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ADN-based Formulations Analysis for Green Solid Propellants

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Abstract

Within this paper, three different ADN-based formulations are analysed for a possible replacement of AP in the solid boosters of Ariane 5. The first two mixtures employ GAP as binder and a double-oxidizer configuration with ADN/HMX or ADN/AN. The third formulation contains a double-binder matrix of GAP and Desmophen. An analysis of thermophysical properties, performance and chemical composition of the combustion products of each mixture is performed. For each formulation, the obtained results are then used to compute the most important features required by a solid rocket motor in order to match the thrust mission profile of the EAP boosters.

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1. Introduction

This study is aimed to provide a detailed insight about ADN-based green propellants. Ammonium dinitramide properties and the ones of currently more advanced ADN-based propellants are hence outlined. Although ammonium dinitramide has already been applied into liquid propelled engines for satellites, still no implementations into solid rockets were obtained. Thus, the present analysis intends to provide an assessment of performance benefits and pollution reduction that a possible future implementation of ADN-based propellants in the boosters of Ariane 5 would imply and to offer a potential baseline for other large-scale applications.

2. Environmental and health concerns about current propellants

The present state-of-the-art technologies for propulsion employ toxic and environmental harmful substances, such as ammonium perchlorate as oxidizer in solid formulations or hydrazine and its derivates in liquid propulsion. The need for new green rocket propellants stems clearly from these considerations and led to intense research during the last years.

Hydrazine (N_2H_4) can be used in both mono- and bi-propellant blends. In the latter case, it is generally employed in combination with nitric acid or nitrogen tetroxide towards which it presents a hypergolic ignition behaviour. In monopropellant systems, several metallic catalysts can be used with hydrazine, one of the most common is the alumina-based "Shell 405". Hydrazine and its organic derivatives, unsymmetrical dimethylhydrazine (UDMH) and monomethylhydrazine (MMH), shares similar physical properties. It is a stable compound with long-term storage capabilities (up to 15 years [1]). These storability and ignition properties determined the large utilization of hydrazine and its derivatives in many upper stages and spacecraft propulsive systems. However, several concerns affect these compounds. Hydrazine has proven to be cancerogenic [2] and harmful effects may result from ingestion, inhalation of vapours or prolonged contact with skin [1]. This toxicity implies advanced and expansive handling techniques in order to guarantee safety of the operators. Moreover, hydrazine presents a certain reactivity with many materials such as iron, copper and its alloys, magnesium, zinc and some aluminium alloys. Thus, care must be taken during the storage not to expose it to these materials and tanks, pipes and valves need to be cleaned from impurities. For these reasons, ESA and NASA are both considering restrictions or prohibition of hydrazine within the near future [3]. In particular, in the European context, several research on the development of green alternatives to hydrazine was conducted, for instance in the framework of the RHEFORM project.

Regarding solid propulsion, ammonium perchlorate (NH_4ClO_4) is the most commonly employed oxidizer. Its success is determined by some desirable properties that this compound possess: a high oxygen content, a high density which implies a good volumetric specific impulse and good combustion and ballistic properties [4]. However, production of AP and combustion of AP-based propellants have a severe impact on environment and human health [4]. Due to its solubility, contamination of groundwater is one of the most concerning issues linked to ammonium perchlorate production. Moreover, its high chemical stability makes the contamination effect persists for years. The hazards for human health are linked to perchlorate interference with thyroid gland activity and thyroidal hormones circulation. Furthermore, combustion of AP-based propellants implies the formation of huge quantities of HCl in the products. This substance is responsible for acid rains, ozone depletion and corrosion around the launching site [5]. For these reasons, alternative propellants have been the subject of intense research worldwide in the last years. In Europe, two of the most important works aimed to develop such green propellants were the HISP and the GRAIL projects.

3. ADN-based propellants: physical and chemical properties

ADN is one of the most promising substances aimed to replace toxic components in both liquid and solid propulsion and its synthesis was acknowledged as one of the most noteworthy discoveries in the field of energetic materials [6]. In the following, ADN structure, synthesis, physical and chemical properties and its implementation in liquid monopropellants and in solid formulations are described.

3.1 ADN molecule structure and properties

ADN ($NH_4N(NO_2)_2$) is a solid salt of dinitramide anion and ammonia cation. Dinitramide anion, which comes from the detachment of a hydronium cation from dinitramidic acid, is particularly stable due to the presence of negative charge that is distributed by resonance over the entire molecular system [7].

There exist two methods for synthesis of ammonium dinitride, the so called "urethane" and "sulfamate" routes [8]. The first one is composed of two steps: synthesis of ammonium nitrourethane (ANU) followed by a nitration reaction performed using dinitrogen pentoxide (N_2O_5) as nitrating agent. The sulfamate route is more suitable for larger

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scale productions. It requires sulfonitric nitrating agents HNO_3/H_2SO_4 and it can be developed with two schemes that involve the formation of different salts of dinitramidic acid, potassium dinitramide (KND) or guanydylazide dinitramide (GUDN), as intermediate products. Between these two schemes, the one involving KND allows to produce higher purity ADN [9], while the GUDN one implies higher quantities and lower costs. The morphology of ADN crystals that are obtained by the described synthesis processes is of needle shape. This is an issue because the shape of the particles influences the loading factor of the oxidizer, the viscosity of the mixture and consequently its casting and processability properties. Thus, a re-crystallization of particles into spheres is of crucial importance.

With respect to other dinitramidic acid salts, ADN decomposition mechanism is way more complex and it is strongly dependant on the nature of chemical surroundings [10]. The initial step is the dissociation into ammonia and dinitramidic acid ($HN(NO_2)_2$) [11]. The next one is a temperature-controlled step. This means that different temperatures lead to different decomposition pathways. The main products ADN decomposition are HNO_3, N_2O, NO_2, NH_3, H_2O, NO, HNO_2, N_2 [10] whose relative amounts vary with temperature, pressure and extent of the reaction. In order to implement it into practical application, due to its decomposition behaviour, ADN requires the usage of stabilization techniques and substances. The most important aspect for stabilization of dinitramide salts is maintaining electron delocalization of the anion [10]. Surface-active species like amines and compounds containing hydroxyl groups are particularly suitable for this scope.

Stindiskii et al. [12] described the burning behaviour of ADN, studying the flame structure, condensed products formation and effects of initial temperature for a pressure range of 0.1 to 40 MPa. At low pressures ADN presents a flame structure (figure 3.1) that is similar to the one of double base propellants. It can be divided in three zones. In the aerosol zone, liquid droplets are dispersed into the gas phase where they decompose. Temperature stays almost equal to the one of the surface in a thin layer close to it, then it presents an almost step-wise increase of 120÷145 K. The thickness of the aerosol layer depends on pressure, shrinking as it increases. As for other energetic materials, a flameless combustion with copious fumes production is observed at low pressures. As pressure increases to 5 bar a flame zone appears with an associated temperature of 1325K that rises to 1475K at 40bar [13]. Stindiskii et al. [12] exploited the c-phase combustion model and thermocouple measurements of the burning surface temperature to compute the rate constant of the rate-controlling reaction in the ADN combustion mechanism. The obtained value, in the range of pressure 0.02÷1 MPa, was: $k = 1016.37 \exp(-39\,000/(RT))$.

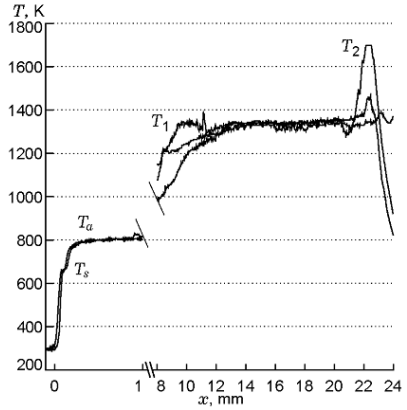

Figure 3.1: ADN combustion wave temperature profile at 0.5 MPa.
T_s = surface temperature; T_a = aerosol temperature; T_1 = 1st flame ; T_2 = 2nd flame

3.2 ADN-based liquid propellants

ADN-based monopropellants have the following advantages compared to hydrazine: a lower life cycle cost, higher specific impulse and higher density. More precisely, Wingborg et al. reported 10% higher values of specific impulse and 60% higher ones of volumetric specific impulse for an ADN/water/hydrocarbon-fuel formulation. There exist two formulations that are considered as the most promising ones: FLP-106 and LMP-103S. Their densities, specific impulses and volumetric impulses are listed in table 3.1.

Table 3.1: Properties of ADN-based liquid monopropellants

Propellant	Density [g/cm^3]	Specific impulse [s]	Volumetric specific impulse [gs/cm^3]
FLP-106	1.362	259	353
LMP-103S	1.240	252	312

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FLP-106 mixture is composed by 64.6% ADN, 23.9% water and 11.5% monomethylformamide (MMF, CH_3NHCHO) [3]. FLP-106 presents better density and specific impulse performance compared to hydrazine. A disadvantage of this formulation is the higher combustion temperature that could not be withstood by Shell 405, the most common ignition catalyst of hydrazine. However, FLP-106 ignites when dropped on a hot plate at 200÷250 °C [6], making thermal ignition a potential alternative to catalytic one for this propellant. Three different heating methods are hence possible: pyrotechnic, conductive or resistive ignition. The latter would exploit the fact that ADN is salt and thus its solutions possess a high electric conductivity. FLP-106 is manufactured in two steps: in the first one the fuel is dissolved in water, in the second ADN is added. The so obtained propellant is then filtered to eliminate possible solid impurities.

LMP-103S mixture is composed by 63% ADN, 13.95% water, 18.4% methanol and 4.65% ammonia [3], its density is 24% higher than the one of hydrazine [14]. As FLP-106, it is harmful if ingested but not toxic [doc 8]. This, together with a low sensitivity, allows a very easy handling and transportation. Specific impulse for this formulation with an expansion ratio of 50 is about 252s [14], nearly 5% more than hydrazine. On the other hand, it has a higher combustion temperature than hydrazine and so it requires the reactor bed, thrust chamber and nozzle to be made of refractory materials that are able to withstand such temperatures. In 2010, LMP-103S was employed in the Swedish PRISMA satellite, the first in-space application of an ADN-based propellant. Ju et al. [15] provided a theoretical and experimental study about LMP-103S characterization and improvement. They tested several mixtures which differed in the employed fuels: methanol, ethanol, acetone, tetraglyme and glycerol. Tetraglyme mixture exhibited the best vacuum specific and volumetric impulse and also better adiabatic decomposition temperature. DSC analysis revealed that the preheating temperatures at which the mixture should be taken before entering the combustion chamber is affected by the catalyst but not by the flash point and auto-ignition temperature of the fuel. Blasting cap tests were also conducted and all propellant formulations exhibited an explosive behaviour similar to the one of ammonium nitrate. It was thus concluded that, given the similar explosive power of the compositions, tetraglyme-based LMP-103S, which achieves the best performances, could be further developed and implemented in satellites.

3.3 ADN-based solid propellants

Development of solid ADN-based formulations proved to be way more challenging than for liquid propulsion. This is mainly due to its incompatibility issues with isocyanates curing agents and to its anomalous solid-state behaviour [10]. The likely cause of such incompatibilities is the ammonium cation tendency to exchange protons with the surroundings. For this reason, the surrounding environment should be polar and capable of hydrogen bonding donation, in order to bind strongly to the surface of ammonium dinitramide and discourage proton exchanges. Another problem of ADN-based formulations is related to excessive values of the burning rate and of the pressure sensitivity. In the recent years, several studies, employing different kinds of binders, were conducted to characterize green propellants and develop solutions to this sort of issues. In this context, HISP (High specific impulse propellant for In-Space Propulsion) and GRAIL GReen Advanced hIgh energy propellants for Launch), two projects funded by the European committee in the framework of the program Horizon 2020, are particularly noteworthy [5]. In reference [13] ammonium dinitramide was tested with inert (HTPB) and active binders (GAP) in order to evaluate theoretical performance compared to AP-based formulations and to gain experimental insight about their ballistic behaviour. The results, reported in figure 3.2, indicated a substantial increment of performance.

	AP/HTPB/Al	ADN/HTPB/Al	AP/HTPB/AlH_3	AP/GAP/Al	ADN/GAP/Al
Density, g/cm^3	1.761	1.682	1.606	1.906	1.812
p_c, bar	70	70	70	70	70
T_f, K	3404	3351	3036	3811	3806
Cp, J/(kg K)	1912.0	2060.2	2203.8	1794.2	1937.52
Sound Velocity, m/s	1072.0	1132.9	1138.6	1036.7	1105.4
C*, m/s	1583.5	1654.4	1644.3	1552.9	1644.6
I_s, s (vacuum with ε=40)	315.17	325.54	320.5	314.47	330.56
I_s, s (70/1)	264.35	274.62	272.17	262.22	275.95
Combustion Products (chamber), $\mathcal{M}_c$, g/mole	25.76	23.09	21.24	29.90	26.71
Combustion Products (chamber), mole/kg	38.82	43.31	47.08	33.44	37.44
Condensed Products (chamber), molar %	7.76	7.33	6.14	9.17	8.35
Combustion Products (exit nozzle), $\mathcal{M}_e$,	26.26	23.45	21.40	32.05	28.15
Combustion Products (exit nozzle), mole/kg	38.08	42.64	46.73	31.20	35.52
Condensed Products (exit nozzle), molar %	8.76	7.82	6.42	10.69	9.39

Figure 3.2: Comparative table of ADN and AP based propellants with inert (HTPB) and energetic (GAP) binders

On the other hand, as it is indicated in figure 3.3, for all the ADN-based formulations either burning rate were too high (especially for the ones that employed GAP as binder) or pressure sensitivities were too large (up to unacceptable levels for the ones that employed HTPB as binder). However, GAP-based formulations proved to have

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good mechanical properties and stable combustion. Thus, glycidylazide polymer is regarded as one of the most promising energetic binders for solid propulsion applications [5]. A possible solution to the excessive burning rate of ADN-based propellants was identified in the employment of a double oxidizer combination with ammonium nitrate [16]. In fact, AN exhibits a much milder burning rate and employing it with ADN allows to combine the properties of each other [4]. Moreover, due to a lower oxygen content, it is impossible to completely replace AP with the sole ammonium dinitramide [16].

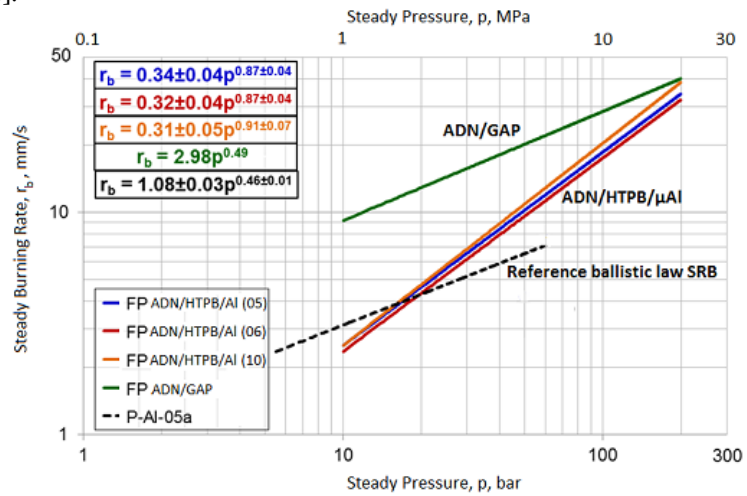

Figure 3.3: Burning behaviour of ADN-based formulations

Tagliabue et al. [16] conducted a study about aluminized double oxidizer compositions with both HTPB and GAP and found out that, for the latter, the specific impulse presents a plateau when varying the oxidizer amount between 51% and 71% (figure 3.4). This allows to tune the oxidizer percentage in the solid mixture in order to obtain desired mechanical and burning characteristics without significant performance losses. HTPB-based formulations provided a higher specific impulse but with a narrower region of best performance (figure 3.5). Moreover, the maximum value is achieved for an oxidizer percentage that would make production and cast of the propellant almost impossible.

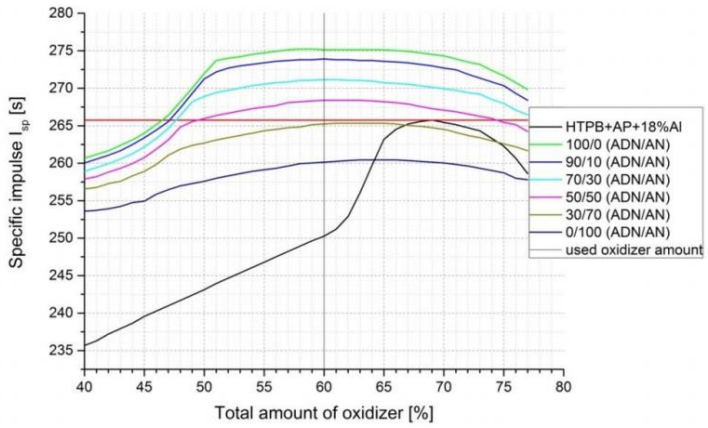

Figure 3.4: Specific impulse of ADN/AN/GAP/Al propellants with different amounts and ratios of oxidizers

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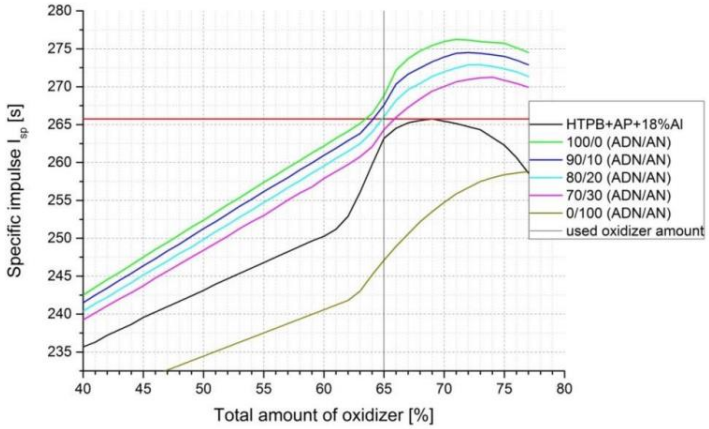

Figure 3.5: Specific impulse of ADN/AN/HTPB/Al propellants with different amounts and ratios of oxidizers

Within the same research, an analysis of the ballistic properties of the formulations was conducted. The results are resumed in the following figure 3.6. It can be clearly observed that the requirements of reducing the burning rate to adequate levels (7÷15 mm/s) and of lowering the pressure exponent to safer values ($n \leq 0.5$) are in competition: an increase in the AN percentage leads to a smaller burning rate but on the other hand it implies either a rise of the pressure sensitivity (up to unacceptable values for HTPB-based formulations) or a specific impulse penalization. However, the pressure exponent enhancing effect is milder for GAP based formulations.

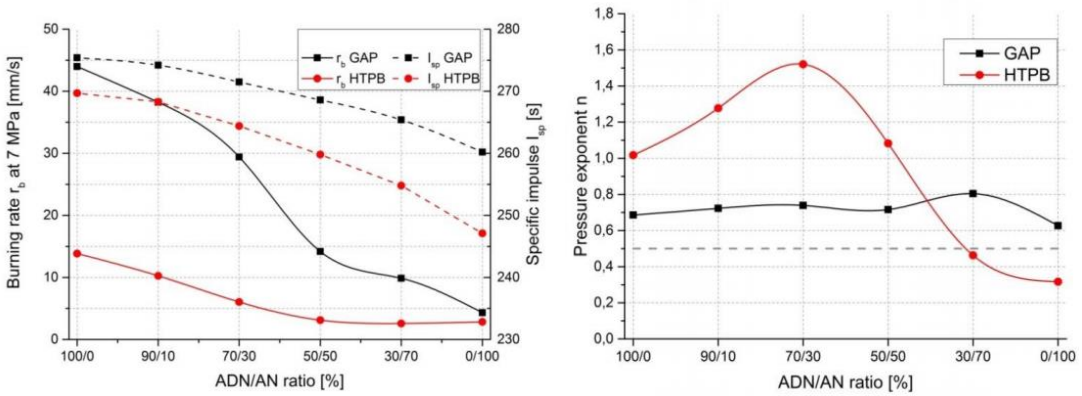

Figure 3.6: Comparison between ballistic properties of ADN/AN based propellants employing HTPB or GAP

Reference [5] resumes the results of several studies about green propellants employing ADN/AN mixture with different binders: GAP, Desmophen D2200, HTPB and a combination of GAP/Desmophen in the ratio 80:20. This latter configuration allowed to obtain better burning rates than with the sole GAP, with just a minor specific impulse penalization and an almost unvaried pressure exponent. Such results are represented in figure 3.7.

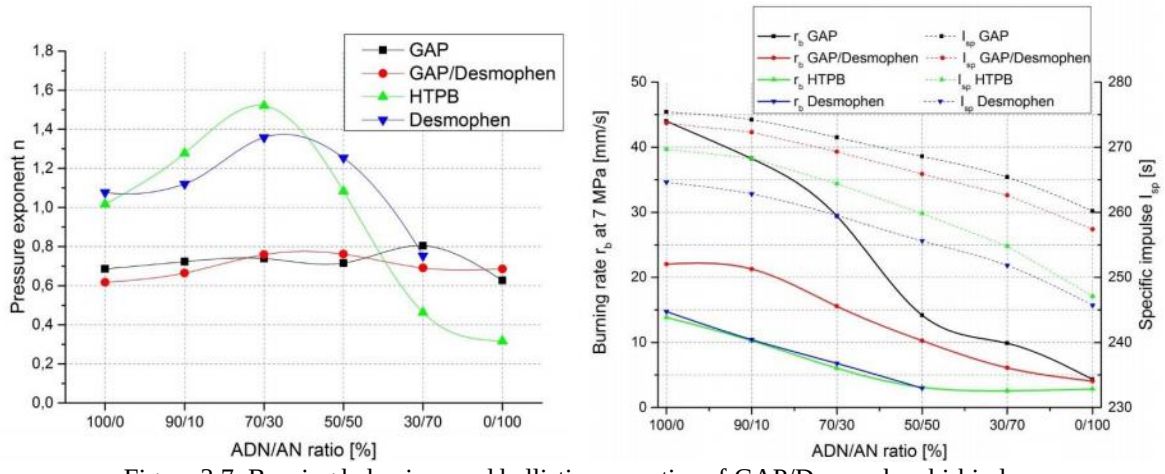

Figure 3.7: Burning behaviour and ballistic properties of GAP/Desmophen bi-binder mixture compared to various ADN/AN-based formulations

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4. Quantitative analysis of possible replacements for AP-based solid propellant

Three different ADN-based formulations were considered. The first two used Glycidylazide polimer (GAP) as binder and a double-oxidizer configuration with ADN/cyclotetramethylenetetranitramine (HMX) in the former and ADN/ammonium nitrate (AN) in the latter; the third formulation contained a double-binder matrix of GAP and Desmophen D2200. Moreover, a further state of the art composition (68% AP, 18% Al, 14% HTPB), based on the Ariane 5 boosters (EAP), was considered as a reference for comparisons. The considered mixtures were selected as the most promising among the ones that were studied in the most important research that were conducted in the last years about green propellants. Analysis of the thermophysical properties, performance and chemical composition of the combustion products of each mixture was performed with the NASA CEA code. The obtained results were then exploited to compute the most important features (mass, volume, combustion chamber pressure etc.) that a solid rocket motor employing each of the investigated formulations, would require to match the thrust profile of the EAP boosters of Ariane 5. Particular attention was paid to both propulsive performances and presence of pollutants agents in the combustion products.

4.1 Characteristics of the analysed mixtures

The mixtures that were analysed within this work are reported in table 4.1 with the names with which they are referred to in the following pages, their composition and principal characteristics.

Table 4.1: Ingredients and characteristics of the investigated formulations

Name	Composition	Characteristics
EAP	68% AP + 14% HTPB +18% Al	Formulation of Ariane 5 EAP boosters
ADN59	55% ADN + 30% HMX+ 19% GAP + 13.4% TMETN + 1.6% stabilizers	Double oxidizer ADN/HMX
ADNAN55	30% ADN + 30% AN + 16.13% GAP + 3.3% BATEG + 18% Al + curing agents	Double oxidizer ADN/AN
ADNAN55 BI-BI (BI-BInder)	30% ADN +30% AN + 12.9% GAP + 3.25% D2200 + 3.3% BATEG +18% Al + curing agents	Double oxidizer ADN/AP and double binder GAP/D2200

The formulation named “EAP” corresponds to the state-of-the-art solid rocket mixture used in Ariane 5 boosters. The formulation named “ADN59” was studied in references [17] and [13] where its good performances and mechanical properties were assessed. Its main characteristic is the usage of HMX as second oxidizer in combination with ADN. Differently from the other analysed formulations, ADN59 does not include metallic fuels. The mixture named “ADNAN55” was studied in references [16]. It presents an ADN/AN weight ratio of 50:50. This ratio was chosen because it is the one that provided acceptable values of burning rate and pressure exponent. In fact, for an augmented percentage of ADN a too high burning rate was obtained while augmenting the AN fraction a decrease in the specific impulse performance was observed. The formulation named “ADNAN55 BI-BI” was studied in references [5]. Its composition presents a weight subdivision between oxidizer, fuel and binder that is equal to the one of formulation ADNAN55. The difference between the two is that ADNAN55 BI-BI employs a double binder matrix with GAP and Desmophen D2200 in a 80:20 ratio. This small variation allows to further lower the burning rate to more suitable values preserving the pressure exponent and with minor penalties in specific impulse.

Combustion of the analysed formulation was described with the Vieille law model (equation 4.1). Such model expresses the burning rate of the propellant ($\boldsymbol{r_b}$) as an exponential function of the pressure in the combustion chamber.

$$\boldsymbol{r_b = aP^n} \quad \textbf{(4.1)}$$

The density and the coefficients of the Vieille law model and the burning rate at a pressure of 60 bar are reported for each formulation in table 4.2.

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Table 4.2: Density and ballistic properties of the analysed formulations

Formulation name	Density [g/cm^3]	a [$mm/(s\ bar^n)$]	n [-]	r_b [mm/s]	Reference
EAP	1.761	1.08	0.46	7.1	[13]
ADN59	1.634	2.37	0.52	20	[13]
ADNAN55	1.841	0.61	0.71	11.2	[16]
ADNAN55 BI-BI	1.837	0.42	0.77	9.8	[5]

4.2 Metodology of the analysis

Some design constrains were established before the beginning of the analysis:

- The exit diameter (2.985 m) and the length of the divergent part of the nozzle (3.374 m) of each designed system is equal to the one of the actual EAP boosters [18].
- The adaptation altitude of each designed system is equal to the one of the actual EAP boosters. Thus, considering the first constrain, the choice of the correspondent area ratio of the nozzle implies a modification of only the throat area.
- A burning time of 130 s.
- The thrust profile of each designed system is equal to the one of the actual EAP boosters.

For all the considered formulations a chemical equilibrium analysis was conducted with the software NASA CEA in order to compute the most relevant thermochemical and rocket performance parameters and the mass fraction of each substance in the combustion products. Such analysis was performed within a range of combustion chamber pressure of 10÷75 bar and with a shifting equilibrium hypothesis for the flow in the nozzle. Such hypothesis neglects the kinematics of the involved reaction and implies that the mixture is able to reach chemical equilibrium at each cross-sectional area of the nozzle in which the properties of the flow. Moreover, Nasa CEA does not consider fluidodynamic losses, hence the specific impulses that are computed tends to be overestimated. For this reason, losses associated to the divergence angle of the nozzle were added subsequently. The EAP formulation was studied with an expansion ratio of 11, the actual value of the nozzle of the boosters. For the other cases, different ranges of ε were analysed: for the ADN 59 between 5 and 11, while for the remaining two cases between 10 and 16. The reason of such choice stands in the fact that a lower mean molar mass of the combustion products and hence a higher specific heats ratio was expected for the non-aluminized ADN59 composition. Thus, for this formulation a lower value of the area ratio is required for the same adaptation altitude of the real case.

The thrust profile that was utilized in the analysis is reported in reference [19]. It is important to notice that the provided data were expressed in terms of vacuum thrust. Thus, to assess the real thrust profile during the mission, the static term, that is generated by the difference between ambient and efflux pressure, needed to be added to the thrust formula. The vacuum and the corrected thrust profiles are reported in figure 4.1.

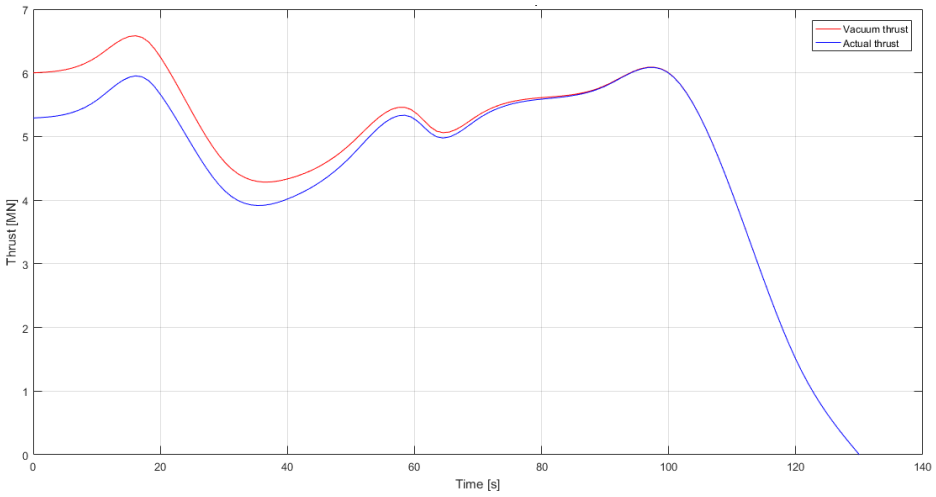

Figure 4.1: In vacuum and actual thrust profile of Ariane 5 boosters

After having computed the adaptation altitude of the boosters (5383 m), such value was imposed to all the other ADN-based formulations in order to find the nozzle area ratio that ensure adaptation at that altitude by

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interpolation within the range of ε. By the hypothesis of isoenthalpic expansion in the nozzle, the efflux velocities for each value in the considered pressure range were computed (4.2) and consequently the propellant mass flow rates (4.3).

$$v_e = (2 (h_{cc} - h_e))^{1/2} \quad (4.2)$$

$$\dot{m}_p = \rho_e A_e v_e \quad (4.3)$$

Thrust was then calculated in various conditions: in vacuum, at optimal expansion and at each of the altitudes (z) that compose the mission profile (5.4), which is reported in figure 4.2. Such computations were performed considering for each ε the losses λ (5.5) associated to the divergence angle of the nozzle.

$$THRUST(z) = \lambda \dot{m}_p v_e + A_e (P_e - P_{amb}(z)) \quad (4.4)$$

$$\lambda = (1 + cos(\vartheta_{nozzle})) / 2 \quad (4.5)$$

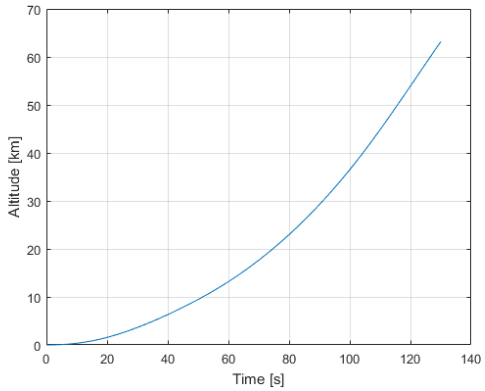

Figure 4.2: Altitude profile during the Ariane 5 boosters mission

At this point, assessing the relation between thrust and combustion chamber pressure at each considered altitude, it was possible to establish for each formulation the values of P_{cc} that are required to match the desired thrust profile of the mission. In a similar manner, it was possible to compute how the other parameters such as the combustion chamber temperature, the mass flow rate of the propellant and the specific impulse vary during the mission. Integrating in time the mass flow rate profile the total mass of consumed propellant of each formulation was obtained. The evolution of the burning rate associated to the variation of combustion chamber pressure was computed exploiting the Vieille law model. Subsequently, from a balance between mass flow produced by combustion of the propellant grain and the one expelled from the nozzle, the klemmung for each formulation was computed (5.6). Knowing the klemmung and the throat areas per each ε, the evolution in time of the burning area was easily obtained (5.7).

$$Kl = P_{cc} / (c^* \rho_{cc} r_b) \quad (4.6)$$

$$A_b = Kl \; A_t \quad (4.7)$$

Data about the mass fraction of the chemical species that are present in the combustion products of each mixture were then employed to compute the mass of each substance that is released into the environment. It is important to notice that the following analysis was performed considering one booster, the obtained data about mass, volume, thrust etc. are hence to be referred to only one solid rocket.

5. Results

The quantitative analysis and the comparison that were performed can be subdivided into three main topics: performance evaluation, burning behaviour and reduction of pollutants.

5.1 Booster performance evaluation

For all the analysed mixtures, the obtained values of thrust at optimal expansion and in vacuum are reported in figure 5.1 (for the EAP propellant, since it was evaluated only for epsilon equal to 11, which is the real value of the

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Ariane 5 booster, a surface graph was not obtained). Vacuum and optimal thrust showed to have similar trends for all the investigated formulations. ADN59 generates the highest thrusts with maximum around 14÷16 MN, while ADNAN55 and its BI-BI version produce similar values, quite aligned with the ones of EAP formulation and with maxima around 8÷9 MN. It is interesting to notice that thrust presents a decrease as ε increases. This is due to the design constrains that were chosen; in fact, since the exit area is constrained, an increase of ε represents a decrease of throat area with a subsequent decrease of the mass flow rate that the nozzle is able to elaborate.

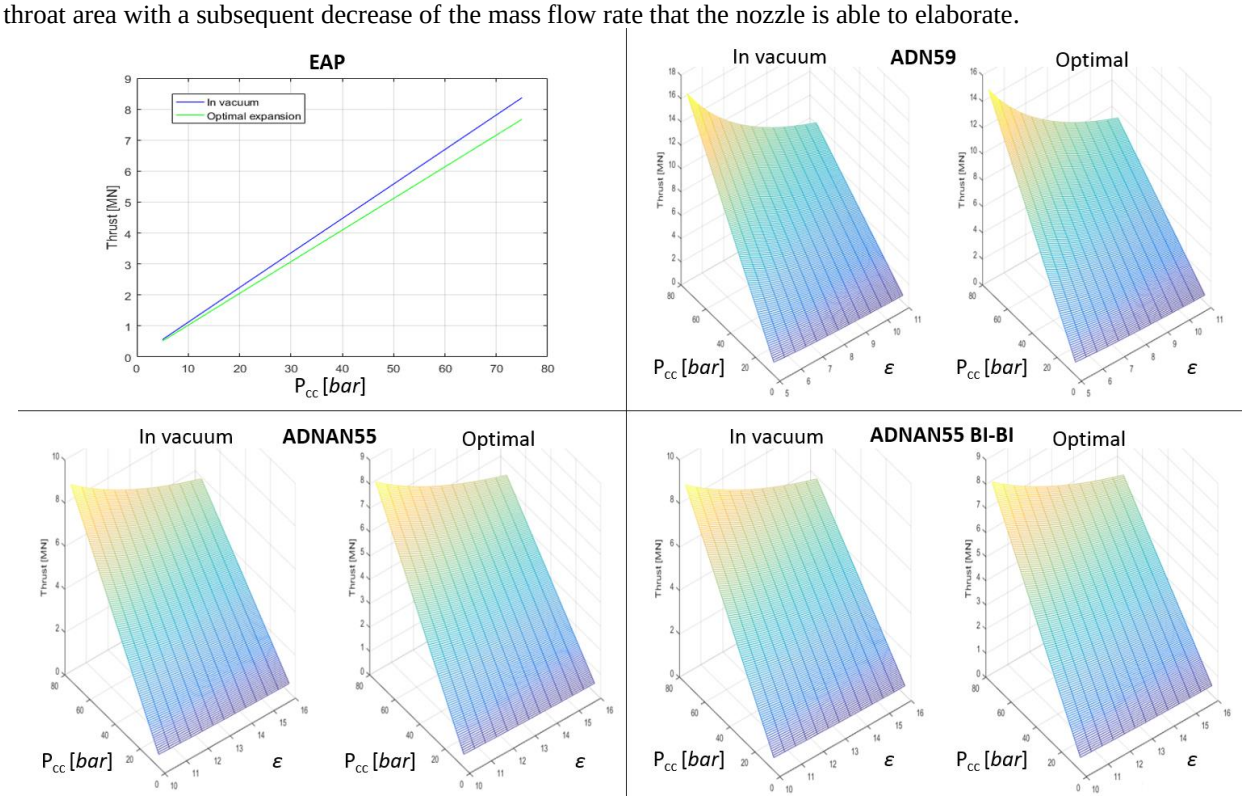

Figure 5.1: In vacuum and optimal thrust of each formulation over pressure in the combustion chamber and area ratio

In figure 5.2 the thrust of the ADN-based formulations at different altitudes and for the range of pressure in the combustion chamber is illustrated, each surface represents a different value of the nozzle area ratio ε.

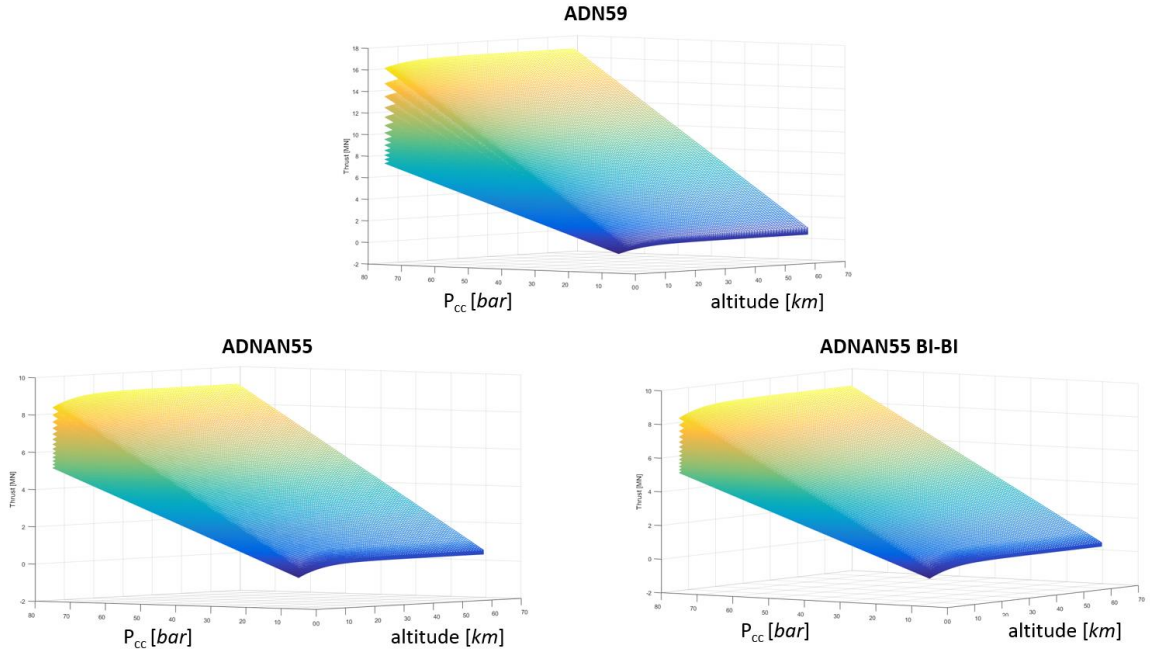

Figure 5.2: Thrust performance for each ε of each ADN-based formulation

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The logic behind the performed computation was to allow a comparison between systems that share the same adaptation altitude (5383 m) of the original one. In this sense, the values of the expansion area ratio of the nozzle were computed for each formulation and the results are resumed in table 5.1.

Table 5.1: Values of the nozzle area ratio that provide adaptation at 5383m for each formulation

Formulation	ε
ADN59	6.23
ADNAN55	11.56
ADNAN55 BI-BI	11.20

Such values are explainable with the ingredients of the different mixtures. In fact, the low ε of the ADN59-propelled system is due to the lack of metallic fuel in its formulation that implies a much lower mean molar mass of the combustion products and hence a higher value of the heat capacities ratio. Thus, a smaller area ratio is required for such formulation. On the other hand, for the aluminized compositions ADNAN55 and ADNAN55 BI-BI, the values of ε are closer to the one of the state-of-the-art propellant.

A comparison between the masses of propellant that are consumed during the mission by each of the analysed systems sharing the same adaptation altitude is provided in figure 5.3 together with a representation of the difference between the mass of the AP-based one and the ADN-based ones that shows the mass save or gain that each formulation provides.

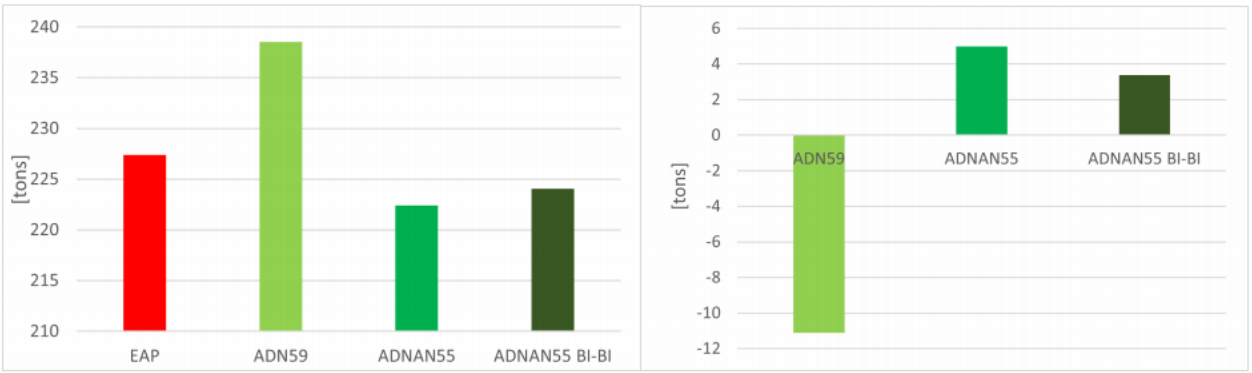

Figure 5.3: Propellant mass of each formulation and mass save/gain of the ADN-based ones with respect to EAP

It can be clearly seen that the two formulations employing ADN and AN as oxidizers provide a saving of propellant mass that is quantifiable in a 2.2% and 1.5% reduction respectively. On the other hand, the non-aluminized ADN/HMX based formulation presents a 4.9% mass increase with respect to the EAP mixture. These trends in the mass performance can be explained by the specific impulse that they provide for the required mission. Mean values of the specific impulse during the mission of the booster are reported for each analysed propellant in table 5.2.

Table 5.2: Time averaged values of I_s during the mission for all the analysed formulations

Formulation	Mean specific impulse [*s*]
EAP	264.4
ADN59	250.1
ADNAN55	270.4
ADNAN55 BI-BI	268.4

The lower mean specific impulses that ADN59 provides during the selected mission profile implies its decreased mass performance. However, a different choice of the design constrains may recover this drawback. In fact, specific impulse data that were obtained with CEA showed that values of about 267 seconds, slightly bigger than the ones of the EAP case, are obtainable for higher nozzle area ratios. Implementing a system with a higher adaptation altitude, and hence a bigger ε, would allow to achieve a saving of propellant mass also for ADN59. Of course, applying such design philosophy also to the other formulations would imply even greater reductions. In fact, results obtained for an area ratio of 16 indicate possible mass savings of about 4.35% for ADNAN55 and about 3.83% for ADNAN55 BI-BI.
Volumes for each of the designed system are resumed in table 5.3. Once again ADN59 presents a performance decrease with respect to the AP-based mixture, while the other two formulations an increase.

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Table 5.3: Propellant volume for each investigated formulation

Formulation	Propellant volume [m^3]
EAP	129.1
ADN59	143.9
ADNAN55	120.8
ADNAN55 BI-BI	121.9

Such trends are obviously associated to the different densities of the solid propellants (see table 4.2). ADN59 density is unsurprisingly the lowest since it does not include metallic fuel in its formulation. Unfortunately, in this case, a better performance than the one of the EAP booster seems not achievable even with a different ε. Analysing the volume performance of ADNAN55 and ADNAN55 BI-BI the tunability properties of such mixtures can be appreciated. In fact, the density of ADN and AN is lower than the one of AP, however this apparent disadvantage is recovered by the possibility that these mixtures offer to reduce the oxidant to fuel ratio without significant specific impulse losses.

5.2 Burning behaviour

The ballistic properties of ADN-based propellants are one of the biggest obstacles to their implementation into real systems. ADNAN55 formulation and its BI-BI version present pressure exponents that, although being lower than the critical value of 1, are still quite high, whereas the value for ADN59 is fairly close to the one of the state-of-the-art AP-based mixture (see table 4.2). Maximum value and the average over mission time of the burning rate are reported for each system in table 5.4.

Table 5.4: Maximum and time averaged values of the burning rate during the mission for all the formulations

Formulation	Max burning rate [*mm/s*]	Mean burning rate [*mm/s*]
EAP	7.1	6.0
ADN59	15.5	12.9
ADNAN55	11.4	9.0
ADNAN55 BI-BI	10.0	7.6

Even though its pressure exponent is the milder among the ADN-based combinations, ADN59 presents an elevated burning rate that is borderline in the generally accepted range for solid rocket propulsion (7÷15 mm/s [4]). Formulation ADNAN55 exhibits better results although still not close enough to EAP ones. ADNAN55 BI-BI was expressly selected because of its better burning rate characteristic with respect to the "mono-binder" version and in facts it achieved the best results in these terms. While its maximum is just one millimeter per second lower than the ADNAN55 one, the average value is very close to the one of the EAP formulation and perfectly aligned to the aforementioned desired range.

Through a mass flow rate balance between combustion chamber and nozzle exit it was possible to obtain the evolution of the burning area in time. Such parameter could be useful in order to design the grain geometry of the solid booster. The 4 analysed propellants exhibited quite different ranges of burning areas with EAP case varying between about 150 and 190 m^2, ADN59 between 80 and 100 m^2, ADNAN55 between 97 and 110 m^2 and ADNAN55 BI-BI between 118 and 130 m^2.

Combustion chamber pressure and temperature are very important parameters since they are associated to design, selection of the materials and dimensioning of the case and of the insulating system. For all the propellant formulations the maximum values were achieved in the first stages of the mission, nearly 15 seconds after the lift-off, when the maximum thrust is required. Maximum and time-average values of pressure and temperature are reported in table 5.5.

Table 5.5: Maximum and time averaged values of combustion chamber pressure and temperature

Formulation	Max P_{cc} [*bar*]	Mean P_{cc} [*bar*]	Max T_{cc} [*K*]	Mean T_{cc}[*K*]
EAP	59.0	43.4	3341.4	3306.6
ADN59	36.8	27.1	3033.4	3009.4
ADNAN55	61.8	45.4	3459.7	3423.0
ADNAN55 BI-BI	60.0	44.1	3402.8	3369.2

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Among the four analysed formulations, ADN59 stems clearly as the one that exhibits the way lowest maximum and average values for both temperature and pressure. It is thus fair to say that this formulation would imply less strict requirements for case and insulation design. The two formulations that employ ADN/AN combination as oxidizer exhibits a pressure trace that is very similar to the one of the EAP booster but with flame temperatures that are 60÷120 K higher. For all of the investigated mixtures it can be noticed that temperature in the combustion chamber seems to stay quite uniform during the mission, with differences of few Kelvins between the maximum and the average. On the other hand, combustion chamber pressure presents larger fluctuations and a wide difference between maximum and mean values.

The characteristic velocity c^* is a parameter of merit of the combustion chamber. All the considered ADN-based formulations exhibit good values of c^* around 1600 m/s which is a slightly better value than the one of the AP-based propellant (around 1578 m/s).

5.3 Analysis of pollutants in the combustion products

Chemical composition of the combustion products of each solid propellant formulation was evaluated with the NAS CEA. Before analysing the obtained results, it is opportune to make some consideration about the hypothesis that were applied. Chemical computations were made with a shifting equilibrium assumption that contemplate the recombination reaction that happen as the pressure decrease in the divergent part of the nozzle. It is important to keep in mind that in its computations, the CEA code does not consider the kinetics of the involved reactions. Masses of the species that compose the combustion products of each formulation are listed in the following table 5.6, while visualizations of the percentage of the compositions is given by the pie graphs of the following figure 5.4.

Table 5.6: Masses of the chemical species in the combustion products of each formulation

Formulation	CO [*tons*]	CO_2 [*tons*]	HCl [*tons*]	H_2 [*tons*]	H_2O [*tons*]	N_2 [*tons*]	Al_2O_3 (α) [*tons*]	Others [*tons*]
EAP	62.8	3.8	47.8	6.4	10.6	18.4	77.3	0.087
ADN59	34.7	50.7	/	2.3	55.6	95.2	/	/
ADNAN55	33.7	6.1	/	5.0	26.2	73.7	77.6	0.056
ADNAN55 BI-BI	36.8	6.5	/	5.3	26.1	71.0	78.2	0.036

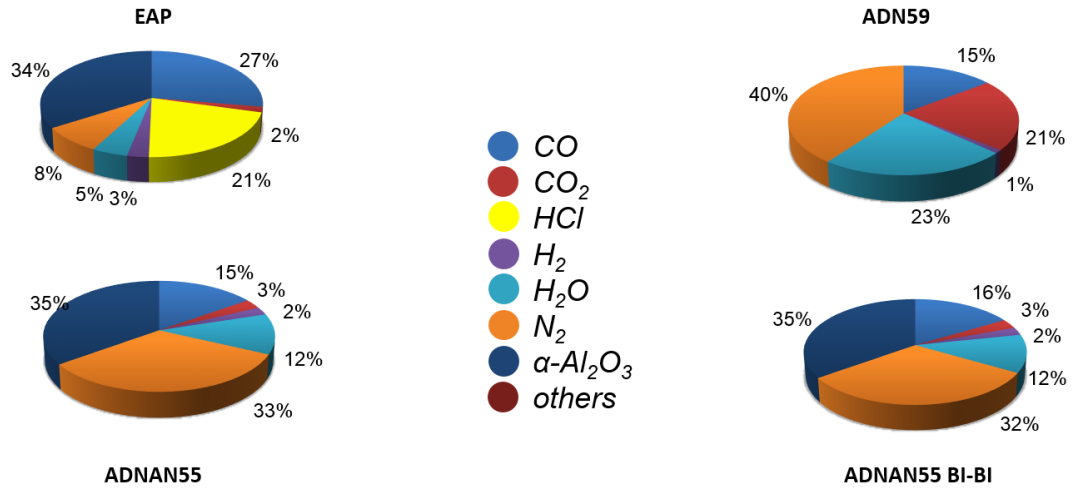

Figure 5.4: Chemical composition of the combustion products of each analysed formulation

As it was expected, the EAP formulation differs from the others for the production of large quantities of hydrogen chloride as a consequence of the presence of ammonium perchlorate as oxidizer. In addition to HCl, other health-hazardous substances can be found in large percentages in the EAP mixture products: α-alumina and carbon monoxide. Moreover, a 2% weight fraction of carbon dioxide was encountered. This substance is naturally present in atmosphere and thus it is not polluting. However excessive concentrations of CO_2 in the atmosphere contribute to the greenhouse effect that traps infrared radiation and causes increments of surface temperature of the Earth. The remining substances that are present in major percentages in the products are non-toxic and non-polluting water and molecular nitrogen and

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hydrogen, while the "others" slice of graph is principally composed by atomic hydrogen and chlorine and aluminium-based compounds.

All the investigated ADN-based formulations do not include chlorinated substances in their ingredients and this allows to eliminate hydrogen chloride from their products. Combustion of propellant ADN59 does not produce polluting compounds with the only concern that is represented by the toxic carbon monoxide. Moreover, this formulation releases the biggest amount of CO_2 between all the investigated propellants. For ADN59 too, the remaining substances that appear in major percentages are non-toxic and non-polluting water and molecular nitrogen and hydrogen, while the presence of other substances besides the most relevant ones appeared to be practically negligible. ADNAN55 and ADNAN55 BI-BI, present combustion products that are very similar by composition and by percentages of the substances. Being aluminized mixtures, their combustion produces aluminium agglomerates that solidify while passing through the nozzle. The amount of this substance is almost equal to the one of the EAP formulation. The other toxic substance in the products is carbon monoxide but its quantity is almost halved with respect to the AP-based formulation. On the other hand, CO_2 is present in a small amount but doubled with respect to the EAP one. As for the other formulations, also for ADNAN55 and ADNAN55 BI-BI, the remaining products that appear in major percentages are non-toxic and non-polluting water and molecular nitrogen and hydrogen.

6. Conclusion and future works

Within the present study an insight about ADN and ADN-based propellants was provided. Whereas it has already been employed in liquid propelled thrusters for satellites, for solid propulsion ADN still lacks of practical applications. ADN presents several advantages with respect to ammonium perchlorate both in terms of theoretical performances and of reduction of polluting products. Furthermore, employing it in combination with other oxidizers can adjust the burning rate and the pressure exponent to more satisfactory levels. In this sense, three different ADN-based solid formulations were analysed and compared to the present state-of-the-art propellant of the Ariane 5 boosters. The main objective was to evaluate whether these mixtures would provide valid alternatives in both ecological and performance terms.

6.2 Comparative remarks between the analysed ADN-based formulations

The three ADN-based propellants exhibited different pros and contra, with none that stemmed as a clearly best option. For the design choice that were assumed, the aluminized formulations resulted to provide an increased performance in term of consumed propellant mass during the mission, with the most savings that were obtained by the ADNAN55 mixture. However, with different design constraints, mass savings with respect to the actual configuration of Ariane 5 boosters could possibly be attained also with the non-aluminized formulation ADN59.

Burning behaviour is one of the most critical aspects in ADN-based propellants. In this sense, ADN59 exhibited the most adequate value for the pressure exponent but a too enhanced burning rate. ADNAN59 BI-BI, which employs a double binder matrix, was expected to present a milder burning rate than the other formulations and in fact its value was the most aligned with the one of the Ariane 5 boosters. Pressure and temperature inside the combustion chamber were computed at every instant of the desired mission profile. Aluminized mixtures presented very similar values between them and thus design criteria for case and insulations are expected to be similar to the ones of the EAP boosters. On the other hand, for ADN59, temperature and pressures resulted to be much lower and hence less strict conditions could possibly be applied.

Since none of the investigated ADN-based formulations required chlorinated ingredients, toxic and polluting hydrogen chloride is not present in the combustion products of each of them. The only hazardous substance that was observed was carbon monoxide that was present with different percentages in all the analysed cases. CO_2 was traced too, as this substance has a strong impact on the greenhouse effect and hence on global warming. It was established that the biggest amount of carbon dioxide is released by ADN59 formulation while for all the other quite similar and relatively low values were observed. The main difference between the combustion products compositions of the ADN-based propellants was represented by the usage of metallic fuel inside the mixture. In fact, great quantities of aluminium agglomerates were observed for ADNAN55 and its BI-BI variant, whereas for the non-aluminized ADN59 this hazardous substance was obviously not present.

In conclusion, although none of them stems as a clear best and besides some drawbacks, each of the analysed formulations exhibited relatively good theoretical performances. This study was intended to provide a baseline for a possible future implementation of green propellants in a larger scale. It has to be noticed that some further aspects, as for example mechanical properties or processability of the propellants, need to be taken into account in order to assess a possible application at industrial level. However, the promising results that were gathered seem to encourage the effort towards such an ambitious and important goal as the large-scale implementation of green propellants in space propulsion systems.

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6.3 Possible future developments

The importance that green propellants are believed to acquire in the near future of space industry motivates a continuous commitment into research and development on this topic. Several improvement areas can be identified. One of the most important is cost reduction. Production of ADN is in fact quite expansive and the synthetised quantities are far from being enough for large scale applications. One reason for such high cost stands in the great volume of solvents that is required. Other key areas for improvement of ADN-based propellants are related to mechanical and ballistic properties and reduction of agglomerate size in case of aluminized compositions. In this sense, one of the most promising possible development would be the usage of stabilized aluminium hydride (AlH_3) as metallic fuel. This substance, which is also known as alane, is in fact believed to provide excellent performances and lower the size of agglomerated particles. According to reference [20], a formulation employing ADN and alane would outperform all the currently available solid propellants in term of specific impulse. On the other hand, alane exhibits a tendency to decomposition into Al and H_2 by an endothermic reaction that makes it long term conservation problematic. Stabilization of alane represent a pre-requisite to obtain the excellent results that are expected from its implementation into solid rocket propellants.

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