

ANALYSIS OF THE COMBUSTION, BURN RATE, AND GRAIN STRUCTURE OF AMMONIUM NITRATE AND BADGE BASED PROPELLANT

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ABSTRACT

A rocket solid propellant is a compacted grain of a mixture of a fuel, an oxidant, and a binder. During the combustion process it produces a flux of hot gases intended to produce work through a rocket propulsion system. Two important and most desirable characteristics of a solid propellant are grain high stability and non-toxic trace. Ammonium nitrate oxidant releases low production of toxic traces, such as nitrogen oxides and chlorinated compounds. As a binder, BADGE presents easy handling and good resistance to shock and humidity when cured in a grain. Grains of ammonium nitrate and BADGE with aluminum and iron oxide III, as catalysts, were built and tested. Three different formulations were tested with fixed 8% in mass of aluminum or iron oxide, and varying ammonium nitrate from 60% up to 75%. The measurements of burn rate were conducted in standard ambient temperature and pressure. Gravimetric comparison of ashes and calculation of burning products via numerical simulation methods were carried out. The results presented a significant relationship between the burn rate and the ammonium nitrate concentration. The use of aluminum and iron oxide modified this relationship due to changes in oxygen consumption dynamics, leading to a change in flame temperature. It was also shown that a presence of aluminum elevates the production of CO, while iron oxide III maintained approximated values of non-catalyzed process. The soot formation was present in all formulations.

Keywords: Combustion, solid-propellant, burn rate, ammonium nitrate

NOMENCLATURE

BADGE bisphenol A diglycidyl ether

HTPB hydroxyl-terminated polybutadiene

HTPE hydroxy-terminated polyether

INTRODUCTION

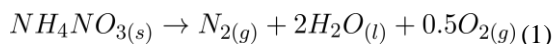
Depending on the number of primary ingredients, solid propellants are categorized in single, double, either as triple-bases, or are denominated composites if consist of a mixture of granules of solid oxidizer with flakes of energetic compounds, metallic additives, plasticizers, stabilizers, and/or burn rate modifiers.

A composite implies the use of a binder, that can be inert or burning-active, to agglutinate the

oxidant and the fuel. The mixture starts as a liquid, and then dried by a chemical process called cure. The result is a homogeneous non-crystalline solid called grain [1].

The current applications of solid propellants require minimum generation of residual solids, high specific impulse, easy handling, and chlorine-free emissions [2]. Compositions based in ammonium perchlorate (NH_4ClO_3 or AP), common choice in commercial solid-fuel rocket engines, show good chemical stability and specific-impulse, but the chlorine residues are an environmental issue that threatens the surrounds of launch centers [3,4]. In this sense the ammonium nitrate (NH_4NO_3 or AN) has been drawing attention because of its low residual solid generation of 8- 12% in mass and its low toxic emissions [5].

The AN thermal decomposition depends on the amount of energy inserted in the system. Equation (1) shows the global reaction of this exothermic decomposition occurring at 550K. It releases nitrogen, oxygen, and 119 kJ.mol⁻¹ of thermal energy, considering liquid water. This reaction injects oxygen in the burning process without generating residues, but before reaction completeness, the AN crystal changes from tetragonal at 256K to orthorhombic at 398K, varying its volume in 95%, thus requiring phase stabilizers as copper or nickel to avoid grain damage during the burn [2,5].



The addition of metals improves the burning characteristics of the ammonium nitrate. Adding iron oxide III (Fe₂O₃) increases the burn rate and ignitability at low pressures for HTPB/AN. The aluminum (Al) causes the same effect to HTPB/AP propellants [6-10].

The BADGE polymers present good corrosion resistance and sufficient rigidity to produce a stable grain. Because of its high-energy content, and presence of only carbon, oxygen and hydrogen in its composition, the BADGE acts as a burning-active binder. The cold-casting technique can be applied as well due the room temperature cure process [11,12].

For a better understanding of this kind of propellant, this work investigates the burning behavior of a composite grain composed of AN as oxidizer, BADGE resin as burning-active binder, and addition of Al and Fe₂O₃ as burning catalysts.

MATERIALS AND METHODS

The work is divided into three main steps: sample manufacturing, burn tests, and simulation analysis.

Sample Manufacturing

The AN was manually macerated before being mixed with Al or Fe₂O₃. After preparation of the mineral mixture, the binder was added with the hardener agent.

There are many different structural formulae for bisphenol-A based resin. For this study was used BADGE resin, that is commercially known as epoxy resin or D.E.R. 332. Its structural formula is shown in Figure (1).

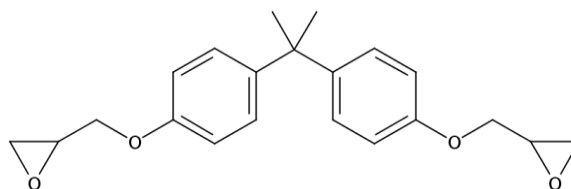


Figure 1. Structural formula of BADGE [12].

Consequently because of the many types of bisphenol-A resins, there are a wide variety of hardener mixtures. The hardener agent used in this work is based in 1,3-propanediamine. Its structure is shown in Figure (2). The resin and the hardener agent present a colorless, crystalline appearance and high viscosity.

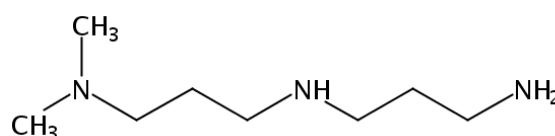


Figure 2. Structural formula of 1,3-propanediamine.

The BADGE resin and the hardener agent were mixed with a proportion of 75% and 25%, respectively. The homogeneous mixtures were shaped into cylindrical grains of 18mm in diameter. The lateral area was coated in bond paper for inhibition and stored in cylindrical molds inside desiccator for 24 hours to cure.

Three different formulations were prepared and tested: non-catalyst AN/BADGE, AN/Al/BADGE and AN/Fe/BADGE. The percentage by mass of AN varies from 60% to 75% and the Fe₂O₃ and Al are fixed at 8% in mass. Except for the non-catalyst samples, the adopted criteria to name the samples were to have the catalyst symbols coming first, followed by the resin identification, and its percentage information, i.e., Al/BADGE40 means aluminum catalyst with 40% of binder and 60% AN. In Table (1) are shown the samples identifications, and also the Oxidizer/Fuel proportion. The O/F proportion was obtained assuming AN as the only oxidizer and all the other components, BADGE and Al or Fe₂O₃, as fuel.

Table 1. Formulations of the tested grains.

Formulation	% Ammonium nitrate	O/F
<u>BADGE40</u>	<u>60</u>	<u>1.5</u>
<u>BADGE35</u>	<u>65</u>	<u>1.85</u>
<u>BADGE30</u>	<u>70</u>	<u>2.28</u>
<u>BADGE25</u>	<u>75</u>	<u>2.93</u>
<u>Al/BADGE32</u>	<u>60</u>	<u>1.50</u>
<u>Al/BADGE26</u>	<u>65</u>	<u>1.86</u>
<u>Al/BADGE22</u>	<u>70</u>	<u>2.31</u>
<u>Al/BADGE17</u>	<u>75</u>	<u>2.96</u>

<u>Fe/BADGE32</u>	<u>60</u>	<u>1.50</u>
<u>Fe/BADGE26</u>	<u>65</u>	<u>1.86</u>
<u>Fe/BADGE22</u>	<u>70</u>	<u>2.30</u>
<u>Fe/BADGE17</u>	<u>75</u>	<u>2.89</u>

Burn Tests

In Figure (3) are aligned all the samples that reached a total cure. In the third row are the grains of BADGE formulations, in middle row are Fe/BADGE, and the first row the Al/BADGE. The burn rate was measured at constant pressure of 101,4kPa and temperature of 293K and the results are presented in grams per second ($\text{g}\cdot\text{s}^{-1}$). The ignition was established by using a LPG burner over the uninhibited area that was able to reach 2200K.

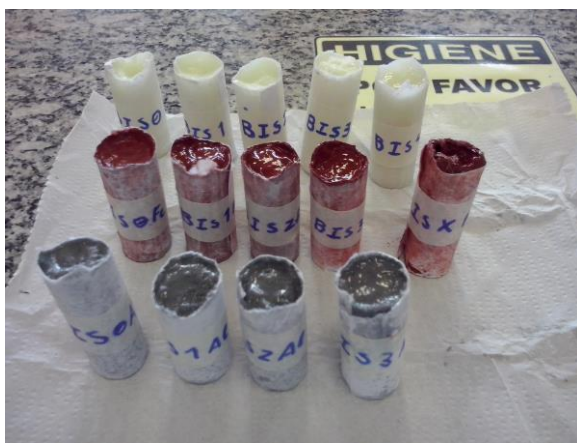


Figure 3. Test grains cured, marked and inhibited.

Burn Tests

The simulation analysis was made with the objective of estimate the combustion products, adiabatic flame temperature and gas-phase temperature in order to understand the burning process.

The method used was the Gibbs free energy minimization by numerical approximation. The chosen software was Ponomarenko's Rocket-Propulsion Analysis (RPA), configured to simulate the burning inside a solid-fuel engine chamber with a nozzle for gas acceleration and generation of thrust [13]. The methodology was to assume pressure and temperature of 101,4kPa and 293K, respectively, inside chamber. The nozzle exit was configured as pressure of 90kPa and Mach equals to 1 at nozzle throat.

RESULTS AND DISCUSSION

For all samples tested, the ignition took place 18 seconds after the flame incidence. Since no

significant ignition-time difference was noticed in any grain sample, it is safe to say that Fe_2O_3 or Al as catalysts does not change ignitability at room temperature and pressure. This result was in accordance with previous works by Naya et al [9] that shows a minimum pressure for deflagration of samples with 80% of AN in mass at 2MPa utilizing heated aluminum plate [7-9]. This behavior is due to the AN being not flammable at solid state, needing extra heat for melting the crystals and releasing flammable gases. This thermal decomposition happens at 430K and requires $181\text{kJ}\cdot\text{mol}^{-1}$ [10].

The grain flame exhibited a distinct pattern among the different formulations. The grain with Fe_2O_3 showed a yellow long and asymmetric flame. Grains containing Al showed a yellow but short symmetric flame with incandescent Al particles being ejected from the sample. The grains with no catalysts showed a short and symmetric flame with constant shape during all the burning process. All the formulations featured a clean burn without smoke or soot formation, only ashes at the end.

The results of the measured burn rates are presented in Figure (4). The first behavior noticeable in all curves is the low burn rate. All grains burned under $0,0450\text{g}\cdot\text{s}^{-1}$, with an average time of 527s for a complete burn. It happens because of two reasons. The first reason is for the fact that AN is a low reaction rate oxidizer due its necessity of being melted before releasing oxygen and the high pressure, at least 1MPa, required by AN to perform a better burn rate. Second reason is the choice of BADGE polymer as binder. Previous works by Lengellé et al and Costa et al [3,12] recommends binders with high mass fractions of oxygen, such as HTPE. A high mass fraction of oxygen is required because AN does not inject enough oxygen for a stoichiometric burn reaction with a poor oxygen fuel. When such binder is employed, the burn rate is low and the combustion is incomplete, forming larges amount of carbonaceous fragments and ashes. The Figure (6) illustrates the solid residues left after an Al/BADGE17 burning test.

It also can be seen in Figure (4) that the burn rate results presented a better performance for Fe/BADGE (round dots), followed by Al/BADGE (inverse triangles), and with the lowest performance results came the BADGE (triangles). The burn rate is a function of the amount of AN, and consequently the results are crescent curves. The higher the percentage of AN in mass, the faster the grain burns. Comparing Fe/BADGE17, Al/BADGE17 and BADGE25, i.e. the grains with the highest burn rate results, the Fe/BADGE17 grain burned at $0,0443\text{g}\cdot\text{s}^{-1}$, which is faster than the Al/BADGE17 with a burn rate of $0,0341\text{g}\cdot\text{s}^{-1}$. The BADGE25 grain presented a burn rate of $0,0247\text{g}\cdot\text{s}^{-1}$.

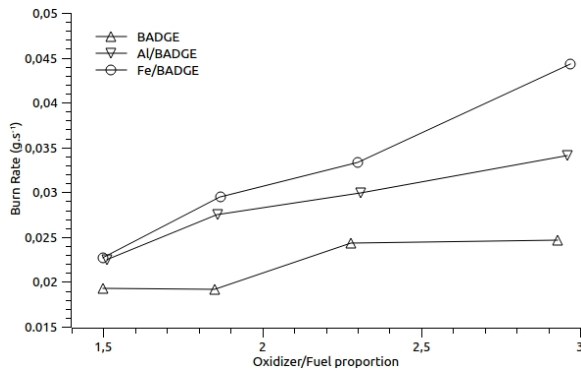


Figure 4. Burn rate results.

The factors affecting directly the burn rate are the oxygen limitation and the activation energy of the reactants. This is shown by the crescent burn rate as the AN content increases as well. The higher the amount of AN the higher the supply of oxygen and energy.

The combustion wave structure for HTPB/AN propellant shown in Figure (5) is similar to the combustion wave observed in AN/BADGE grain tested in this work. It consists of a solid-phase zone, a condensed-phase zone and gas-phase zone where the combustion reaction takes part, after comes the luminous flame zone.

During the burning of the grain, the initial heat injected melts the surface of the sample, creating the condensed-phase reaction zone and starting the thermal decomposition of AN, and the binder that creates the gas-phase reaction zone. The oxygen released by AN attacks the binder molecules in a reaction of combustion, leading to generation of carbon dioxide, water, carbon monoxide, and molecular nitrogen, secondary combustion products, and heat. Part of this heat is lost to the flow of hot gases while other part feeds the thermal decomposition, creating a self-sustaining combustion. For the catalysts-free grains the burn rate is little affected by the supply of oxygen, shown in Figure (4), but this is not observed in the catalysts content grains, where the burn rate shows a much crescent and steeper curve. This phenomenon is due to the changes in the oxygen consumption dynamics.

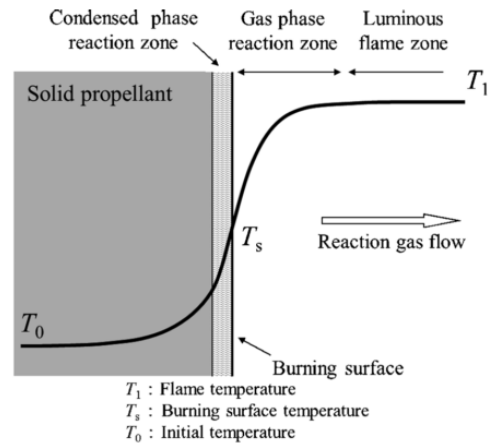


Figure 5. Combustion wave structure of an AN/HTPB propellant [9].

Figure (7) shows the results of H₂ (vertical line), CO (inversed triangle), CO₂ (triangle), N₂ (square) and H₂O (cross) mole fractions in the combustion products. The carbon gases and water vapor were from the BADGE combustion. Nitrogen gas was from the AN decomposition. Also other gaseous and solid products were generated such as aluminum oxide (Al₂O₃), iron (Fe), and traces of hydrocyanic acid (HCN), ammonia (NH₃) and nitrous oxides (NOX). For evaluation of the combustion, CO and H₂ indicate the quality of the combustion reaction, i.e., the higher the mole fraction of these gases, the lesser oxygen available for a complete combustion. This phenomenon is observed in the three formulations as a consequence of the higher percentage of oxidizer. As the O/F proportion increases better and more energetic burning is observed, indicating more formation of H₂O. This is better observed at Al/BADGE and Fe/BADGE formulations, where there is a strong correlation between the water vapor generation and adiabatic flame temperature.



Figure 6. Solid residues left after burn test of Al/BADGE17 burn test.

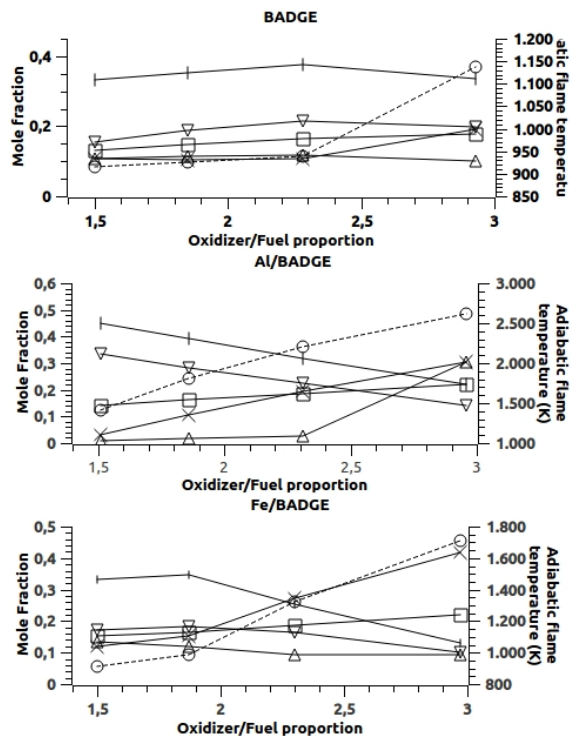


Figure 7. Adiabatic flame temperature (traced line - circles) and products composition of the tested formulations: CO (inversed triangle), CO₂ (triangle), N₂ (square), H₂O (cross) and H₂(vertical line).

However in catalyzed formulations the CO and CO₂ curves decrease as O/F increases, and this is a strong evidence of poor binder decomposition.

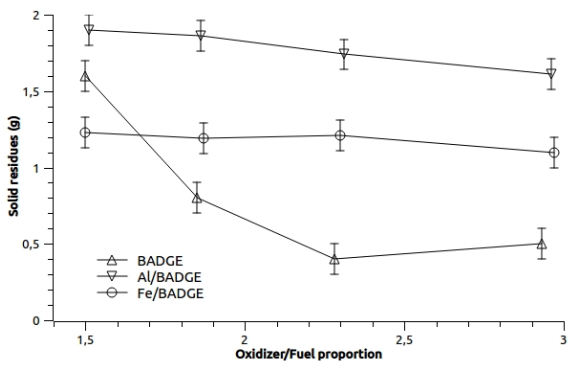


Figure 8. Solid residues left after combustion.

The BADGE resin presented a low capacity of receiving mineral loads, such as AN, Al and Fe₂O₃ tested. This characteristic prevent to get a test with a stoichiometric oxygen supply by AN, because values under 17% in mass of BADGE lead to a grain with spongy structure when dry or even not drying at all. This is the reason all samples were limited to an O/F proportion of 2.93 and generated high amount of solid residues after burning, as the results shown in

the Figure (8). The minimum O/F proportion recommended by the Ponomarenko's RPA software was 11.0. This level was impossible to reach with the casting technique used in this work.

CONCLUSIONS

The smokeless burn featured by AN was not altered by the use of BADGE resin and Al or Fe₂O₃ as propellant components. However, the burn rate and flame characteristics vary according to the combination of such compounds. The Al/BADGE and Fe/BADGE grains burned faster with a higher adiabatic flame temperature, showing that this catalysts change the oxygen consumption dynamics during the burning process, consequently changing the combustion products.

Due to the limitation of sample manufacturing technique and the BADGE limitations, the formulations tested in this work presented a high generation of solid burning residues. This is a severe disadvantage when it comes to application to solid rocket engines. This behavior can lead to structural damage by two-phase flow, erosive burning, and in extreme cases, explosion due to nozzle clogging.

The tests carried out in this work were important to understand the casting and burning behavior of BADGE and AN burning together, but further tests are necessary, since tests with different pressures and atmospheres conditions were not conducted. The samples used in this work may vary their behavior in such tests.

REFERENCES

1. Sutton, G., Biblarz, O. "Rocket Propulsion Elements", 8th edition, 2010, ISBN: 978-0-470-08024-5.
2. Chaturvedi, S., Dave, P. N. "Review on Thermal Decomposition of Ammonium Nitrate" Journal of Energetic Materials, 2013, doi: 10.1080/07370652.2011.573523.
3. Lengellé, G. Duterque, J., Trubert, J. "Combustion of solid propellants", France, Office national d'études et de recherches aérospatiales (ONERA), 2002.
4. Kubota, N. Okuhara, H. "Burning rate temperature sensivity of HMX propellants" Journal of Propulsion and Power, 1989, doi: 10.2514/3.23169.
5. Andrade, J. et al "Estudo da decomposição térmica de propellente sólido compósito de baixa emissão de fumaça" Química Nova, 2008, doi: 10.1590/S0100-40422008000200021.
6. Brewster, M. Q., Ishihara, A., Sheridan, T. A. "Ammonium nitrate magnesium propellant combustion and heat transfer mechanisms"

- Journal of Propulsion and Power, 1992, doi: 10.2514/3.23547.
7. Murata, H. et al “The effect of Magnalium (Mg-Al alloy) on combustion characteristics of ammonium nitrate-based solid propellant” Japan, Science and Technology of Energetic Materials, 2000.
 8. Singh, G., Felix, S. P. “Studies on energetic compounds. Part 36. Evaluation of transition metal salts of NTO as burning rate modifiers for HTPB-AN composite solid propellants” Combustion and Flame, 2003, doi: 10.1016/S0010-2180(03)00156-1.
 9. aya, T., Kohga, M. “Burning characteristics of ammonium nitrate-based composite propellants supplemented with Fe₂O₃” Propellants, explosives, pyrotechnics, 2013, doi: 10.1002/prop.201200159.
 10. Kubota, N. “Propellants and explosives: Thermochemical aspects of combustion”, 2nd edition, 2006, ISBN: 978-3527314249.
 11. Nakka, R. “RNX Composite propellant” United States of America, 2010.
 12. Costa, M. L., Rezende, M. C., Pardini, L. C. “Estudo da influência do diluente reativo PGE na cinética de cura de resina epóxi utilizada em compósitos estruturais” Química Nova, 2000, doi:10.1590/S0100-40422000000300008.
 13. Ponomarenko A. “RPA: Tool for liquid propellant rocket engine analysis” Russia, 2010.