Thermo-analytical study of 2,2,2-trinitroethyl-formate as a new oxidizer and its propellant based on a GAP matrix in comparison with ammonium dinitramide

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ABSTRACT
A new high energy dense oxidizer (HEDO) 2,2,2-trinitroethyl-formate (TNEF) was prepared and characterized by nuclear magnetic resonance (NMR). A new propellant based on glycidyl azide polymer (GAP) and TNEF was prepared. Thermo-analytical study of TNEF in comparison with ammonium dinitramide (ADN) and their propellant formulations based on GAP were investigated. The decomposition gaseous products and the combustion characteristics of the propellants were determined by using thermodynamic code (EXPLO5_V6.03). Scanning electron microscope (SEM) technique was applied to clarify the crystal morphology of the oxidizers in addition to the homogeneity of the propellants ingredients. Impact and friction sensitivities of the oxidizers and the GAP binder were measured. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) techniques were used to study the pyrolysis of the oxidizers as well as the prepared propellants. The decomposition kinetics were determined by Kissinger and Kissinger-Akahira-Sunose (KAS) methods. The thermal degradation of ADN is faster than TNEF oxidizer. ADN and TNEF have melting temperatures at 95.5 and 127.1 °C and maximum decomposition temperature at 183.5 and 210.1 °C respectively. In addition, TNEF has activation energy in the range of 131–146 kJ mol⁻¹, while ADN has activation energy in the range of 114–117 kJ mol⁻¹. TNEF has specific impulse (250.1 s) higher than ADN (202.4 s). TNEF is a promising oxidizer to be used in composite solid rocket propellants.

1. Introduction
Solid rocket propellants (SRP) have a wide range of applications in space launcher boosters, airplane ejection seats, tactical rockets and even amateur hobby rockets [1]. Due to the simplicity, reliability and low cost of propulsion system of the SRP, they are preferred over liquid and hybrid propellants [2,3]. Composite solid rocket propellants (CSRP) are composed of an oxidizer embedded in a polymeric matrix where a metal powder might be included as a secondary fuel to increase the specific impulse. One of the most usable propellant formulation for more than 60 years contains hydroxyl-terminated polybutadiene (HTPB) as polymeric matrix, ammonium perchlorate (AP) as oxidizer and aluminum (Al) as metal powder [2,4–6]. In 1972, a new trend of energetic binders such as 3,3-Bis(azidomethyl)oxetane (BAMO), poly 3-nitratomethyl-3-methyl oxetane (poly NIMMO) and glycidyl azide polymer (GAP) was appeared, which enhanced the properties of composite rocket propellant to a great extent [7]. On the other hand, many scientists and researchers are working to develop new oxidizers for replacing AP because of its toxicity. AP-based propellants produce large amount of hydrochloric acid (HCl(g)) as a gaseous product during its burning that contaminate the atmosphere. In addition, Urbansky et al. stated that the drinking water obtained from southwestern USA might include perchlorate anion (ClO₄⁻), which cause a problem in some regions of the United States [8]. Also, the formation of aluminum oxide (Al₂O₃) from the combustion of CSRP is a source of toxicity to humans, animals and plants [9,10]. Synthesis of new compounds is one of the priorities for the scientists all over the world [11,12] in addition to testing of new formulations [13–15] to overcome the toxicity of the traditional SRP and to fulfill the requirements of CSRP that impart high performance, thermal stability and environmentally safe during the manufacture process. Many CSRP formulations based on GAP as energetic binder and different high energy materials as oxidizers have been studied during last year’s [16–20]. ADN is one of the most promising green oxidizer to be used in SRP with GAP (which has high performance characteristics and good thermal stability) [21–28]. 2,2,2-trinitroethyl-formate (TNEF) is a new interesting high-energy dense...
oxidizer (HEDO) that has been prepared by Klapötke’s group [29]. It has high performance parameters and good thermal stability. Actually, there is no information about the application of TNEF neither as a plastic bonded explosive nor as a composite solid rocket propellant [30–33]. In addition, the thermal behavior and reaction kinetics of the new oxidizer (TNEF) have not been studied yet. As a result, TNEF were prepared and characterized. In addition, a new CSRP formulations based on TNEF/GAP was prepared and the thermal decomposition kinetics of both TNEF and its propellant formulation were studied. ADN and the traditional propellant based on ADN/GAP were studied for comparison.

2. Experimental

2.1. Materials

Glycidyl azide polymer GAP diol L-996, 3 M, St. Paul, MN. (Molecular weight (Mn): 2900 g/mol). Hexamethylene diisocyanate (HMDI) as a curing agent with an NCO equivalence value of 11.83 meq g⁻¹, 1,1,1-Tris(hydroxymethyl)propane as a crosslinking agent, Dibutyltin dilaurate as a catalyst, Chloroform and Anhydrous iron(III) chloride were obtained from Sigma-Aldrich. Ammonium dinitramide (ADN) and 2,2,2-trinitroethanol were prepared in our laboratories. ADN was prepared by nitration of potassium sulfamate according to the method discussed in ref [34].

2.2. Preparation of 2,2,2-trinitroethyl-formate (TNEF)

2,2,2-trinitroethanol (12.5 g, 70.0 mmol) was dissolved in dry chloroform (25 mL), anhydrous iron(III) chloride (1.0 g, 6.15 mmol) was added carefully to avoid the moisture. The mixture was heated under reflux in an oil bath at 85 °C for 120 h. The content of reaction, after cooling, was poured into diethyl ether (300 mL). The ether solution was washed with cold water (3 × 100 mL) and dried over magnesium sulfate. After removing the solvent, a creamy coloured crude product was left, which was recrystallized from dichloromethane to yield 9.5 g (74% yield) of colorless crystals of 2,2,2-trinitroethyl-formate (Scheme 1).

2.3. Preparation of propellant formulations

GAP was mixed with crosslinking agent (1,1,1-Tris(hydroxymethyl)propane) and dibutyltin dilaurate was added, the mixture was stirred under vacuum in a vertical mixer (500 mL) for 30 min at 40 °C. TNEF was added in three portions and stirred for another 30 min. Then, the mixture was cured by adding HMDI at 50 °C and mixing process remained for another 30 min. Finally, the prepared propellant samples were poured in a specific mold and were cured in a vacuum oven at 60 ± 2 °C for seven days. The weight percentage of the oxidizer to the binder system was 86:14 wt%. The selected percentage of each propellant will be discussed in 4.1 theoretical calculation results.

2.4. Experimental techniques

JEOL Eclipse 400 instrument was used to determine the NMR spectra of TNEF. The chemical shifts were obtained based on the external standards Me₄Si (1H, 399.8 MHz; 13C, 100.5 MHz) and MeNO₂ (14N, 28.8 MHz). Impact sensitivity was measured by using BAM falling hammer test obtained from OZM Company, while the friction sensitivity was determined by using BAM friction test [35–37]. The morphology of the studied crystals as well as the homogeneity of the prepared propellant were studied by using SEM (FEI – Helios G3 UC). EXPLO5 thermodynamic code version 6.03 was used to determine the combustion characteristics of the propellant samples. The combustion conditions are based on the ideal gas equation of state with 70 atm combustion chamber pressure and under isobaric combustion. The gaseous products and the specific impulse of the propellant samples were calculated. The thermal decomposition kinetics of the samples were studied using Thermogravimetric Analysis (Perkin-Elmer, TGA 4000) where 1–3 mg samples were examined at different heating rates of 1, 3, 5 and 7 K min⁻¹ in the temperature range 30–500 °C under a flow of dynamic nitrogen of 20 mL min⁻¹. The thermal behavior was determined by using LINSEIS DSC – PT10 with samples of approximately 3 mg placed in an aluminum pan with a pin-hole cover at a heating rate of 5 K min⁻¹ in a temperature range of 25–400 °C.

3. Theoretical

3.1. Kinetic analysis

The determination of the kinetic triplets which are pre-exponential factor (A), kinetic model (f(α)) and the activation energy (Ea) are very important for the kinetic analysis, which should be determined for complete description of the kinetics. Many analytical methods are available nowadays that can be used to determine the kinetic parameters of solid-phase reactions. Model-fitting and isoconversional (model-free) methods are considered the two main methods to determine the kinetic parameters, which can be used either isothermally or nonisothermally [38–41].

![Fig. 1. Relation between the oxidizer weight percentage in each propellant and its specific impulse.](image1)

![Fig. 2. Reaction gaseous products at the nozzle exit.](image2)
3.2. Activation energy calculation

The activation energy (Ea) of the decomposition reaction of the samples can be calculated from Kissinger’s method (Eq. (1)) [42].

\[
\frac{E_a}{R} = \frac{d \ln \left( \frac{\beta}{T_p^2} \right)}{d(1/T_p)}
\]

Where \( \beta \) is the heating rate and \( T_p \) is the DTG peak temperature at that rate. The activation energy can be calculated from the slope of the straight line of \( \ln \left( \frac{\beta}{T_p^2} \right) \) versus \( 1/T_p \). Such rough integral approximation of the temperature may cause an inaccurate calculated values of \( E_a \) [43,44]. More accurate equation was presented according to Starink [45] to calculate \( E_a \) which is commonly called the Kissinger–Akahira–Sunose (KAS) equation [46]:

\[
\ln \left( \frac{\beta}{T_p^{0.5}} \right) = \text{const} - \frac{E_a}{RT_p}
\]

4. Results and discussion

4.1. Theoretical calculation results

The performance characteristics of the new competitor oxidizer (TNEF) and its GAP-based propellant formulation were calculated by using EXPLO5 V_6.03. The theoretical calculations of the best formulation based on ADN/GAP and TNEF/GAP are presented in Fig. 1. The optimum weight percentage of each oxidizer in the propellant formulation was selected to prepare the propellant formulation. It is clear that ADN with 84 wt% presents the highest specific impulse of the ADN/GAP propellant while TNEF with 86–88 wt% has the highest specific impulse of all the TNEF/GAP studied formulations. As a result, percentage of the oxidizer selected in the preparation of ADN/GAP propellant formulation was 84 wt%, while the TNEF percentage in the prepared TNEF/GAP propellant was 86 wt%.

In order to check the gaseous products produced from the combustion of each propellant, Fig. 2 shows the calculated mole percentage of the reaction gaseous products at the nozzle exit for the TNEF/GAP propellant formulation in comparison with the ADN/GAP propellant. It is clear that the TNEF/GAP propellant produced percentage of CO2.
higher than ADN/GAP propellant (more than double the amount produced from ADN/GAP propellant). While the percentage of H2O(g) is higher in case of ADN/GAP. As a result, it was predicted that the energy produced from the combustion of TNEF/GAP should be higher than that produced from ADN/GAP (heat of formation of CO2 is higher than that of H2O(g)). In addition, the new oxidizer TNEF has specific impulse (Iₛ = 250.1 s) and characteristic exhaust velocity (C* = 1408 m s⁻¹), which are higher than that of ADN (Iₛ = 202.4 s) and (C* = 1243 m s⁻¹) respectively, which give it a feature of high combustion characteristics.

4.2. Characterization of TNEF

The new oxidizer (TNEF) was characterized by 1H, 13C, and 14N NMR spectroscopy. The CH2C(NO2)3 singlet moiety in the 1H NMR spectra can be determined at δ = 5.49 ppm in [D₆]acetone. The methylene groups carbon resonances (CH₂) could be observed at 63.7 ppm, while the carbon atom of the formate group was identified at 113.6 ppm and the trinitromethyl groups C(NO2)₃ at 124.7 ppm in the 13C NMR spectra. The nitrogen atom of C(NO2)₃ group was found at −33.1 ppm in 14N NMR spectra.

SEM was used in order to study the crystal morphology of the obtained TNEF. The prepared TNEF has irregular crystals with sharp edges. As a result, solvent/anti-solvent recrystallization techniques were applied to improve the morphology of TNEF. Three different solvents (acetonitrile, acetone and chloroform) and two anti-solvents (water and hexane) were used. It was concluded that the system based on acetone as a solvent and water as anti-solvent with ratio 1:10 vol percentage respectively was the best selection to obtain spherical crystals. The obtained crystals have average particle size of 50 μm with rough surface and uniform shape as shown in Fig. 3. After mixing of TNEF with the GAP polymeric matrix, it was observed that the crystals of TNEF were almost disappeared and a homogenous mixture of TNEF/GAP propellant was obtained as shown in Fig. 4b. In case of ADN/GAP propellant, the irregular shape of ADN crystals were collected with each other (aggregation of ADN crystals) and coated by the GAP polymeric matrix as shown in Fig. 4a. By comparing the SEM photos of TNEF/GAP and ADN/GAP propellants, the homogenous mixing of TNEF/GAP is
clear and it might be possible to predict the smooth burning behavior of TNEF/GAP propellant. In case of ADN/GAP propellant if the GAP matrix does not fill the entire space between the ADN crystals, the burning behavior could be uncontrolled due to the presence of voids. On the other side, it is predicted that the homogeneity of the prepared propellants will affect their thermal degradation process.

The sensitivity of the individual materials was studied where the results of impact and friction sensitivities measurements are presented in Table 1. The reported values are the 50% probability of initiation obtained by the Probit method [47]. Here, the impact sensitivity resulted from uniaxial compression and friction sensitivity resulted from shear slide at certain constant volume for all the studied samples are presented. It is clear that the impact sensitivity of TNEF has been significantly decreased after the recrystallization process. While a small effect on the friction sensitivity appeared. This result is compatible with the results of SEM, where the spherical crystals of TNEF has lower sensitivity to impact than the raw crystals. The AND was used without recrystallization. The prepared propellants have low friction sensitivity (>360 N), while the impact sensitivity of TNEF/GAP is lower than ADN/GAP, this result is also confirmed by the SEM photo of TNEF/GAP propellant which shows homogeneous mixture of the TNEF/GAP propellant formulation.

4.3. Thermogravimetric studies

TG/DTG thermograms of TNEF, ADN, TNEF/GAP and ADN/GAP were recorded at four different heating rates 1, 3, 5, and 7 K min⁻¹ (see Figs. 5 and 6).

From the TG thermograms (Fig. 5), it is clear that TNEF starts its mass loss at temperature higher than that of ADN. The DTG curves presented on Fig. 6 showed maximum decomposition peaks at 206.2 °C for TNEF and 187.5 °C for ADN at 5 K min⁻¹ heating rate. One-step decomposition process was observed for both TNEF and ADN. Regarding to the GAP binder, two steps decomposition stages were observed. The GAP polymer has rate of mass loss less than 75% where the mechanism of decomposition of the two decomposition stages are different. This might be due to the azido group decomposition at the first peak followed by the degradation of the main structure of the polymer.

Fig. 6. DTG curves of TNEF, ADN, GAP, TNEF/GAP and ADN/GAP under heating rates of 1, 3, 5 and 7 K min⁻¹.
The nonisothermal TG/DTG data of TNEF, ADN, GAP, TNEF/GAP and ADN/ GAP.

<table>
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<tr>
<th>Material</th>
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<th>TG curves</th>
<th>DTG peaks</th>
</tr>
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<tr>
<td></td>
<td>Tₐ₀ (°C)</td>
<td>T_i (°C)</td>
<td>Mass Loss (%)</td>
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<tr>
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<td>182.3</td>
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<tr>
<td></td>
<td>3.0</td>
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</tr>
<tr>
<td></td>
<td>5.0</td>
<td>190.7</td>
<td>202.6</td>
</tr>
<tr>
<td></td>
<td>7.0</td>
<td>195.3</td>
<td>206.8</td>
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<tr>
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<td></td>
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<td>7.0</td>
<td>186.4</td>
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<tr>
<td>GAP</td>
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<tr>
<td></td>
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<td>235.8</td>
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<tr>
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<td>164.3</td>
</tr>
<tr>
<td></td>
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<td>157.6</td>
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<td></td>
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<td>167.0</td>
<td>171.7</td>
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<tr>
<td></td>
<td>5.0</td>
<td>174.5</td>
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<td></td>
<td>7.0</td>
<td>181.3</td>
<td>185.9</td>
</tr>
</tbody>
</table>

Note: Tₐ₀: onset decomposition temperature; Tₚ: initial thermal decomposition temperature; Tₜₑ: the maximum peak temperature; Mass Loss: from initial temperature to end temperature.

4.4. Thermal decomposition kinetics

4.4.1. Kinetic parameters obtained by kissinger method

The thermal decomposition kinetics of the individual oxidizers as well as the propellant formulations were studied using nonisothermal TGA technique and their activation energies were determined using the conventional Kissinger method by applying Kissinger equation (Eq. (1)). The activation energy were obtained from the slope of the straight line from plotting ln(β/T²) versus 1/T at the four selected heating rates, where T is the decomposition peak temperature which obtained from the DTG thermogram (Fig. 6). The activation energies of the TNEF and ADN were 146.4 kJ mol⁻¹ and 117.2 kJ mol⁻¹ respectively, while the activation energies of the propellant samples TNEF/GAP and ADN/GAP were 145.1 kJ mol⁻¹ and 134.1 kJ mol⁻¹ respectively. From this result, it is clear that the new oxidizer TNEF and its propellant TNEF/GAP have higher activation energy values than that of the ADN and its GAP-based propellant formulation, which give the advantage for TNEF.

4.4.2. Kissinger–Akahira–Sunose (KAS) method

The activation energy at the different fractional conversion was determined by using modified Kissinger–Akahira–Sunose (KAS) method. The Kinetic parameters of the individual energetic materials (ADN, TNEF, GAP) in addition to the prepared propellants (TNEF/GAP and ADN/GAP) are presented in Tables 3 and 4. Fig. 7 shows the variations of the activation energy for the studied samples from reaction step to another. The mean values of activation energies were calculated at α interval from 0.3 to 0.7 due to the increased of inaccuracy from the tail peak of DTG [49–51]. The mean value of the activation energy of TNEF was found to be 132.1 kJ mol⁻¹, which is higher than ADN (115.3 kJ mol⁻¹). In case of ADN, the activation energy increased until 0.3 fractional conversion, then it starts to be nearly constant until 0.7 fractional conversion followed by decreasing at the end of the reaction conversion. The propellant based on ADN/GAP has the same behavior as ADN until 0.3 fractional conversion with higher activation energies but it continue to increase slightly as the fractional conversions increase until it reached nearly 130 kJ mol⁻¹ at 0.8 fractional conversion. On the other side, the activation energy of TNEF increases as the fractional conversion increases. At 0.1 fractional conversion, the activation energy of TNEF is 124 kJ mol⁻¹ and slightly increases until reached maximum value at 0.8 fractional conversion (136 kJ mol⁻¹). The new propellant TNEF/GAP has different behavior, an obvious increase in the activation energy with increasing of the fractional conversion. TNEF/ GAP has activation energies ranging from 98 to 154 kJ mol⁻¹. By comparing the activation energies of the studied samples with the GAP
binder, it is clear that GAP binder has the highest activation energy of all the studied samples at the same reaction conversion. The significant reduction of the activation energies at each conversion shows the effect of the decomposition of GAP binder (nitrene) \(^{[48]} \) on the studied oxidizers and it might be due to the dissolution of the oxidizers in the intermediate decomposition products of the propellants, which cause the autocatalytic degradation products. It is well known that the decomposition of energetic materials represents a complex process and the difference in the activation energies of propellants and their individual components might be due to the complexity of the decomposition behavior.

The values of the activation energy of the studied samples by the different methods are presented in \(\text{Table 5} \). The results obtained by Kissinger methods is slightly higher than that obtained by KAS method except for GAP binder. The maximum difference between the two methods is less than 12%. The average activation energy of TNEF and its propellant is very close to each other and lower than the GAP binder. While the average activation energy of ADN is lower than its propellant where ADN/GAP has average activation energy lies between the activation energy of both GAP and ADN.

4.5. DSC studies

The DSC thermograms of all the studied samples studied at heating rate \(5.0 \text{ K min}^{-1} \) are presented in Fig. 8. In case of the pure ADN, a melting peak (endothermic) appeared at 95.5 °C as a max. peak followed by onset exothermic decomposition peak at 165.9 °C and maximum decomposition peak at 183.5 °C. While ADN/GAP propellant has melting peak at 93.1 °C, which is lower than that of ADN. The decrease of the melting temperature of the mixture may be due to the use of technical GAP which might acts as impurity and decreased the melting temperature of the pure ADN. In addition, the maximum peak decomposition temperature of ADN/GAP is 186.4 °C, which is higher than that of the pure ADN. This might be due to the high decomposition temperature of the pure GAP (245.7 °C max. peak temperature at heating rate \(5.0 \text{ K min}^{-1} \)) which acts as inhibitor in this case and increased the decomposition temperature of the propellant ADN/GAP. Table 6 includes the data of DSC measurements for the studied samples at heating rate of 5.0 K min\(^{-1}\). In addition, it was found that the oxidizer TNEF has endothermic melting peak at 127.1 °C and followed by onset decomposition peak at 189.6 °C and maximum decomposition peak at 210.1 °C. It is obvious that TNEF has higher thermal stability compared with the oxidizer ADN. Regarding to the new propellant TNEF/GAP it was found that the maximum decomposition temperature of the propellant is lower than the pure TNEF by nearly 15 °C. It means that GAP binder decreased the decomposition temperature of TNEF even that GAP has decomposition temperature at 245.7 °C. This result confirms that TNEF might be dissolved in the polymeric matrix, which affects its thermal stability. Still the new propellant has decomposition temperature higher than the traditional propellant based on ADN/GAP.
2,2,2-Trinitroethanol-formate (TNEF) is a new interesting competitor as a high energy dense oxidizer (HEDO) which has higher performance characteristics and thermal stability than the common ammonium nitrate (ADN). The thermochemical calculations showed that TNEF has specific impulse of 250.1 s, which is higher than that of ADN (202.1 s). In addition, it has green decomposition gaseous products (chlorine-free) comparing with other common used oxidizer (ammonium perchlorate AP). The impact sensitivity of TNEF was improved through an easy and fast recrystallization process to decrease its impact sensitivity than ADN. The SEM photos showed high homogeneity degree of TNEF after recrystallization process with the energetic GAP matrix in comparison with the ADN oxidizer. The thermal study proved the higher thermal stability of TNEF that melts at 127.1 °C and decomposes at 210.1 °C in comparison with ADN that melts at 95.5 °C and decomposes at 183.5 °C. The kinetic study showed activation energy of TNEF (in the range of 132–146 ± 0.5 kJ mol⁻¹) higher than that of ADN (in the range of 114–117 ± 0.2 kJ mol⁻¹). TNEF is a promising high-energy dense oxidizer, which might have applications in future.

5. Conclusion

2,2,2-trinitroethanol-formate (TNEF) is a new interesting competitor as a high energy dense oxidizer (HEDO) which has higher performance characteristics and thermal stability than the common ammonium nitrate (ADN). The thermochemical calculations showed that TNEF has specific impulse of 250.1 s, which is higher than that of ADN (202.1 s). In addition, it has green decomposition gaseous products (chlorine-free) comparing with other common used oxidizer (ammonium perchlorate AP). The impact sensitivity of TNEF was improved through an easy and fast recrystallization process to decrease its impact sensitivity than ADN. The SEM photos showed high homogeneity degree of TNEF after recrystallization process with the energetic GAP matrix in comparison with the ADN oxidizer. The thermal study proved the higher thermal stability of TNEF that melts at 127.1 °C and decomposes at 210.1 °C in comparison with ADN that melts at 95.5 °C and decomposes at 183.5 °C. The kinetic study showed activation energy of TNEF (in the range of 132–146 ± 0.5 kJ mol⁻¹) higher than that of ADN (in the range of 114–117 ± 0.2 kJ mol⁻¹). TNEF is a promising high-energy dense oxidizer, which might have applications in future.

Acknowledgments

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References


Table 6

<table>
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<tr>
<th>Sample</th>
<th>Exothermic peak</th>
<th>Endothermic peak</th>
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<tbody>
<tr>
<td></td>
<td>( T_p ) (°C)</td>
<td>( T_d ) (°C)</td>
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<tr>
<td>TNEF</td>
<td>189.6</td>
<td>216.1</td>
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<tr>
<td>ADN</td>
<td>165.9</td>
<td>183.5</td>
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<td>195.4</td>
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<tr>
<td>ADN/GAP</td>
<td>169.8</td>
<td>186.4</td>
</tr>
</tbody>
</table>

Note: \( T_p \): onset decomposition temperature; \( T_d \): decomposition peak temperature; \( T_m \): the end decomposition temperature; \( T_{mp} \): melting onset temperature; \( T_{mp} \): melting peak temperature.
1702–1706.


