

Study of Energetic Materials of Double Base Propellant for Small Caliber Ammunition

Khevinadya Ramadhani Runtu^{1,a}, Leni Tria Melati^{2,b}, Igara Triregina^{3,c}, Gathut Imam Gunadi^{4,d}, Prita Nur Wahyu^{5,e}, Ice Fahmi^{6,f}, Nanang Hary Soebakgijo^{7,g}, Mas Ayu Elita Hafizah^{8,h}, Yayat Ruyat^{9,i}

^{a,b,c,d,e,f,g,h,i} Republic of Indonesia Defense University, Bogor, Indonesia

¹khevinadya.runtu@tp.idu.ac.id*, ²leni.tria@tp.idu.ac.id, ³triregina.igr@gmail.com, ⁴jejaklangkah82@yahoo.com, ⁵pritanurwahyu@gmail.com, ⁶icefahmi77@gmail.com, ⁷nahesu94@gmail.com, ⁸masayu.elita@gmail.com, ⁹yayat.ruyat@idu.ac.id

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ABSTRACT

Double Base Propellants (DBP) has been frequently utilized in the fields of rocket propellant and gun propellant. DBP has various advantages over conventional propellants, including easy formulation, high energy, and smoke lessness. The research conducted in literature studies was applied by referring to the various energetic materials for DBP. The composition of a DBP consists of energetic raw material of Nitrocellulose (NC) and Nitroglycerin (NG). According to data analysis, NC can be manufactured from the raw material Nata de Coco, which has a nitrogen content of more than 12,5% in NC, which is in line with the levels of conventional military and propellant raw materials. Meanwhile, SMX (1,4-dinitrate-2,3-dinitro-2,3bis (nitroethylene) butane) or GAP (Glycidyl Azide Polymer) on double-base propellants is suggested as potential alternative energy sources that can be utilized to substitute NG. The choice of new energetic material is influenced by the fact that Nata de Coco is abundant in Indonesia, while SMX and GAP in terms of manufacturing and handling are safety. The several parameters to characterize double-base propellants include thermal analysis, microstructure, surface area, burning rate value, and gaseous product. The results of thermal properties by DSC analysis on a DBP based on NC+NG+TiO₂-trifluoroacrylate showed a change in exothermic decomposition at a temperature of 199.2°C. Meanwhile, TGA analysis of a DBP based on NC+NG+GAP showed mass decomposition at temperature 199,3°C. Furthermore, it was found that thermoplastic elastomers GAP have a significant effect on increasing the low-temperature mechanical properties of double-base propellants. As a result, the literature studies approach, which includes consideration of alternative energetic raw materials and characterization for double-base propellants, is the recommendation for obtaining a superior performance double-base propellants with energetic materials.

Keywords:
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Energetic Materials
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I. Introduction

The propellant is one of the 10 strategic programs in the field of defense equipment's for Indonesian defense industry. In manufacturing and developing propellant technology independently, the first step needs to be supported by various researches related to propellants. Various studies have been carried out to support the latest advances in propellant technology. The current development of propellant technology makes it possible to use new energetic materials, simple formulations, high energy, and smokeless [11]. The use of this new energetic material is used for more modern propellant applications.



Propellant or propulsion is the most important part of munitions. A propellant is an explosive that burns continuously in a controlled manner and produces a large volume of hot gas. The hot gases produced are then used for pressure as a driving agent in a ballistic propulsion system [1]. In general, solid propellants consist of double-base propellants (DBP), composite propellants, and composite modified double-base propellants (CMDB). Double Base Propellant (DBP) in general has a long history of use in the rocket propellant and armament industries. In comparison to other propellants, DBP has a variety of benefits, including easy formulation, high energy, and smokelessness.

The composition of the double-base propellants consists of energetic materials of Nitrocellulose as the main component, Nitroglycerin as a plasticizer, ballistic stabilizers, combustion catalysts, and other additives [16]. Nitrocellulose synthesis can be performed by titrating cellulose obtained from synthetic or natural raw materials. The manufacture of nitrocellulose includes the steps of nitration of cellulose with a nitration solution consisting of a mixture of nitric acid with a concentrated sulfuric acid catalyst, separation of nitrocellulose from the nitration solution, washing, and stabilization. Nitroglycerin (glycerol trinitrate) is an energetic material that resembles oil and is colorless. Nitroglycerin synthesis is obtained by the nitration of glycerin with a Sulfonitric mixture [2].

Several studies have been carried out to obtain double base energetic propellant materials, one of which is the synthesis of nitrocellulose from synthetic or natural raw materials. Jori *et al.*, (2021) showed that *Nata de Coco* could be used for the synthesis of cellulose for nitrocellulose in double-base propellants. It's known that the combination of Nitrocellulose with other energetic materials in the form of a new solid nitrate ester (SMX) and Glycidyl Azide Polymer (GAP) produces a new propellant technology with good safety characteristics and improves propellant performance [11,15].

Several parameters of double-base propellant characterization can be measured and analyzed using laboratory instruments. Zhao *et al.* (2015) showed that the characteristics of the thermal properties, microstructure, and gaseous product propellant double base were tested. Several other studies also analyzed other characteristics such as burning rate, surface area, and rheological properties tests. It should be noted that in addition to testing for mechanical and viscoelastic properties, additional testing parameters must also be carried out such as visual inspection, chemical stability assessment, and internal ballistic tests.

In Indonesia, since double-base propellants manufacturing plant is not existed, currently Indonesia still really on imported the products. There is a manufacturing plant for producing nitrocellulose in Indonesia, unfortunately for industrial application. In order to realize the independence of the defense industries, it's necessary to study of various energetic raw materials as the main component for double base propellants. The results of the research regarding double-base propellants technology can be applied in future research and development of propellants technology.

II. Method

The research was conducted by applying qualitative research methodology. Literature studies was applied referring to the various energetic raw materials of double-base propellants. Literature studies are carried out by reviewing previous research journals and then reviewing and discussing them. The results and discussion were obtained by collecting various data from references to the results of relevant journal reviews.

Furthermore, the results of the energetic raw materials regarding double-base propellants technology from several previous research journals can be compared to produce comprehensive and useful data and information that can be used in future research and development of propellant technology.

During the last 10 years, there have been several journals related to energetic raw materials of double-base propellants. From these publications, there are composition, manufacturing and characterization of double-base propellants produced by Yolhamid *et al.* (2018); Gismatulina *et al.*

(2018); Jamal *et al.* (2020); Jori *et al.* (2021); Reese *et al.* (2014); Zhao *et al.* (2015); Pourmortazavi *et al.* (2016); Zhang *et al.* (2019); Zou *et al.* (2020).

III. Results and Discussion

A. Double-base Propellant Composition: Energetic Raw Materials

The composition of double-base propellants consists of energetic material in the form of 40-70% Nitrocellulose and 15-41% Nitroglycerin [1] which is added with ballistic stabilizer, combustion catalyst, and other additives [16]. While Reese *et al.* (2014) made a double-based propellant with a composition based on Nitrocellulose and SMX (1,4-dinitrate-2,3-dinitro-2,3bis(nitratomethylene)butane). In the study of Zhao *et al.* (2015) and Zou *et al.* (2020), it was found that the energetic thermoplastic elastomer GAP (Glycidyl Azide Polymer) can act as a component of the double-based propellant.

Based on the several research, there are differences in the double-based propellant plasticizer materials used. Nitroglycerin is generally used as a plasticizer in double-based propellants. The use of Nitroglycerin turned out to cause stability and performance problems for the double base propellant because Nitroglycerin might migrate from the stored propellant and soften it at higher inclusion levels. Furthermore, because of NG's low melting point (287°K), its quantity in the propellant must be carefully considered to avoid excessive grain strength degradation [11].

Therefore, this problem can be overcome by substituting new energetic alternative materials that are stable, oxygen balance, lower sensitivity, has the potential to reduce migration, and improve the physical properties of the propellant.

Nitrocellulose

Nitrocellulose (NC) is the main energetic material for double-base propellants. The nitration process of cellulose produces nitrocellulose, namely the process of substitution of the –OH group with the –ONO₂ group. The synthesis of nitrocellulose was carried out by nitration the cellulose. Cellulose can be obtained from synthetic or natural main raw materials such as plants, non-woody raw materials, and another alternative bacterial cellulose [12]. The use of natural materials aims to obtain raw materials that are abundantly available in Indonesia. Table 1 shows data from several studies related to nitrogen percent in the synthesis of nitrocellulose produced.

Table 1. Percent Nitrogen in Nitrocellulose (%)

Author (Year)	Material	% Nitrogen
Yolhamid <i>et al.</i> (2018)	<i>Rhizophora</i>	11.40
Gismatulina <i>et al.</i> (2018)	<i>Miscanthus</i>	11.85
Jamal <i>et al.</i> (2020)	Bacterial Cellulose	12.10
Jori <i>et al.</i> (2021)	<i>Nata de Coco</i>	12.75

Based on Table 1, shows that based on the results of various studies, several natural plant materials and bacteria can be utilized for the synthesis of nitrocellulose for double-base propellants (DBP). The NC criteria for DBP depend on the nitrogen content in the NC. Although materials with nitrogen content reaching 11,8-12,3% in NC can be used in military applications [9], nitrocellulose with low nitrogen content (< 12,5%) is more likely to be used in industrial applications, such as pharmaceuticals and ink bases. Meanwhile, to meet the criteria for standard military raw materials, the nitrogen content must be 12,5 to 13,5% in nitrocellulose.

Therefore, this type of nitrocellulose which is classified as a high nitrogen content NC can be used as energetic materials such as rockets and guns propellants [3]. The data in Table 1 shows that *Rhizophora*, *Miscanthus*, and bacterial cellulose belong to low nitrogen content NC. While the latest study by Jori *et al.* (2021) showed that *Nata de Coco* was able to produce the highest nitrogen content (12.75%), it can be concluded that the Nitrocellulose synthesis carried out can be used as a propellant, raw material in military applications. In addition to nitrogen content, it's necessary to

consider other parameters required in the manufacture of DBP, such as the cellulose content must be 92% in nitrocellulose can be used in military applications.

Nitroglycerin

Nitroglycerin (NG) is used as an energetic plasticizer in double-base propellants. Nitroglycerin or glycerol trinitrate can be synthesized by nitration of glycerin by a sulfonitric mixture [2]. The use of Nitroglycerin turned out to cause stability and performance problems for the double base propellant because Nitroglycerin could migrate from the propellant during storage, and soften it at high inclusion levels.

Therefore, a new alternative energetic material is used to replace nitroglycerin in the double base propellant, which can make the resulting propellant have flexible and homogeneous propellant characteristics to improve the propellant performance.

Based on several research, the addition of new energetic material SMX (1,4-dinitrate-2,3-dinitro-2,3bis(nitratomethylene)butane) and GAP (Glycidyl Azide Polymer) as a substitute for NG results in the physical characteristics of a double-base propellant with a structure homogeneous. SMX is also soluble with the plasticizer DEGDN, propellant based on NC+SMX+DEGDN 25%-wt produce a homogeneous propellant that is flexible and exhibits superior performance, and is easier to process.

Energetic materials of SMX and GAP can be considered because they have energy that is equivalent to NG. It's known that SMX and GAP have good oxygen balance so they are smokeless. The oxygen balance value for the propellant containing GAP is 0.623 [16]. GAP is also well-known for its non-volatility and higher heat stability [15]. It can be concluded that substituting Nitroglycerin with SMX or GAP is proven to result in a new propellant technology with good safety characteristics and superior propellant performance. In Table 2, the results of the physics microstructure of propellants double-base based on new energetic material (SMX and GAP) characteristics are shown.

Table 2. Characteristics Physics of Propellants Double-base Based on New Material Energetic

Author (Year)	Materials	Microstructure
Reese <i>et al.</i> (2014)	NC + SMX	Homogeneous structure
Zhao <i>et al.</i> (2015)	NC + GAP	Homogeneous structure

B. Characterization Propellant Double Base

From the data obtained, there are several parameters to characterize the double base propellant, including thermal analysis, microstructure, surface area, burning rate value, and gaseous product. These characterization parameters were measured and analyzed using laboratory instruments. The results of the double base propellant characterization from several previous studies have been summarized in Table 3.

Table 3. Double-base Propellants Characterization Results

Author (Year)	DBP Raw Material	Parameter Characterization	Instruments	Result
Reese <i>et al.</i> (2014)	NC + SMX + DEGDN	Thermal Properties	DSC	$T_{\text{exo}} = 62,6^{\circ}\text{C}$
		Microstructure	SEM	Homogeneous
		Surface Area	BET	$1.9 \pm 0.03 \text{ m}^2\text{g}^{-1}$
Zhao <i>et al.</i> (2015)	NC + GAP	Thermal Properties	TGA	Mass decomposition at temperature 192,9-194,6°C
		Microstructure	SEM	Homogeneous

Author (Year)	DBP Raw Material	Parameter Characterization	Instruments	Result
Pourmortazavi <i>et al.</i> (2016)	NC + NG + DAG	Gaseous Products	FTIR	NO, NO ₂ , CO, CO ₂ , NH ₃ , CH ₄ , HCN, N ₂ , CH ₂ O and C ₂ H ₄ O
		Thermal Properties	DSC	T _{exo} = 188,74°C
		Burning Rate	-	17.54 mm/s ⁻¹ (at Pressure 15 MPa)
Zhang <i>et al.</i> (2019)	NC + NG + TiO ₂ -3F	Thermal Properties	DSC	T _{exo} = 199,2°C
		Gaseous Products	FTIR	CO, CO ₂ , CH ₄ , NO, H ₂ O
Zou <i>et al.</i> (2020)	NC + NG + GAP	Thermal Properties	TGA	Mass decomposition at temperature 199,3°C

Based on Table 3, the results of some research there are several parameters results of characterization of the double-base propellant produced. A Double-base propellant composition with NC+SMX 40 wt-%+ Additive DEGDN (Diethyleneglycol dinitrate) 25%-wt, a flexible double-base propellant was produced with homogeneous physical characteristics and good sensitivity. It is known that increasing the addition of SMX into the propellant also increases the specific impulse value of the propellant [11]. The rise in the particular impulse value implies that double-base propellants are being used more effectively and efficiently.

A double-base propellant based on NC+GAP 40% and NC+GAP 50% is better than the double-base propellant based on NC+GAP 30%, which indicates that increasing the composition of GAP can improve the quality of the double-base propellant. In addition, it's known that a propellant based on NC+GAP are homogeneous [15]. A double-base propellant with alternative substitution of Nitroglycerin with a new compound (SMX/GAP) can produce new propellant technology with good safety characteristics and increase the performance of the propellant.

From the results of this study, the gas product produced by the propellant was also measured by analyzing it using FTIR. The results of the FTIR analysis revealed that the major gas decomposition of the propellant based on NC+NG, with additive TiO₂-3F (TiO₂-trifluoroacrylate) produced gases in the form of NO₂ and NO. The addition of fluorine-containing additives is known to reduce the concentration of CO toxic gas (Zhang *et al.*, 2019). Meanwhile, research by Zhao *et al.* (2015) revealed that the major gas decomposition in NC+GAP propellants were O-NO₂ groups and N₃ groups and main chains.

The DSC-TGA analysis instrument was used to carry out the thermal properties of the double-base propellant. Based on previous research, the results of DSC analysis of double-based propellants based on NC+SMX+DEGDN exothermic decomposition at DEGDN 25-wt% of 62.6°C [11]. A double-base propellant based on NC+NG, with additive DAG (Diaminoglyoxime) on thermokinetic results showed an increase in the decomposition enthalpy, apparent activation energy, and a change in the function of the decomposition reaction mechanism.

The results of DSC analysis showed exothermic decomposition at 188.74°C. Meanwhile, the results of DSC analysis on a double-base propellant based on NC+NG+TiO₂-3F showed a change in exothermic decomposition at a temperature of 199.2°C. The thermal stability of a DBP increased after the addition of the TiO₂-3F additive.

TGA analysis on a double-base propellant based on NC+GAP revealed that the initial decomposition temperature ranged from 192.9-194.6°C, indicating that the replacing of NG with GAP resulted in a double-based propellant with safe storage and good process operation [15]. Meanwhile, the results of TGA analysis on a double-base propellant based on NC+NG+GAP showed mass decomposition at temperature 199,3°C. Furthermore, it was found that thermoplastic elastomers GAP have a significant effect on increased the low-temperature mechanical properties of a double-base propellants [16].

IV. Conclusion

The research conducted in literature studies was applied by referring to the various energetic raw materials for double-base propellants (DBP). The composition of a DBP consists of energetic raw material of Nitrocellulose (NC) and Nitroglycerin (NG).

According to data analysis, NC can be manufactured from the raw material *Nata de Coco*, which has a nitrogen content of more than 12,5% in NC, which is in line with the levels of conventional military and propellant raw materials. Meanwhile, SMX or GAP on double-base propellants is suggested as potential alternative energy sources that can be utilized to substitute NG. The choice of new energetic material is influenced by the fact that *Nata de Coco* is abundant in Indonesia, while SMX and GAP in terms of manufacturing and handling are safety.

The several parameters to characterize double-base propellants include thermal analysis, microstructure, surface area, burning rate value, and gaseous product. The results of thermal properties by DSC analysis on a DBP based on NC+NG+TiO₂-3F showed a change in exothermic decomposition at a temperature of 199.2°C. The thermal stability of a DBP increased after the addition of the TiO₂-3F additive. Meanwhile, TGA analysis of a DBP based on NC+NG+GAP showed mass decomposition at temperature 199,3°C. Furthermore, it was found that thermoplastic elastomers GAP have a significant effect on increased the low-temperature mechanical properties of double-base propellants.

As a result, the literature studies approach, which includes consideration of alternative energetic raw materials and characterization for double-base propellants, is the recommendation for obtaining a superior performance double-base propellant with energetic materials.

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