Performance of advanced composite solid rocket propellants based on novel oxidizers

Mohamed Abd-Elghany¹, Ahmed Elbeih²,³, Thomas M. Klapötke¹ and Mahmoud Abdelhafiz²

¹ Department Chemie, Ludwig-Maximilians Universität München, 81377 München, Germany
² Military Technical College, Kobry Elkobbah, Cairo, Egypt
³ Email: elbeih.czech@gmail.com

Abstract: Three novel high energy dense oxidizers (HEDO), Bis(2,2,2-trinitroethyl)oxalate (BTNEOx), 2,2,2-Trinitroethyl-nitrocarbamate (TNENC), 2,2,2-Trinitroethyl-formate (TNEF) have been prepared and studied as oxidizers in composite solid rocket propellants (CSRPs). For comparison, traditional CSRPs containing ammonium perchlorate (AP) bonded by hydroxyl-terminated polybutadiene (HTPB) binder system was studied. The optimum oxidizer percentage with respect to the specific impulse was determined using the thermodynamic code (EXPLO5_V6.03). In addition, the optimum oxidizer mixture based on the novel oxidizers with AP was studied. The combustion properties and gaseous products of the optimum propellant compositions were calculated. A selected composition was prepared in the lab. scale and the burning rate was measured by the strand burner method. It was concluded that TNEF based propellant possess the maximum specific impulse of all the studied compositions. In addition, TNEF based propellant has a higher burning rate than the traditional CSRPs.

Keywords: TNEF, TNENC, BTNEOx, Propellant, Performance

1. Introduction
Solid rocket propellant compositions are famously used as boosters in the military applications. Simplicity, reliability, and stability during long-time storage favor their usage in tactical missions, such as space launches, missiles, and guns, over the higher performance and the more controllable liquid-propellant formulations [1]. However, improving their performance still challenging and motivated many researchers to investigate this issue [2]. Solid propellant formulations are classified into two main categories; homogeneous and heterogeneous mixtures [3]. Homogeneous CSRPs are those obtained by the chemical mixing of ingredients forming a homogeneous physical structure, such as single base, double-base, and triple-base propellants [4]. On the other hand, the heterogeneous rocket propellant formulations are fabricated through the physical mixing of ingredients forming a heterogeneous physical structure [5,6].

A solid rocket propellant formulation consists of a range of different chemical ingredients such as oxidizers, fuels, binders, plasticizers, curing agents, stabilizers, and cross-linking agents. The type of ingredients tolerates the output physical and chemical properties of the mixture, thus controlling the
performance and the combustion properties of propellant formulation [7,8]. Nitrocellulose (NC) is the common energetic polymer used in rocket propellant compositions. However, its inflexible nature restricts processing and thus limits its applications [9]. For that reason, liquid nitroglycerine (NG) was introduced to plasticize NC to improve the processing and to increase the energy output leading to the fabrication of the traditional double-base propellants [10]. The high sensitivity and low thermal stability of NG increased its hazards during handling and manipulation, this lead to the replacement of NG by modern energetic plasticizers [11].

In composite solid rocket propellant (CSRP), ingredients are crystalline particles which act as either oxidizers or fuels. Oxidizers, such as Ammonium perchlorate (AP) and fuel solid particles, such as aluminum powder (Al) are bound together in a polymeric matrix called binder [12-14]. Binders could be inert, such as the conventional Hydroxyl-terminated polybutadiene (HTPB), or could be energetic such as NG or modern azide polymers; Glycidyl azide polymer (GAP), 3,3-Bis-azidomethyl oxetane (BAMO), and 3-Azidomethyl-3-methyl oxetane (AMMO) [15-17]. The performance, availability, and compatibility of Ammonium perchlorate (AP) with other propellant ingredients make AP the most commonly used oxidizer in the rocket propellant field [18-20]. However, the economics of inorganic nitrates, such as Ammonium Nitrate (AN), and their ability to produce smokeless exhaust facilitate their usage as low-performance oxidizers [21,22]. Developing a new family of oxidizers has motivated many researchers to work in this field. Challenging was to develop thermally stable oxidizers that have a relatively high oxygen content and able to produce smokeless, non-toxic and environmentally safe exhaust [18].

Recently, a new family of green oxidizers has been prepared called high-energy dense oxidizers (HEDOs) [23-25]. These oxidizers interestingly are thermally stable and have high-performance parameters. However, their applications as energetic oxidizers in the composite solid propellant formulations have not been studied yet. In this work, three novel high-energy dense oxidizers (HEDOs); 2,2,2-trinitroethyl-formate (TNEF), 2,2,2-trinitroethyl-nitrocarmamate (TNENC) and bis(2,2,2-trinitroethyl)oxalate (BTNEOx) were fabricated and characterized [26-28]. The influence of these novel HEDOs on the performance of CSRP was studied in comparison to the traditional CSRP based on ammonium perchlorate (AP) and hydroxyl-terminated polybutadiene (HTPB) binder system.

2. Experimental

2.1. Preparation of bis(2,2,2-trinitroethyl)-oxalate (BTNEOx)
Firstly, 5.7 g 2,2,2-trinitroethanol was dissolved in 10 ml of 1,2-dichloroethane. Then, 1.0 g oxalyl chloride and 0.1 g AlCl3 were added. The solution was subjected to heating for 5 h under reflux. After reaction completion, the solution was left to cool until colorless BTNEOx crystals were precipitated [29].

2.2. Preparation of 2,2,2-trinitroethyl-nitrocarmamate (TNENC)
Chlorosulfonyl isocyanate (CSI) was added to a solution of 2,2,2-trinitroethanol (TNE) dissolved in acetonitrile. The mixing molar ratio of CSI:TNE was 1:1.07. After mixing for 1.5 h at room temperature, the reaction mixture was left to cool with continuous stirring. After 10 min, a colorless precipitate of 2,2,2-trinitroethylnitrocarmamate was formed. After nitration, 2,2,2-trinitroethyl-nitrocarmamate crystals were obtained with an approximate yield percentage of 99% [30].

2.3. Preparation of 2,2,2-trinitroethyl-formate (TNEF)
70 mmol of 2,2,2-trinitroethanol was dissolved in 25 ml chloroform. Then, 6.15 mmol anhydrous iron(III) chloride was added to the reaction mixture. Heating at 85 °C in an oil bath was then applied under reflux. After 120 h, the mixture was cooled then mixed with 300 ml diethyl ether. After washing with cold water, drying over magnesium sulfate and then recrystallization from dichloromethane, creamy-colored crystals of 2,2,2-trinitroethyl-formate were obtained with a 74% yield [31].
2.4. Preparation of propellant formulations
Hydroxyl-terminated polybutadiene (HTPB) with a 14 wt. % was used as a prepolymer. Then, 86 wt% of each oxidizer; TENF and AP were added carefully and mixed with the prepolymer in a 400 mL vertical mixer for 25 minutes at 50 °C under vacuum. Afterward, Hexamethylene diisocyanate (HMDI) was added at 60 °C as a curing agent. The reaction medium was kept under continuous mixing for 30 min. Finally, the fabricated propellant samples were dispensed in a specific mold and left in a vacuum oven 60 °C for a week until curing occurs.

2.5. Experimental techniques
Calculations of the combustion properties of the fabricated propellant formulations were achieved using the thermodynamic code EXPLO5 version 6.03. The reaction conditions were adjusted according to the ideal gas equation of state, where the pressure of the used combustion chamber was kept constant at 70 atm. EXPLO5 software was used to develop the specific impulse as well as the resultant gaseous products for each propellant sample. The burning rates of the prepared samples were measured by the Strand burner method using the Crawford bomb [32].

3. Results and discussion
3.1. Theoretical calculation of the specific impulse of CSRP based on different percentages of individual oxidizers
The performance features of the HTPB-based propellant formulations based on different percentages of the fabricated novel high energy dense oxidizers (HEDOs), bis(2,2,2-trinitroethyl)oxalate (BTNEOx), trinitroethyl-nitrocarbamate (TNENC), 2,2,2-trinitroethyl-formate (TNEF) were calculated by using EXPLO5 V_6.03. As shown in Figure 1, it was found that the percentage of any of the three new HEDOs is directly proportional to the theoretical values for the specific impulse (Is) of the resultant propellant formulation. Interestingly, TNEF as an energetic oxidizer showed the highest specific impulse values in comparison to the corresponding results obtained at the same weight % of either TNENC or BTNEOx. As a result, it is recommended to favor the usage of TNEF as an interesting candidate for replacing the traditional AP oxidizer in rocket propellant formulations to obtain high-performance with the advantage of the production of the smokeless exhaust.

Figure 1. Changing the wt % of the oxidizers in the propellants with their specific impulse
3.2. Theoretical calculation of the specific impulse of CSRP based on oxidizer mixtures

In this part, an oxidizer mixture was used instead of a single component. Motivation beyond that was to evaluate the relationship between the AP weight % and the output specific impulse of the propellant formulation. Three different mixtures were examined; BTNEOx/AP, TNENC/AP, and TNEF/AP mixtures. The performance characteristics of the propellant formulations based on these oxidizer mixtures were calculated by using EXPLO5 V_6.03. Results, as shown in Figure 2, exhibited that increasing the AP weight % in either BTNEOx/AP or TNENC/AP formulations lead to increasing the specific impulse of propellant. On the other hand, TNEF/AP mixture showed the opposite behavior, where the higher the AP weight percentages resulted in lower specific impulse values. However, the values of the specific impulse of the propellant formulations based on the TNEF/AP mixture still the highest ones among the whole study. These results confirmed the significant influence of the usage of TNEF as an oxidizer instead of AP.

![Figure 2. Changing the wt% of the oxidizers to AP wt% in the studied propellants with their specific impulse](image)

3.3. Theoretical calculation of the combustion properties and gaseous products of selected CSRP

Herein, the theoretical calculation of the gaseous products resulted during the combustion of both AP/HTPB and TNEF/HTPB propellant formulations were determined using EXPLO5 V_6.03. This work was done as a trial to cultivate new oxidizers for substituting AP to avoid its disadvantages such as toxicity and the production of a large amount of hydrochloric acid (HCl(g)) that contaminates the atmosphere. Figure 3 shows the gaseous products obtained at exit of the nozzle after the combustion of the TNEF/HTPB propellant composition and the AP/HTPB propellant. Results showed that the AP/HTPB formulation produces 18.4 mol% of HCl(g) as a gaseous product. However, HCl(g) disappeared in the gaseous products obtained in the case of burning the TNEF/HTPB propellant formulation. This concludes that the usage of TNEF as a novel oxidizer instead of AP will help to obtain a smokeless exhaust.

In addition, results, as summarized in Table 1, show that the propellant composition based on the new oxidizer TNEF has a specific impulse (I_s = 250.1 s) which is greater than that of the conventional AP/HTPB (I_s = 245.9 s). This could be attributed to the production of a higher molar percentage of gaseous products (41.126 mol.kg\(^{-1}\)) in case of TNEF/HTPB in comparison to the 39.765 mol.kg\(^{-1}\) obtained in the case of AP/HTPB. Also, the characteristic exhaust velocity obtained from the novel
TNEF/HTPB formulation ($C^* = 1532.6 \text{ m.s}^{-1}$) was found to be higher than that of AP/HTPB ($C^* = 1484.4 \text{ m.s}^{-1}$), which improves its combustion characteristics over the conventional AP/HTPB formulation.

### Table 1. Comparison between the combustion characteristics of AP/HTPB and TNEF/HTPB formulations

| Propellant Formulation | $I_s$ (s) | $C^*$ (m.s$^{-1}$) | $C_T$ | $T_e$ (K) | $Mol_e$ (mol.kg$^{-1}$) |
|-------------------------|----------|------------------|-------|----------|----------------------|
| AP/HTPB                 | 245.9    | 1484.4           | 1.62  | 1360.5   | 39.765               |
| TNEF/HTPB               | 251.2    | 1532.6           | 1.61  | 1331.8   | 41.126               |

$C_T$...Thrust Coefficient, $T_e$...The temperature at the nozzle exit, $Mol_e$...mole of gaseous products

#### 3.4. Results of burning rate measurements

Crawford bomb was used to measure the burning rate of the prepared propellants. Strands have been prepared with a dimension of 6 mm diameter and 80 mm length. The strand was coated by an inhibitor to prevent side burning and placed vertically in a pressure tank. Two fuse wires were embedded in the strand itself with 50 mm distance between them. The wires were connected to the electronic timer. The strand was ignited from the upper side of the strand by electrical current. The time taken to burn the 50 mm between the two wires was calculated using a data acquisition system. Nitrogen was used to increase the pressure inside the bomb. The burning rate was determined by dividing the burning part between the two wires (50 mm) by the time recorded. The burning rates of the studied samples are reported at 7 MPa. The burning rate of AP/HTPB is 10.64 mm.s$^{-1}$ at 7 MPa while the burning rate of TNEF/HTPB is 12.11 mm.s$^{-1}$ at 7 MPa. The new propellant TNEF/HTPB has a burning rate higher than the traditional AP/HTPB by 14%.

#### 4. Conclusion

By comparing the performance of the three novel interesting oxidizers, BTNEOx, TNENC and TNEF, it was concluded that TNEF has the highest performance. TNEF has a specific impulse higher than AP and the other studied oxidizers. On the other side, it has been observed that there is no HCl(g) produced in the gaseous products of TNEF/HTPB while AP/HTPB formulation produced 18.4 mol% of HCl(g). The burning rate of TNEF/HTPB is higher than the AP/HTPB. It means that TNEF/HTPB is an interesting smokeless composite propellant; it has performance higher than the traditional AP/HTPB. It is recommended to scale up the production process and test the propellant practically on a large scale.
References

[1] DeLuca L T 2016, Eurasian Chemico-Technological Journal 18(3), 181-196.

[2] Guery J-F, Chang I-S, Shimada T, Glick M, Boury D, Robert E, Napier J, Wardle R, Pérou C and Calabro M 2010, Acta Astronautica 66(1), 201-219.

[3] D'Andrea B, Lillo F, Faure A and Perut C 2000, Acta Astronautica 47(2-9), 103-112.

[4] Zayed M A, Mohamed A A and Hassan M A 2010, Journal of hazardous materials 179(1), 453-461.

[5] Rashkovskii S 1999, Combustion, Explosion and Shock Waves 35(5), 523-531.

[6] Yan Q L, Zeman S, Sánchez Jiménez P E, Zhang T L, Pérez-Maqueda L A and Elbeih A 2014, J. Phys. Chem. C 118, 22881–22895.

[7] Cerri S, Bohn M A, Menke K and Galfetti L 2014, Propellants Explosives Pyrotechnics 39(2), 192-204.

[8] Abd-Elghany M, Elbeih A and Hassanain S 2016, Central European Journal of Energetic Materials 13, 349-356.

[9] Pourmortazavi S, Hosseini S, Rahimi-Nasrabadi M, Hajimirsadeghi S and Momenian H 2009, Journal of hazardous materials 162(2), 1141-1144.

[10] Chin A, Ellison D S, Poehlein S K and Ahn M K 2007, Propellants explosives pyrotechnics 32(2), 117-126.

[11] Agrawal J and Singh H 1993, Propellants Explosives Pyrotechnics 18(2), 106-110.

[12] Ma Z, Li F and Bai H 2006, Propellants Explosives Pyrotechnics 31(6), 447-451.

[13] Abd-Elghany M, Klapötke T M and Elbeih A 2018, RSC Advances 8(21), 11771-11777.

[14] Abd-Elghany M, Klapötke T M, Elbeih A and Zeman S 2017, J. Anal. Appl. Pyrolysis 26, 267-274.

[15] Gaur B, Lochab B, Choudhary V and Varma I 2003, Journal of Macromolecular Science, Part C: Polymer Reviews 43(4), 505-545.

[16] Abd-Elghany M, Elbeih A and Klapötke T M 2018, Journal of Analytical and Applied Pyrolysis 133, 30-38.

[17] Hussein A K, Zeman S and Elbeih A 2018, Thermochimica Acta 660, 110-123.

[18] Trache D, Klapötke T M, Maiz L, Abd-Elghany M and DeLuca L T 2017, Green Chemistry 19(20), 4711-4736.

[19] Boldyrev V 2006, Thermochimica Acta 443(1), 1-36.

[20] Memon N K, McBain A W and Son S F 2016, Journal of Propulsion and Power 32(1), 682-686.

[21] Kohga M and Okamoto K 2011, Combustion and Flame 158(3), 573-582.

[22] Abd-Elghany M, Klapötke T M, Elbeih A and Zeman S 2017 J. Anal. Appl. Pyrolysis 26 267-274.

[23] Silva G D, Rufino S C and Iha K 2013, Journal of Aerospace Technology and Management 5(2), 139-144.

[24] Talawar M, Sivabalan R, Mukundan T, Muthurajan H, Sikder A, Gandhe B and Rao A S 2009, Journal of Hazardous Materials 161(2-3), 589-607.

[25] Elbeih A, Abd-Elghany M and Klapötke T M 2017, Propellants, Explosives, Pyrotechnics 42(5) 468-476.

[26] Abd-Elghany M, Klapötke T M and Elbeih A 2017, Journal of Analytical and Applied Pyrolysis 128 397-404.

[27] Abd-Elghany M, Klapötke T M and Elbeih A 2017, Propellants Explosives Pyrotechnics 42(12) 1373-1381.

[28] Abd-Elghany M, Klapötke T M, Krumm B and Elbeih A 2018, ChemPlusChem 83(3) 128-131.

[29] Klapötke T M, Krumm B and Scharf R 2016, European Journal of Inorganic Chemistry 19 3086-3093.

[30] Axthammer Q J, Klapötke T M, Krumm B, Moll R and Rest S F 2014, Zeitschrift für anorganische und allgemeine Chemie 640(1) 76-83.
[31] Klapötke T M, Krumm B, Moll R and Rest S F 2011, Zeitschrift für anorganische und allgemeine Chemie 637(14-15), 2103-2110.

[32] Mukesh R, Sivasubramaniyam R, Elangovan R, Sree A, Harish R, Rajashree D and Kanhar S K 2017, Advances in Aerospace Science and Technology 2(4), 48-72.