



## **Analysis of Thermal Decomposition of Solid Rocket Propellants**

Marcin CEGŁA<sup>1\*</sup>, Janusz ZMYWACZYK<sup>2</sup>,  
Piotr KONIORCZYK<sup>2</sup>

<sup>1</sup>*Military Institute of Armament Technology,  
7 Prymasa Stefana Wyszyńskiego Str., 05-220 Zielonka, Poland*

<sup>2</sup>*Military University of Technology, Faculty of Mechatronics and Aerospace,  
2 gen. Sylwestra Kaliskiego Str., 00-908 Warsaw, Poland*

*\*Corresponding author's e-mail address and ORCID:  
ceglam@witu.mil.pl; <https://orcid.org/0000-0002-6056-6175>*

*Received by the editorial staff on 04 October 2018*

*The reviewed and verified version was received on 27 May 2019*

DOI 10.5604/01.3001.0013.2115

**Abstract.** The paper presents results of thermal decomposition analysis of selected solid rocket propellants. Homogeneous propellant PAC and heterogeneous propellant H2 were subjected to simultaneous thermal analysis with the use of NETZSCH STA 2500 Regulus device with five heating rates of 2.5, 5, 7.5, 10 and 15 K/min. The method combines TG, DTG and DTA analytical techniques in a single measurement. The aim of the conducted experiments was to study thermal decomposition of these energetic materials as well as to determine activation energy of the decomposition process and the preconditioning factor from the TG curves.

The tested materials properties and chemical composition along with a brief description of the experimental procedure are described. The inverse procedure of calculating the activation energy, based on the Ozawa-Flynn-Wall model is described. Finally, the results of thermal decomposition of two tested solid rocket propellants are presented along with maximum decomposition rates and percentage of mass loss.

**Keywords:** solid rocket propellants, thermal decomposition analysis, activation energy

## 1. INTRODUCTION

Solid rocket propellants are a group of high energy materials containing flammable and oxidizing substances, enabling them to be combusted in the anaerobic atmosphere. Modern solid rocket propellants have a number of properties desirable for efficient and safe operation. The most important are: high chemical durability, good mechanical properties, high heat of combustion, low sensitivity to ignition and detonation, low coefficient of thermal expansion, low molecular weight of combustion products. Good repeatability of their thermal and mechanical properties is also essential for their safe handling and production [1, 2].

Considering chemical content and the connection between ingredients two general types of solid propellants can be distinguished. These are homogeneous (double-base) and heterogeneous (composite) solid rocket propellants. The homogeneous propellants have a uniform physical structure whereas in heterogeneous ones, the oxidizer and fuel are physically mixed and do not have chemical bonds. Typical double base rocket propellants consist mainly of nitrocellulose 50-60% and nitroglycerine 30-49%. Heterogeneous solid rocket propellants are mixture of a solid oxidizer (ammonium perchlorate – AP) and liquid combustible substances (binders) mostly synthetic rubber with functional groups, a cross-linking agent and various kind plasticizers and additives. Both types of propellants may contain high energy additives like cyclotrimethylenetrinitroamine and cyclotetramethylenetetranitroamine (RDX, HMX). Due to the complex nature of solid rocket propellants it is important to know their thermal and mechanical properties which may affect the proper operation of the rocket motors [3, 4].

Simultaneous thermal analysis (STA) in which TG/DTG and DTA signals are recorded for exploring thermal decomposition of the propellant during a single measurement allows determination of decomposition rates as well as percentage of mass loss. Commonly used model-free kinetics such as the Friedman model or the Ozawa-Flynn-Wall model (OFW) allow to determine the activation energy  $E_a$  occurring in the Arrhenius equation without the knowledge of the function determining the course of the reaction. In addition, assuming that the reaction is the first order, the preconditioning factor  $A$  can be specified.

STA of solid rocket propellants and determination of thermokinetic parameters allows the prediction of the behaviour of the propellant under various storage and operating conditions.

## 2. MATERIALS AND METHODS

### 2.1. Tested solid rocket propellants

The tested solid rocket propellants represent two main groups of these materials, namely, the homogeneous and heterogeneous. Main chemical composition of propellants is presented in Table 1.

Table 1. PAC and H2 main chemical composition

PAC, $\rho = 1.1 \text{ g/cm}^3$ *		H2, $\rho = 1.77 \text{ g/cm}^3$ *	
Ingredient	Content %	Ingredient	Content %
Nitrocellulose	47.7	Ammonium perchlorate	70
Nitroglycerine	28.4	Aluminium powder	15
Dinitrotoluene	7.3	BKN, additives, stabilizers ect.	15
Polyoxymethylene	7.3		
Other additives	9.3		

\* The densities  $\rho$  of solid rocket propellants samples were determined with the use of RADWAG XA 60/220/X analytical balance and the double-weight method.

### 2.2. Experimental procedure

Thermal decomposition of homogeneous PAC and heterogeneous H2 solid rocket propellants was performed using NETZSCH STA 2500 Regulus which combines thermogravimetry TG/DTG with DTA. The STA testes were carried out in the temperature range from 30 °C to 1000 °C with the heating rates of 2.5; 5; 7.5; 15 K/min to determine activation energy of the thermal decomposition process and also 10 K/min to study the occurring phenomenon.

### 2.3. Inverse approach to the kinetics of thermal decomposition

The basic kinetic equation for the degree of mass loss  $\alpha$  for thermal degradation has the following form [5]:

$$\frac{d\alpha}{dt} = k(T)f(\alpha)h(p) \quad (1)$$

where:

$\alpha$  – the degree of mass loss of the sample (conversion rate), which for a given point on the TG curve equals

$$\alpha_i = \alpha(t_i) = \frac{m(t_0) - m(t_i)}{m(t_0) - m(t_f)},$$

$t$  – time, s

$k(T)$  – the reaction rate constant described by the Arrhenius equation:

$$k(T) = A \exp\left(-\frac{E_a}{R \cdot T}\right), \text{ s}^{-1}$$

$E_a$  – activation energy (at a given conversion rate  $\alpha$ ),  $\text{kJ} \cdot \text{mol}^{-1}$

$R$  – universal gas constant,  $R = 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$

$f(\alpha)$  – reaction model

$h(p)$  – pressure function  $p$ , assumed in calculations as  $h(p) = 1$

$T$  – absolute temperature, K

$m(t_0)$  – mass of the sample at the initial moment, mg

$m(t_i)$  – mass of the sample at the final moment, mg.

The conversion rate  $\alpha$  is conveniently related to the heating rate,  $\beta = dT/dt$ , which brings the equation (1) to the form of (2)

$$\frac{d\alpha}{dt} = \frac{d\alpha}{dT} \frac{dT}{dt} = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \Rightarrow \frac{d\alpha}{f(\alpha)} = \left(\frac{A}{\beta}\right) \exp\left(-\frac{E_a}{RT}\right) dT \quad (2)$$

Integrating the equation (2), leads to the dependence (3)

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \left(\frac{A}{\beta}\right) \int_{T_0}^T \exp\left(-\frac{E_a}{RT'}\right) dT' \quad (3)$$

The expression on the right of equation (3) can be reduced to the form (4) using a variable:

$$z = \frac{E_a}{RT} \Rightarrow dz = -\frac{E_a}{RT^2} dT = -\frac{R}{E_a} z^2 dT \Rightarrow dT = -\frac{E_a}{R} \frac{dz}{z^2}$$

$$g(\alpha) = \left(\frac{A}{\beta}\right) \int_0^T \exp\left(-\frac{E_a}{RT'}\right) dT' = \left(-\frac{A E_a}{\beta R}\right) \int_\infty^z \frac{\exp(-z')}{z'^2} dz' \quad (4)$$

where the change of the lower limit of integration with  $T_0$  to 0 in formula (4) is the result of the assumption that if the thermal reaction of degradation starts above the temperature  $T_0$  it can be assumed to be equal to zero at  $T_0$ . The integral occurring in equation (4) after applying the integration method by parts is reduced to the form (5)

$$\begin{aligned} \int_{\infty}^z \frac{\exp(-z')}{z'^2} dz' &= \left( \begin{array}{l} u = \exp(-z'), \quad v' = z'^{-2} \\ u' = -\exp(-z'), \quad v = -z'^{-1} \end{array} \right) = -\frac{\exp(-z')}{z'} \Big|_{\infty}^z - \int_{\infty}^z \frac{\exp(-z')}{z'} dz' = \\ &= -\frac{\exp(-z)}{z} - \int_{\infty}^z \frac{\exp(-z')}{z'} dz' = -\left( \frac{\exp(-z)}{z} - \int_z^{\infty} \frac{\exp(-z')}{z'} dz' \right) \end{aligned} \quad (5)$$

After introducing the exponential integral  $p(z)$  defined as

$$p(z) = \frac{\exp(-z)}{z} - \int_z^{\infty} \frac{\exp(-z')}{z'} dz' \quad (6)$$

the equation (3) using (4) and the exponential integral (6) takes the form:

$$g(\alpha) = \left( \frac{A E_a}{\beta R} \right) p(z) \quad (7)$$

From the logarithm of the relationship (7) we obtain:

$$\ln g(\alpha) = \ln \left( \frac{A E_a}{R} \right) - \ln \beta + \ln p(z) \Rightarrow \ln \beta = \ln \left( \frac{A E_a}{R} \right) - \ln g(\alpha) + \ln p(z) \quad (8)$$

The dependence given by formula (8) is the basis for free models of determining activation energy. In the OFW model it is assumed that the exponential integral  $p(z)$  can be approximated by the expression proposed by Doyle [6]  $p(z) \cong -5.3305 - 1.052z$ , which in the range

$$31 < z = \frac{E_a}{RT} < 47$$

provides an approximation error less than 1% [7].

Decreasing the approximation error of the exponential integral to 0.03% for  $5 < z < 100$  is possible after applying the correction given by Senum and Yang [8] in the form:

$$p(z) \cong \frac{\exp(-z)}{z} \frac{z^3 + 18z^2 + 88z + 96}{z^4 + 20z^3 + 120z^2 + 240z + 120} \quad (9)$$

The activation energy of the thermal decomposition process of the propellant can be determined from the model-free kinetics based on the TG measurement results carried out for several heating rates  $\beta_j$ . For this purpose, measuring points for the determined value of conversion rate  $\alpha_i$  corresponding to different heating rates  $\beta_j$  must be placed on the graph with coordinates  $(\ln(\beta) - (1/T))$ , and then the angular coefficient of the slope of the straight line regression has to be found.

As follows from the formula (10)

$$\ln \beta = \ln \left( \frac{AE_a}{R} \right) - \ln g(\alpha) - 5.3305 - 1.052 \frac{E_a}{RT} \quad (10)$$

the angular factor  $m$  of the regression line is associated with the activation energy by the following relationship:

$$m = -1.052 \frac{E_a}{R} \Rightarrow E_a = -\frac{m \cdot R}{1.052} \quad (11)$$

It should be noted that the activation energy determined by means of free models does not require knowledge of the kinetic model of the process as well as the type of reaction. It should also be emphasized that the calculation of the preconditioning factor  $A$  from the free model is possible, assuming the form of the function defining the reaction model  $f(\alpha)$  which is most commonly adopted in the form describing the reaction of the  $n^{\text{th}}$  order [9].

### 3. RESULTS AND DISCUSSION

The thermogravimetric experiment results for PAC double base propellant is presented in Figure 1.

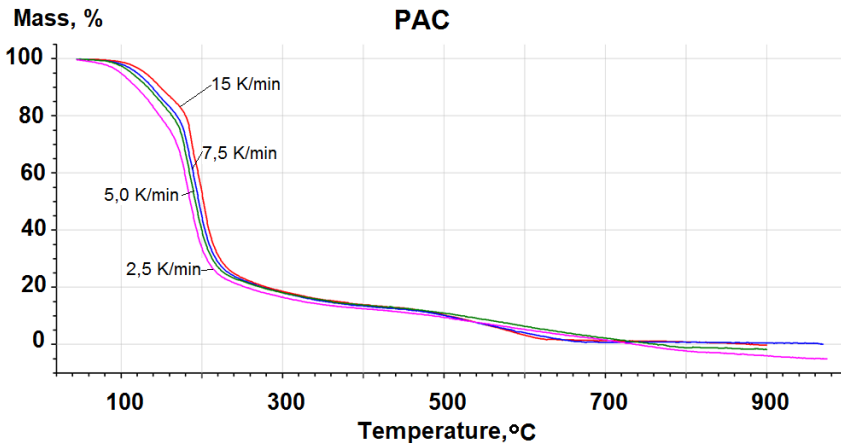


Fig. 1. The percentage loss of mass with temperature for double base propellant PAC obtained for the heating rates of 2.5; 5.0; 7.5; 15 K/min

According to the recommendation of the ASTM E1641 standard, the activation energy and the preconditioning factor were calculated from the TG curves representing the dependence of the percentage of mass loss on the temperature for the conversion rate  $\alpha = 5\%$  as equal:

$$E_a = 73.75 \pm 3.61 \text{ [kJ/mol]}, \quad \log(A, \text{ s}^{-1}) = 6.36$$

Figure 2 and Table 2 show the dependency of the activation energy  $E_a$  and the preconditioning factor  $A$  on the conversion rate  $\alpha$  for PAC, based on the OFW model-free kinetics. As can be seen in Figure 2, the activation energy of the thermal decomposition process in PAC has two local maximum – one for  $\alpha = 0.12$  and the other for  $\alpha = 0.34$ . This indicates that the thermal decomposition reaction in the PAC is at least two-step process. This is also due to simultaneous NG evaporation and NC and NG decomposition processes in the double base propellant [10].

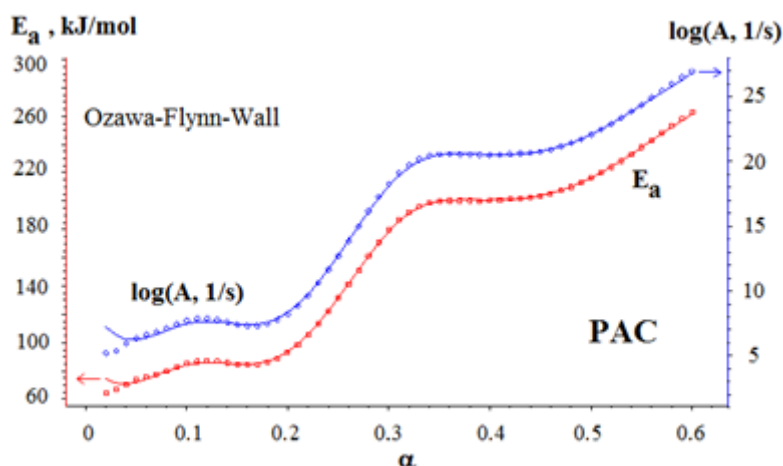


Fig. 2. The dependence of the activation energy  $E_a$  and the preconditioning factor  $\log(A)$  on the conversion rate  $\alpha$  for PAC

Table 2. Activation energy  $E_a$  and the preconditioning factor  $\log(A)$  values obtained for double base rocket propellant PAC

Conversion rate $\alpha$	Activation energy $E_a$ [kJ/mol]	Preconditioning factor $\log(A, s^{-1})$
0.02	$64.68 \pm 6.81$	5.22
0.05	$73.75 \pm 3.61$	6.36
0.10	$85.15 \pm 5.24$	7.71
0.20	$93.20 \pm 6.34$	8.22
0.30	$179.40 \pm 4.74$	18.27
0.40	$200.51 \pm 6.43$	20.50
0.50	$216.34 \pm 5.94$	22.08
0.60	$262.87 \pm 8.27$	26.97

The TG/DTG-DTA results obtained at the heating rate of 10 K/min for PAC shown in Figure 3 indicate that the thermal degradation process occurs in two stages.

In the first stage, the highest decomposition rate of  $-15.67\%/min$  takes place at  $T = 184.5^\circ C$  while in the second stage, the maximum decomposition rate of  $-14.30\%/min$  takes place at  $T = 196.5^\circ C$ .

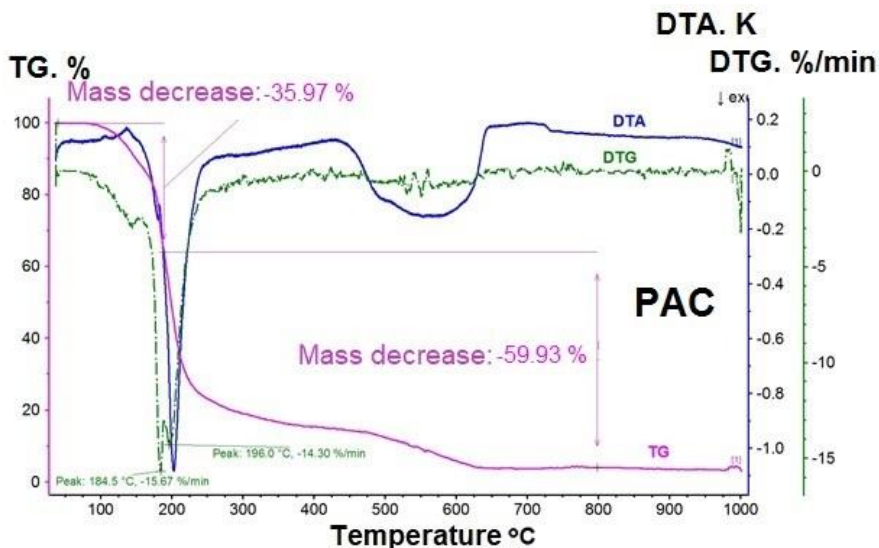


Fig. 3. Thermogram TG/DTG-DTA for PAC homogeneous propellant

The process starts with evaporation, afterwards the thermal decomposition is faster in the first stage than in the second one. The sample mass decrease in the temperature range from  $40.0^\circ C$  to  $184.5^\circ C$  was  $-35.97\%$ , and in the range from  $188.5^\circ C$  to  $800^\circ C$  it was  $-59.93\%$ .

The TG thermogravimetric result for heterogeneous H2 propellant is shown in Figure 4.

The activation energy and the preconditioning factor for the heterogeneous H2 propellant were calculated from the TG curves representing the relationship between the percentage loss of mass and temperature for the conversion rate  $\alpha = 5\%$  as:

$$E_a = 48.94 \pm 4.01 \text{ [kJ/mol]}, \log(A, s^{-1}) = 1.73$$



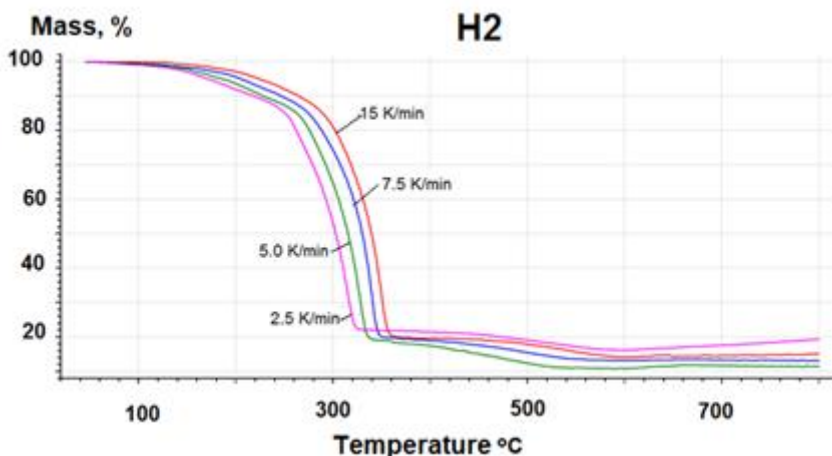


Fig. 4. The percentage loss of mass with temperature for heterogeneous propellant H<sub>2</sub> obtained for the heating rates of 2,5; 5,0; 7,5; 15 K/min

The results of activation energy  $E_a$  and  $\log(A, \text{s}^{-1})$  for H<sub>2</sub> in the function of conversion rate  $\alpha$  are shown in Figure 5 and Table 3.

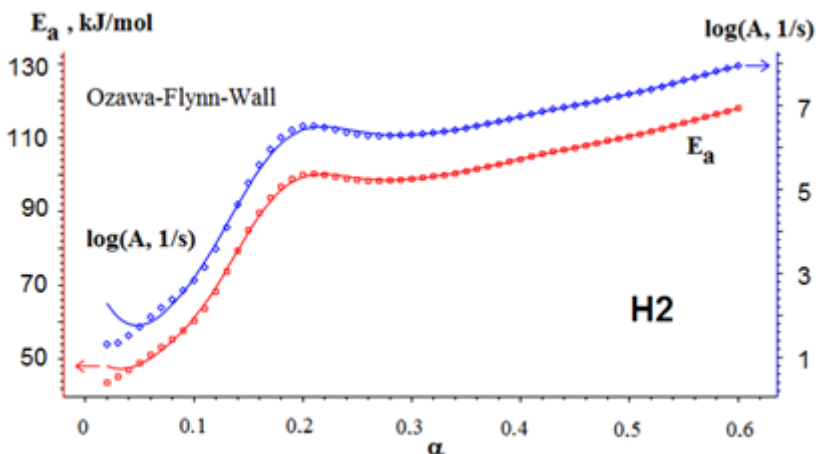


Fig. 5. The dependence of the activation energy  $E_a$  and the preconditioning factor  $\log(A)$  on the conversion rate  $\alpha$  for H<sub>2</sub>

Figure 6 shows the TG-DTG-DTA thermogram obtained at a heating rate of 10 K/min for H<sub>2</sub> propellant. Unlike the previously presented double base propellant, the H<sub>2</sub> thermal degradation process occurs at a maximum decomposition rate of -22.83%/min at 343°C. The percentage loss of H<sub>2</sub> mass in the temperature range from 40.0°C to 343.0°C was -65.84%, and in the range from 343.0°C to 800°C it was 18.62%.

Table 3. Activation energy  $E_a$  and the preconditioning factor  $\log(A)$  values obtained for heterogeneous propellant H2 presented in Figure 6.

Conversion rate $\alpha$	Activation energy $E_a$ [kJ/mol]	Preconditioning factor $\log(A, s^{-1})$
0.02	43.53±2.40	1.31
0.05	48.94± 4.01	1.73
0,10	60.27± 4.13	2.83
0.20	99.92± 6.37	6.50
0.30	98.88±10.79	6.30
0,40	104.20±14.38	6.73
0.50	110.36±15.86	7.26
0.60	117.99±16.00	7.94
0.70	126.22±15.63	8.70
0.80	133.58±15.01	9.39
0.90	142.24±14.98	10.21

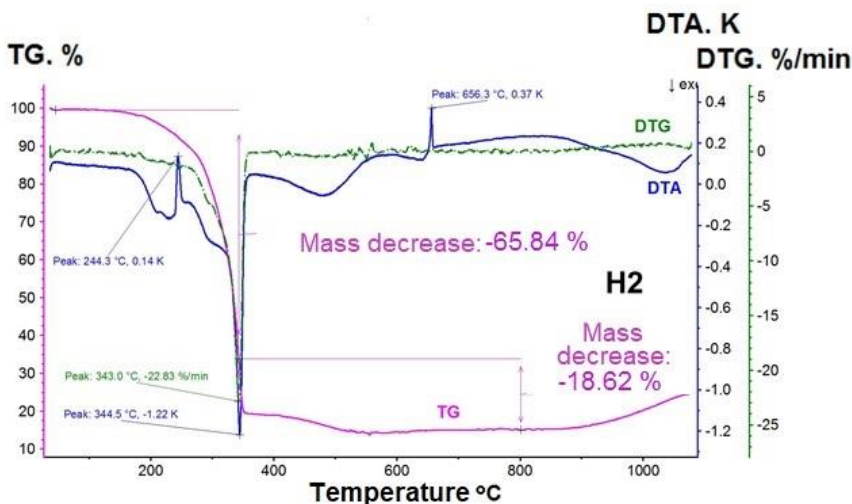


Fig. 6. Thermogram TG/DTG-DTA for H2 heterogeneous propellant

#### 4. CONCLUSIONS

The analysis of thermal decomposition of PAC homogeneous rocket propellant and H2 heterogeneous rocket propellant was conducted with the use of Netzsch STA 2500 Regulus analyser. Maximum decomposition rates and percentage of mass loss were determined for both types of propellants. It was found that the PAC thermal decomposition occurs in two steps.

Activation energy  $E_a$  of the thermal decomposition process on the basis of experimental TG thermograms obtained at the heating rate  $HR = 2.5; 5.0; 7.5; 15$  K/min in the temperature range from 30°C to 1000°C, was calculated on the basis of the Ozawa-Flynn-Wall (OFW) free-kinetic model. It's values for the conversion rate  $\alpha = 5\%$  were:  $73.75 \pm 3.61$  [kJ/mol] and  $48.94 \pm 4.01$  [kJ/mol] for PAC and H2 propellants respectively.

A more detailed analysis of the thermal decomposition processes of solid rocket propellants requires additional testing of reaction products by mass spectrometry or FTIR (Fourier Transform Infrared Spectroscopy).

## FUNDING

This work was supported financially by the European Regional Development Fund under the Operational Programme Innovative Economy 2007-2013, POIG.02.02.00-14-022/09.

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## **Analiza rozkładu termicznego stałych paliw raketowych**

Marcin CEGŁA<sup>1</sup>, Janusz ZMYWACZYK<sup>2</sup>,  
Piotr KONIORCZYK<sup>2</sup>

<sup>1</sup>Wojskowy Instytut Techniczny Uzbrojenia  
ul. Prymasa Stefana Wyszyńskiego 7, 05-220 Zielonka  
<sup>2</sup>Wojskowa Akademia Techniczna im. Jarosława Dąbrowskiego  
ul. gen. Sylwestra Kaliskiego 2, 00-908 Warszawa

**Streszczenie.** W pracy przedstawiono wyniki analizy termicznej dekompozycji wybranych stałych paliw raketowych. Homogeniczne paliwo raketowe PAC i heterogeniczne paliwo raketowe H2 poddano badaniom za pomocą techniki jednoczesnej analizy termicznej przy użyciu urządzenia NETZSCH STA 2500 Regulus, wykorzystując pięć szybkości ogrzewania próbki wynoszących 2,5, 5, 7,5, 10 i 15 K/min. Wspomniana metoda łączy analizy TG, DTG i DTA w jednym pomiarze. Celem eksperymentów było zbadanie rozkładu termicznego tych materiałów energetycznych, a także określenie energii aktywacji procesu rozkładu i współczynnika przedwykładniczego z krzywych TG. Omówiono podstawowe właściwości oraz skład chemiczny badanych stałych paliw raketowych, warunki prowadzenia eksperymentu oraz opisano procedurę odwrotną obliczania energii aktywacji termicznego rozkładu paliwa na podstawie krzywych TG, dla kilku szybkości ogrzewania próbki. Przedstawiono wyniki analizy termicznego rozkładu dwóch badanych stałych paliw raketowych wraz z maksymalnymi współczynnikami dekompozycji i procentowym spadkiem masy, a także wyznaczone wartości energii aktywacji ich termicznej dekompozycji. Uzyskane w wyniku badań wyniki są istotne w doborze bezpiecznych warunków magazynowania i eksploatacji silników raketowych napędzanych paliwem stałym.

**Słowa kluczowe:** stałe paliwa raketowe, analiza rozkładu termicznego, energia aktywacji