Green Advanced High Energy Propellants for Launchers (GRAIL) - First results on the Burning Behavior of AN/ADN Propellants

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Abstract

Solid rocket motors are today the most cost effective, competitive and reliable propulsion technology for space launch systems. State of the art solid rocket propellants are based on the oxidizer ammonium perchlorate, AP, and aluminum powder, embedded in a polymer binder matrix. Unfortunately, AP has a negative impact on the environment and on personal health due to ozone depletion, thyroid gland interference and acid rain formation. The paper gives a short overview on the objectives of the GRAIL project [1] which received funding from the European Union's Horizon 2020 research and innovation programme and started in February 2015. GRAIL seeks for a replacement of AP by using a mixture of the new green high energy density oxidizer ammonium dinitramide, ADN, in combination with the low cost oxidizer ammonium nitrate, AN.
Furthermore the paper focuses on first results in respect to the burning behavior of aluminized AN/ADN propellants with different oxidizer ratios of AN and ADN embedded in different binder systems.

1. Introduction

In 2014, The European Commission, ESA (European Space Agency) and EDA (European Defence Agency) launched a new round of the European Non-Dependence Process with a view to establishing a list of actions on critical space technologies for European non-dependence to be implemented in the time frame of 2015-2017 [2]. "Non-dependence" refers to the possibility for Europe to have free, unrestricted access to any required space technology. One item are the development of low cost, solid green propellants which will reduce application costs and environmental friendly while providing the same or similar efficiency as current propellant in use at the same time.
The solid propellant formulations, commonly used for space access until today, contain mostly ammonium perchlorate in combination with hydroxyl terminated polybutadiene (AP/HTPB). One of the main combustion products is hydrogen chloride (HCl) that should be considered critical under pollution aspects, since it contributes to acid rains and causes environmental damage and corrosion around the launch base. The boosters that contain this type of solid propellants, burn in the order of tons per second, releasing large quantities of HCl, which can reach more than 20% of the reaction products at the nozzle. Also aluminum chloride and other intermediate reaction products, which are not more than 2% [3], will cause additional serious problems when the huge quantities of expelled mass are considered. Furthermore there are some health concerns regarding AP. The perchlorate ion is toxic for human beings and animals, the production is contaminating the groundwater and perchlorate was found in fruits and vegetables [4-7].
In order to develop a green solid propellant AP has to been replaced by a chlorine-free oxidizer. Unfortunately the number of oxidizer is limited and only two oxidizers for the preparation of green propellants exist: ADN and AN. Ammonium dinitramide [ADN, $NH_4N(NO_2)_2$] has a dual advantage over the workhorse oxidizer AP in terms of clean combustion and superior heat of combustion. Due to lower oxygen content it is not possible to replace AP by ADN one-to-one and for high performance ADN has to be combined with an energy-rich binder. Ammonium nitrate [AN, NH_4NO_3] is the other one. AN is usually not used in high performance propellants due to the low performance and low burning rate. Neither ADN, nor AN are able to replace AP on its own. Table 1 summarized and compared some properties of AN and ADN [1, 8]

Table 1. Properties of AN and ADN [1, 8]

Property	AN	ADN
Performance (Isp)	Low	High
Burning rate	Low	High
Explosive hazard	Low	High
Cost	Low	High
Environmental impact	Low	Low

A combination of both suggests that the properties and performance of AN/ADN based propellants are equal or even exceed the properties of AP based propellant and match the requirements for space applications.

2. GRAIL

GRAIL stands for "Green advanced high energy propellant for launchers" and is a research project funded by the European Union's Horizon 2020 research and innovation programme under the grant agreement number 638719.
The objective of the GRAIL project is to determine if it is feasible to replace AP by using a mixture of the new high energy density oxidizer ammonium dinitramide, ADN, and the low cost oxidizer ammonium nitrate, AN.
This will be done by developing a solid propellant based on ADN/AN, aluminum powder and a polymer binder. To obtain high performance high energy fuels such as aluminum hydride and nano aluminum will also be used.
The high energy density green solid propellant developed will be compared with state of the art solid propellants with respect to:

- Safety
- Performance
- Cost

to determine if replacing AP with ADN/AN is a feasible option [1].
The work in the project is carried out by seven partners and coordinated by FOI (Swedish Defence research Agency, Sweden). Partner are: Avio S.p.A (Italy), Eurenco Bofors AB (Sweden), FOI, Fraunhofer Institute for Chemical Technology (FhG-ICT, Germany), The Inner Arch (France), Politecnico di Milano (Italy) and the Institute of Chemistry of Poitiers: Materials and Natural Resources at the Centre National de la Recherche Scientifique (CNRS-IC2MP, France).
The project started in February 2015 and the first results about the burning behavior of ADN/AN based propellant are presented below.

3. Ingredients

ADN was used in a spherical form of 48µm, 212 µm and 218µm nominal particle size in order to have a bimodal distribution in the propellants; ADN was purchased from Eurenco Bofors and prilled at ICT. AN was used in a spherical form stabilized either with KNO_3 (KNO_3-PSAN, 30µm) or NiO (NiO-PSAN, 120µm). The phase stabilized AN was produced at ICT. Two different particle size of aluminum were used for better processing. The finer aluminum powder has a nominal diameter of 4µm and it´s called Alcan400 while X81 is a 20µm aluminum powder. The amount of aluminum is fixed at 18%. GAP (Glycidyl azide polymer, Eurenco), HTPB (R45HTLO, MACH I INC.), Desmophen 2200 (polyester, BayerMaterial Science) and a mixture GAP/Desmophen2200 (80:20) are the selected binder system. GAP and GAP/Desmophen mixture were cured with Desmodur N100 and E305 (BayerMaterial Science). The standard curing agent IPDI was used to cure HTPB, while Desmodur N100 was used for Desmophen 2200. To achieve higher solid loads plasticizer agents were used. In order to lose not too much energy content, an energetic plasticizer (not disclosed) for GAP and GAP/Desmophen formulations was added. The viscosity of HTPB based formulation was lowered by DOA while triacetin was used in Desmophen.

4. Thermodynamic calculations

All thermodynamic calculations were performed by ICT code [9]. The thermochemical data of the ingredients were taken from ICT´s database [10]. The software works with ideal thermochemistry, so the dimensions of substances involved are not considered. All calculations were made for a chamber pressure of 7 MPa and expansion ratio of 70:1. The following chapters present the calculated specific impulse, under the hypothesis of shifting equilibrium, as a function of the ADN/AN ratios and different oxidizer contents. These calculations give a guideline for the amount of oxidizer needed in order to achieve the maximum performance. The computed values are compared to a standard Al/AP/HTPB (18/68/14) composite propellant.

4.1 GAP

Al/ADN/AN propellants based on GAP binder exhibit a kind of plateau for a total oxidizer content between 51% and 70%. Comparing the ADN/AN ratio at different amount of oxidizer, the differences of the specific impulse is less than 1.5 sec, except the one with AN only. This enables a broad range of formulations for adapting the mechanical properties and processing. If needed it´s possible to change the amount of binder without loss of performance. In comparison to the Al/AP/HTPB reference propellant, superior performances are obtained in wide range of ADN/AN ratios. The amount of ADN can be decreased down to 35% of the total amount of oxidizer and the computed specific impulse is still better than AP based propellant (266.15 s vs 265.8 s). The best performances are achieved at an oxidizer content of 60%. The position of the maximum performance slightly slides to the right when the amount of ammonium nitrate increases due to its lower oxygen content. The difference is not significant, for example for an oxidizer content of 60% with an ADN/AN ratio of 90/10 to 62% with a ratio of 40/60 it can be hardly noticed because of the flattening of the values.

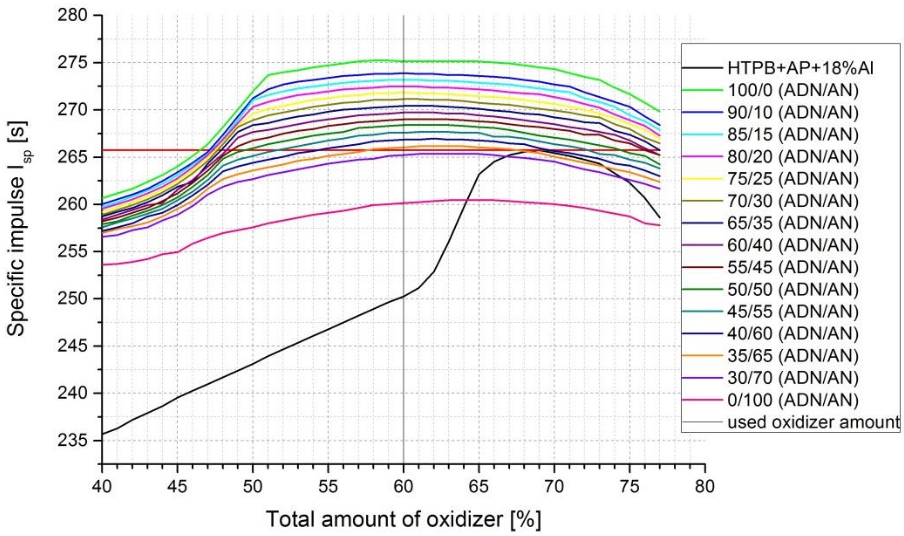

Figure 1. Thermodynamic calculations of Al/ADN/AN/GAP propellants

4.2 GAP-Desmophen 2200

Al/ADN/AN propellant based on a binder mixture of Gap-diol and Desmophen in a ratio of 80 to 20 shows a similar behavior like pure GAP based propellants. The plateau is less pronounced but is still present. This mixture is chosen on the one hand to improve the mechanical properties of the GAP binder and on the other hand to decrease the high burning rates which are known from ADN/GAP based propellants. The drawback is a smaller specific impulse but the decrease is not dramatic and around 1.33 s (-0.58%). The highest I_{sp} is obtained at an oxidizer content of 62% while the reference propellant is matched at a ADN/AN ratio of 45/55 (I_{sp}=266.05 s).

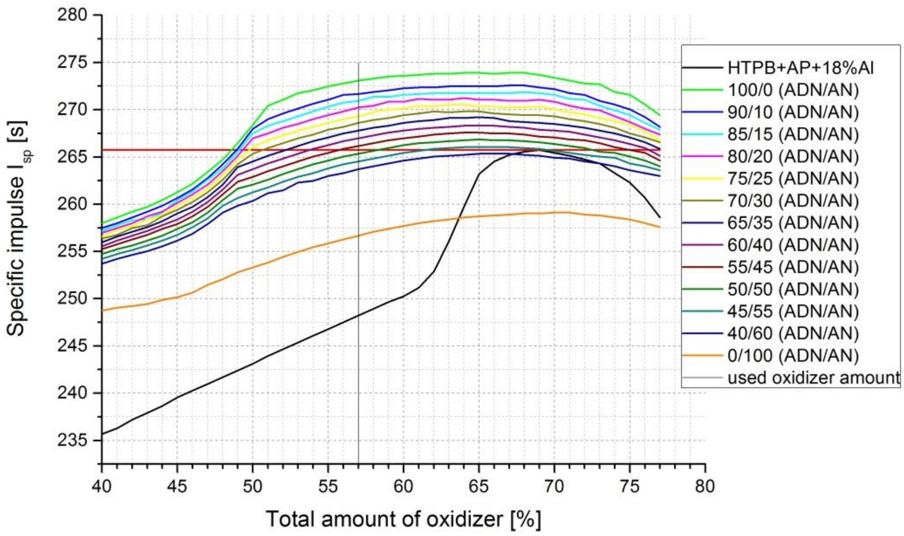

Figure 2. Thermodynamic calculations of Al/ADN/AN/GAP/Desmophen 2200 propellants

4.3 HTPB

The maximum specific impulse of the Al/ADN/AN/HTPB is around an oxidizer content of 72%. Together with Al, a total filler content of 90% will be reached. The theoretical specific impulse of the HTPB based propellant reveals to be the highest among all investigated formulations with different binders.

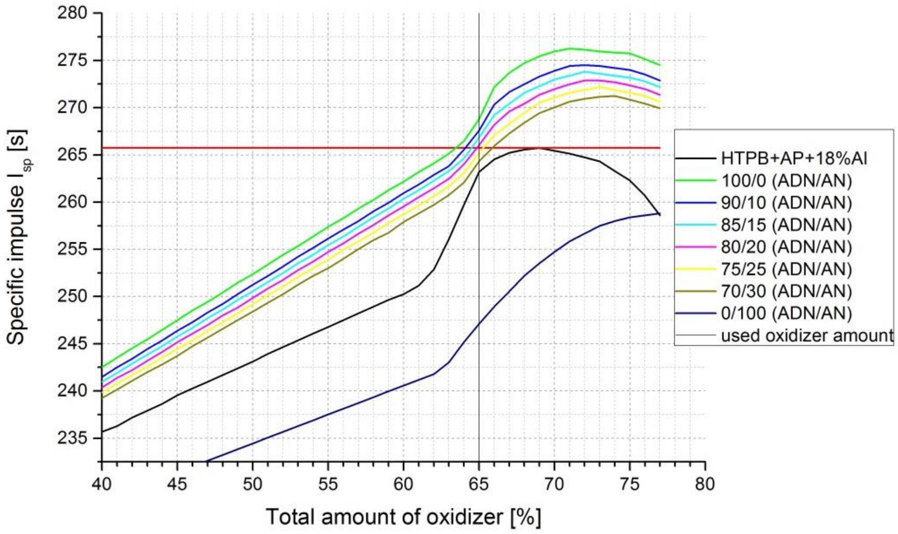

Figure 3. Thermodynamic calculations of Al/ADN/AN/HTPB propellants

4.4 Desmophen 2200

Its behavior is smoother than the AP based referent propellant, which shows a strong increase at an AP content of 62%. The maximum specific impulse of the Al/AP/HTPB propellant is attained at an oxidizer content of 68%. With the same total amount of oxidizer the AP based propellant´s performance, is reached with an ADN/AN ratio of 70/30 (266.6 s vs 265.8 s). The maximum specific impulse is achieved with a total oxidizer content of 73%.

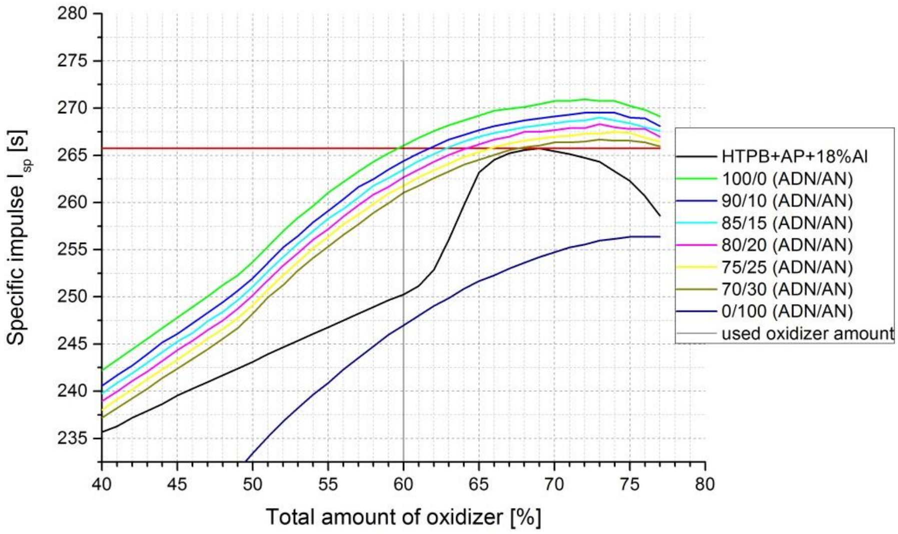

Figure 4. Thermodynamic calculations of Al/ADN/AN/Desmophen 2200 propellants

5. Investigated Formulations

For every binder the maximum amount of filler was determined which was processable. It was tried to get as close as possible to the oxidizer amount of the highest specific impulse. This leads to various total amounts of oxidizer for different binder. When a processable amount was found the ADN/AN ratio was varied by keeping the total amount of oxidizer and the ratio of coarse/fine particle distribution (70/30) constant.
The amount of aluminum was fixed at 18% of the total mass for all formulations. The mass fractions of the ingredients are reported in detail in the following tables.

5.1 GAP

A solid load of 78% (60% oxidizer and 18% Al) was achieved by the addition of 3.3% of plasticizer to the binder

Table 2. Composition GAP based propellants

Label	**ADAN52**	**ADAN53**	**ADAN54**	**ADAN55**	**ADAN56**	**ADAN50**
ADN/AN ratio	100/0	90/10	70/30	50/50	30/70	0/100
GAP	16.13	16.13	16.13	16.13	16.13	16.13
E305	0.29	0.29	0.29	0.29	0.29	0.29
N100	2.28	2.28	2.28	2.28	2.28	2.28
Energetic plasticizer	3.3	3.3	3.3	3.3	3.3	3.3
ADN	60	54	42	30	18	-
PSAN	-	6	18	30	42	60
Al	18	18	18	18	18	18

5.2 GAP-Desmophen 2200

For the binder mixture a total amount of oxidizer of 57% could be achieved only. It is not far away from the amount with the best performance (62%). To achieve this solid load of 57% of oxidizer and 18% of aluminum, 3.75% of energetic plasticizer was needed for processing, similar to the GAP based propellants.

Table 3. Composition GAP-Desmophen 2200 based propellants

Label	ADAN61	ADAN62	ADAN63	ADAN64	ADAN65	ADAN66
ADN/AN ratio	100/0	90/10	70/30	50/50	30/70	0/100
GAP	14.53	14.53	14.53	14.53	14.53	14.53
Desmophen	3.63	3.63	3.63	3.63	3.63	3.63
E305	0.35	0.35	0.35	0.35	0.35	0.35
N100	2.74	2.74	2.74	2.74	2.74	2.74
Energetic plasticizer	3.75	3.75	3.75	3.75	3.75	3.75
ADN	57	51.3	39.9	28.5	17.1	-
PSAN	-	5.7	17.1	28.5	39.9	57
Al	18	18	18	18	18	18

5.3 HTPB

With HTPB the highest solid load (83%) of the all investigated propellant was obtained. Despite that the oxidizer content is far from the required value but, it was not possible to produce a propellant with a total oxidizer content of 72% which leads to a total solid load of 90% in these first investigations.

Table 4. Composition HTPB based propellants

Label	ADAN74	ADAN75	ADAN76	ADAN77	ADAN78	ADAN79
ADN/AN ratio	100/0	90/10	70/30	50/50	30/70	0/100
HTPB	13.23	13.23	13.23	13.23	13.23	13.23
IPDI	1.22	1.22	1.22	1.22	1.22	1.22
DOA	2.55	2.55	2.55	2.55	2.55	2.55
ADN	65	58.5	45.5	32.5	19.5	-
PSAN	-	6.5	19.5	32.5	45.5	65
Al	18	18	18	18	18	18

5.4 Desmophen 2200

Desmophen was quite difficult to handle. It was possible to process an oxidizer amount of 60% if 8.8% of triacetin was added to the binder. With this solid load the theoretical performance is quite low, except for the propellant with ADN only.

Table 5. Composition Desmophen 2200 based propellants

Label	ADAN100	ADAN101	ADAN102	ADAN103	ADAN106	ADAN107
ADN/AN ratio	100/0	90/10	70/30	50/50	30/70	0/100
Desmophen	10.92	10.92	10.92	10.92	10.92	10.92
N100	2.28	2.28	2.28	2.28	2.28	2.28
triacetin	8.8	8.8	8.8	8.8	8.8	8.8
ADN	60	54	42	30	18	-
PSAN	-	6	18	30	42	60
Al	18	18	18	18	18	18

6. Mixing of Propellant ingredients

A planetary centrifugal mixer "THINKY MIXER ARV-310" was used to prepare the formulations. This device exploits two centrifugal forces (rotation and revolution) for mixing the materials without shearing. Vacuum can be also added to remove air bubbles caught in the materials. Thinky mixer is generally used to produce small amount of propellants because it is much faster than conventional kneader and there is no need to clean (no blades). The temperature during the mixing has to be controlled in order to avoid voids inside the propellant. Due to the impossibility to control it, the mixing time was adjusted experimentally while the RPM was set at 1600. Vacuum was used only after the addition of curing agent.

Figure 5. Thinky Mixer ARV-310

7. Experimental Setup

The burning behavior of each formulation was studied through burning tests at room temperature in the ICT´s window bomb floated with nitrogen [11]. Strands of propellant (5x5x20 mm) were burned at different pressure (1, 2, 4, 7, 10 and 13 MPa). The ICT´s window bomb allows conducting analysis in a pressure range from 0.1 MPa to 15 MPa in different atmospheres: air, argon, oxygen and nitrogen (as used here). The combustion tests are performed under constant gas flow in order to improve the recording quality removing smoke. There are 4 windows: 2 rectangular and 2 circular. The latter one is used for spectroscopy analysis and it gives the possibility to change the glass type in order to change the absorption peak and therefore it allows performing spectroscopy investigations at different wavelengths. The ignition was performed by a hot wire enhanced with a small charge of booster mixture. The combustion was recorded with a Redlake Motion Pro X 24 bit color high speed camera. The frame rate (25-64000 fps) and the exposure time can be set by the operator. Both parameters were set experimentally depending on the combustion time and the brightness of the flame respectively.

Figure 6. Experimental setup of window bomb and camera

The movies were processed with the software AVICOR32 and ABBRANDv2, both developed at ICT. The first one converts the time history of the burning surface in a sort of intensity histogram (Figure 7).

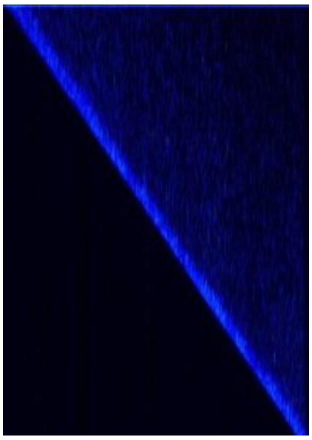

Figure 7. AVICOR32

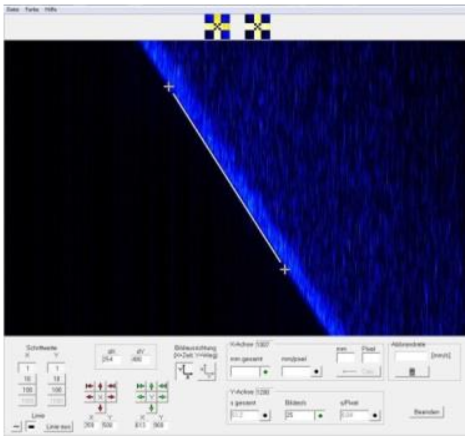

Figure 8. ABBRANDv2

ABBRANDv2 (Figure 8) allows to evaluate the slope of the line and by knowing the frequency and the equivalence between pixel and mm (obtained by a calibration picture) the combustion´s speed can be calculated. This procedure is described and in more detail by Weiser in [12].

8. Burning Behavior

8.1 GAP

Al/ADN/AN/GAP combustion was characterized by a high smoke production which, in some cases, could completely hide the combustion itself .This behaviour can be particularly noticed at high pressure (above 7 MPa) and with a high amount of ADN (above 70% of the total amount of oxidizer). This issue was solved adjusting experimentally the nitrogen mass flow during the combustion. The measurements were characterized by high scattering, especially at high pressure and high ADN content. This may be explained considering that ADN based propellants showed a mesa effect, a changing of slope of Vieille law, in the range of 7-10 MPa. Unfortunately it was measured just once for sample ADAN50 (100% of AN) at 1 MPa because of difficult ignition.

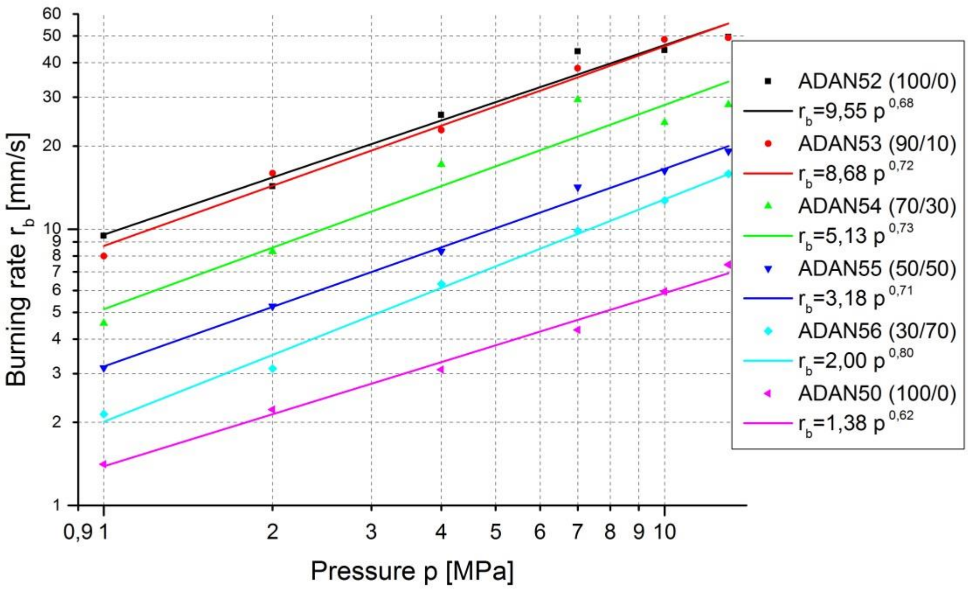

Figure 9. Burning behaviour of Al/ADN/AN/GAP/energetic plasticizer propellants

Table 6. Vieille Law's parameter, r_b and I_{sp} GAP based propellants

Label	**ADN/AN ratio**	**A [mm/s*MPa]**	**n**	**r_b at 7 MPa [mm/s]**	**I_{sp} [s]**
ADAN52	100/0	9.55	0.68	43.9	275.4
ADAN53	90/10	8.68	0.72	38.2	274.2
ADAN54	70/30	5.13	0.73	29.4	271.5
ADAN55	50/50	3.18	0.71	14.1	268.6
ADAN56	30/70	2.00	0.80	9.8	265.4
ADAN50	0/100	1.38	0.62	4.3	260.2

In Figure 9 the burning behaviour of GAP based propellants as a function of different ADN/AN ratios are reported while the Vieille´s Laws parameters, the burning rates at 7 MPa and the theoretical specific impulse can be found in Table 6. It was found that the burning rate of the propellant containing ADN only as an oxidizer is quite high (43.9 mm/s at 7 MPa) and a gain of almost 10 s in the theoretical specific impulse compared to the reference propellant. There are little differences in the behaviour between the ADN/AN ratio 100/0 and 90/10. The burning rate is 5.7 mm/s at 7 MPa (-13.05%) lower and the loss in the theoretical in the specific impulse is 1.2 s (-0.43%). This isn´t that dramatic, but the propellant is quite too fast for space application. In order to have an appreciable reduction in the burning rate, at least 30% of AN must be added, with which was reached 29.4 mm/s. In order to slow down the burning rate to 15 mm/s, the ADN ratio has to be lowered till 50%. ADAN55 and ADAN56 are in the range of 15-7 mm/s, with 14.1 mm/s and 9.8 mm/s respectively. The ballistic exponents are around 0.7 and barely acceptable for a practical use. One reason for the high burning rates could be the influence of the energetic plasticizer. It seems that the pressure exponent increases when both ADN and AN are present. The pressure exponent increase form 0.68 (ADAN52, ADN/AN ratio 100/0) to 0.73 (ADAN54, ADN/AN ratio 70/30). ADAN56 shows an anomalous value of 0.80 that is not in line with the other value. The measurements look good and a valid explanation was not found yet. The reason of the growth of ballistic exponent when both ADN and AN are present is not clear. It was supposed that it was influenced by the development of the eutectic but this thesis is not supported by clear evidences and more analysis are needed. It can be noticed that also the pressure exponent of ADAN50 (ADN/AN ratio 0/100) is quite high and not so far from the one computed for ADN oxidizer only (0.62 and 0. 68 respectively). This indicates that the ballistic response of the propellant is mainly ruled by the binder rather than oxidizer. ADAN52 can be compared with a similar formulation investigated in the former project HISP [13, 14]. The Al/ADN/GAP (16/60/24) propellant, without energetic plasticizer, exhibit a burning rate around 25 mm/s at 7 MPa with a pressure exponent of 0.58. This is quite different from the results achieved in this work: r_b is almost doubled, the ballistic exponent is increased. Considering that the particle sizes of the ingredients were very similar, the change in the burning rate could be ascribed to the energetic plasticizer used to produce the propellant.

8.2 GAP-Desmophen

These propellants burnt less smoky than the pure GAP based formulation. It showed also a good reproducibility also at high pressure and high ADN content.

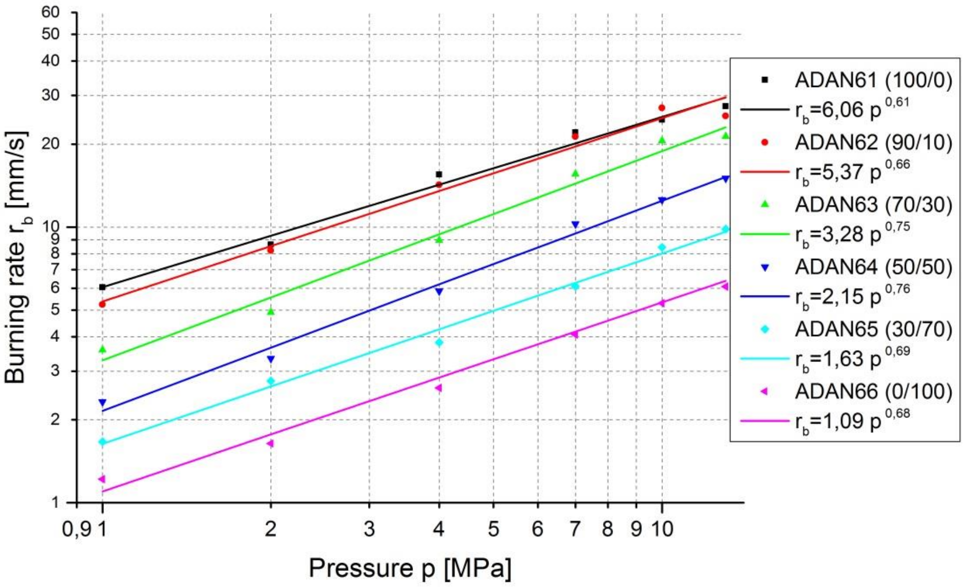

Figure 10. Burning behaviour of Al/ADN/AN/GAP/Desmophen/energetic plasticizer propellants

Table 7. Vieille Law's parameter, r_b and I_{sp} of GAP/Desmophen based propellants

Label	ADN/AN ratio	A [mm/s*MPa]	n	r_b at 7 MPa [mm/s]	I_{sp} [s]
ADAN61	100/0	6.06	0.61	22.0	273.7
ADAN62	90/10	5.37	0.66	21.2	272.3
ADAN63	70/30	3.28	0.75	15.5	269.3
ADAN64	50/50	2.15	0.76	10.2	265.9
ADAN65	30/70	1.63	0.69	6.0	262.6
ADAN66	0/100	1.09	0.68	4.0	257.4

In Figure 10 and Table 7 it can be noticed that the burning rates of ADAN61 and ADAN62 are very similar to each other (22.0 mm/s vs 21.2 mm/s) despite there is a difference of 10% in the ADN content and the loss of specific impulse is around 1.4 s. The burning rates are slower than the ones measured for the GAP based propellants but still too high for space booster application even if the energetic binder was decreased to 80% of the total binder and the filler content was just 75%. ADAN63 and ADAN64 show interesting values about both r_b and the theoretical specific impulse is superior to the reference propellant, computed under the same assumption. The pressure exponent is quite high for the all of the propellants and show similar behaviour as the ADAN5x series. The characteristic of increasing when both ADN and AN are present holds steady. A ballistic exponent of 0.61 is determined for ADAN61 (ADN/AN ratio 100/0) while ADAN64 (ADN/AN ratio 50/50) showed 0.76. ADAN65 and ADAN66 show almost equal values and the propellant with AN as oxidizer has a higher pressure sensitivity than the corresponding ADN propellant (ADAN61). Again the explanation of this trend is not clear and it has to be considered that it was used an energetic plasticizer which could influence the computed values.

8.3 HTPB

It was difficult to ignite the HTPB based at low pressure, especially with a high content of ADN. For this reason further pressure steps (2 and 3 MPa) were added. The Al/AN/HTPB propellant (ADAN79) could be ignited at 1 MPa while in present of ADN the lowest PDL (pressure deflagration limit) was 2 MPa. At 2 MPa ADAN75 could be ignited only ones on several attempts.

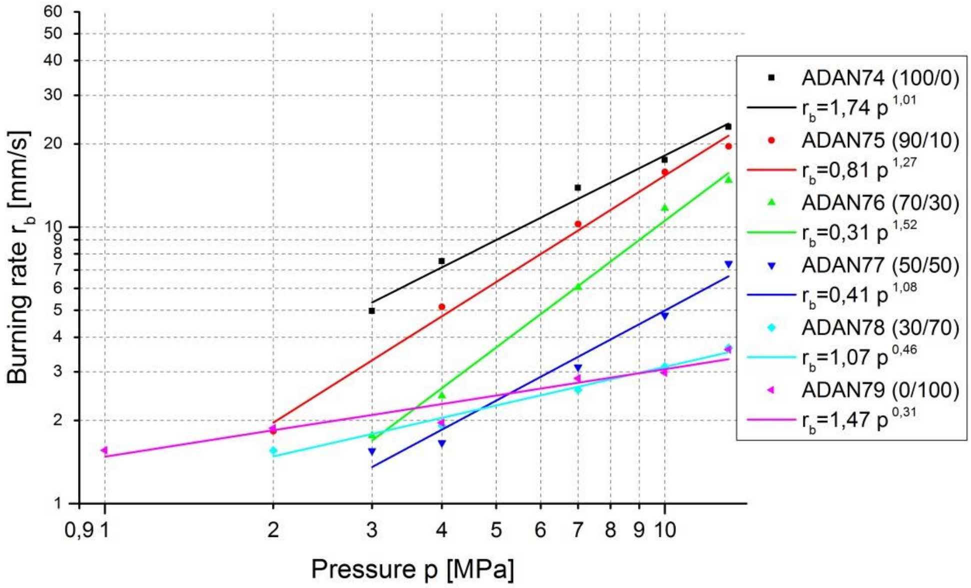

Figure 11. Burning behaviour of Al/ADN/AN/HTPB/DOA propellants

Table 8. Vieille Law's parameter, r_b and I_{sp} HTPB based propellants

Label	ADN/AN ratio	A [mm/s*MPa]	n	r_b at 7 MPa [mm/s]	I_{sp} [s]
ADAN74	100/0	1.74	1.01	13.8	269.7
ADAN75	90/10	0.81	1.27	10.2	268.3
ADAN76	70/30	0.31	1.52	6.0	264.4
ADAN77	50/50	0.41	1.08	3.1	259.8
ADAN78	30/70	1.07	0.46	2.5	254.8
ADAN79	0/100	1.47	0.31	2.8	247.1

Figure 11 showed the best fit received from the average of the measured burning rates while in Table 8 the Viellie law, average burning rate at 7 MPa and the theoretical specific impulse are reported. ADAN74 (ADN/AN ratio 100/0) shows a pressure exponent around 1 and a decent burning rate of 13.8 mm/s. The burning rate of ADAN75 (ADN/AN 90/10) is still good enough for launcher applications, the specific impulse is also suitable but the pressure exponent greater than one is too high for solid propellant rocket motor applications. The propellants with the higher amount of AN are not interesting due to low burning rates. Remarkable is the burning rate of ADAN79 (ADN/AN ratio 0/100) which reveals faster than the propellant with an ADN/AN ratio of 30/70 (ADAN78). The discussion of the pressure sensitivity is more intriguing. If a relative small amount of ammonium nitrate is added, the value of n increases. With the ADN/AN ratio of 90/10 n becomes 1.27 while with ADAN76 (ADN/AN ratio 70/30) it is 1.52, with a ratio of more than 50% compared is similar to ADAN74 (ADN/AN ratio 100/0). At an equal amount of ADN and AN, the ballistic exponent reduces to a value around one while when the amount of ammonium nitrate further increased (ADAN78-79) the propellants show a stable combustion with an intended low pressure exponent of 0.46 and 0.31 respectively. The formulation with ADN as oxidizer only (ADAN74, Al/ADN/HTPB binder 18/65/17) can be compared to a similar propellant discussed by De Flon [15]. In this work the formulation Al/ADN/HTPB 15/60/25 showed a pressure exponent of 0.87 and a burning rate of 11.5 mm/s at 6 MPa. Considering the higher solid load of ADAN74 the achieved results (n=1.01, r_b=13.8 mm/s) can be considered consistent.

8.4 Desmophen 2200

Desmophen showed a good reproducibility in the whole pressure range but the strands could not be ignited at 1 MPa. The PDL increases with the ammonium nitrate content. The propellant with pure ADN as oxidizer (ADAN100) could be ignited at 2 MPa, an ADN/AN ratio of 70/30 showed a combustion at 3 MPa and the PDL increased to 7 MPa for ADAN103 and 10 MPa for ADAN106 (ADN/AN ratio 30/70) respectively. ADAN107 (pure AN oxidizer) could be ignited only once at 13 MPa despite several attempts. It was unsuccessfully tried to ignite ADAN101 at 3 MPa.

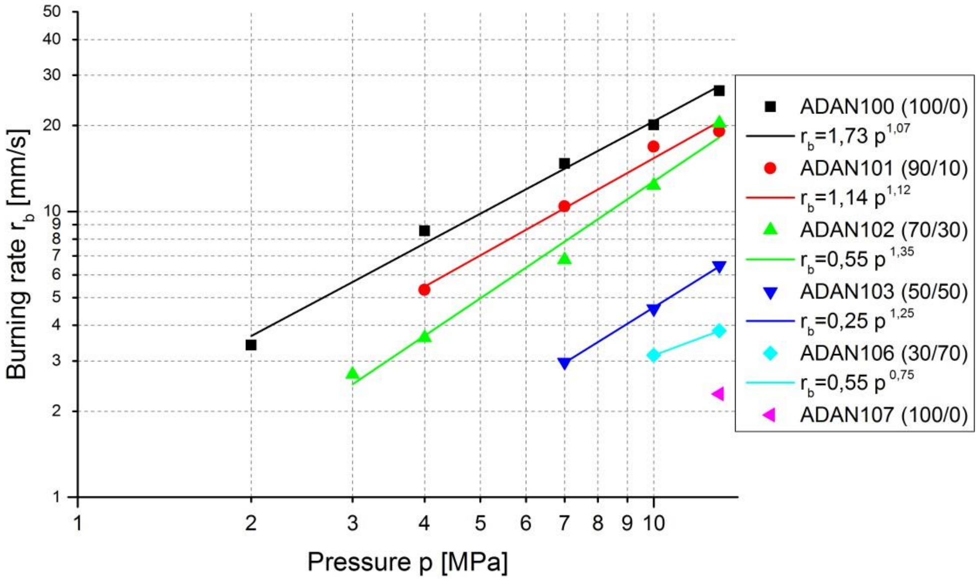

Figure 12. Burning behaviour of Al/ADN/AN/Desmophen/Triacetin propellants

In Figure 12 the Vieille Law is reported, while its parameters are reported in Table 9. Obviously it was not possible to compute a best fit for ADAN107 (pure AN oxidizer) from a single value. Also the parameters of ADAN106 must be handled with care because of the lack of data.

Table 9. Vieille Law's parameter, r_b and I_{sp} Desmophen 2200 based propellants

Label	ADN/AN ratio	A [mm/s*MPa]	n	r_b at 7 MPa [mm/s]	I_{sp} [s]
ADAN100	100/0	1.73	1.07	14.7	264.6
ADAN101	90/10	1.14	1.12	10.4	262.8
ADAN102	70/30	0.55	1.35	6.7	259.5
ADAN103	50/50	0.25	1.25	2.9	255.6
ADAN106	30/70	0.55	0.75	-	251.8
ADAN107	0/100	-	-	-	245.7

The low level of solid load achieved by preparation of the propellants led to poor values for the specific impulse. In the best case, with pure ADN (ADAN100), there is a loss of a second in comparison to the AP based reference propellant (265.7 s). Increasing the amount of ammonium nitrate reduces the I_{sp} significantly. The measured burning rates are quite good for ADAN100 and ADAN101, 14.7 mm/s and 10.4 mm/s respectively, but with 50% of ammonium nitrate of the total oxidizer content it drops to 2.9 mm/s. ADAN106 (ADN/AN ratio 30/70) and ADAN107 (ADN/AN ratio 0/100) do not burn at 7 MPa. The ballistic exponent is in the order the propellant with pure ADN (ADAN100) and it increases till 1.35 at an ADN/AN ratio of 70/30 (+26%) and decreases to 0.75, for ADAN106 (ADN/AN ratio 30/70). For more than 70% of AN, the pressure exponent gets almost acceptable but samples with such high amount of AN did not ignite.

9. Conclusion

In this work 24 different formulations based on three binder were investigated changing the ratio of ADN and AN but keeping the same amount of oxidizer in the all sets in order to create some preliminary results on a dual oxidizer propellant. All data have to be confirmed since this project is still in the first stages of development. An overview of the obtained results is presented in Figure 13 and Figure 14

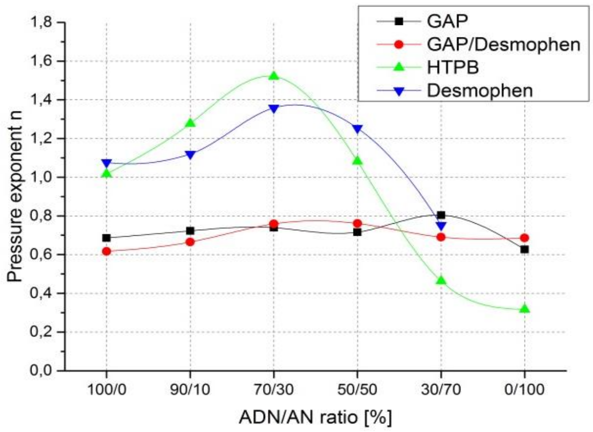

Figure 13. Pressure exponents

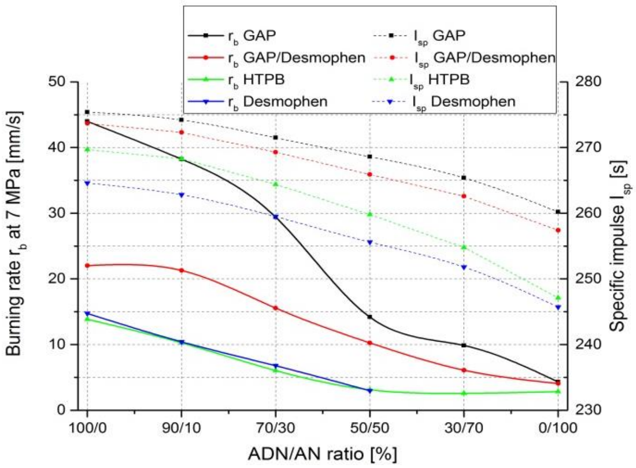

Figure 14. Burning rates and specific impulses at 7 MPa

It has been found that replacing a fraction of ADN with AN leads to reduced propellant burning rates without a dramatic reduction of the theoretical specific impulse. A drastic effect on the pressure sensitivity was discovered when ADN and AN are mixed together. The ballistic exponents tend to increase with increasing ADN/AN ratios in comparison to pure ADN as oxidizer. This behaviour is less correlated to the type of energetic binders and their mixtures (~+20%), but it leads to almost acceptable values for the pressure exponent. It becomes even higher amongst the inert binder. For the inert binder it has been found an increase of the ballistic exponent of 50% with HTPB and +26% with Desmophen by decreasing ADN/AN ratio in comparison to ADN oxidizer only. Especially for the formulation with promising values of specific impulse and burning rates the pressure exponent is too high. The partial replacement of GAP by an inert polymer has a good influence on the burning rate. It was nearly able to bisect the burning rate in a wide range of ADN/AN ratios.

Even if there are a lot of outstanding issues regarding the usability of the aluminized ADN/AN based propellants the initial investigations of the burning behaviour indicate that these propellants could be a potential replacement for Al/AP/HTPB propellants.

10. Upcoming Work

In the future the chemical stability of ADN/AN based propellants has to be investigated in more detail. It is reported in literature that mixtures of ADN and AN decompose and an eutectic is formed, decreasing the melting temperature of the compound till 60°C and increase ADN decomposition [16].

Another promising possibility, found during this this work, is to replace parts of the GAP binder by an inert binder. It has been proven that this can reduce the burning rate in comparison to GAP based propellants. Further inert binder shall be investigated. The use of a different particle size will help to increase the filler content and may also modify the pressure exponent and the burning rate. For the reduction of the pressure exponents burning rate modifiers will be needed too.

Furthermore the mechanical properties of the propellants have to be adapted

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Abbreviations and symbols

ADN	Ammonium dinitramide
AN	Ammonium nitrate
AP	Ammonium perchlorate
CNRS-IC2MP	Institute of Chemistry of Poitiers: Materials and Natural Resources at the Centre National de la Recherche Scientifique
DOA	Di-isooctyl-adipate
EDA	European Defence Agency
ESA	European Space Agency
FhG-ICT	Fraunhofer Institute for Chemical Technology
FOI	Swedish Defence Research Agency
GAP	Glycidyl azide polymer
GRAIL	Green advanced high energy propellant for launchers
HISP	High performance solid propellants for In-Space Propulsion
HTPB	Hydroxy terminated polybutadiene
IPDI	Isophorone diisocyanate
Isp	Specific impulse
n	Pressure exponent
N100	N-hexylmethylene diisocyanate – trimer (HDI biuret)
PDL	Pressure deflagration limit
PSAN	Phase stabilized ammonium nitrate
$\mathbf{r_b}$	Burning rate
RPM	Revolution per minute