Comparing AP- and AN-based propellants with low Aluminum content

M. Fassina, S. Dossi, L. Galfetti and L. T. DeLuca
**Politecnico di Milano, Dept. of Aerospace Science and Technology*
34, Via La Masa, 20156 Milan, Italy

Abstract

The increasing interest to environmental conditions during last years has prompted efforts from several research groups to identify alternative and less polluting solid rocket propellant formulations. The growing interest and utilization of this mature technology both for civil and military application requires a review in frame of cleaner emissions. A comparison between thermo-chemical analysis and burning rate test to evaluate performance and exhaust emissions is carried on for three propellants loaded with 4% of nano-Aluminum: 1) AP-based; 2) AN-based; 3) dual-oxidizer propellants. Results show advantages adopting AN and dual-oxidizer in terms of emissions, even if performance are not totally satisfactory.

1. Introduction

Nowadays environmental issues are becoming more and more pressing in each scientific and technical field. Along this path some research projects are dealing with the development of new and innovative solid rocket propellant formulations more environmentally friendly. Actually Ammonium Perchlorate (AP) plays a leading role in space propulsion as oxidizer because it has several pros, such as high oxidation power, high density, no phase transition (during production and stock phase) and high reliability [1].

On the other hand the main drawbacks are the generation of Chlorine products during the combustion, especially HCl, which are responsible for acid pollution nearby the launch sites. A huge quantity of smoke is ejected by nozzles, which could affect and disturb local communication because of the emission of free electrons in the plumes and Al_2O_3 dispersed particles could react and deteriorate ozone layer [2] [3] [4]. Thus new formulations as well as AP substitutes are under study in order to reduce launch environmental impact, as, for examples, energetic binder as GAP, PNIMMO, BAMMO/AMMO or chlorine-free oxidizer as Cl20, AND, AN, HNF [5] and dual-oxidizer, as AP/AN mixtures, are all good options. Ammonium Nitrate (AN) is a promising substitute because it generates Chlorine-free and environmentally friendly combustion products and it is a very low-cost oxidizer, this allows a dramatic reduction of operative and production costs [6]. However AN presents different drawbacks:

- high grade of hygroscopicity [7] [8], due to this issue strong quality controls are required to avoid the contaminations in a humid ambient, during production, stocking and utilization,
- low density [7], (performance reduction in terms of volumetric specific impulse),
- limited oxidation capability [7],
- low efficiency in burning Al particles [8],
- several highly endothermic transition phases [8] [9] [10]; AN crystal has 5 crystalline phase (-18°C; 32.1°C; 84.2°C; 125.2°C),
- liquid phase at 169.6°C that endures till evaporation at 210°C [7] [11],
- necessity to intensify the thermal decomposition [9] [12],
- low value of burning rate, gravimetric and volumetric specific impulse, when used in solid rocket propellants (in comparison with AP) [7].

Some of these issues have already been investigated and some solutions are already available. The transition phase at 32.1 °C, for example, represents a severe problem since not only it is very close to ambient temperature, but it can also produce cracks inside the grain due to density variations. This peculiarity can be hindered adding some additives such as MgO, NiO, CuO and ZnO capable to eliminate the transition phase at across 32.1°C [8] [9] [10]. To increase the thermal decomposition, as Fe_2O_3 or $Fe(NO_3)_3$ [9], have been studied as well.

The presence of a thick liquid layer on the burning surface generated by AN melting [7] [11], reduces the heterogeneity on the surface itself, but dramatically reduces the burning rate and, at the same time, increases the

effect and the action time of the retaining forces allowing the formation of large agglomerates [12], consequently strongly reducing performance.
In this thick liquid layer is present a mixture of liquid Al and Al_2O_3 [13] [14] bringing to the generation of large agglomerates which are responsible of important two-phase flow losses, concentrated mainly in the nozzle. These big particles also cannot be completely burnt passing through the combustion chamber, producing an additional loss caused by the poor combustion of the aluminum particle.
The introduction of nAl has the aim to reduce the size of the agglomerates, thus reducing losses due to the two-phase flow and the incomplete combustion of the metal fuel [13], making the system more efficient.
Dual-oxidizer propellants (AP/AN mixtures) have some advantages in comparison with AN-based propellants and solve some of the problems connected with AN.
The presence of AP increases the burning rate, the gravimetric and the volumetric specific impulse thanks to a higher oxidation power of AP, which makes the propellant more reactive. AN, decomposing, generates Nitrogen oxides, which are catalysts for the decomposition of AP, so the decomposition process of the whole propellant in enhanced [9]. Increasing the decomposition process involves the increment of the overall performance.
A higher burning rate means also a reduction of the residence time of the agglomerates over the burning surface, so they have less time to grow, that is why dual-oxidizer propellants have smaller agglomerates than AN-based propellants. This fact reduces the two-phase flow losses and increases the combustion efficiency of Al particles [9] [12]. Moreover, the introduction of AP makes the propellant less sensitive to the pressure oscillation and lowers the pressure deflagration limit (PDL) [12].

2. Thermo-chemical analysis

A thermo-chemical analysis is carried on to point out the relationship between performance and exhaust composition for solid rocket propellant with different ratios of AN and AP.
At first, considering a generic formulation composed by 14% of binder (HTPB+DOA+IPDI), 4% of nAl (Al_01_i, EEW, uncoated) and 82% of oxidizer, we made a parametrical analysis on the performance and the theoretical plume exhaust composition substituting AN to AP range from 0% to 82% in mass of the solid rocket propellant.
The thermo-chemical simulation has been made with the CEA code, developed by NASA. The reference condition selected are pressure inside the combustion chamber (P_c) of 70 bar, the area ratio (A_e/A_t) of 40 and the shifting equilibrium condition.

Table 1: Exhaust gases composition from the parametrical analysis varying AP and AN mass fraction. Simulation conditions considered: P_c=70 bar; A_e/A_t=40; Shifting equilibrium flow.

	AN 82% AP 0% [%]	**AN 72% AP 10% [%]**	**AN 62% AP 20% [%]**	**AN 52% AP 30% [%]**	**AN 42% AP 40% [%]**	**AN 32% AP 50% [%]**	**AN 22% AP 60% [%]**	**AN 12% AP 70% [%]**	**AN 0% AP82% [%]**
AlCl	-	-	-	-	-	-	0.001	0.003	0.009
$AlCl_2$	-	-	-	-	-	-	-	0.001	0.004
$AlCl_3$	-	-	-	-	0.001	0.002	0.005	0.001	0.021
AlOCl	-	-	-	-	-	-	0.005	0.002	0.005
AlOH	-	-	-	-	-	0.001	0.002	0.004	0.01
AlOHCl	-	-	-	-	-	-	0.001	0.003	0.009
$AlOHCl_2$	-	-	0.001	0.004	0.013	0.028	0.054	0.096	0.17
$Al(OH)_2$	-	-	-	-	-	-	0.001	0.002	0.003
$Al(OH)_2Cl$	-	-	0.002	0.005	0.011	0.020	0.034	0.054	0.085
$Al(OH)_3$	0.001	0.002	0.003	0.006	0.012	0.017	0.023	0.031	0.042
CO	19.982	20.235	20.396	20.472	20.466	20.312	20.156	19.920	19.542
CO_2	12.124	11.727	11.475	11.356	11.364	11.606	11.851	12.221	12.815
Cl	-	0.001	0.003	0.009	0.026	0.055	0.128	0.273	0.601
ClO	-	-	-	-	-	-	-	-	0.001
Cl_2	-	-	-	-	-	-	0.001	0.002	0.005
H	-	-	0.001	0.001	0.002	0.004	0.006	0.010	0.017
HCl	-	3.103	6.203	9.296	12.373	15.432	18.434	21.346	24.65
HOCl	-	-	-	-	-	-	-	-	0.001
H_2	2.324	2.129	1.940	1.757	1.580	1.415	1.251	1.095	0.923
H_2O	29.545	29.087	28.570	27.995	27.363	26.631	25.875	25.034	23.889
NH_3	0.005	0.004	0.003	0.003	0.001	0.001	0.001	-	-

NO	-	-	-	-	0.001	0.002	0.005	0.013	0.030
N_2	28.817	26.510	24.203	21.897	19.590	17.282	14.973	12.662	9.885
O	-	-	-	-	-	-	-	0.001	0.005
OH	-	0.001	0.002	0.005	0.013	0.025	0.057	0.117	0.251
O_2	-	-	-	-	-	-	-	-	0.011
$Al2O_3$	7.202	7.201	7.199	7.193	7.182	7.166	7.138	7.094	7.013

Results show that the substitution of AP in place of AN slightly change the production during the combustion process of the chemical species CO and CO_2. The effect oxidizer change is more evident focusing on the species H_2, H_2O and N_2, where it is possible to notice a constant depletion, and a constant increment of HCl, and other chlorinated elements caused by AP. In Figure 1 the trend of these species is reported with the ratio AP/AN.

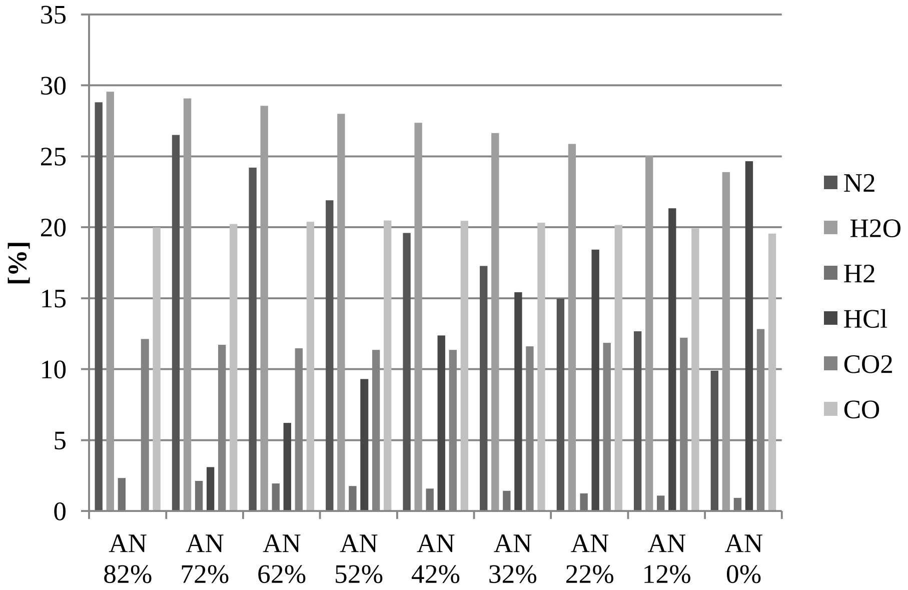

Figure 1: Comparison of the most relevant combustion products

It is evident from Figure 1 how the substitution is almost irrelevant on the production of CO and CO_2 because of the reaction with the binder, instead the generation of N_2 is strongly reduced with AN, essentially, due to the different nature of the two oxidizer. Figure 1 shows the production of HCl is really high, and it can reach almost a quarter of all the total amount of the products. This leads to the consequence of a very polluting plume exhaust, which could deplete ozone, and generate local pollution with a high concentration of acid species very dangerous for the environment. This is a relevant drawbacks that should be solved.

Gravimetric specific impulse in vacuum and under shifting equilibrium condition shows a trend of constant growth with the increasing presence of AP in the solid propellant formulation. This is due to the fact that AP is able to produce higher exothermic reactions, which allow to reach also higher temperature in the combustion chamber. AN presents also highly endothermic phase transitions, which require a certain amount of energy to take place, and this fact, with a lower reactivity of AN itself determine a lower specific impulses. In the Figure 2 and Table 2 this phenomenon is illustrated in detail.

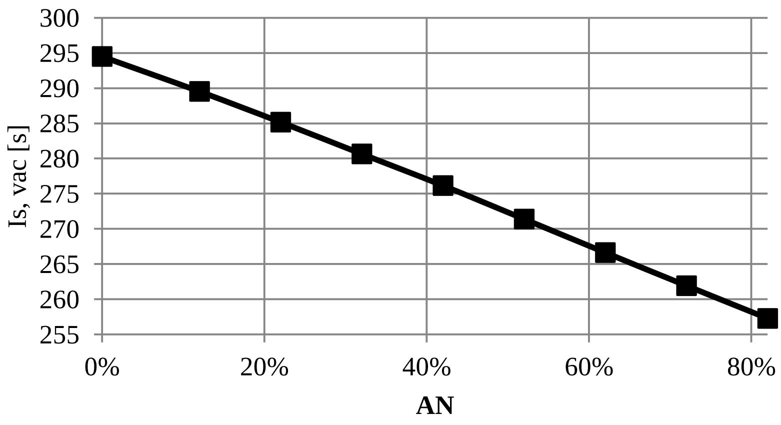

Figure 2: Gravimetric specific impulse vs. AN percentage

Table 2: Gravimetric specific impulse in vacuum trend with AN concentration

	AN 82%	**AN 72%**	**AN 62%**	**AN 52%**	**AN 42%**	**AN 32%**	**AN 22%**	**AN 12%**	**AN 0%**
$I_{s,vac}$ [s]	257.27	261.92	266.63	271.39	276.15	280.64	285.16	289.52	294.49

Actually AN-based propellant performance cannot be yet comparable to AP-based propellant performance. Gravimetric specific impulse decreases with the addition of AN in place of AP in the formulation and also the same trend is even enhanced considering the volumetric specific impulse because AP presents a higher density than AN.
In Figure 3 is reported the trend for the temperature in the combustion chamber obtained from the numerical simulation, it presents the same behavior seen with $I_{s,vac}$.

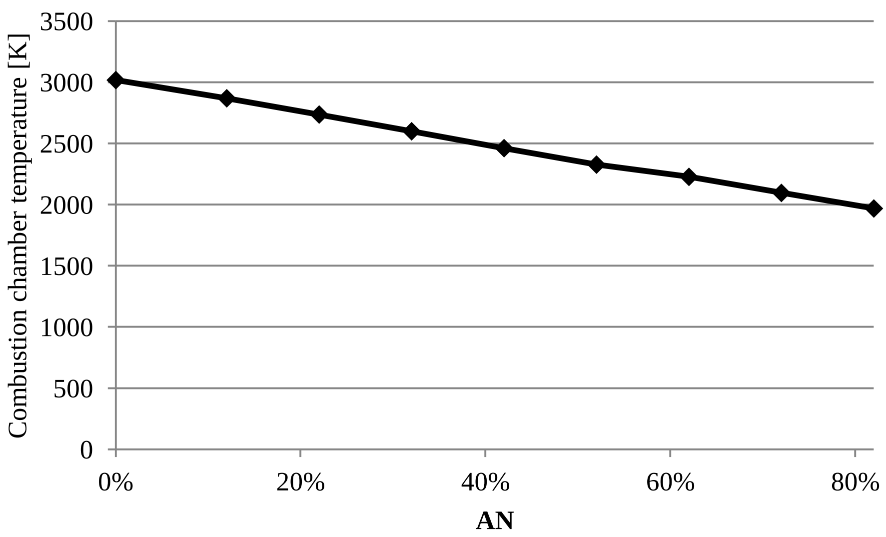

Figure 3: Decreasing combustion chamber temperature dependence on increasing concentration of AN

In the present work three different compositions were analyzed: 1) containing only AP as oxidizer; 2) containing only AN as oxidizer and 3) containing the dual-oxidizer (AP/AN), with a ratio AN/AP equal to 60/40, selected as optimum from previous research activities conducted at SPLab [9] [12], as reported in Table 3.

Table 3 - Formulation tested

	Average size [μm]	**1**	**2**	**3**
Binder	-	14.0 %	14.0 %	14.0 %
AP coarse	200	72.0 %	0.0 %	38.8 %
AP fine	<10	10.0 %	0.0 %	4.0%
AN coarse	200	0.0 %	72.0 %	43.2 %
AN fine	<10	0.0 %	10.0%	6.0 %
nAl	0.1	4.0 %	4.0 %	4.0 %

As before, the comparison between the three formulations was done comparing performance and exhaust compositions. In Table 4 the compositions of the plume exhausts are reported.

Table 4: Plume exhaust chemical compositions of the three propellants tested

	1 [%]	**2 [%]**	**3 [%]**		**1 [%]**	**2 [%]**	**3 [%]**
AlCl	0.009	-	-	ClO	0.001	-	-
$AlCl_2$	0.004	-	-	Cl2	0.005	-	-
$AlCl_3$	0.021	-	-	H	0.017	-	0.001
AlOCl	0.005	-	-	HCl	24.65	-	10.160
AlOH	0.01	-	-	HOCl	0.001	-	-
AlOHCl	0.009	-	-	H_2	0.923	2.324	1.707
$AlOHCl_2$	0.17	-	0.006	H_2O	23.889	29.545	27.824
$Al(OH)_2$	0.003	-	-	NO	0.03	-	-
$Al(OH)_2Cl$	0.085	-	0.006	N_2	9.885	28.817	21.251
$Al(OH)_3$	0.042	0.001	0.008	NH_3	-	0.005	0.002
CO	19.542	19.982	20.478	O	0.005	-	-
CO_2	12.815	12.124	11.345	OH	0.251	-	0.007
Cl	0.601	-	0.012	O_2	0.011	-	-

Data for the most relevant combustion products (HCl, H_2O, CO_2, CO, H_2, N_2 and Cl) are also illustrated in Figure 4.

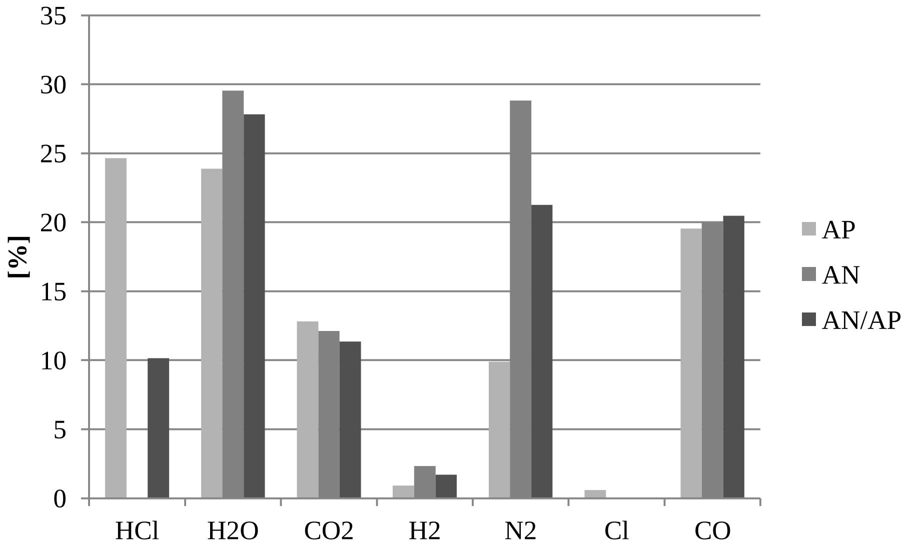

Figure 4: Exhaust chemical composition for the three selected oxidizers

It is evident, and obvious, that reducing the quantity of AP there is a strong reduction of acid pollution. Indeed the presence of HCl goes from almost the 25 %, with only AP as oxidizer, to, naturally 0, with only AN as oxidizer; in the middle there is the dual-oxidizer propellant, with a strong reduction of HCl (and all the other chlorine products as well). AN-based propellants present more than a half of the species generated during the combustion constituted by

N2 and H2O, gases totally environmentally friendly, that is why even if AN still has some important drawbacks, it represents one of the most suitable substitute for AP leading to a “greener” propulsion technology.

Concerning performance, the better efficiency of AP in oxidizing Aluminum particles and higher exothermic reactions during the combustion, plus the presence of several endothermic transition phases of AN, place AP in a better position in comparison to AN. The corresponding ideal gravimetric specific impulses are reported in Table 5 for the three formulation tested.

Table 5: Ideal gravimetric specific impulse in vacuum for the formulations analyzed

	1	**2**	**3**
$I_{s,vac}$ [s]	294.49	257.27	272.72

Propellant 1 shows an increment in the performance of about 12.64 % comparing to the propellant 2, meanwhile the propellant 3 has an increment of 5.67%.

3. Experimental results

The propellants samples needed for ballistic testing were prepared with a new technique available in SPLab. Instead of the typical mechanical mixer, the Resodyn Acoustic Mixer LabRAM was used. This new tool allows some advantages with respect to the former technique, as the possibility to work under vacuum (reachable range of 0.2 – 0.15 bar) during all the production process, and the reduced chance of inclusion of external elements that could happen during the mixing with blades. Moreover it is proven that mixing time and speed of the blades can modify the oxidizer particle granulometry [15] that could possibly lead to unexpected results under certain circumstances. There are no studies yet which show a similar effect of the mixing with an acoustic mixer on the oxidizer particle size.

3.1 Burning rate facility

The windowed strand burner technique has been used in order to obtain results about the burning rate (r_b). The pressure regime adopted for the tests goes from 5.5 bar up to 40 bar. The pressurizing gas is Nitrogen. The scheme of the testing apparatus is sketched in Figure 5.

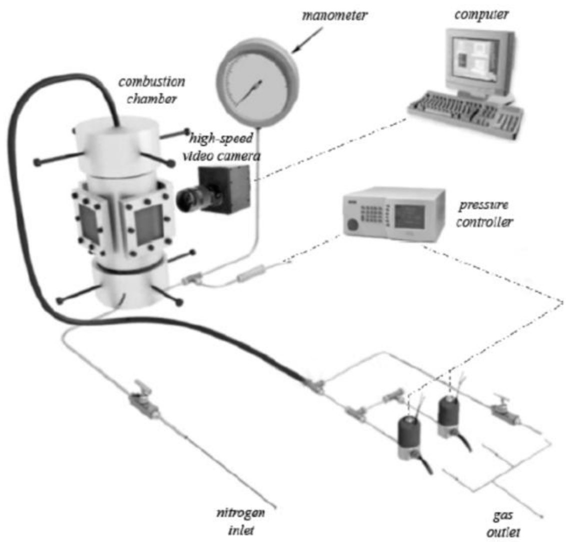

Figure 5: Burning rate apparatus scheme

As it is possible to see in Figure 5, the experimental apparatus is composed by:

- combustion chamber
- pneumatic system
- high-speed video-camera
- acquisition system/pressure controller.

Videos have been recorded at 60 fps in order to have a good quality during the image processing to evaluate the burning rate. The shutter regulation was determined each time depending on the natural luminosity of the propellant flame.

3.2 Samples preparation

Propellants are cut into samples having a shape of a rectangular parallelepiped with sizes of 4 mm x 4 mm x 30 mm. Once cut, it is necessary to inhibit the lateral surface in order to guarantee a regular combustion. The inhibitors used are Paraloid B72, dissolved in Methyl Ethyl Ketone (MEK), with a mass ratio of 1:5, for propellants 1 and 3; instead to inhibit propellant 2 an hydrocarbon with low molecular weight was used.

3.3 Combustion tests

The standard procedure is to achieve (at least) three valid combustion tests for each pressure. The pressures considered are 5.5 bar; 10 bar; 20 bar; 30 bar; 40 bar. Ignition is given by a Nichrome wire, using the Joule effect, which ignites the sample, starting the combustion. Data from the combustion tests are reported in Table 6 and 7, in the form of the classical Vieille law: $r_b=a\cdot\exp(n\cdot\ln(P_c))$.

Tab. 6: Burning rate data obtained from the combustion tests for the three tested formulations

P_c [bar]	1 [mm/s]	2 [mm/s]	3 [mm/s]
5.5	3.2825	-	-
5.5	3.3686	-	-
5.5	3.3356	-	-
10	4.6376	0.7712	-
10	4.7372	0.8066	-
10	4.6166	0.7110	1.2594
20	7.0339	1.2924	2.3058
20	6.9384	1.2811	2.3155
20	6.9284	1.3018	2.2981
30	8.4728	1.7034	3.1462
30	8.4439	1.7481	3.1253
30	8.4760	1.6277	3.1266
40	10.2020	1.9539	3.5582
40	10.2570	1.9854	3.6969
40	10.3900	1.9882	3.7742

Table 7: Vieille law coefficients for the three tested formulations

	a	n	R2
r*	1.08	0.49	0.992
1	1.28	0.56	0.999
2	0.16	0.70	0.989
3	0.31	0.68	0.988

* [16]

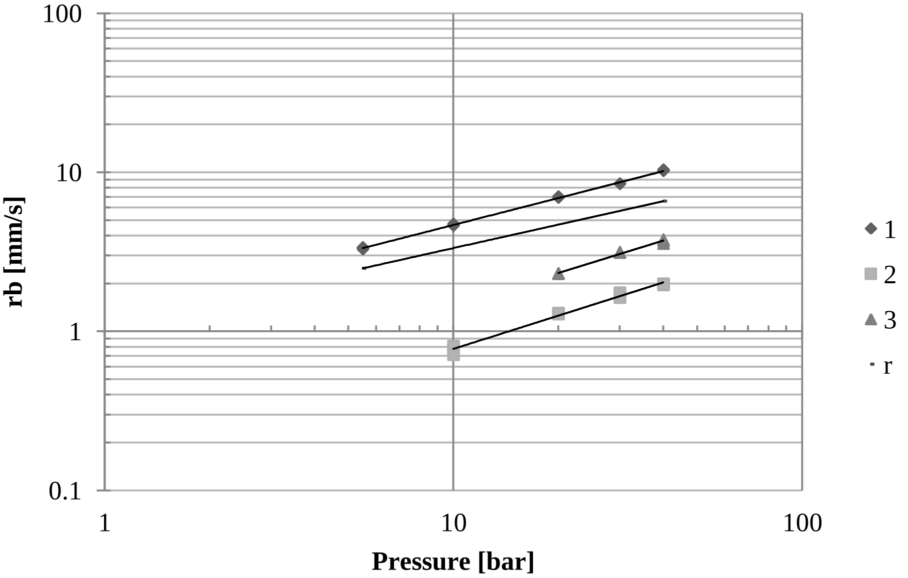

Figure 6: Burning rate for the three tested formulations

The results of the combustion tests are presented in Figure 6. The propellant 1 shows a regular behavior along all the pressure range, it has also a value of the ballistic exponent lower than the other propellant tested, that means a propellant with less sensitivity to pressure fluctuations.
Propellants 2 and 3 have shown bad behaviors during the combustions with absence of combustion and self-quenching combustion at lower pressure (5.5 and 10 bar). With these pressures it has been difficult to complete valid burning tests due to the oscillating behavior of the samples during the combustion.
Propellants 2 and 3 present a high value of the ballistic exponent “n”, 0.70 and 0.68 respectively. This means that propellants charged with AN show a higher sensitivity to the pressure fluctuations. They also has a higher value of PDL due to the difficulty in igniting and maintaining the combustion process sustained, because of the intrinsic nature of AN.
Propellant r [16] has the following composition: 14% binder (HTPB+DOA+IPDI), 82% AP (72% coarse, 10% fine), and 4% Al (30 µm spherical, space-grade type III). It has been introduced in Figure 6 to compare the effects of nAl and µAl into solid rocket propellants charged with low quantity of metal fuel.

Propellant 1 has a higher value of the ballistic exponent n respect with the propellant r, so leading the propellant to be more reactive, because with nAl there is the exploitation of the chemical energy with a less thermal inertia in comparison with micrometric Aluminum. On the other hand higher n means a system more sensitive to pressure fluctuations.

4. Conclusion and final remarks

Some technical issues regarding an extensive use of AN as oxidizer in solid rocket propellant systems have been solved, as the problem of the phase stabilization and the problem of increasing its thermal decomposition, by adding different additives. However, the performance that an AN-based propellant could reach is still to be satisfactory for the specifications required by the current space launchers. More effort is still necessary to abandon AP in order to substitute it with other oxidizers environmentally more friendly and with cleaner emission.

A dual-oxidizer formulation presents several advantages in comparison with the AN-based propellant from the point of view of the performance, with higher burning rate and specific impulses, and fewer losses for incomplete Aluminum combustion and for the multiphase flow.

A dual-oxidizer formulation presents also advantages in comparison with AP-based propellant with a strong reduction of the acid and toxic emission which could affect the environment nearby the launch site as well as the atmosphere surrounding it, by the intake of HCl and fine Al_2O_3 from the plume exhaust, which could generate an acid fall-out due to acid rain and could create local detriment of the ozone layer.

The introduction of a low quantity of Al powder, in comparison with most common values of 16-19%, has been adopted to guarantee a minimum level of high frequency pressure oscillation dumping, with the intent to keep low the production of Al_2O_3; in fact Al condensed combustion products have the helpful ability to damp acoustic pressure instabilities in solid rocket propellants [17].

To complete this investigation future activities include the analyses of the agglomeration process by visualization technique and the collection of the combustion residuals from one side, and from the other side to test propellant modified by additives for phase stabilization and increment of thermal decomposition.

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