

Kinetic Study and Thermal Decomposition Behavior of Magnesium-Sodium Nitrate Based on Hydroxyl-Terminated Polybutadiene

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ABSTRACT: This paper has been utilizing the simultaneous ThermoGravimetric analysis and Differential Scanning Calorimetry (TG–DSC) to investigate the thermal decomposition of magnesium-sodium nitrate pyrotechnic composition based HTPB resin. The thermal behaviors of different samples with various fuel-oxidizer ratio contents were determined. Decomposition kinetic was investigated by evaluating the influence of DSC heating rate (4, 7, 10, 13 °C/min) on the behavior of the illumination flares. The results as expected showed that the decomposition temperature of the illumination flares decreases with the increase in the DSC heating rate, while thermal decomposition of the sample followed the first-order law. Furthermore, Magnesium-sodium nitrate illumination flares with HTPB resin have been studied for luminous efficiency by varying fuel/oxidizer ratio. The kinetic and thermodynamic parameters of the illumination flares decomposition under ambient pressure were obtained from the resulted DSC data via non-isothermal methods proposed by ASTM E698 and Flynn-Wall-Ozawa. Also, the critical temperature of ignition temperature was estimated at about 455 °C.

KEYWORDS: Pyrotechnic; Thermal decomposition; kinetic; Non-isothermal; Luminous efficiency.

INTRODUCTION

Principal constituents of the illuminating pyrotechnic composition are magnesium, sodium nitrate and binder. The role of fuel and oxidant is much more understood, but the binder is less known. Control the performance characteristics of the mixtures, as well as the duration of their service life, cohesion between particles aiding consolidation significant efforts to introduce new types of binders. Various types of binders are used in illuminating flares to improve the luminous output the performance [1-3],

ignition and the burning rate [4, 5], chemical stability and service life [5]. In order to develop new compositions with better performance, a number of compositions were studied by varying magnesium/sodium nitrate ratio in the presence of Hydroxyl-terminated polybutadiene (HTPB) as the binder. HTPB is the most popular polymer binder which used in propellants and explosives. Since HTPB has a low viscosity, it allows high solids loading. This polymer binder acts by sticking the solid filler which

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gives improved mechanical and safety properties furthermore allows the formulation to be cast into massive cases [6]. Thermal analysis investigation on high energetic materials is suitable to appreciate the kinetic and the mechanism of their thermal decomposition and evaluate the potential hazards of their exothermic decomposition during processing, handling, and storage [7-9]. Furthermore, thermokinetic studies afford interesting information on thermal stability and shelf life of the energetic materials to store at definite conditions [10, 11]. The aim of this work was to study the endothermic or exothermic changes of Mg/NaNO₃/HTPB pyrotechnic mixture heated in nitrogen atmosphere through TG/DSC measurements and to obtain some information on the correlation between exothermicity and luminous efficiency, kinetic and the mechanism of their thermal decomposition and evaluate the potential hazards of their exothermic decomposition during processing, handling and storage characteristic. To the best of our knowledge, there is no report on this field.

EXPERIMENTAL SECTION

HTPB (R45-M, the number-average molecular weight of 2600, Zibo Qilong Chemical Co., China) and IPDI (Bayer Material Science, Germany) were used as purchased. Analytical grade sodium nitrate and magnesium powder were purchased from Merck Company and Tangshan Weihao Magnesium Powder Co. Ltd, respectively. Sodium nitrate was ground with 0.5 % MgO to prevent agglomeration in a mortar to produce a fine powder and then dried at 80 °C for 2 h. The particle size of magnesium and sodium nitrate powders are shown in Fig. 1. The particles size of sodium nitrate and magnesium powders are seen about in the range of 20 and 200 microns respectively. The DSC experiments were carried out on pyrotechnic samples containing Mg/NaNO₃/HTPB prepared based on their stoichiometric ratio (as shown in Table 1). Thermochemical behaviors were characterized by a METTLER TOLEDO differential scanning calorimeter (Model: TG/DSC 1) at different heating rates (4, 7, 10, 13 °C/min). The pyrotechnic samples were analyzed by DSC/TG using an aluminum crucible under a nitrogen atmosphere with the purge flow rate of 50 mL/min at the temperature range of 50 to 700 °C. The sample mass used in each test was 5.0 mg. The luminosity and burning time were measured

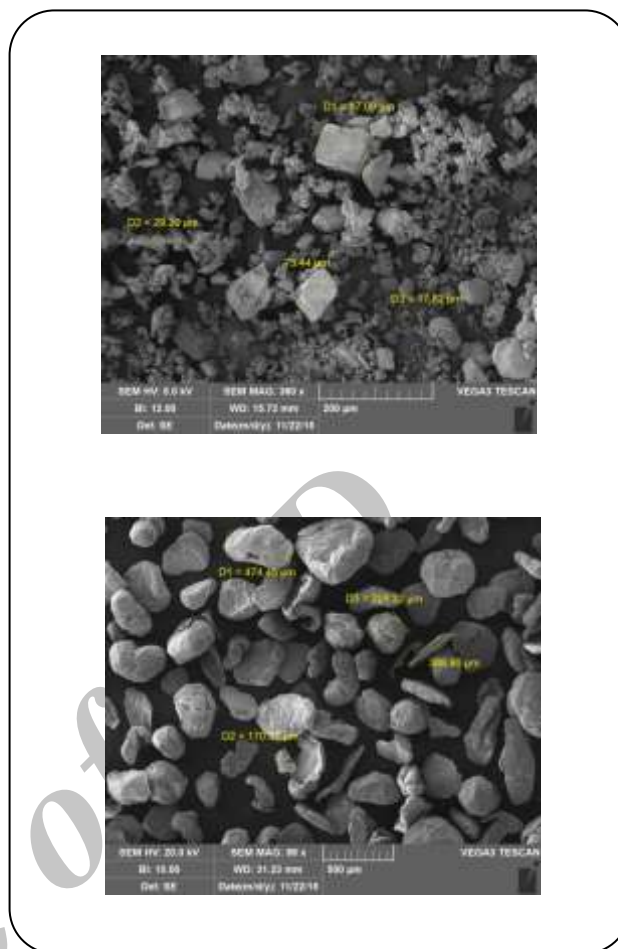


Fig. 1: Particle size of a sodium nitrate and b magnesium

by Lurton photometer model 2006. All compositions (500 g) were pressed into paper tubes of ID 78 mm at 8000 psi.

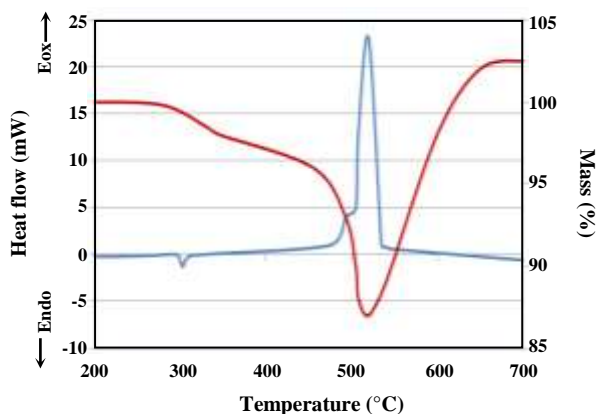
RESULTS AND DISCUSSION

Luminous Efficiency and Thermal Decomposition

As shown in Table 1, there is a direct correlation between luminous efficiency and heat of decomposition of pyrotechnic samples. It was found that the luminous efficiency of samples increases with increase in the heat of decomposition obtained from the DSC peak area. Fig. 2 shows the resulted TG/DSC curves of the pyrotechnic sample (4) heated at the rate of 10 °C/min. The curve for this composition shows a small endothermic peak near 305 °C which is due to the melting of the sodium nitrate present in the pyrotechnic mixture. The second peak which is highly exothermic in nature appears at a temperature of 495 °C. This peak represents the ignition of magnesium fuel due to reaction with oxygen released

Table 1: Composition, luminous efficiency, and heat of decomposition of the pyrotechnic samples.

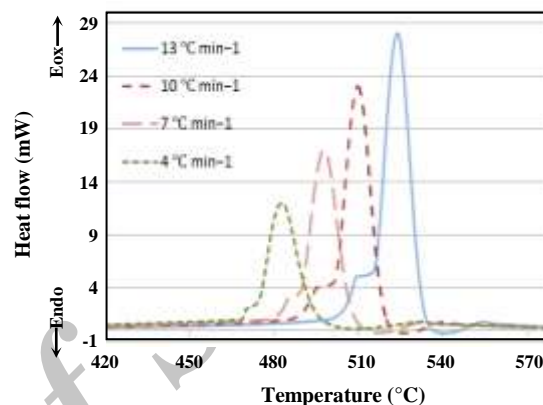
Sample	Composition (Wt%)			Luminous Efficiency(cd s/g)	Heat of Decomposition (J/g)
	Mg	NaNO ₃	HTPB		
1	57.42	37.62	4.95	45611	2347
2	58.37	38.24	3.38	49615	2470
3	59.27	37.17	3.55	49187	2448
4	57.30	39.18	3.51	51659	2503

**Fig. 2: TG/DSC curve of pyrotechnic composition (sample 4) under the heating rates of 10 °C/min.**

as a result of oxidizer decomposition. The endothermic peak at 305 °C is not clearly visible because of the small heat flow value and it has been masked due to very high heat flow value of the ignition peak. The mass loss curve of pyrotechnic composition remains stable till 280 °C. There is nearly 2 percent mass loss between temperature ranges of 280 °C and 340 °C. This mass loss is due to the removal of chemically bonded water due to thermal decomposition of magnesium hydroxide. There is a gradual mass loss above 340 °C till 490 °C due to slow decomposition of the HTPB resin present in the pyrotechnic composition. There is a rapid increase in the mass of the sample above 490 °C due to oxidation of the magnesium fuel by the oxygen released due to the thermal decomposition of the oxidizer. The curve stabilizes again near 650 °C.

Effect of Heating Rate

The effect of several heating rates (4, 7, 10, 13 °C/min) on the heat flow curve of the pyrotechnic sample (4) is shown in Fig. 3. It is seen that the small the endothermic peak corresponding to the melting of

**Fig. 3: Effect of multiple heating rates on the heat flow curve of pyrotechnic composition (Sample 4).**

sodium nitrate does not shift with increasing heating rates. This peak has been masked because the ignition peak has a very large heat flow value as compared to the endothermic peak. The exothermic peak related to the ignition of the magnesium fuel shifts to higher temperatures when the heating rates are increased. These shifts in the values of onset temperature and maximum peak temperature are shown in Fig. 4. On the other hand, considering the results of our study shows that as the DSC heating rate was increased, the heat of decomposition resulted from the peak area was increased. These increments in the heat of decomposition are presented in Fig. 5.

Kinetic of Thermal Decomposition

The kinetic analysis corresponding to the thermal decomposition of the pyrotechnic sample (4) was carried out by DSC data and using the ASTM method E698 [12]. The DSC curves of the pyrotechnic sample obtained at different heating rates were given in Fig. 3. The resulted data from this figure was used to plot the $\ln(\beta/T_p^2)$ versus $1/T_p$ and the obtained plot is presented in Fig. 6. It could be found that plotting of $\ln(\beta/T_p^2)$ against $1/T_p$ was

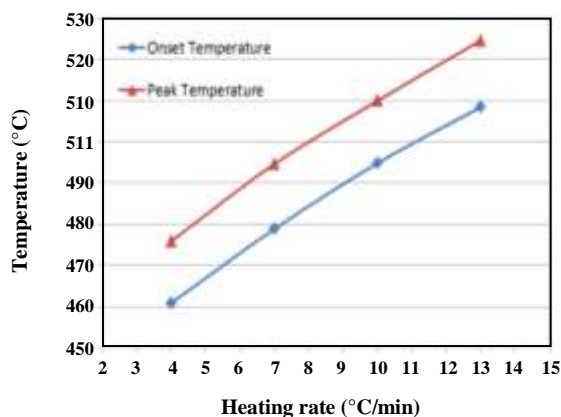


Fig. 4: Variation of the peak temperature and onset temperature of pyrotechnic composition (sample 4) by changing the heating rate

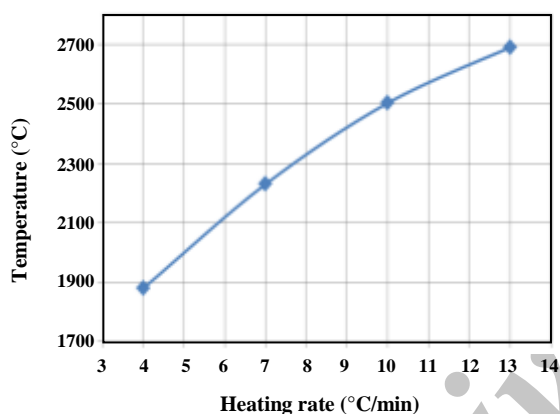


Fig. 5: Effect of multiple heating rates on the heat of decomposition of pyrotechnic composition (sample 4).

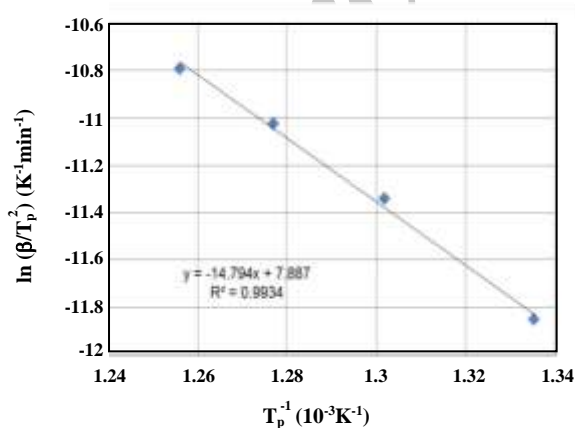


Fig. 6: The plot of $\ln \beta T_p^{-2}$ versus T_p^{-1} for the pyrotechnic composition (sample 4).

a straight line for the studied pyrotechnic sample, which indicates that the mechanism of a thermal decomposition reaction is the first order [13].

As proposed by the ASTM method, the slope of this line is equal to $-E_a/R$. Therefore, the value of the activation energy (E_a) was obtained from the slope of this graph, while the pre-exponential factor, $\log(A/s)$, as another Arrhenius parameter was computed from the following expression is given in ASTM E698:

$$A = \beta (E_a/RT_m^2) \exp(E_a/RT_m) \quad (1)$$

The calculated values of activation energy and frequency factor for the pyrotechnic sample (4) are listed in Table 2. Also, a second method was utilized to achieve the activation energy and frequency factor values for comparison. Based on the kinetics equations used for heterogeneous chemical reactions, Flynn-Wall-Ozawa (FWO) [14, 15] has been proposed a method to determine the kinetic parameters using TG/DSC curves, which so-called isoconversional method. The FWO method is based on the isoconversional principle which describes the rate of reaction at a constant extent of the conversion is only a function of the temperature. The Flynn, Wall and Ozawa method could be described by the following equation:

$$\log \beta = \log \frac{AE_a}{Rg(\alpha)} - 2.315 - 0.4567 \frac{E_a}{RT_m} \quad (2)$$

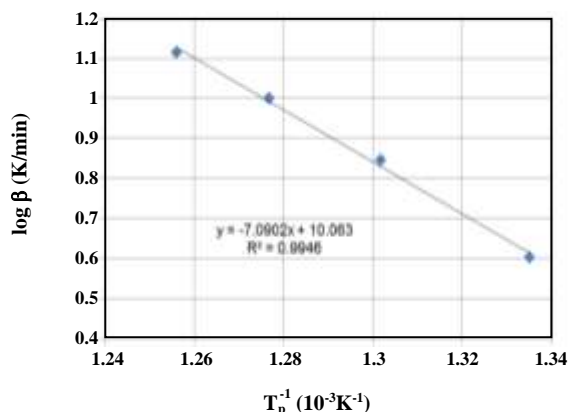
Where $G(\alpha)$ is the conversion functional relationship and the other terms possess their usual meaning. The degree of conversion could be defined as $\alpha = (m_0 - m)/(m_0 - m_f)$, while m_0 , m , and m_f are corresponding to the initial, actual and the final mass of the sample. FWO as the isoconversional method permits evaluation of the dependence of the activation energy on the degree of conversion without the precise knowledge about $G(\alpha)$ [16]. At the maximum peak temperature, the degree of conversion (α) at different heating rates possesses a constant value [14]. Thus, de Doyle's approximation [15] could be applied on Eq. (2) to simplify it and hence Flynn-Wall-Ozawa rewrote this equation as:

$$\log \beta = \text{Const.} - 0.4567 \frac{E_a}{RT_m} \quad (3)$$

The value of activation energy corresponding to the decomposition of the pyrotechnic sample (4) was predicted using the FWO method.

Table 2: Kinetic and thermodynamic parameters of the pyrotechnic composition (sample 4) by ASTM and Ozawa methods.

Methods	Activation energy (kJ/mol)	Frequency factor log A (min ⁻¹)	Linear regression (r)	ΔG^\ddagger (kJ/mol)	ΔH^\ddagger (kJ/mol)	ΔS^\ddagger (J/mol)	Half-life (S ⁻¹)	T _b (°C)
ASTM	122.99	29.30	0.9934	103.0	116.0	16.9	18.71	455.25
FWO	123.23	29.35	0.9946	104.0	117.0	16.5	19.51	455.13

Fig. 7: The plot of $\log \beta$ versus T_p^{-1} for the pyrotechnic composition (sample 4).

As seen in Fig. 7, plotting of the logarithm of heating rate values against reciprocal of the maximum peak temperature for the pyrotechnic sample (4) yields a straight line with $R^2 = 0.9946$. This result confirms that the thermal decomposition mechanism undergoes no variation at the studied rates [17]. Meantime, the value of the frequency factor (A) for the sample might be computed via the Eq.(1). The resulted kinetic data are presented in Table 2. The resulted data by both methods were compared. It was found that the calculated values by ASTM are faintly lower than those by FWO method. Furthermore, thermodynamic parameters of the activation for the decomposition reaction of the pyrotechnic sample (4) are calculable from the resulted kinetic parameters (E_a and A), using the following equations [14, 18]:

$$A \exp \frac{-E_a}{RT} = v \exp \frac{-\Delta G^\ddagger}{RT} \quad (4)$$

$$\Delta H^\ddagger = E - RT \quad (5)$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (6)$$

Where, ΔG^\ddagger , ΔH^\ddagger and ΔS^\ddagger represent the free energy, enthalpy and entropy of the activation, receptivity; $v = k_B T/h$ (while k_B and h are respectively the Boltzmann

and Plank constants). Calculated values of thermodynamic parameters for the pyrotechnic sample (4) are also presented in Table 2.

Half-Life Determination

Considering the first-order decomposition, the equation to determine the half-life is:

$$t_{1/2} = 0.693 k^{-1} \quad (7)$$

The rate constant (k) for decomposition reaction could be calculated by the following equation [19]:

$$\log k = \log A - E_a 2.3 R^{-1} T^{-1} \quad (8)$$

Which for the temperature of 50 °C and using activation energies (E_a) and frequency factors (A) obtained in the above; the equation was solved for k . Table 2 listed the half-life for sample 1. By considering half-lives calculated for nitrocellulose using kinetic parameters obtained by different methods, this compound at 50 °C has a half-life about 19 years.

Critical Ignition Temperature

The critical ignition temperature is considered to be an important parameter pertaining to the thermal stability and safety of energetic materials. It is the minimum temperature beyond which there is a chance of thermal runaway reaction for the energetic materials. It can be effectively used as a thermal safety standard for the propellants explosives and pyrotechnics. The energetic composition is assumed to be safe for handling and storage if the critical ignition temperature is adequately higher than the ambient temperature at which the composition is to be stored. The critical ignition temperature can be estimated by using the thermal and kinetic parameters and employing the under mentioned formulae [20-22]. In order to obtain the critical temperature of thermal ignition (T_b), the following equations were used [23].

$$T_e = T_{e0} + b\beta_1 + c\beta_1^2, \quad i=1-4 \quad (9)$$

$$T_b = \frac{E_a - \sqrt{E_a^2 - 4E_a R T_{e0}}}{2R} \quad (10)$$

Where b and c are the coefficients, while β_i is the utilized heating rate, R is the value of the universal gas constant, and E_a represents the activation energy. T_{e0} is representing the onset temperature, or T_e when $\beta_i \rightarrow 0$ and is given by Eq. (9). The computed value of T_{e0} is 441.15 °C for the pyrotechnic sample (4). Then, the value of the critical temperature (T_b) was predicted from Eq. (10). The resulted values were 455.25 and 455.13 °C respectively by the employment of corresponded ASTM and FWO data.

CONCLUSIONS

Thermal and kinetic evaluation of pyrotechnic composition containing magnesium and sodium nitrate has been carried out to elucidate the decomposition processes and to evaluate their stability and reactivity. This study indicates that the thermal decomposition process of Mg/NaNO₃/HTPB pyrotechnic mixture obeys the first-order law in the investigated temperature range. Also, the influence of the different heating rates on the DSC behavior of the pyrotechnic composition was verified. It was found that thermal stability increased as the heating rate increased. As well as, experimental results showed that the higher luminous efficiency is achieved for the pyrotechnic composition with the higher heat of decomposition. The kinetic and thermodynamic parameters for thermal decomposition calculated by ASTM method are in good agreement with those of the FWO method. Based on the resulted data, the half-life at the temperature of 50 °C was calculated about 19 years.

Nomenclature

HTPB	Hydroxyl-Terminated Polybutadiene
Mg	Magnesium
NaNO ₃	Sodium Nitrate
TG	Thermogravimetric Analysis
DSC	Differential Scanning Calorimetry
FWO	Flynn-Wall-Ozawa
E_a	Activation Energy
B	Heating Rate
A	Frequency Factor
K	Rate Constant
T_p	Critical Ignition Temperature

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REFERENCES

- [1] Palaiah R., Joshi P., Deo S., Jawale D., Valiv M., Somayajulu M., [Luminous Efficient Compositions Based on Epoxy Resin](#), *Def. Sci. J.* **56**(3): 339-343 (2006).
- [2] Koch E.C., [2006–2008 Annual Review on Aerial Infrared Decoy Flares](#), *Prop. Explos. Pyrotech.*, **34**(1): 6-12 (2009).
- [3] Göçmez A., Yilmaz G.A., Peke F., Özkar S., [Development of MTV Compositions as Igniter for HTPB/AP Based Composite Propellants](#), *Prop. Explos. Pyrotech.*, **24**(2): 65-69 (1999).
- [4] Toader G., Rotariu T., Rusen E., Tartiere J., Esanu S., Zecheru T., [New Solvent-free Polyurea Binder for Plastic Pyrotechnic Compositions](#), *MAT. PLAS.*, **54**(1): 22-28 (2017).
- [5] Barros L.D., Pinheiro A.M., Câmara J.E., Iha K., [Qualification of Magnesium/Teflon/Viton Pyrotechnic Composition Used in Rocket Motors Ignition System](#), *J. Aerosp. Technol. Manag.*, **8**(2): 130-136 (2016).
- [6] Abusaidi H., Ghorbani M., Ghaieni H.R., [Development of Composite Solid Propellant Based on Nitro Functionalized Hydroxyl-Terminated Polybutadiene](#), *Prop. Explos. Pyrotech.*, **42**: 1-6 (2017).
- [7] Badgujar D., Talawar M., Asthana S., Mahulikar P., [Advances in Science and Technology of Modern Energetic Materials: an Overview](#), *J. Hazard. Mater.*, **151**(2): 289-305 (2008).
- [8] Agrawal J.P., [Some New High Energy Materials and Their Formulations for Specialized Applications](#), *Prop. Explos. Pyrotech.* **30**(5): 316-328 (2005).
- [9] Agrawal J.P., [Recent Trends in High-Energy Materials](#), *Prog. Energ. Combust.* **24**(1): 1-30 (1998).
- [10] Millar R., Colclough M., Desaii H., Golding P., Honey P., Paul N., [Novel Syntheses of Energetic Materials Using Dinitrogen Pentoxide](#), *Chem. Inform.* **27**(40): 104-121 (1996).
- [11] Millar R., Colclough M., Golding P., Honey P., Paul N., Sanderson A., [New Synthesis Routes for Energetic Materials Using Dinitrogen Pentoxide](#), *Phys. Eng. Sci.* **339**(15): 305-319 (1992).

- [12] ASTM E698-16, [Standard Test Method for Arrhenius Kinetic Constants for Thermally Unstable Materials Using Differential Scanning Calorimetry and the Flynn/Wall/Ozawa Method](#), (2005).
- [13] Sunitha M., Reghunadhan Nair C., Krishnan K., Ninan K., [Kinetics of Alder-ene Reaction of Tris \(2-allylphenoxy\) Triphenoxycyclotriphosphazene and bismaleimides—A DSC Study](#), *Thermochim. Acta.* **374**(2): 159-169 (2001).
- [14] Yi J-h., Zhao F-q., Xu S-y., Zhang L-y., Gao H-x., Hu R-z., [Effects of Pressure and TEGDN Content on Decomposition Reaction Mechanism and Kinetics of DB Gun Propellant Containing the Mixed Ester of TEGDN and NG](#), *J. Hazard. Mater.* **165**(1): 853-859 (2009).
- [15] Tonglai Z., Rongzu H., Yi X., Fuping L., [The Estimation of Critical Temperatures of Thermal Explosion for Energetic Materials Using Non-Isothermal DSC](#), *Thermochim. Acta.*, **244**: 171-176 (1994).
- [16] Salla J., Morancho J., Cadenato A., Ramis X., [Non-Isothermal Degradation of a Thermoset Powder Coating in Inert and Oxidant Atmospheres](#), *J. Therm. Anal. Calorim.* **72**(2): 719-728 (2003).
- [17] Ma H., Yan B., Li Z., Guan Y., Song J., Xu K., [Preparation, Non-Isothermal Decomposition Kinetics, Heat Capacity and Adiabatic Time-to-Explosion of NTO-DNAZ](#), *J. Hazard. Mater.* **169**(1):1068-1073 (2009).
- [18] Pourmortazavi S., Hosseini S., Rahimi-Nasrabadi M., Hajimirsadeghi S., Momenian H., [Effect of Nitrate Content on Thermal Decomposition of Nitrocellulose](#), *J. Hazard. Mater.* **162**(2): 1141-1144 (2009).
- [19] Tompa A.S., Boswell R.F., [Thermal Stability of a Plastic Bonded Explosive](#), *Thermochim. Acta.*, **357**: 169-175 (2000).
- [20] Pickard J.M., [Critical Ignition Temperature](#), *Thermochim. Acta.* **392**: 37-40 (2002).
- [21] Tonglai Z., Rongzu H., Yi X., Fuping L., [The Estimation of Critical Temperatures of Thermal Explosion for Energetic Materials Using Non-Isothermal DSC](#), *Thermochim. Acta.* **244**: 171-176 (1994).
- [22] Abusaidi H., Ghaieni H.R., [Thermal Analysis and Kinetic Decomposition of Nitro-Functionalized Hydroxyl-Terminated Polybutadiene Bonded Explosive](#), *J. Therm. Anal. Calorim.* **127**(3): 2301–2306 (2017).
- [23] Abusaidi H., Ghaieni H.R., Pourmortazavi S.M., Motamed-Shariati S.H., [Effect of Nitro Content on Thermal Stability and Decomposition Kinetics of Nitro-HTPB](#), *J. Therm. Anal. Calorim.* **124**(2): 935-941 (2016).