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Optimization of ignition properties and agglomeration features of the main metal-based fuel candidates

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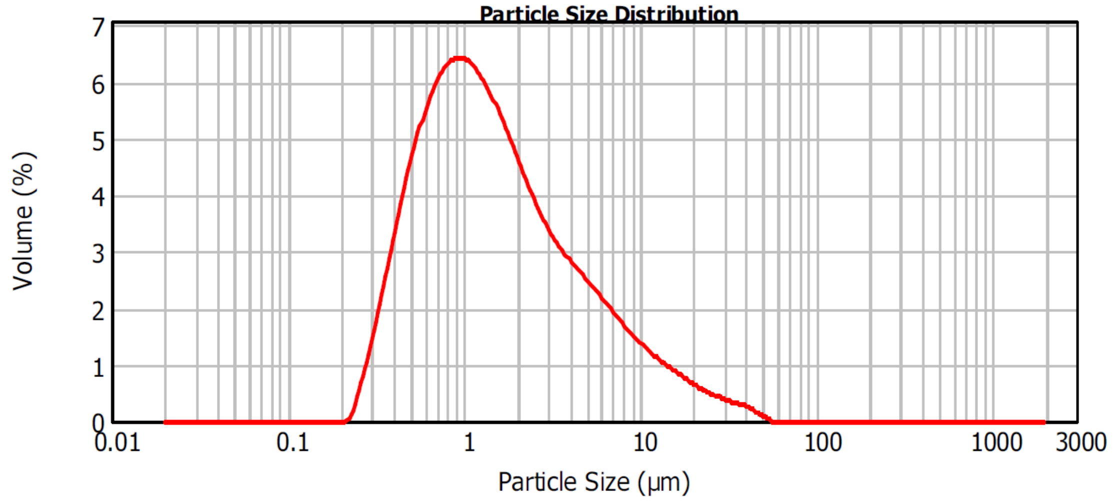

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Image on the front page:
Particle size distribution of the condensed combustion products produced by a propellant fuelled with nanoaluminum burning at 10 bar.

Summary

HISP project aims at the development of solid rocket propellants with high specific impulse, leveraging on the proper choice of binder, oxidizer and fuel. Work package 5 focuses on the use of metal as high-energy density fuels. In previous deliverables, physical and chemical characterization of ingredients as well as analyses of combustion properties for relevant AP/HTPB/Metal propellants were performed. This set of investigations allowed for a relative grading among the tested group and a more detailed screening was focused on a set of three ingredients: one type of nanometric aluminum (nAl-03), one type of activated aluminum (actAl-02), and a baseline micrometric aluminum (µAl-03). Initial optimization of fuel mixes was also performed.

From this preliminary set of data, a good compromise between metal content, processability, reactivity, agglomeration, and steady burning rate was found to be represented by blends of micrometric and nanometric aluminum powders.

The present report focuses on the analysis of such behavior. Nanoaluminum content is now varied across a narrow range in proximity of the initially selected nAl fuel mass fraction and combustion properties are investigated. The analysis carried out comprises steady burning rate assessment, ignition delay, and condensed combustion residues.

Contents

1 Introduction

HISP project aims at developing high specific impulse solid rocket propellants, taking advantage of proper modifications in propellant formulations. From one side, the objective is accomplished by addressing an ADN/GAP baseline formulation which grants itself a higher specific impulse, when compared to standard AP/HTPB propellants. On the other side, the use of high-energy density ingredients should contribute to specific impulse increment by increasing its ideal value and/or reducing 2P flow losses. In a first stage of the work, from the initial list of tested materials (details are given in Table 1), only actAl-02 and nAl-03 powders were selected for further characterization.

Table 1. High energy density fuels tested during HISP project. Conversion table nomenclature for chemical ingredients.

New Label	**Old Label**	**Nom. Size**	**Description**
nAl-01	n-Al01	50 nm	Industrial ALEX^{TM} nanoaluminum naturally coated by aluminum oxide.
nAl-02	n-Al02	100 nm	Industrial ALEX^{TM} nanoaluminum naturally coated by aluminum oxide.
nAl-03	n-Al03	100 nm	Industrial ALEX^{TM} nanoaluminum coated by fatty acid (stearic or palmitic) before air exposure.
actAl-01	A-Al01	3 μm	Activated aluminum powder 1 from Valimet.
actAl-02	A-Al02	3 μm	Activated aluminum powder 2 from Valimet.
actAl-03	A-Al03	3 μm	Activated aluminum powder 3 from Valimet.
Valimet	Valimet	3 μm	Spherical aluminum produced by Valimet, H3 cut.
μAl-01	Al-01	15 μm	Space-grade spherical aluminum.
μAl-02	Al-02	70 μm	Industrial-grade aluminum with shape of flakes produced by Metalpolveri S.p.A.
μAl-03	Al-03	30 μm	Space-grade spherical aluminum (added after the first plenary meeting).
AlH_3	AlH_3		Aluminum hydride

Standard AP/HTPB/Metal propellant combustion analysis was performed using the reference formulation described in Table 2. Full details and compositions addressed in the past work are listed in Table 3.

Table 2. General propellant formulation.

Id.	**Mass fraction, %**	**Description**
AP 200	58	Oxidizer, nominal size: 200 μm
AP 10	10	Oxidizer, nominal size: 10 μm
HTPB	14	HTPB-based elastomer
Metal Fuel	18	---

Table 3. Propellant labels and relevant details of the fuel with conversion table nomenclature. Quantities are expressed on a mass-basis and referred to the whole propellant mass.

New Id.	Old Id.	Details of fuel
P-µAl-01	P-Al-01	18% of µAl-01
P-µAl-02	P-Al-02	18% of µAl-02
P-µAl-03	P-Al-03	18% of µAl-03 (baseline)
P-Valimet	P-Valimet	18% of Valimet
P-actAl-01	P-A-Al01	18% of actAl-01 (for comparison)
P-actAl-02	P-A-Al02	18% of actAl-02
P-nAl-03	P-n-Al03	18% of nAl-03
P-MIX--µAl-03—actAl-02	P-MIX-Al-03-A-Al02	15% µAl-03 and 3% actAl-02
P-MIX--µAl-03—nAl-03	P-MIX-Al-03-n-Al03	15% µAl-03 and 3% nAl-03
P-MIX--µAl-03--nAl-03—actAl-02	P-MIX-Al-03-n-Al03-A-Al02	15% µAl-03, 1.5% nAl-03 and 1.5% actAl-02
P-MIX—actAl-02—nAl-03	P-MIX-A-Al02-n-Al03	15% actAl-02 and 3% nAl-03

From the whole set of analysis, the most promising compositions consisted of the nanoaluminum-microaluminum (µAl-nAl) blends which resulted in a compromise between low agglomeration tendency, mild increment of burning rate, as well as reduced metal content loss due to aluminum passivation.

The interest of the present document focuses on the optimization of propellant formulation P-MIX--µAl-03--nAl-03 which was selected in a first tentative study. Fine tuning of nAl content is still required.

It should be noted that, in the body of WP6, parallel combustion analyses on ADN/GAP- and AP/HTPB-based propellants demonstrated that different behavior may occur for metal fuel and conclusions resulting from one propellant family cannot be blindly generalized. Some peculiarities (now under investigation) are emerging. However, the interest in such ingredients and in this type of formulations is still high due to the fact that these fuels can be used to obtain a sensible combustion improvement in standard propellants. *De-facto*, they represent a key point for increase of deliverable specific impulse if a change in the basic matrix (oxidizer/binder) technology is not envisaged.

2 Propellant formulations

The fine tuning of propellant composition is accomplished by taking as a reference the formulation reported in Table 2, commonly adopted in all tested propellants. Starting from P-MIX--µAl-03--nAl-03 which has 3% by mass of nAl-03 and 15% by mass of µAl-03, fractions of µAl and nAl are progressively varied in the proximity of the previously tested value to obtain P-MIX--µAl-03--nAl-03-1.5% (containing 1.5% of nAl) and P-MIX--µAl-03–nAl-03-4.5% (containing 4.5% of nAl). For a matter of comparison, this document also reports data about propellants P-nAl-03 (containing 18% of nAl-03) and P-µAl-03 (with baseline Al-03 powders), which were discussed in detail in the previous deliverables. A summary of composition details is reported in Table 4.

Table 4. Details of tested propellants for nAl fine tuning.

Id.	Details of fuel
P - μAl-03	18% μAl-03 (baseline)
P - nAl-03	18% nAl-03 (data available)
P-MIX--μAl-03-- nAl-03-1.5%	16.5% μAl-03 and 1.5% nAl-03
P-MIX--μAl-03--nAl-03	15% μAl-03 and 3% nAl-03 (data already available)
P-MIX--μAl-03--nAl-03-4.5%	13.5% μAl-03 and 4.5% nAl-03

All formulations have been characterized using the procedures and the experimental techniques already addressed in deliverables D5.2 and D5.3, which can be considered for reference by the reader.

3 Density measurement

Measurement is performed by means of hydrostatic weighting technique, using commercial grade ethyl alcohol (95% concentration) as working fluid. Three valid tests for each propellant are used for the estimation of density. Results and relevant uncertainties are reported in Table 5, along with porosity. The theoretical propellant density (TMD), assuming 100% of aluminum in the fuel, is 1.761 g/cm^3.

Table 5. Density characterization of propellants. Uncertainty is computed assuming a t-student distribution and a 95% of confidence level.

Id.	Density, g/cm^3	ρ/TMD, %
P - μAl-03	1.751 ± 0.010	99.4
P - nAl-03	1.729 ± 0.005	98.2
P-MIX -- μAl-03 -- nAl-03-1.5%	1.699 ± 0.013	96.5
P-MIX -- μAl-03 -- nAl-03	1.745 ± 0.006	99.1
P-MIX -- μAl-03 -- nAl-03-4.5%	1.721 ± 0.011	97.7

4 Ballistic characterization

Following up some advancements implemented on the experimental rig during the HISP project, the ballistic characterization has been performed in an improved strand burner of about 2 liter internal volume. The basic concept of the experimental setup is unchanged and consists of a vertical strand burner, where combustion of samples progresses along a top-bottom direction. Ignition, pressure control system, test conditions, and procedures are unchanged. Detailed description and schemes are available in Deliverable 5.3, section 2. As for previous characterizations, combustion tests covered a pressure range between 5 to 40 bar. Data representation as well as detailed Vieille's law are available in Figure 1.

The progressive introduction of small fractions of nAl in a standard propellant formulation appears to be responsible for a monotonic increase of burning rate. Though, as expected, the increment is not proportional and the effect tends to be lower as the amount of nanometric powder increases. Results in such direction are in agreement with previous results available in the literature and were already discussed in Deliverable D5.1 [1]. Going into details, halfway improvements are already obtained for the repacement of 1.5% of µAl with nAl. Gains with respect to the baseline are in the order of 20-30% depending on the operating pressure. This curve also presents an anomaly in the pressure exponent of Vieille's law which appears to decrease from 0.46 to 0.38. At this time, a confirmed explanation for this effect is missing, as discussed in Sec. 7.

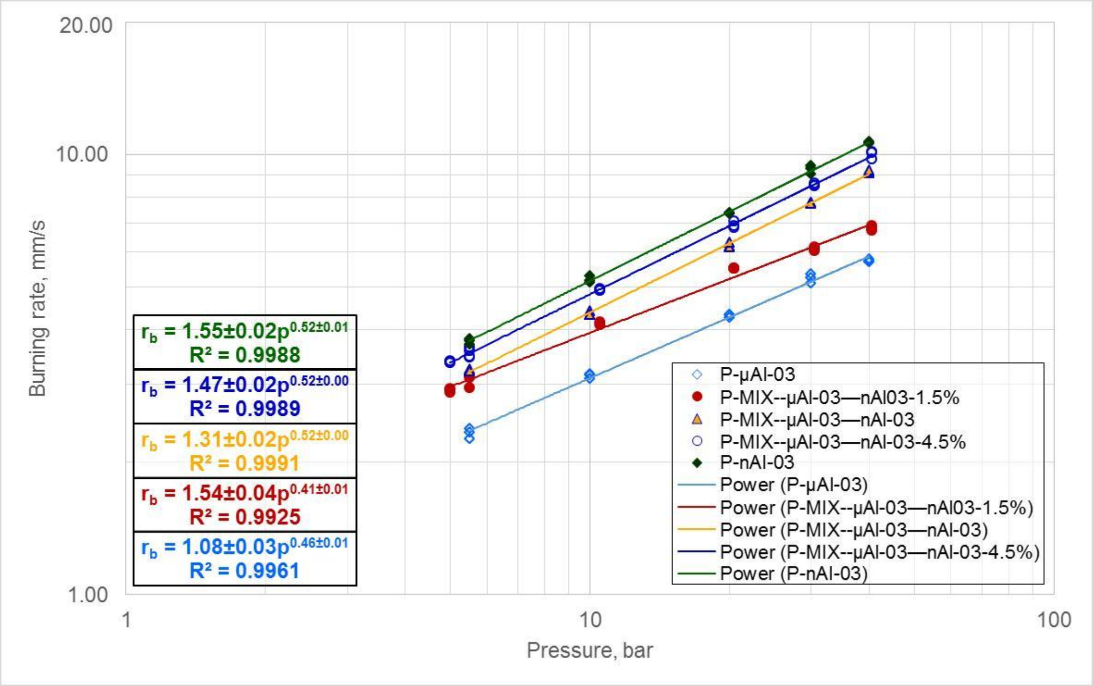

Figure 1. Ballistic characterization of propellants fueled with µAl-nAl mixes.

Once nAl content is increased to 3%, the gain in burning rate sets in the range 40-60% while, for 4.5%, propellant ballistics approaches the behavior of composition P-nAl-03, fueled with nAl only. Experimental data reveal gains in the order, respectively 55-75% for the former composition and 60-80% for the latter.

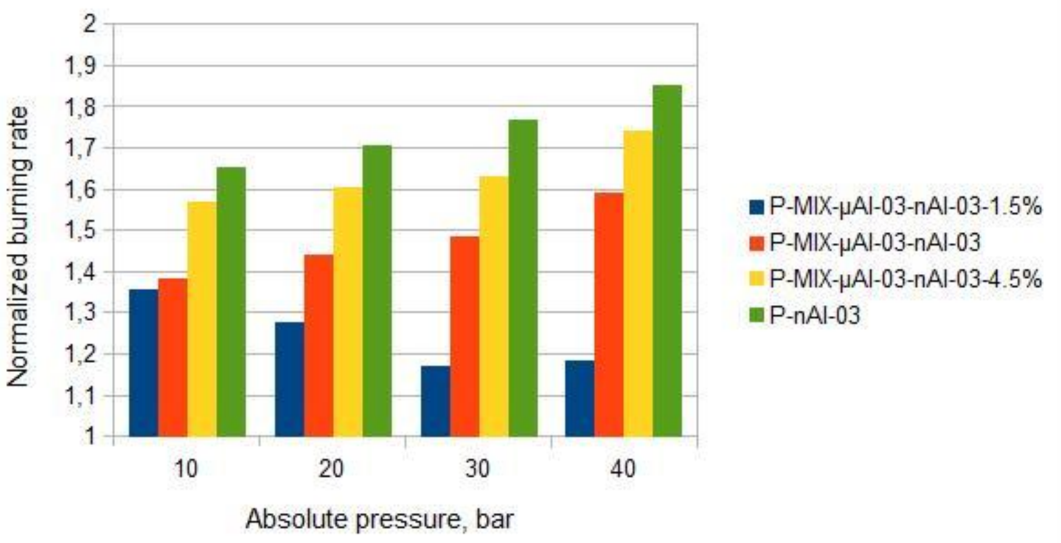

Figure 2. Normalized burning rate of tested propellants. Normalization is performed with respect to P - µAl-03 baseline propellant.

The comparison can be better appreciated if Figure 2 is taken as reference. The plot reports the mean experimental burning rates for each pressure, normalized with respect to the value obtained for the baseline propellant P -- µAl-03. Especially at higher pressure, it is evident that the largest regression rate increase is granted by 3% nAl content, while 4.5% of nAl allows a ballistic performance which is comparable with a propellant containing 18% of nAl.

5 Ignition delay

As already described in Deliverable D5.3, ignition delay is measured by the time lapse between an energetic stimulus and the propellant response. The energy source consists of a CO_2 laser operating in the far infrared at 10.6 µm wave length. The reader is encouraged to consult Deliverable 5.3 for the description of the experimental rig and of the testing procedure. With respect to the previous experimental data, the baseline was re-investigated due to a suspected problem in original data.

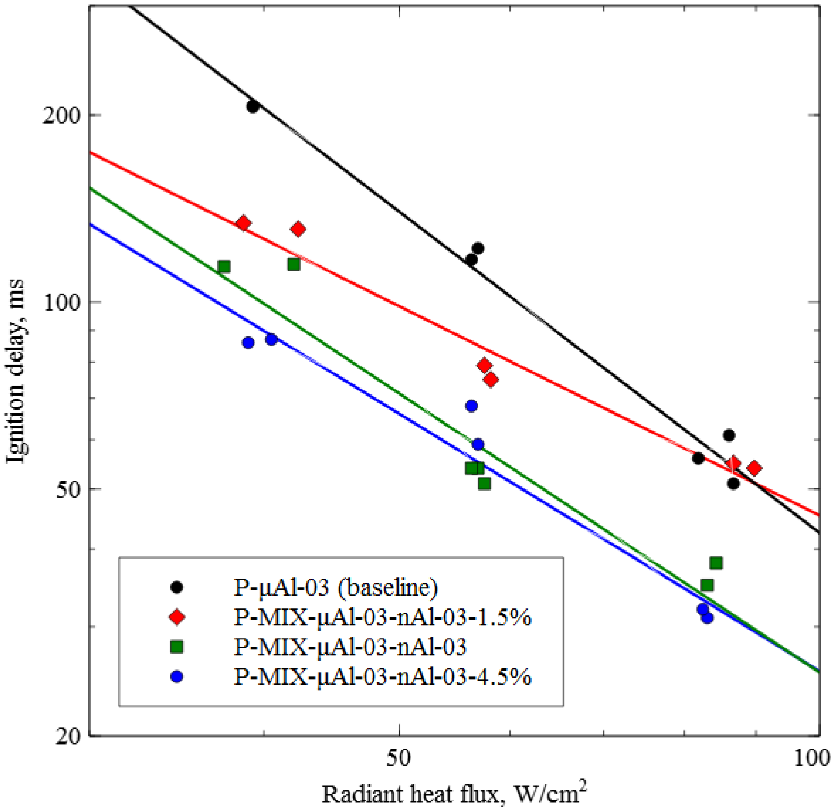

Figure 3. Summary of ignition delay analysis.

Table 6. Ignition delay power fitting. Time t_{ign} in milliseconds, heat flux I_0 in W/cm^2. Uncertainty is computed using 95% confidence level.

Id.	Ignition Delay fitting curve
P -- µAl-03	$t_{ign} = 116203 \pm 28646\ I_0^{-1.719\pm0.060}$
P-MIX -- µAl-03 -- nAl-03-1.5%	$t_{ign} = 7838 \pm 2352\ I_0^{-1.119\pm0.073}$
P-MIX -- µAl-03 -- nAl-03	$t_{ign} = 24438 \pm 8692\ I_0^{-1.492\pm0.088}$
P-MIX -- µAl-03 -- nAl-03-4.5%	$t_{ign} = 14471 \pm 3924\ I_0^{-1.378\pm0.067}$

With respect to the baseline, all propellants feature a reduced ignition delay thanks to the addition of even small quantities of nAl. A saturation effect is obtained for the formulation containing 3% of nAl, which has a behavior comparable to the one with 4.5% nAl content. A different trend is attributed to the composition P-MIX -- μAl-03 -- nAl-03-1.5% whose experimental data coincide with the results of the baseline propellant at low radiant fluxes. For high fluxes halfway performance between baseline and P-MIX -- μAl-03 -- nAl-03-4.5% is obtained.

6 Collection and analysis of condensed combustion products (CCP)

In addition to the previous characterizations, this deliverable contains an improved analysis of the condensed combustion residues which is complementary to the visualization technique, already addressed in the previous reports.

Unlike the visual analysis of the CCP, collection techniques do not allow direct observation of agglomeration process and evolution. However, limitations on particle visibility are overcome by the capability of collecting residues which are measured through a laser granulometer. Thus, an extension towards lower CCP size is easily achieved.

6.1 Description of the technique

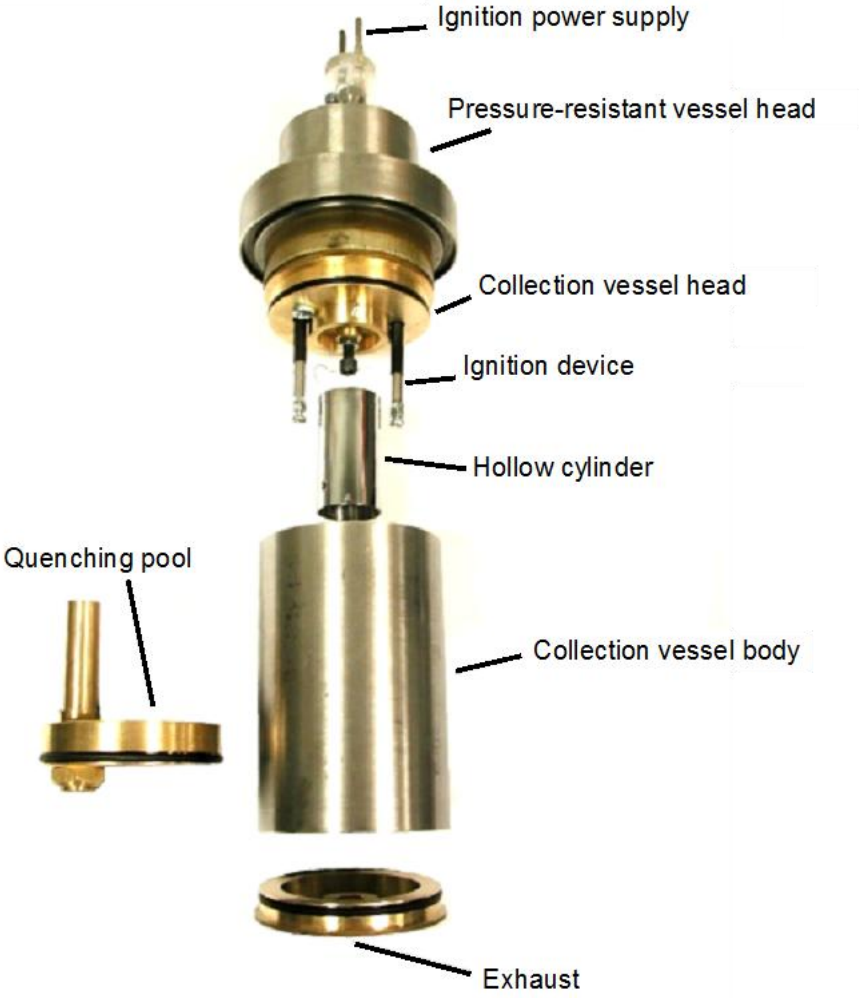

Figure 4. Assembly of the CCP collection facility.

The combustion is performed by burning a propellant strand upside down and starting the combustion using hot wire ignition. A detailed representation of the rig is given in Figure 4. The process occurs in a pressure vessel with a volume of 1414 cm^3, where a set of electrovalves is actuated to maintain the pressure constant. The vessel is pressurized with nitrogen gas, after proper purging. The condensed combustion products (CCPs) originated from the specimen combustion are quenched in a pool filled with proper liquid. The collection of CCPs is made after at least 3/4 tests at a given pressure. Residuals are then treated by removing the excess quenching media and the unburned pyrolyzed polymer, as much as possible. During this process, the sample is also pre-dispersed in the measurement medium without drying it. In the current version, the combustion chamber can operate up to 40 bar. Combustion tests are performed at 10 bar.

The particle size distribution and relevant average parameters are evaluated using a Malvern Mastersizer 2000 with Hydro liquid dispersion unit. An updated procedure recently replaced the dry-dispersion technique and grants a higher sensitivity. After condensed combustion product collection and treatment, the suspension medium is replaced by the measurement medium. In the dispersion unit the sample is treated with ultrasounds and, if needed, dispersants. After the stabilization of optical parameters (obscuration of the laser beam), a sequence of measurements is performed and averaged, after proper post-processing (typically 10 to 20 tests). The selection is based on criteria of stability for the optical properties and of measurement residuals, which is a numeric parameter of the measurement rating the quality of the obtained result.

6.2 Detailed results

In the following paragraphs, particle size distributions obtained by the CCP analysis collected after 10 bar combustion of different propellants are presented. Data refer to baseline P--µAl-03 (Figure 5), nAl-fuelled propellant P--nAl-03 (Figure 6), and mixed µAl-nAl compositions (Figure 7, Figure 8, and Figure 9).

6.2.1 P--µAl-03

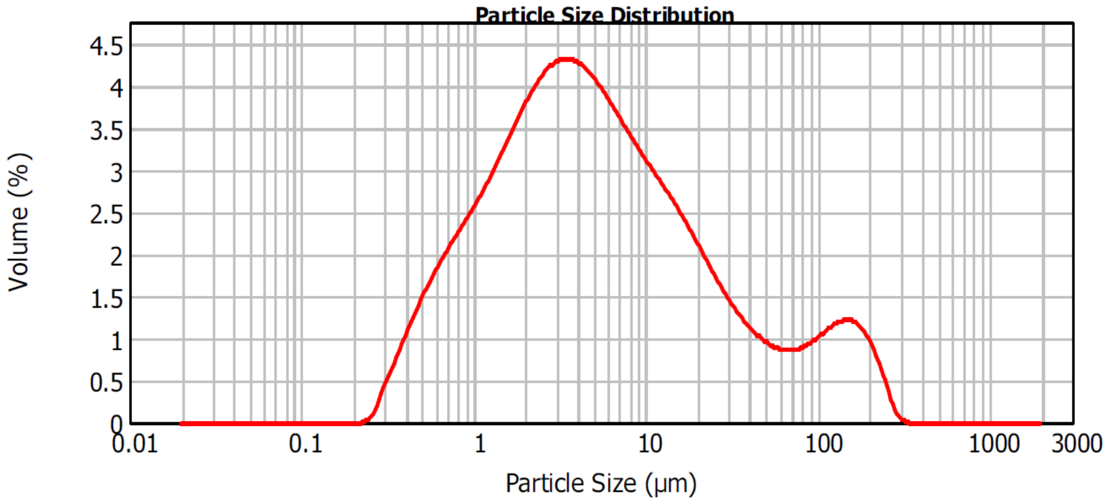

Figure 5. P--µAl-03 CCP analysis; combustion at 10 bar.

6.2.2 P--nAl-03

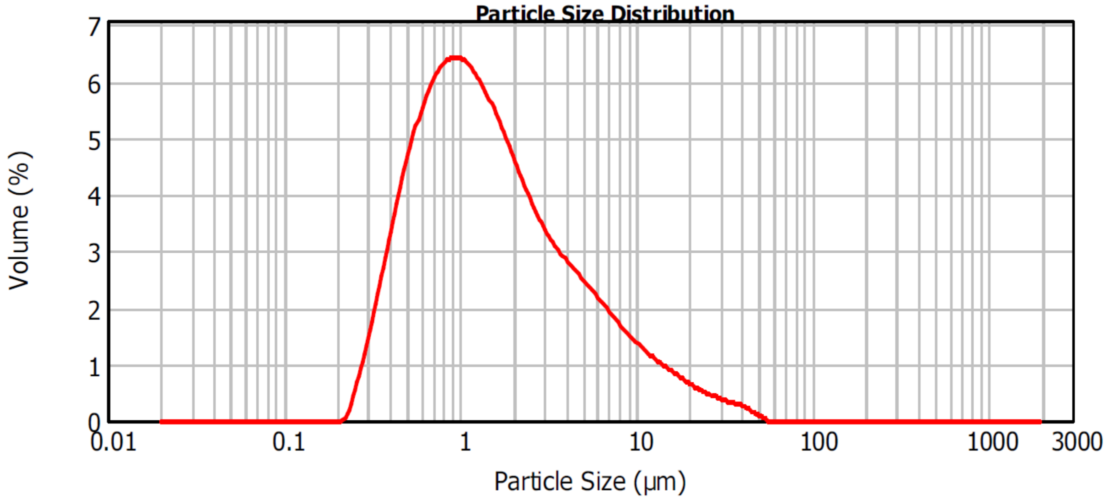

Figure 6. P--nAl-03 CCP analysis; combustion at 10 bar.

6.2.3 P-MIX--µAl-03--nAl-03-1.5%

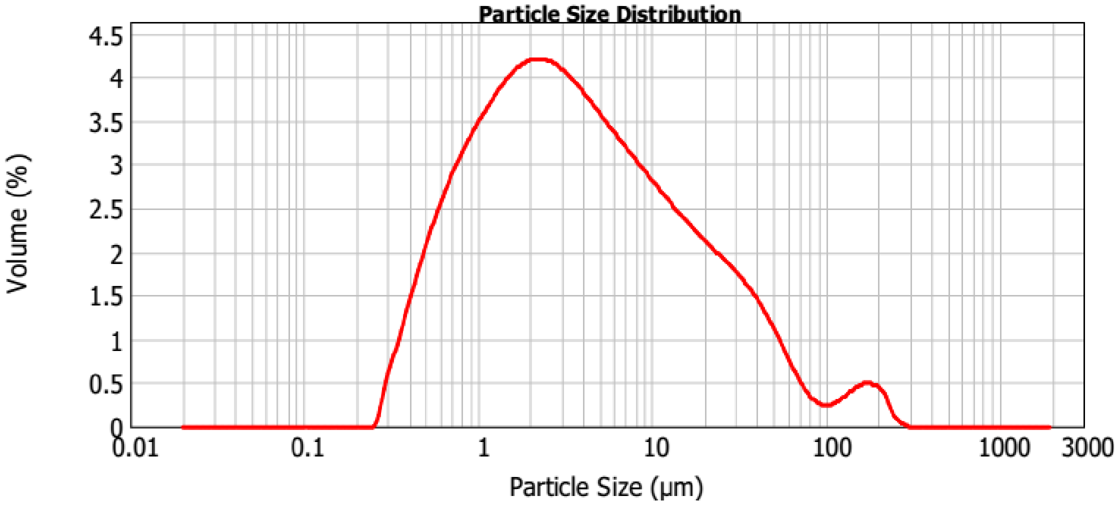

Figure 7. P-MIX--µAl-03--nAl-03-1.5% CCP analysis; combustion at 10 bar.

6.2.4 P-MIX--µAl-03--nAl-03

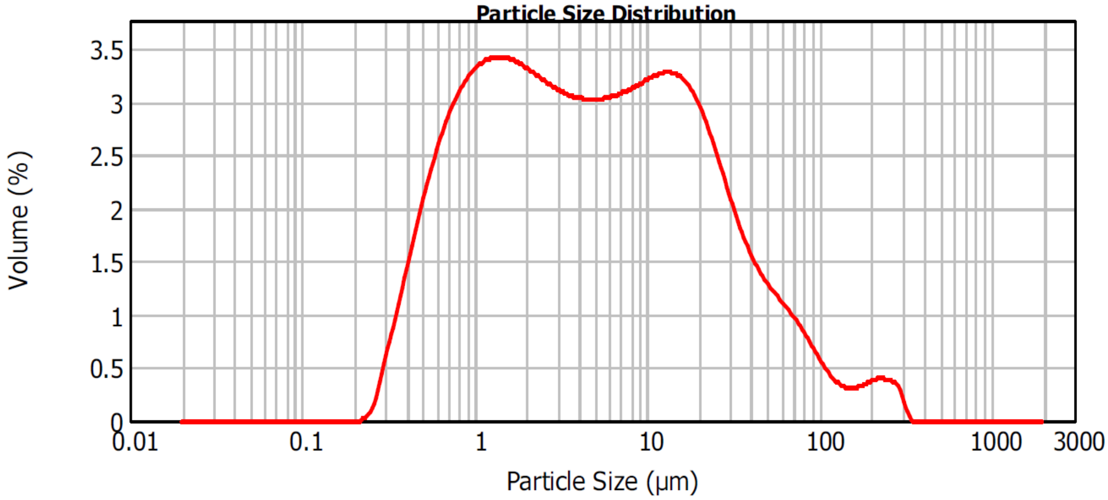

Figure 8. P-MIX--µAl-03--nAl-03 CCP analysis; combustion at 10 bar.

6.2.5 P-MIX--μAl-03—nAl-03-4.5%

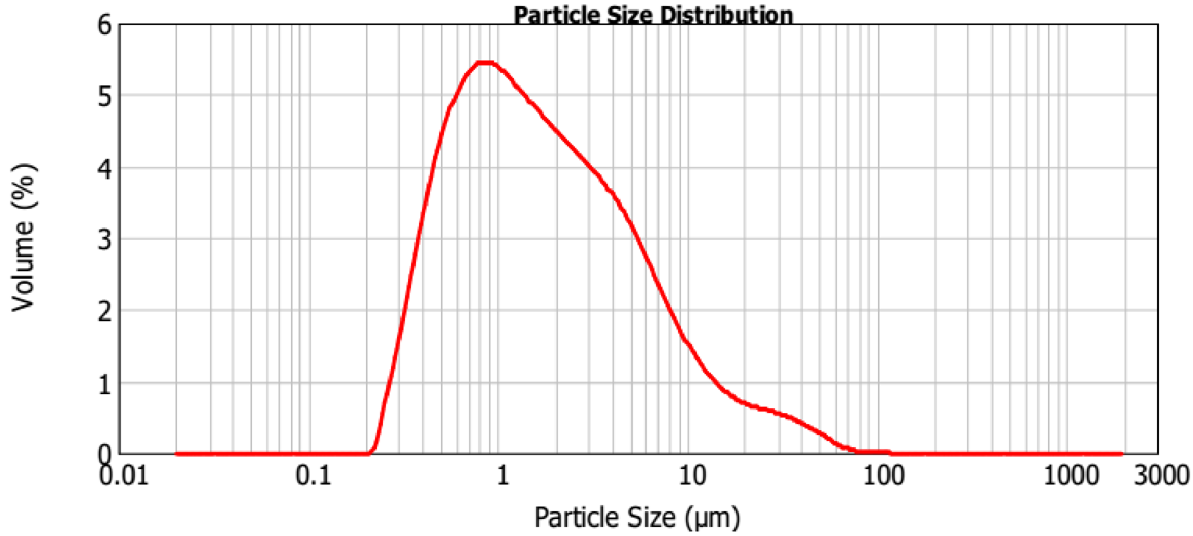

Figure 9. P-MIX-μAl-03-nAl-03-4.5% CCP analysis; combustion at 10 bar.

6.3 Result summary

From the analysis of Table 7, it is clear that a substantial presence of nAl decreases the size of condensed combustion products. Agglomerates for P--nAl-03 feature about 3 μm of mass-weighted mean diameter which is sensibly lower than the value measured for the baseline P--μAl-03 which is around 20 μm.

A different matter is observed in propellants containing μAl-nAl fuel mixtures. The presence of small fractions of nAl does not seem to carry out advantages at the tested conditions, in terms of mass-weighted mean diameter. If a detailed curve comparison is taken as reference (Figure 10), some differences can be observed in the coarse range where a reduction of largest agglomerates is obtained passing from P--μAl-03 to the P-MIX series. That is, actually, the range which can be perceived by the incipient agglomerate visualization techniques. However, once the amount of nAl is set to 4.5%, the distribution curve becomes very similar to that obtained for the propellant containing only nAl, also underlined by the mass-mean diameter.

Table 7. Mass-weighted mean diameters for CCP samples collected after 10 bar combustion.

Name	D_{43} [μm]
P--nAl-03	3.174
P--μAl-03	20.207
P-MIX--μAl-03--nAl-03 1.5%	12.427
P-MIX--μAl-03--nAl-03	15.980
P-MIX--μAl-03--nAl-03 4.5%	3.863

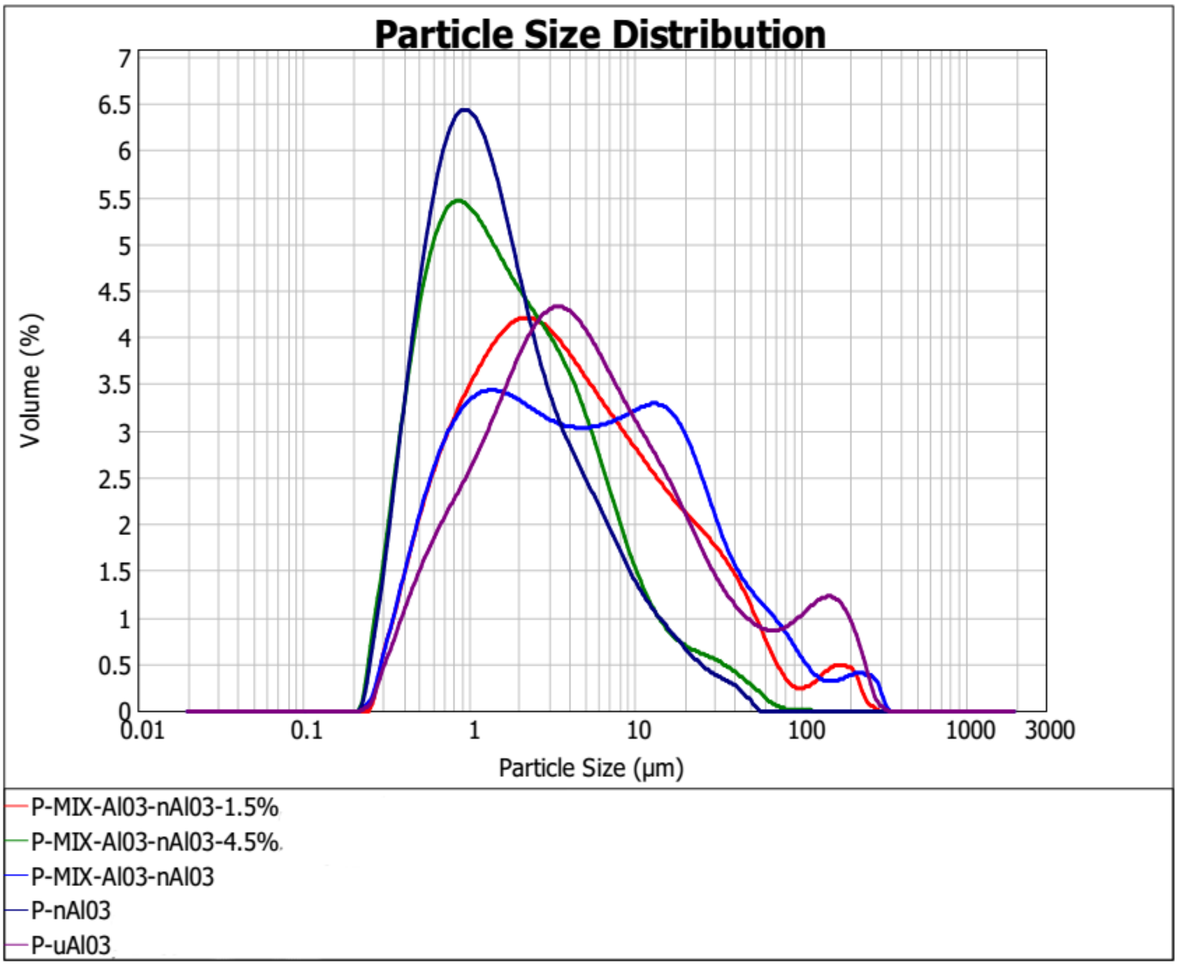

Figure 10. Detailed comparison among mixed μAl-nAl compositions at 10 bar.

7 Comments on results

From the ensemble of the results available for P-MIX propellant series it appears that the step-up performance gain is obtained for a nAl content between 1.5 and 3%. Further increase above 3% of nAl leads to reduced gains in both burning rate and ignition delay. Moreover, the performance of the formulation containing 4.5% nAl are almost levelled with behaviour of propellant P-nAl-03, fully fuelled with nAl.

A different matter is observed for CCP analysis, where it appears that a qualitative leap is obtained only when the nAl content is set to 4.5% or above. In fact, under the tested reference conditions, formulation P-MIX—Al03—nAl03 4.5% demonstrated a CCP size distribution very similar to the one exhibited by propellant P—nAl03. Only minor improvements were obtained for the larger agglomerate fraction by other P-MIX propellants. Focusing on D_{43} measurement, it appears that P-MIX with 1.5% of nAl has smaller agglomerates with respect to the formulation with 3% of nAl. However, the discrepancy is minimal and might can be introduced either by CCP collection/treatment process or by issues in the formulation itself. Further investigations are needed and still in progress, especially for combustion at higher pressure.

A clear explanation for the anomalous behaviour of P-MIX--µAl-03--nAl-03 1.5% is still missing. A discrepancy was observed for almost all of the investigated properties: steady burning rate, radiant ignition delay and CCP size distributions. Burning rate pressure dependence was found to be lower than expected. The same happened for the absolute value of the power exponent in the ignition delay vs. radiant flux fitting. Finally, the D_{43} measured from CCP laser granulometry did not strictly follow the expected trend, though such discrepancy was limited. The fact that anomalies occur for the same propellant formulation under different tests may suggest that the samples burned were affected by some quality issues. A symptom of possible manufacturing problems stems from porosity measurement which is the highest in the group, as shown in Table 5.

8 Conclusions

The activity of optimization confirmed that, for propellant formulations containing multimodal µAl-nAl blends, a trade-off between nAl content and combustion propertied can be found. Performance of propellants containing only nAl fuel can be almost reached with µAl-nAl blends where the fine fraction does not exceed 3-4.5% by mass of the whole formulation. In such a way, an enhancement of combustion properties is obtained, but the well-known problems connected with difficult processablity and reduced metal content are appreciably mitigated.

The choice of the exact optimal point depends on the scope of the propellant. In the frame of the HISP project, low burning rate with high specific impulse is envisaged so formulation containing 1.5% or, at most, 3% of nAl can be recommended. For a sensible agglomerate reduction, 4.5% of nAl is required. If propellant burning rate is still high, it might be possible to introduce an oxidizer with lower oxygen content than ammonium perchlorate (namely, ammonium nitrate), though maintaining good combustion quality by taking advantage of improvements granted by nAl content.

9 References

1. Olivani A. et al. Aluminum Particle Size Influence on Ignition and Combustion of AP/HTPB/Al Solid Rocket Propellants. Advances in Rocket Performance Life and Disposal, Paper 31, NATO MP-091, 2002.