On the replacement of traditional stabilizers by guaiacol in environmentally safe nitrocellulose-based propellants

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Abstract
In this work we investigated the possibility of substituting diphenylamine (DPA) by the natural product 2-methoxy phenol, known as guaiacol (CAS 90-05-1), as a stabilizer for nitrocellulose (NC)-based propellants. Stability evaluation, using heat flow calorimetry, revealed lower heat flows associated with our guaiacol-stabilized propellant samples when compared to those of propellants stabilized with the traditional stabilizers. Also, pressure vacuum stability tests showed that our propellant exhibited lower evolved gas volumes. Traditional tests, such as the German Test, and the Bergmann-Junk Test, scored a NO volume, after titration, of 0.87 ml (below the limit-value for acceptance, which is 2.0 ml), and the Storage Test, showed that our samples are stable and do not degrade until 3 days when submitted to a constant temperature of 100 °C. The homogeneity, stability and compatibility of our samples were evaluated through scanning electron microscopy, differential scanning calorimetry, and isothermal thermogravimetry. Ballistic parameters were estimated using a closed vessel along with computational codes developed by our research group, for comparison purposes. Finally, the high-performance liquid chromatography method allowed inferring the stabilizer consumption after artificial ageing of samples. This method also showed that the material met the corresponding stability criteria of AOP-48. Concluding, our results clearly indicate that guaiacol is an effective and efficient substitute for DPA as a propellant stabilizer for single-base NC-based propellants, making them more environmentally friendly.

Graphical abstract

Keywords Energetic materials · Stabilizer · Green propellant · Guaiacol

Extended author information available on the last page of the article
**Abbreviations**

2-NDPA  2-Nitrodiphenylamine  
AK-II  Akardite-II  
BDE  Bond dissociation energy  
DPA  Diphenylamine  
DSC  Differential scanning calorimetry  
EC  Ethycentralite  
F  Force  
HFC  Heat flow calorimetry  
HPLC  High-performance liquid chromatography  
MENA  N-(2-Methoxyethyl)-P-nitroaniline  
NC  Nitrocellulose  
N–NO  N-Nitrous group  
PVST  Pressure vacuum stability test  
SEM  Scanning electron microscopy  
TGA  Isothermal thermogravimetry  
UFLC  Ultra-fast liquid chromatography  
UV  Ultra-violet  
\( \eta \)  Co-volume

**Introduction**

Nitrate esters, such as nitrocellulose (NC), are extensively used in propellants due to some unique characteristics, such as their high energetic potential and nearly smokeless burning. However, over time, several catastrophic accidents resulting from the NC decomposition have demonstrated that the chemical stability is an important aspect to ensure a safe use and storage of propellants (de Klerk 2015; Defanti et al. 2020). This NC degradation was identified as being intrinsic to the nitrate esters, depending on temperature and time, and happens mainly due to denitration reactions based on the chemical detachment of –NO2 groups caused by thermal decomposition and hydrolysis reactions involving the residual moisture present in the propellant material (Bohn 2007). The products formed during this decomposition are mostly NO2, NO, HNO3 and HNO2, which promote consecutive reactions in an auto-catalytic process of degradation. As the decomposition process is exothermic in total, the rate of degradation of the propellant increases with temperature by self-heating (Vogelsanger 2004), and such synergistic processes can even lead to the spontaneous combustion of the material. Therefore, chemical stabilizers are necessary to ensure an adequate shelf life of NC-based propellants, by capturing the generated radicals or by interrupting, over a period of time, the auto-catalytic process of decomposition. The most commonly used stabilizers are diphenylamine (DPA), ethycentralite (EC), methylcentralite, akardite-II (AK-II) and 2-nitrodiphenylamine (2-NDPA). However, as these compounds are amines and secondary amides, the degradation process leads to the formation of R–R’–N–N=O (where R is an alkyl radical and R’ an aryl radical), which are suspected of being carcinogenic (Lin 1990).

DPA is the most used stabilizer for single-base (SB) gunpowder and is quite standard for small guns ammunition. It has been cited by the European Union as a recalcitrant pollutant, leading to the development of standards to evaluate and control the environmental risks associated with its use (Mendonça-Filho et al. 2019). Substances produced within the stabilization process, especially N-nitroso-DPA, which is a major product formed during the degradation of NC-based propellants, have carcinogenic, mutagenic and toxic to reproduction properties, according to toxicological tests (Jain et al. 2020; Rodrigues et al. 2018).

Mestankova et al. (2014) reported that dialkyl N-nitrosamines are known to have a common mutagenic mechanism, triggered by the enzymes of the cytochrome P450, which increase the polarity and water solubility of the substances, through the hydroxylation of the carbon adjacent to the N-nitroso group (see Fig. 1).

Araújo et al. (2000) also reported that N-nitrosoamides, which are the degradation products of EC and AK-II, undergo a hydrolysis process which is similar to the N-nitroso-hydroxylamine decomposition (Fig. 2), producing diazo-alkanes which are able of interacting with DNA.

The use of natural substances as stabilizers for energetic materials comes up as an excellent alternative to reduce...
environmental impacts, besides the fact that they are prone to generate products that might be, in thesis, less harmful to humans. This is particularly important in training facilities, destruction sites and, of course, in manufacturing plants, where ammunition is, respectively, employed, decommissioned and produced for decades. In this context, some studies have suggested the complete replacement of traditional stabilizers by "green" alternatives, especially those that can be found in natural products (Langlet et al. 2007; Dejeaifve et al. 2018).

Moving in this direction, Krumlinde et al. (2017) investigated new stabilizers that were not prone to form by-products containing nitrosamines, concluding that bis(2,6-dimethoxyphenyl)triethylene glycol was the most promising one. Cherif et al. (2020a; b) also studied natural stabilizers, lignin in particular, due to its availability via sustainable processes. The aromatic rings present in this amorphous biomacromolecule, exhibit great potential to capture –NO₂ groups during NC degradation, being an attractive option. Chelouche et al. (2019) studied a binary eutectic mixture of N-(2-methoxyethyl)-p-nitroaniline (MENA) and DPA, aiming to minimize the number of toxic products resulting from the decomposition of DPA. This molecule was considered compatible and functional as a stabilizer for NC-based propellants. Dejeaifve et al. (2020), in addition to their previous works, analyzed potential (natural) substances, such as alpha-tocopherol, alpha-ionone and curcumin for replacing DPA, using Heat Flow Microcalorimetry (HFC) to predict their shelf life when compared to AK-II stabilized propellants. In previous works of our research group, we also found promising results for NC-based propellants stabilized with 1.0% of curcumin (Rodrigues et al. 2019, 2021), while very recent research on the use of alpha-ionone as stabilizer (Damseaux et al. 2021), has demonstrated its effectiveness, with the main derivative products identified as: 3-oxo-α-ionone, 4-oxo-β-ionone and 4,5-epoxy-α-ionone.

Still aiming for new green stabilizers, the main goal of the present work was to propose a naturally based stabilizer as a substituent for synthetic stabilizers that would exhibit equal or superior stabilizing properties. Guaiacol was chosen due to the fact that this molecule does not exhibit amine or amide groups, which indicates a lower tendency to produce carcinogenic, mutagenic or toxic to reproduction derivatives during the stabilization process. Another important aspect is the possibility of improving the propellant shelf life, searching for formulations with shelf-lives as long as 10–15 years, which are longer than the ones related to conventional ammunition. This can lead to lower costs in several aspects, once it lowers the replacement rates besides demanding less tests and destruction operations.

Guaiacol (Fig. 3), the common name of 2-methoxyphenol, C₆H₄(OH)(OCH₃), is an organic compound that, in its pure state, is found as an oily and colorless liquid, with molar mass of 124.137 g/mol and a melting point of 28 °C. It is water soluble (17 g/L at 15 °C) and can be found in the guaco (Mikania glomerata) leaves and in wood-tar creosote.

Guaiacol has been cited (Hartman and Morton 1981) as a potential NC stabilizer along with many other molecules exhibiting at least one aromatic ring substituted with alkoxy groups, such as: 1,3,5-trimethoxy benzene, 2-methoxy-naphthalene (nerolin), catechol, 1,2 dimethoxy benzene (veratrol), and 1,4 dimethoxy benzene (hydroquinone dimethyl ether). No direct investigation has been conducted yet on the products that could be formed during the degradation process of NC stabilized by guaiacol, but Kroflič et al. (2015) reported that the guaiacol originated from biomass burning, can interact with nitrite present in the atmosphere, resulting in 4-nitroguaiacol, 6-nitroguaiacol and, after a short interval of time, 4,6-dinitroguaiacol (Kroflič et al. 2015).

In order to investigate the substitution of DPA by guaiacol as a stabilizer, we conducted a set of six performance tests employed for comparison. The stability was first evaluated through HFC, three classical stability tests (Bergmann Junk test, German test and Storage Proof), pressure vacuum stability test (PVST), and ballistic parameter estimation using a closed vessel device along with a regression tool developed by our research group. Finally, the guaiacol concentration depletion after a 10/15-years artificial aging was analyzed using high-performance liquid chromatography coupled with ultra-violet detection (HPLC/UV).

Aiming the best analytical scrutinizing procedure of the NC propellants under study, the techniques were employed and analyzed in conjunction in order to complement each other, and to collect possible pros and cons. The PVST monitors the evolved gas from a fixed-volume system, being a reliable and accurate test for stability. HPLC/UV was used to determine the remaining amount of the stabilizer after an induced/artificial ageing protocol. A solvent extraction procedure was used, once the residual stabilizer content is crucial for inferring on the propellant shelf life. The traditional stability tests, such as the Bergmann-Junk Test, the German Proof and the Storage Test are also based on analysis performed during an artificial ageing of the material that follow different protocols of time and temperature, according to the type of propellant. Such tests aim to mimic, in the sample, the actual conditions of a given (aged) ammunition,
as demonstrated by Bohn (2010) through the measuring of the mass loss of SB propellants from 70 to 110 °C until the end of stabilization was reached (which is useful to compare propellants stabilized by different substances). However, these tests exhibit some intrinsic deficiencies such as being too dependent on the experimenter’s skill, as well as on the quality of the indicator paper employed (Trache and Tarchoun 2019; Bohn 2010).

**Experimental methods**

**Sample preparation**

The inputs used in the sample preparation were: a 2:1 mixture of a NC with low nitrogen content (ranging from 10.8 to 12.3 mass-%, according to the supplier, IMBEL – Brazil) and a NC with high nitrogen content (ranging from 12.5 to 13.4 mass-%, according to the supplier, IMBEL – Brazil); traditional stabilizers DPA and EC, used in the reference samples, and guaiacol, all supplied by Sigma-Aldrich (USA); Acetone analytical grade (CAS Nº 67-64-1, analytical grade > 99.5%), supplied by Isofar (Brazil), which was used for the NC gelatinization and also as a vehicle for incorporating the stabilizers in the propellant mass.

Samples were produced according to the procedures depicted in Fig. 4. Both NCs (with high and low nitrogen content) were mechanically mixed with a spatula and the mixture was air dried (25 °C) for 72 h to reduce the moisture content. The equivalent of 1.0 mass-% of both DPA and guaiacol were weighted in beakers, solubilized in 30 ml of acetone and added to the mass, along with enough acetone to gelatinize the NC. As 1.0% is the typical percentage of DPA found in commercial products available in Brazilian ordnance, we decided to apply it for comparison purposes. Besides, this concentration is considered economically feasible for the new commercial products that might be developed based on this study. It must be said that this leads to 36% more active molecules when using guaiacol, due to the difference between the molar mass values (guaiacol: 124.137 g mol$^{-1}$; DPA: 169.23 g mol$^{-1}$). However, 1 mol of DPA can catch up to 4 mols of $-\text{NO}_2$, while guaiacol only 2. Therefore, some compensation can be expected when using a mass base for this comparison, which can even be conservative, if all “active sites” in both molecules are used.

After, the mixture was macerated for 1 h and the acetone excess was evaporated by letting the mixture rest, until a consistency that allowed lamination and cutting was observed. The lamination was conducted by passing the mass through unheated stainless-steel cylinders, resulting, at each pass, in sheets that were repeatedly grouped and reprocessed, to ensure good dispersion and sample homogeneity. Finally, the sheets were sliced, and the slices had their edges cut, for the standardization of samples. After cutting, the average grain size of the samples was $1.40 \times 0.73 \times 15.00$ mm.

**Stability tests**

**Heat flow microcalorimetry**

The heat-flow calorimeter employed was a TNO-HFC Mod. P0810, which allows to determine the total heat generated during the artificial ageing process of 5 g samples of each propellant and detects the heat generation rate in a microwatt scale (μW). Well-established protocols (NATO Standardization Agency 2007) on chemical stability states that SB propellants with a heat generation rate of less than 201 μW/g at 85 °C are considered, by safety standards, to have a minimum of 10-years shelf life, when stored at 25 °C.
Classical chemical stability tests (German test, storage proof, and Bergmann–Junk test)

The classical chemical stability tests consist of heating propellant samples at different temperatures and time periods to simulate its natural ageing and infer whether the stabilizer is able to ensure the stability of the propellant during its actual storage time. A brief description of each classical method used in this work is made below.

German chemical stability test (methyl violet test) The German chemical stability test consists in heating a 5 g sample up to 120 °C, when analyzing a double-based (DB) propellant, and up to 134.5 °C, when analyzing a SB propellant. The test is conducted in sealed test tubes, placed inside a metallic thermostatic block, in which a litmus indicator paper is inserted. After the desired temperature is reached, a time count is started and, when the indicator paper turns salmon-red, the time is recorded as the “turning point”. In the second stage of the test, a diluted solution of iodine (0.01 N) is added to each test tube and another time count is started. When the solution becomes reddish-brown, due to the evolution of nitrous vapors, the time is recorded as the “vapor point”. In the last step, the time required for the ignition or detonation of the sample is recorded as “explosion point”, which is noted as EXP > 360 min if that doesn’t take place within 6 h. For analysis of the results, these three times noted will allow scoring the propellant. These points are converted to scores that take into account other stability tests (presented in the following sections), according to specific standards (Exército Brasileiro 2007), and the NC-based propellants are classified as having “good”, “fair” or “poor” stability.

The storage proof The storage test consists in heating 10 g samples up to 100 °C in test tubes also placed in a thermostatic block. The tubes remain open for the first 8 h to simulate its natural ageing and one for the 15-year simulated ageing; the samples are under residual air with a pressure smaller than 670 Pa, according to the prevailing standards STANAG 4556 (NORTH ATLANTIC TREATY ORGANIZATION—NATO 1999). In the preset experimental runs all tests were initiated at 26 °C and ended at 27 °C, after the test time followed by cooling.

The volume of gas evolved is reported as "cold-cold" when it refers to the entire experiment, from initial heating until cooling to room temperature. On the other hand, the volume of gas calculated as "hot-hot" is the amount of gas evolved during the 100 °C step. The STANAG-4556 uses the “cold-cold” gas volume for approval criteria and the standard MIL-STD-1751A (USDoD 2001) uses the “cold-cold” gas volume for approval criteria and the standard MIL-STD-1751A (USDoD 2001) uses, as an approval criterion, that samples of 5.00 ± 0.01 g of propellants under heating at 100 °C for 40 h, which should produce less than 2 mL/g of gas evolved. The equipment used was a Deltima Delti Vac Mil (Praha, Czech Republic) and the test followed the standards as mentioned above.

Bergmann-Junk Stability Test The Bergmann-Junk stability test consists in heating, for 5 h, a 5 g sample up to 120 °C, when analyzing a DB propellant, and up to 132 °C, when analyzing a SB propellant. The samples are placed in special tubes equipped with bulbs that receive a 4.5% (in mass) potassium iodide (KI) solution and are further placed in a thermostatic block. The nitrous vapors that evolve from the samples oxidize the iodide to iodine (I₂) which is then titrated with a 0.01 N solution of sodium thiosulfate (Na₂S₂O₃) using starch as indicator. When the blue solution turns colorless, the volume of Na₂S₂O₃ consumed (VNa₂S₂O₃ in mL) is used to calculate the volume of nitrous vapors evolved (VNO in mL/g of sample) according to the formula in Eq. (1), where NO is considered as an ideal gas, and fNa₂S₂O₃ is the correction factor of the 0.01 N sodium thiosulfate solution.

\[ V_{NO} = 0.224 \times f_{Na_2S_2O_3} \times V_{Na_2S_2O_3} \]  

Pressure vacuum stability test (PVST)

The PVST was performed in duplicate with samples of both propellants: the reference one—stabilized by DPA (1.00 mass-%)—and the one stabilized by guaiacol (1.00 mass-%). This test consists in heating the samples inside tubes, which are evacuated to a low-level vacuum (250 Pa) and measuring the volume of gas evolved. Initially, the samples are under residual air with a pressure smaller than 670 Pa, according to the prevailing standards STANAG 4556 (NORTH ATLANTIC TREATY ORGANIZATION—NATO 1999). In the preset experimental runs all tests were initiated at 26 °C and ended at 27 °C, after the test time followed by cooling.

The volume of gas evolved is reported as "cold-cold" when it refers to the entire experiment, from initial heating until cooling to room temperature. On the other hand, the volume of gas calculated as "hot-hot" is the amount of gas evolved during the 100 °C step. The STANAG-4556 uses the “cold-cold” gas volume for approval criteria and the standard MIL-STD-1751A (USDoD 2001) uses, as an approval criterion, that samples of 5.00 ± 0.01 g of propellants under heating at 100 °C for 40 h, which should produce less than 2 mL/g of gas evolved. The equipment used was a Deltima Delti Vac Mil (Praha, Czech Republic) and the test followed the standards as mentioned above.

Stabilizer concentration depletion test

Once again, an artificial ageing was conducted, operating the Deltima Delti Vac Mil heating block at a constant temperature of 90 °C. The protocol establishes that, in order to simulate a 10-year ageing, the temperature must be kept for 3.43 days, while for a 15-year simulation, 5.145 days are necessary. Two 5 g samples of the propellant stabilized by DPA were weighed-in, one for the 10-year simulated ageing and one for the 15-year simulated ageing; the same was carried out for the propellant stabilized by guaiacol. All samples were admitted to glass tubes in a
loading density of 0.25 g/cm$^3$ and closed with glass stoppers containing silicone grease without applying any force/pressure.

The aged samples were then compared, in terms of the residual stabilizer content, to fresh ones using HPLC–UV analysis. For that, 0.8000 g of all propellants (unaged, 10-year aged and 15-year aged) were weighed and treated with 200 ml of methanol analytical grade in a beaker to extract the stabilizers and their reaction products. To ensure in depth extraction, ultrasonic vibration was employed (using an Unique Ultrasonic Cleaner) for 4 h at 25°C, avoiding exposure to sunlight. After extraction, the solution was diluted to 250 ml with Methanol analytical grade and the supernatant liquid from each sample was percolated through a 0.45 μm polypropylene filter with PVDF membrane (Agilent). Aliquots of 10 μL were injected into the HPLC instrumentation using an ACE5-C18-HL (Octadecyl) 150 x 4.6 mm reverse phase column with 5 μm diameter particles.

The HPLC analysis was performed on a Prominence LC (Shimadzu, Kyoto, Japan) Ultra-Fast Liquid Chromatography (UFLC) system equipped with a SIL-20AC self-injector, two LC-20AD solvent pumping units and a DGU-20A. Data were acquired using the Labsolution software (Shimadzu, Kyoto, Japan). The mobile phase was composed of HPLC grade methanol and distilled water (75:25, v/v) for isocratic elution at a flow rate of 0.8 ml/min; the column temperature was kept at 20 °C and the UV detector was set at a wavelength of 272 nm.

According to AOP-48 (NATO 2008), a maximum reduction (after ageing) of 80% of the stabilizer concentration with respect to the initial concentration and a remaining minimum of 0.2 mass-% of the initial stabilizer amount were established as the stability criterion.

For quantitative purposes, calibration curves for each stabilizer were constructed, using the same chromatographic method and conditions. For this, solutions with 0.003, 0.01, 0.0305 and 0.0609 mg/ml, were produced from successive dilutions of a stock solution of 0.6092 mg/ml.

**Ballistic parameters estimation**

Pressure *versus* time data of a confined burn of the propellants under evaluation were acquired in a 200 cm$^3$ HPI Closed Vessel B-180.2 (High Pressure Instrumentation, Graz, Austria) at a loading density of 0.1 g/cm$^3$. This was used to calculate the propellants vivacity (roughly the first derivative of the pressure with respect to time), as well as to estimate the parameters of Vieille-Saint Robert burning (rate) law along with the co-volume of the Nobel-Abel equation of state and the specific force; this set will be, henceforth, referred as the “ballistic parameters” of the propellant.

The fitting algorithm was based on a Maximum Likelihood criterion and was implemented in SciLab (a free, open-source software available in https://www.scilab.org), producing coherent and unbiased estimates, along with their variances (Rodrigues et al. 2006).

**Differential scanning calorimetry and thermogravimetry**

Samples of NC stabilized with 1 mass-% of either DPA or guaiacol were analyzed through Differential Scanning Calorimetry (DSC) and Thermogravimetry (TGA). The chemical compatibility between components in energetic materials can be evaluated by thermal studies (DSC and TGA) as a complement to VST. Thermal analysis gives fast results and requires lower amounts of sample, although may not be representative of the whole propellant grain. Nevertheless, DSC and TGA provide good hints about the compatibility when new molecules are being tested to be used as stabilizers, and it was already reported in the literature (Chelouche et al. 2020; Krabbendam-La Haye et al. 2003; Li et al. 2020; Trache et al. 2019).

These studies were performed in Shimadzu Thermal Analysis systems, models DSC-60 and DTG-60 H, under a 50 ml/min nitrogen gas purge. For the DSC it was used a heating rate of 2 °C/min from ambient temperature up to 280 °C, with a sample mass around 1 mg (0.75 mg for pure NC) in an aluminum crucible. For the TGA experiment, a heating rate of 5 °C/min was used to heat an amount of 3 mg of each sample in a platinum open crucible, up to an isotherm of 145 °C for 150 min.

**Results and discussion**

**Stability tests**

**Heat-flow microcalorimetry**

Results depicted in Fig. 5 were obtained at 85 °C and indicate that all formulations of SB propellants would pass the approval criteria established by the standard STANAG 4582 (NATO Standardization Agency 2007). It must be noticed that the formulation stabilized by guaiacol exhibits a smaller area below the heating isotherm, when compared to the ones of the traditional formulation with DPA and EC. According to the prevailing literature (Bohn 2009), this can be associated with a longer shelf life, even though the heat generation rates is a combined effect of the reaction enthalpies and the reaction rates. The proposed deduction of the useful life from the amount of heat released during the ageing of the energetic material compares the area predicted by the
procedure described in STANAG – 4582 for 10 years of artificial ageing with the area of the propellant investigated.

**Traditional chemical stability**

According to Table 1, all SB propellant samples would be approved by the traditional chemical stability. The temperatures in which each test was conducted are indicated in Table.

**Pressure vacuum stability**

Vacuum stability tests (PVST) were ran in duplicate with the DPA and guaiacol propellant samples and results in Table 2 show the average between the values found for the volume of gas released per propellant sample.

**Stabilizer concentration depletion**

Figures 6 and 7 depict the HPLC–UV calibration curves for DPA and guaiacol, built as described in the methodology. As can be seen, both exhibited adequate adherence to a linear model, according to their respective coefficients of determination \(R^2\).

The procedure of HPLC–UV used for the determination of DPA and guaiacol in propellants was successfully established before (Rodrigues et al. 2021) and within this work showed again to be pertinent, fast, simple and specific for
DPA and guaiacol analysis. The standard peaks can be found in Figs. 8 and 9.

Table 3 shows the result of the maximum peak area decrease of each stabilizer for the unaged and aged (10 years and 15 years) propellant samples, where concentrations were calculated using the calibration curves determined in Figs. 3 and 4.

Following the AOP-48 (NATO Standardization Agency 2008) criterion, the final stabilizer concentration (after artificial ageing) should be not less than 80% of the initial concentration. A second stability criterion states that at least 0.20 mass-% of stabilizer should remain in the material for a propellant to be approved.

The last column in Table 3 shows the remaining amount of stabilizer in relation to the initial concentration after artificial ageing. Both samples were approved, but the propellant stabilized by guaiacol exhibited lower levels of stabilizer depletion, indicating that this propellant may be stored for longer times (or be more safely stored) than the reference.
propellant with DPA. Such difference was especially acute when comparing the results associated with 15 years of (artificial) ageing.

One must be aware of the possibility of the decomposition of guaiacol (Nguyen et al. 2018). The reaction products of guaiacol with the decomposition products of NC are still a subject to be studied. However, they are expected to be less toxic than the ones formed by DPA stabilizers (Mestankova et al. 2014), despite this assumption has still to be confirmed through toxicity studies, since the products are nitrated aromatic compounds.

Regarding the products of the stabilizing reactions between NC and DPA, Itkis and Bohn (2021) pointed out that it is not yet clear which mechanism generates such compounds. They argue that possibly, the first radical is formed through the N–H bond, which is the weakest (357.4 kJ/mol). Thus, the nitration of the aromatic ring takes place by shifting the radical function into the ring (Itkis and Bohn 2021).

In guaiacol, it is still unknown which primary radical is the most effective in forming the activated radical ring system. The possibilities are: H abstraction at OH, at the CH₃ group, or finally at the –CH₃ from the O–CH₃ group. It has been reported that the O–H and O–CH₃ bonds within the guaiacol chemical structure present bond dissociation enthalpies ranging from 243 to 364 kJ/mol (Nowakowska et al. 2018). In addition, the radicals formed from guaiacol may be stabilized by the electron delocalization of the aromatic ring and recombination with NO₂ could also be possible, as described by Itkis and Bohn (2021) for DPA.

### Ballistic parameters estimation

As described previously (Rodrigues et al. 2006) three tests must be conducted with different loading densities for the estimation of the force (F) and co-volume (\( \eta \)) of each propellant. Therefore, 6 shots were fired, three with the reference propellant and three with the proposed propellant.

Each set of such pressure versus time data (examples can be found in Fig. 10) was then used as input to a nonlinear fitting algorithm based on a Maximum Likelihood criterion used in the regression of a semi-empirical model comprised of material balances and the Vieille–Saint Robert’s burning law (\( v = \beta \cdot P^\alpha \)). When convergence was achieved, model parameters were estimated, along with the model variance (\( S^2 \)), and the values obtained can be found on Table 4.

It can be noticed that the sets of ballistic parameters of the propellants do not differ in a great extent from each other, indicating that slight adjustments in grain dimensions can compensate for differences.

Figure 11 depicts the vivacity and Table 5 reports some relative vivacity of both propellants, which are both related to the derivative of the pressure and characterize the burning of a propellant, confirming the slight increase in pressure of the guaiacol sample and its quickness compared to DPA.

These results indicate that the use of guaiacol can motivate a change in the grain ballistic length (in this case, the thickness), in order to correct its relative quickness when compared to the reference propellant. This adjustment can also be carried out by changing the shape of the grain, modifying the formulation or even the load density.

### Differential scanning, calorimetry (DSC) and thermogravimetry (TGA)

Regarding the DSC, the test followed STANAG 4147 (NATO Standardization Agency 2001) to give a preliminary analysis on compatibility. If the peak related to the exothermic decomposition of the samples with stabilizer deviates by 4 °C or more from the decomposition temperature of the pure NC, that is an indication that the stabilizer is not compatible with NC. In addition to that, any change in the curve profile is considered as an indication of incompatibility. On the other hand, the isothermal TGA has being used as a method to indicate if a stabilizer is efficient to delay the mass loss at a temperature close to the main decomposition of the energetic material (Trache et al. 2019; Chelouche et al. 2020; Rodrigues et al. 2021; Krabbendam-La Haye et al. 2003; Li et al. 2020). In addition to that, the TGA is also helpful to evaluate comparatively the chemical compatibility of different formulations once the lack of compatibility may induce an increase in the rate of decomposition at high temperatures.

Figure 12 shows that the exothermic decomposition measured in DSC is similar for all samples (pure NC and with stabilizers), with only one main decomposition event occurring at a very narrow temperature range (less than 4 °C). Table 6 depicts the results of the thermal analysis, and
the mass loss curves of the samples analyzed for 150 min at 145 °C are shown in Fig. 13. Both stabilized NC presented a continuous decomposition with no thermal runaway or any unexpected spontaneous decomposition. The NC stabilized with guaiacol presents slightly better performance, i.e., less mass loss after 150 min at 145 °C and lower decomposition rate, although the comparison with DPA-stabilized NC is still statistically similar.

Studies reported that the decomposition of pure guaiacol starts around 375 °C (Nguyen et al. 2018; Nowakowska et al. 2018). This indicates that the stabilizer decomposition during the TGA experiment is negligible. In general, the results indicated that this stabilizer delays the decomposition rate and provides a good thermal stability to NC.

**Conclusion**

The development of green propellants is a modern initiative in the field of energetic materials aimed to extinguish the use of substances used in propellants suspected of being harmful to humans and the environment. This research has addressed this concern, studying a substance as possible stabilizer that exhibit potentially lower risks, prioritizing formulations with longer shelf life due to better chemical stability.

From the results obtained here, it can be concluded that the green propellant stabilized with guaiacol is potentially viable to replace the DPA-stabilized propellant. All samples passed the stability tests, with better quantitative results than the DPA-stabilized sample. Regarding the estimation of ballistic parameters, the propellant stabilized with guaiacol was the fastest in burning behavior. However, this can be corrected through simple alterations in the propellant grain size, especially thickness, which should adjust its combustion speed proportionally to the DPA-stabilized propellant.

Future works will be devoted to analytically elucidate the chemical composition of the degradation products from the propellant stabilized with guaiacol, aiming at a deeper knowledge of the guaiacol stabilization mechanism. During the revision process of the present work, an interesting procedure to compare long term stabilization was proposed by the reviewers and is left here as a suggestion for similar works. Basically, it consists in heating samples to 90 °C up to the time when the mass loss strongly increases. This should capture effect of the decrease of reactivity of the sites at the aromatic ring when NO₂ are bonded to it.

At this point, a pilot batch will be scheduled to take place in an industrial facility, which will be of assistance for additional tests, including the shooting of real rifle rounds, in which the muzzle velocity, ash content and residues will be measured and evaluated.

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**Table 4** Fitted ballistic parameters for propellants stabilized by DPA and guaiacol

| Sample       | $\alpha$ (m/s) | $\beta$ (Pa) | $\eta$ (m³/kg) | $F$ (J/kg) | $S^2$ (Pa) |
|--------------|----------------|--------------|----------------|------------|------------|
| DPA (1.0%)   | $1.0001 \pm 10^{-4}$ | $(2.7 \pm 0.1)10^{-9}$ | $0.0010 \pm 10^{-4}$ | $806,377 \pm 2.10^5$ | $2.554.10^{13}$ |
| Guaiacol (1.0%) | $1.0140 \pm 10^{-4}$ | $(2.6 \pm 0.1)10^{-9}$ | $0.0010 \pm 10^{-4}$ | $751,225 \pm 2.10^5$ | $1.482.10^{13}$ |

**Table 5** Relative vivacity of the propellant’s samples stabilized with DPA and guaiacol

| Pressure (MPa) | DPA $dP/dt$ (MPa/ms) | Guaiacol $dP/dt$ (MPa/ms) |
|---------------|----------------------|--------------------------|
| 7             | 4.88                 | 6.63                     |
| 14            | 7.42                 | 10.28                    |
| 21            | 9.11                 | 12.05                    |
| 28            | 10.48                | 13.05                    |
| 35            | 11.78                | 14.29                    |
| 35–70         | 12.78                | 15.04                    |
| 70 – 100      | 2.65                 | 5.38                     |
Fig. 12 DSC analysis of the NC and NC-stabilizers samples

Table 6 Results of the thermal analysis of the NC and NC-stabilizers samples

| Sample                  | DSC exothermic peak (°C) | TGA mass loss after 150 min isothermally at 145 °C (mass-%) | Decomposition rate from TGA (average linear fit-mass-%. min⁻¹) × 10⁻² |
|-------------------------|---------------------------|--------------------------------------------------------------|---------------------------------------------------------------------|
| Pure NC                 | 194.44 ± 0.10             | –                                                            | –                                                                    |
| NC + 1 mass-% DPA       | 193.86 ± 0.27             | 5.04 ± 0.72                                                 | 2.98 ± 0.58                                                         |
| NC + 1 mass-% guaiacol  | 193.91 ± 0.06             | 3.11 ± 1.22                                                 | 1.47 ± 0.93                                                         |

Fig. 13 Isothermal TGA at 145 °C of the NC and NC-stabilizers samples
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Declarations

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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