-conversional method, differential form or Friedman method.

Both methods are model-free which means they provide activation energy for each conversion but they do neither give information about reaction order nor take changing reaction mechanisms into account.

To compensate for this, a kinetic modelling was applied to the different heat flow curves. In the first step, evaporation of volatile compounds and stabilizer consumption are assumed to be of first order and zero order reaction, respectively. The total heat flow is described Equation 3. a is a partitioning factor, that describes the proportion that each heat of reaction contributes to the total heat; k_0 and k_1 are the respective reaction rate constants for both reactions.

$$Q(t) = Q_{max} \cdot ((1 - a)k_0 \cdot t + a \cdot (1 - \exp(-k_1 \cdot t)))$$

Equation 3: Heat flow coming from two reactions of zero and first order.

For the second part of the reaction, a first order autocatalytic reaction is assumed [2] and described in Equation 4.

$$Q(t) = Q_{max} \cdot \left(1 - \left(\frac{\beta_1}{k_a + \beta_2 \cdot \exp(\beta_1 \cdot t)} \right) \right)$$

$$\beta_1 = k_1 + (F_0 + 1) \cdot k_a$$

$$\beta_2 = k_1 + F_0 \cdot k_a$$

Equation 4: Heat flow coming from a first order reaction with subsequent autocatalytic reaction

F_0 is the initial concentration of autocatalytic substance. The change of reaction mechanism is determined by the dip in the heat flow curves as can be seen in Figure 2.

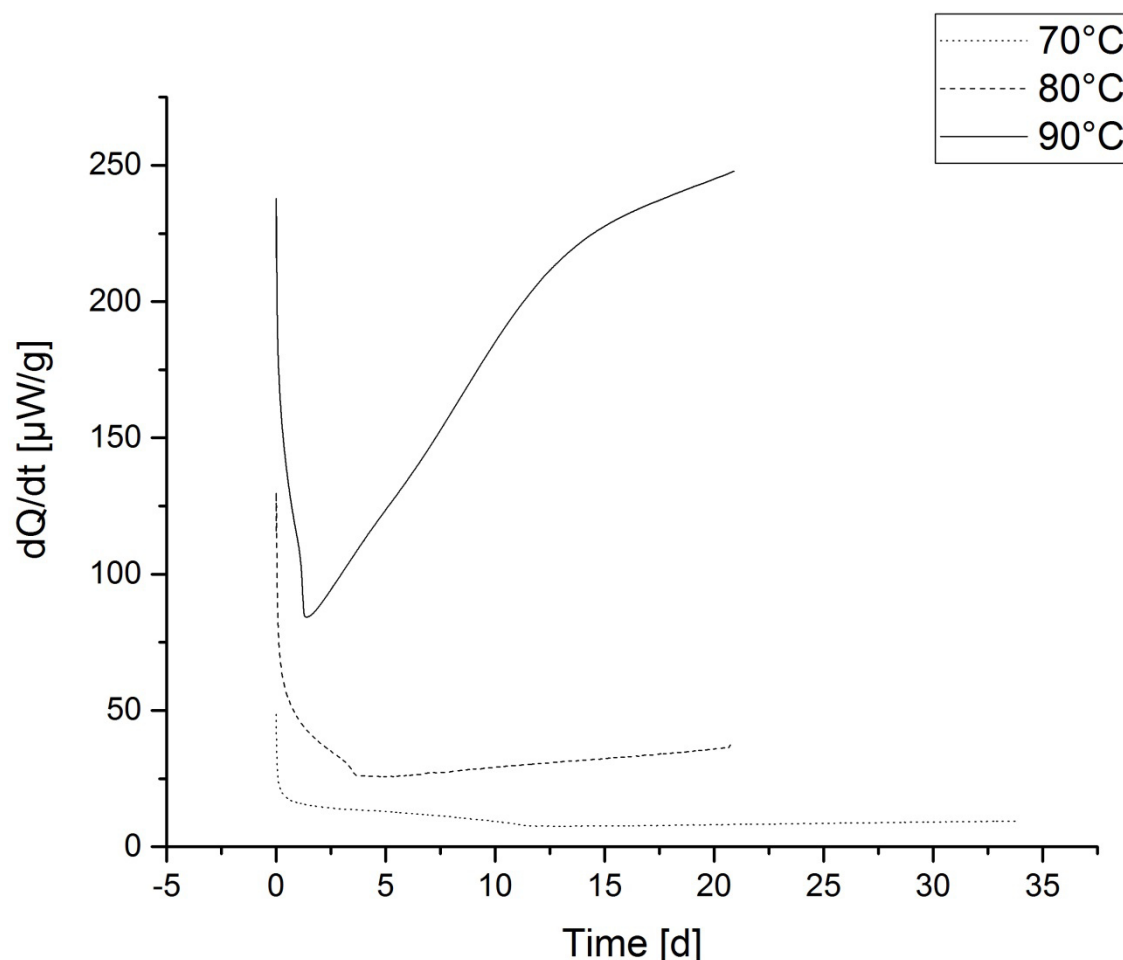


Figure 2: Example of heat flow for different temperatures, in this case FG 1909. The dip in heat flow that serves as point of changing reactions can be clearly seen.

The activation energies of the iso-conversional methods are shown in Figure 3 to Figure 5. Since the model-free kinetics does not lead to constant activation energies for domains of reaction, the activation energies vary at low values of α . However, in most cases both models converge at a certain activation energy that can be used to compare these results to those obtained with modelled reactions.

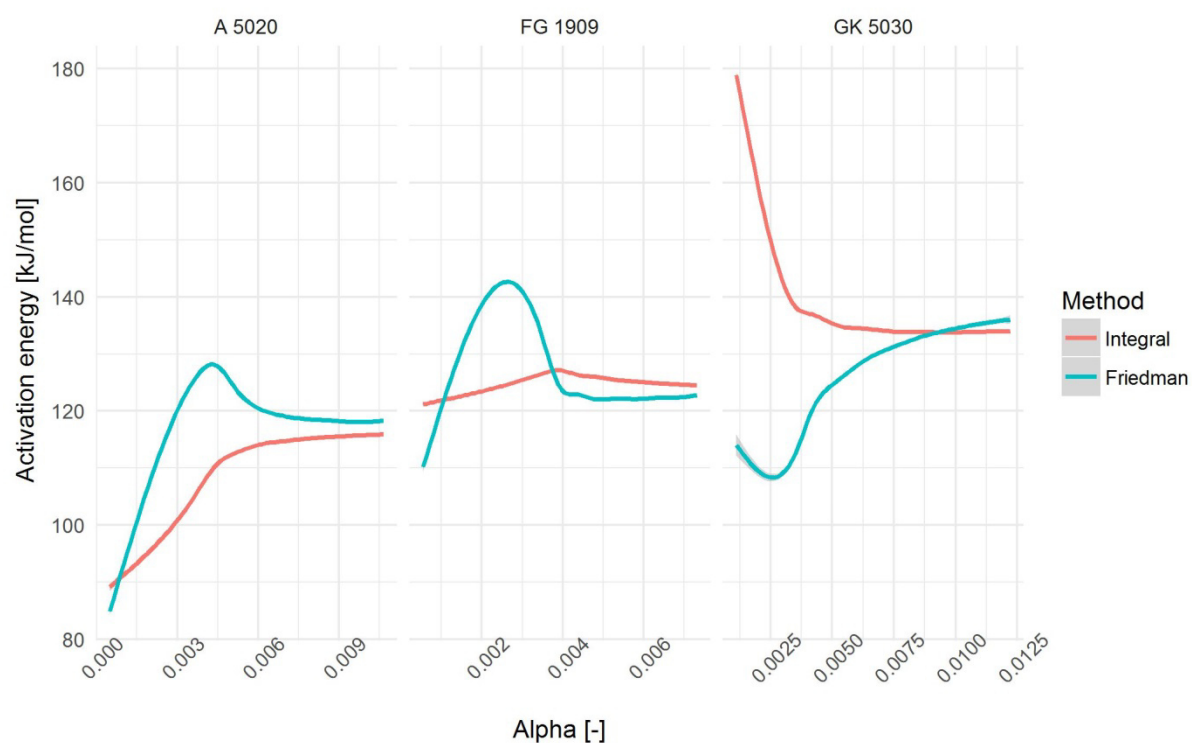


Figure 3: Activation energies of three different gun propellants with model-free kinetics.

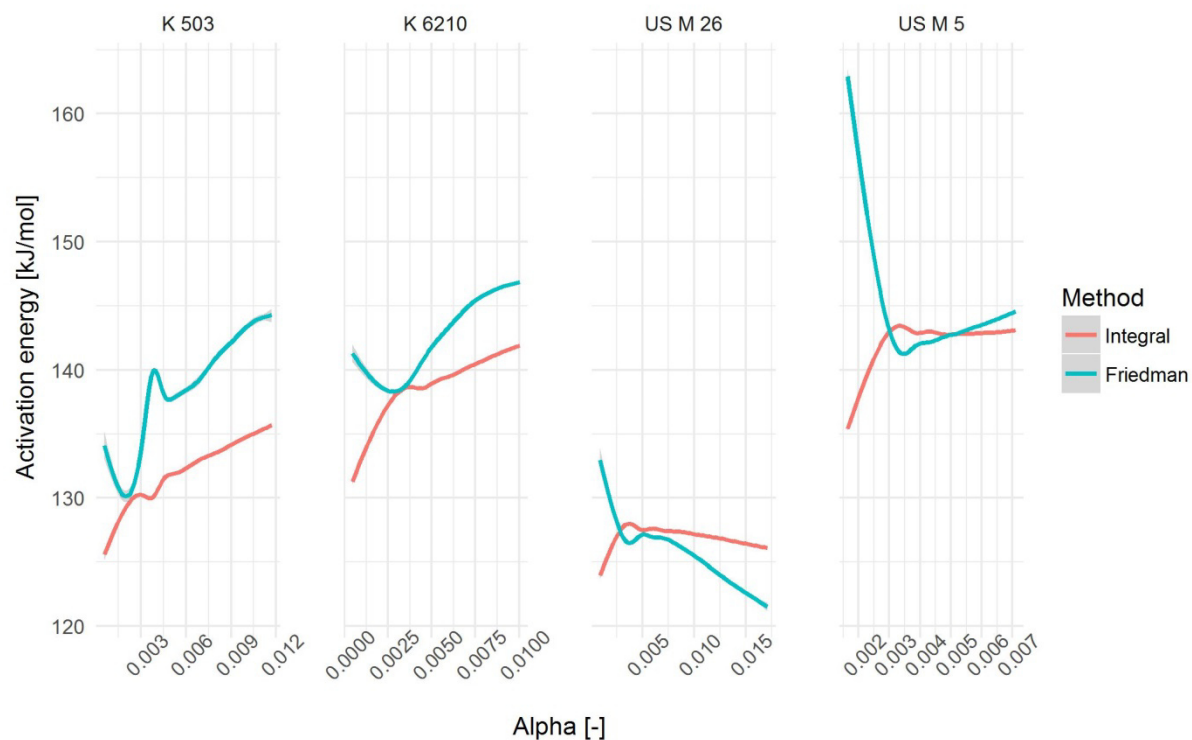


Figure 4: Activation energies of four different gun propellants with model-free kinetics.

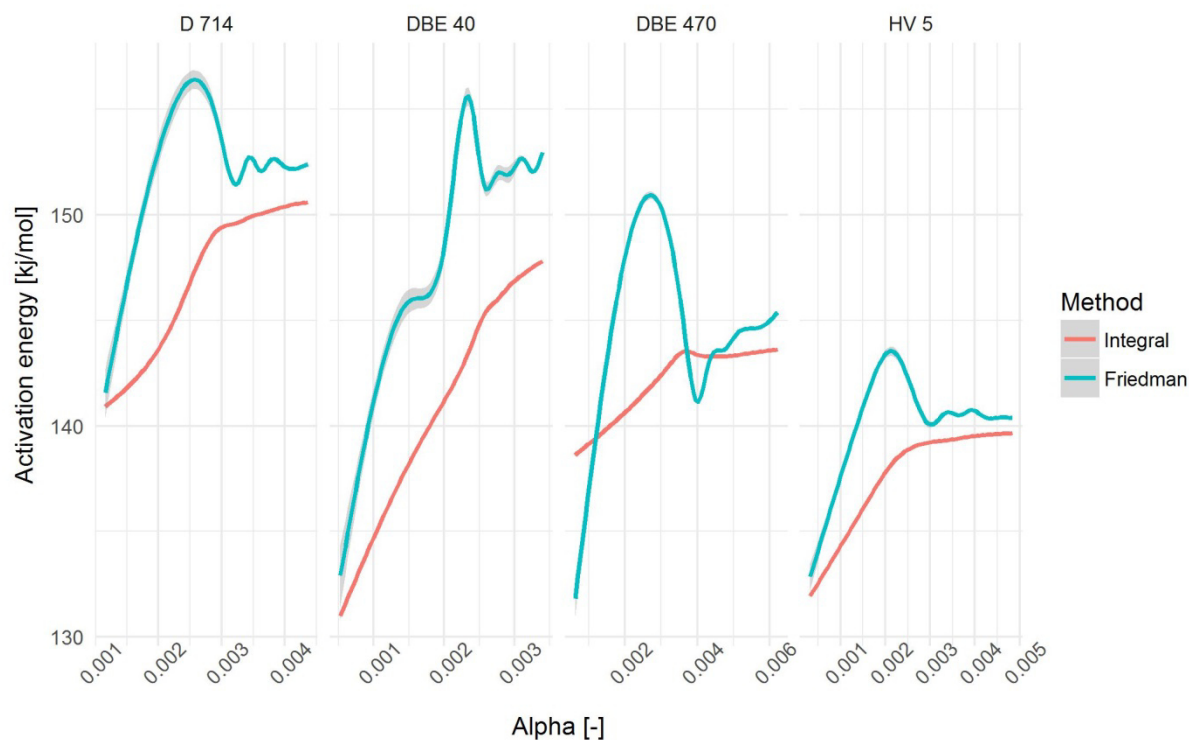


Figure 5: Activation energies of four different rocket propellants with model-free kinetics.

The different iso-conversional methods show different characteristics, particularly in the beginning at low values of α . In theory, both methods should lead to the same result, but it seems that the Friedman method shows more detail, whereas the integral method is more robust. For example the activation energy of D 714 shows some kind of oscillation. Nearly all Friedman curves exhibit some kind of peak (positively or negatively), which might be due to this property or because there is some kind initial reaction. This is not explained by the measurements here. The integral method is not as detailed but does not show a tendency to possibly overshoot.

For each propellant another model can be applied to calculate the activation energy: The heat flow curve of each propellant at each temperature is modelled using Equation 3 and Equation 4. The point, at which the change of reaction mechanism occurs, has been already discussed. The time of reaction mechanism change can also be used to estimate the activation energy using Equation 5:

$$\ln \frac{1}{t_{\text{switch}}(T)} = \ln A - \frac{E_a}{RT}$$

Equation 5: Calculation of activation energy from time to reach mechanisms change

This is a quick and easy way to estimate the activation energy of the decomposition process of a propellant. However it is not describing any mechanisms that may occur. A summary is

given in Figure 6. Since the y-scale is large due to some outliers, a more detailed plot between 100 kJ/mol and 200 kJ/mol is shown in Figure 7.

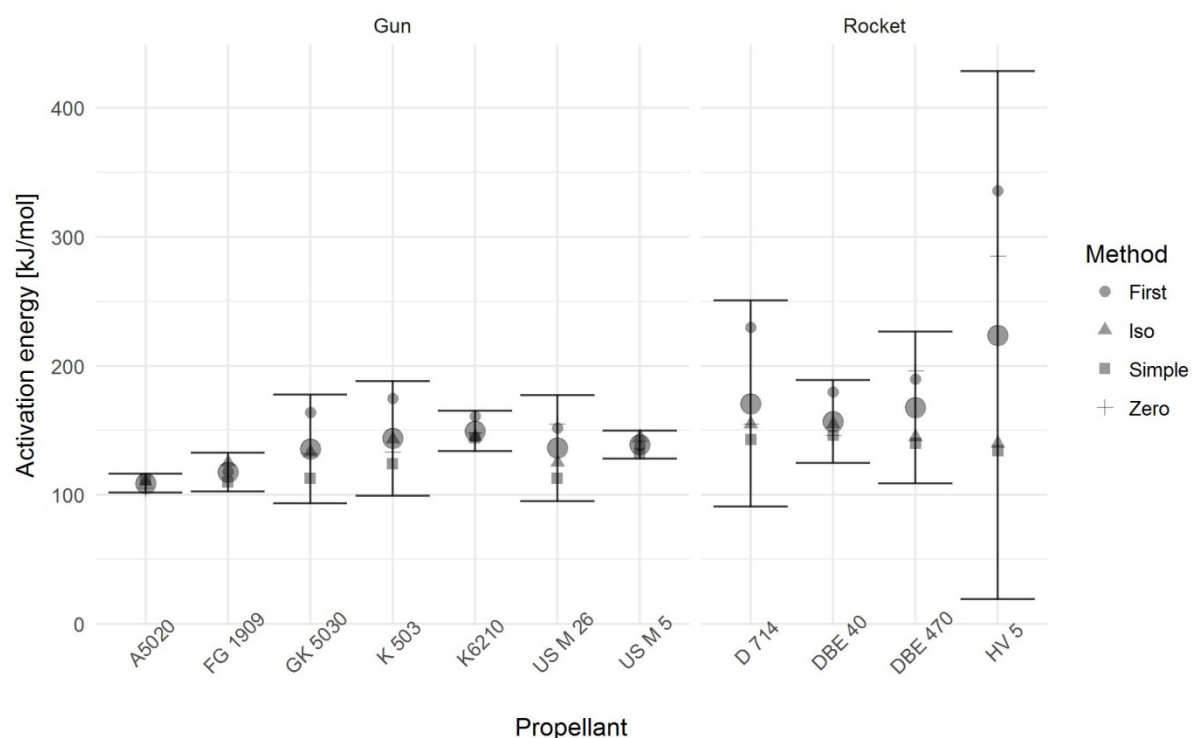


Figure 6: Comparison of activation energies obtained by different methods. Additionally, the mean and standard deviation are given.

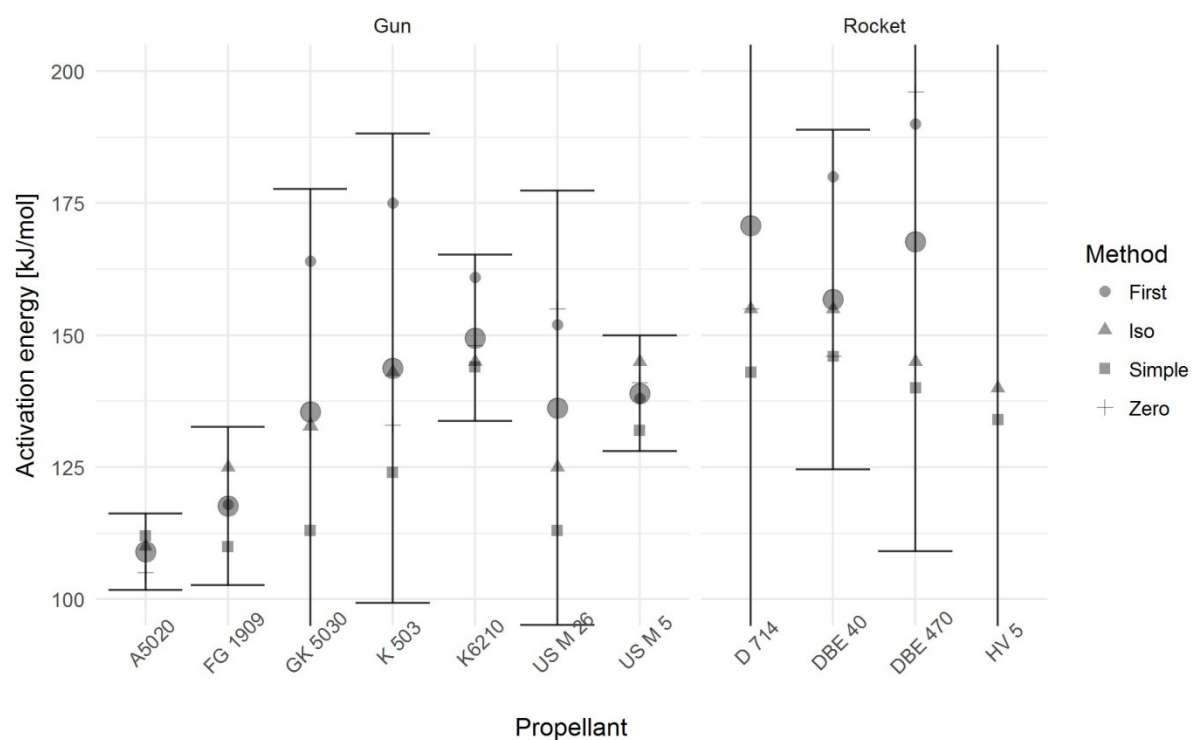


Figure 7: Same as Figure 6, with limited y-scale to show more details.

It is notable that the activation energies obtained by first order decomposition, i. e. decomposition of NC after stabilizer consumption, is in most cases than those obtained by other methods. The activation energy derived from the convergence of the iso-conversional methods and those derived by the simple model of time of reaction mechanism change are mainly similar. For the activation energy derived from zero order stabilizer consumption, no trend can be observed.

Mass loss

Mass loss measurement is performed at 90 °C in a glass vial with a loosely inserted stopper as already reported [3]. The mass loss is only measured at one temperature, so no kinetic parameters can be calculated. However, a general assessment based on the form of mass loss curve can be made. Normally, a mass loss curve shows a mixture of a small but fast mass loss, mostly due to evaporation, and a slow linear mass loss due to stabilizer consumption. If the stabilizer is fully consumed, mass loss increases dramatically, because autocatalytic decomposition of NC takes place. Examples for mass loss curves with and without autocatalytic behavior are shown in Figure 8 and Figure 9.

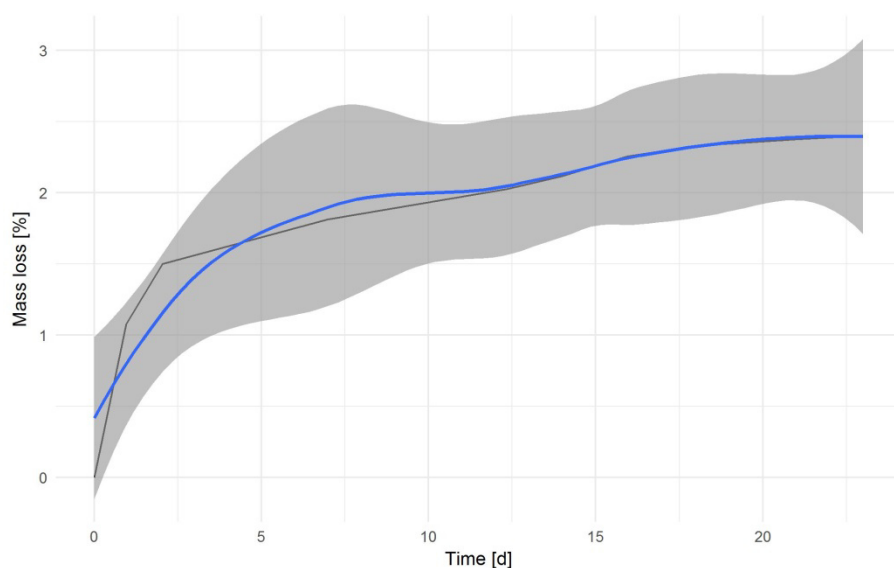


Figure 8: Mass loss curve of A 5020 at 90 °C. The exact values are shown as well as the smoothed curve. No autocatalysis is observed.

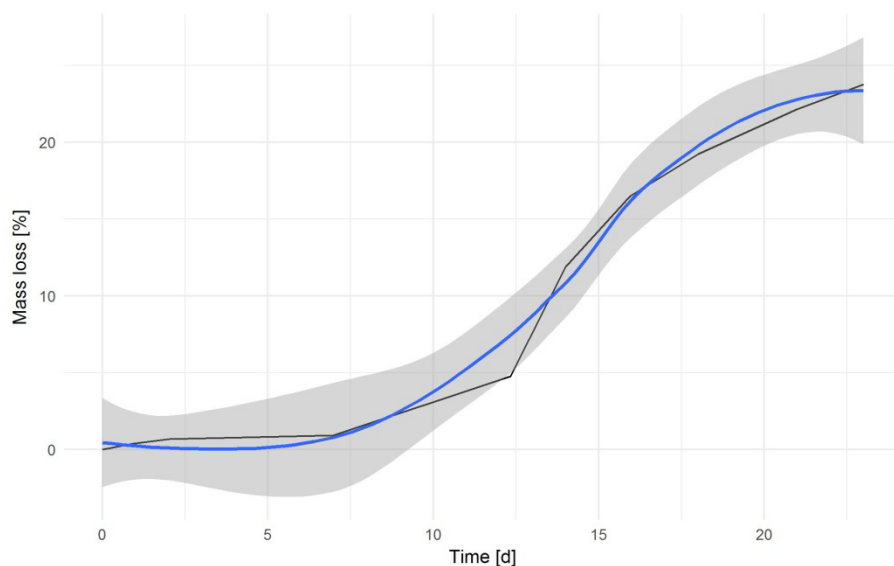


Figure 9: Mass loss of K 6210 gun propellant at 90 °C. The exact values are shown as the thin line, the smoothed curve with standard error is also provided. Autocatalysis is observed after about 7 days.

In both curves the first reaction mechanism, fast first order evaporation and slow zero order reaction can be observed. K 6210 in Figure 9 however shows autocatalytic behavior after approx. 7 days, resulting in a large increase in mass loss with the typical sigmoid shape.

Figure 10 shows the mass loss of all investigated propellants.

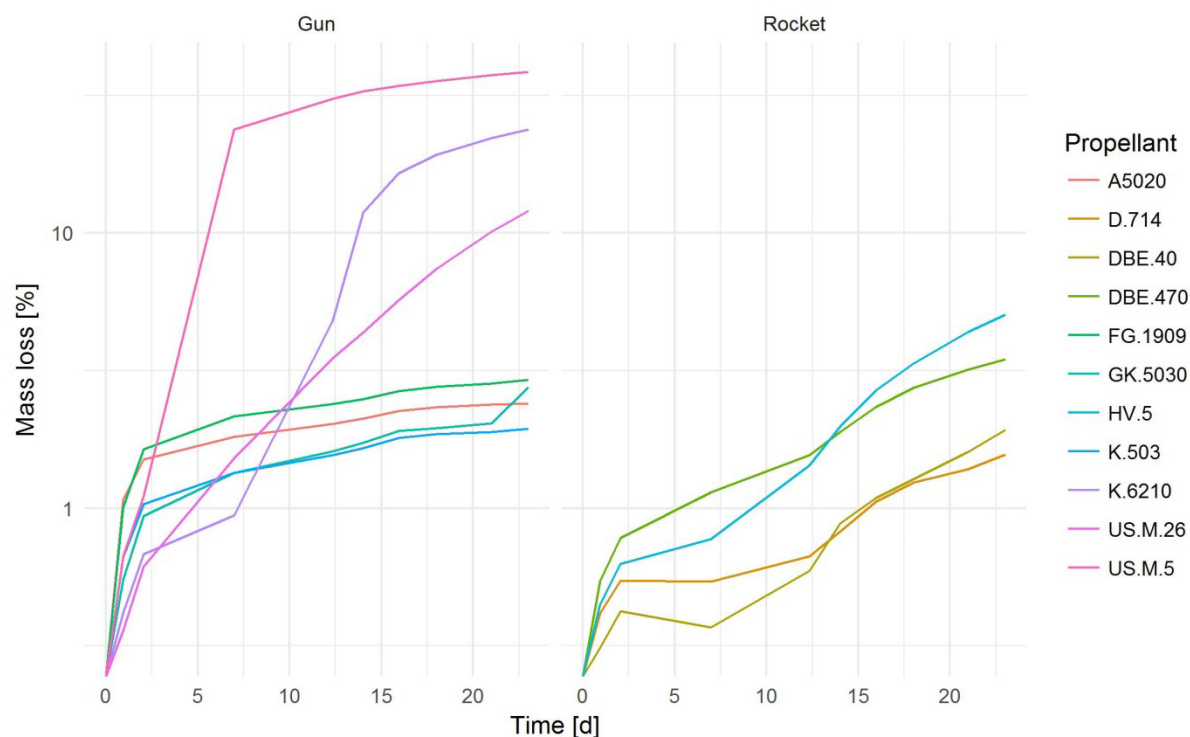


Figure 10: Mass loss curves at 90 °C of all investigated propellant, separated by type. Note the logarithmic y-axis.

A propellant is in this work considered critical, if it shows autocatalytic decomposition within 20 days.

Conclusion

Stability is assessed by several criteria: First is the maximum allowed heat flow from STANAG 4582 Heat Flow Calorimetry, in which is stated that the maximum heat flow in the respective time (34.8 d, 10.6 d and 3.43 d) is not allowed to exceed 34.5 $\mu\text{W/g}$, 114 $\mu\text{W/g}$ and 350 $\mu\text{W/g}$, respectively. As already mentioned, a propellant is considered unstable, if autocatalytic decomposition occurs within 20 d at 90 °C. The summary is shown in Table 1

It is notable that for the gun propellants the results are unambiguous. Several propellants are exceeding maximum heat flow for one temperature but not at others. Only US M 26 is considered unstable in most assessments. This shows that several measurements at different conditions or different methods are useful to determine if a propellant is still fit for service.

Table 1: Assessment of stability of different propellants. The criteria for assessment are mentioned above.

Propellant	HFC (70 °C)	HFC (80 °C)	HFC (90 °C)	Mass loss
A 5020	44	47	142	
Feldgeschütz 1909	13.6	53	136	
GK 5030	23.2	94	317	
K 503	20.3	88	368	
K 6210	19	64	248	
US M 26	42	141	522	
US M 5	10	44.8	167	
D 714	13.7	51	77	
DBE 40	13.6	43	59	
DBE 470	14.6	49	139	
HV 5	10	39	195	

Summary

Different methods to determine activation energies have been applied to naturally aged propellants. The different methods result in different values for activation energies with advantages and drawbacks for each method. Heat flow calorimetry and mass loss have been used to determine stability of the propellants. Despite being several decades old, most propellants are considered stable according to STANAG. For FG 1909 there is no known

manufacturing date. The name suggests an origin before World War I, is t s also of a propellant form that is not used any longer. Its real age could not be determined. Nevertheless it is still considered stable. Also, different methods or conditions help to get a clearer picture, especially when used for old samples.

References

- [1] H. L. Friedman, „Kinetics of thermal degradation of char-forming plastics from thermogravimetry. Application to a phenolic plastic,“ *Journal of Polymer Science*, Bd. 6, Nr. 1, pp. 183-195, 1964.
- [2] M. A. Bohn, „Kinetic Description of Mass Loss Data For The Assessment Of Stability, Compatibility And Ageing Of Energetic Compounds And Formulations Exemplified With CL-20,“ *Propellants, Explosives, Pyrotechnics*, pp. 125-135, 2002.
- [3] M. Heil, K. Wimmer und M. A. Bohn, „Characterization of Gun Propellants by Long-Term Mass Loss Measurements,“ *Propellants, explosives, Pyrotechnics*, pp. 706-711, 2017.