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OVERVIEW OF THE CNES “HIGH PERFORMANCE GREEN MONOPROPELLANT PROJECT”:
REQUIREMENTS, ORGANIZATION & BREAKTHROUGHS

SPACE PROPULSION 2018

BARCELO RENACIMIENTO HOTEL, SEVILLE, SPAIN / 14 – 18 MAY 2018

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ABSTRACT:

CNES, the French Space Agency, has been leading for nearly six years intensive research on alternative green propellants for spacecrafts thrusters. More precisely, research has been focused on premixed monopropellant formulations based on state-of-the-art energetic materials and green chemistry approaches. The goal of this program is to provide an innovative propulsion system to replace standard hydrazine technology, demonstrating total breaking performance, low toxicity and high versatility. Hydrazine, mostly used in its anhydrous form as catalyzed monopropellant, is indeed an old and undoubtedly flight-proven product, but suffers from relatively poor propelling performance and from a high toxicity (both acute and suspected CMR). This paper describes the origins of the project and the main requirements we have imposed on ourselves. It also gives an overview of both the organization and the roadmap of the development plan, then concluding on the achievements and breakthroughs obtained to date.

1. INTRODUCTION

Green propellants have been a hot topic in recent years, mostly since anhydrous hydrazine – which is the current monopropellant of reference – is threatened with a full ban in the European Union. Indeed, due to both its high acute toxicity and suspected CMR status for humans, REACH¹ introduced hydrazine on the “Substances of Very High Concern” (SVHC) list, which is generally a preamble to an outright prohibition of manufacture, importation and use in the EU. In order to anticipate this short- to mid-term risk, CNES decided to initiate a

Research Program dedicated to the development of a green alternative propellant providing many assets compared to both hydrazine and already available green competitors. Among the many imposed technical requirements, the propelling performance must be in total breaking with the current solutions. We are indeed looking for an increase of at least 100% of spacecraft velocity increment (ΔV) compared to standard hydrazine (at equivalent fuel tank volume). To achieve this ambitious objective, a new ultra-high temperature material must be developed so as to sustain the relatively high combustion temperature observed. All this work has been included in a five-year CNES-ONERA joint project called “High Performance Green Monopropellant”.

2. SCOPE OF ACTIVITIES

Our project aims to achieve, with a relative short deadline, a proof of concept on a thruster demonstrator of 10 Newton thrust. This corresponds to a TRL 6/7. To ensure the smooth running of this project and maximize its chances of success, it was therefore necessary to build a comprehensive and consistent roadmap, addressing various but interrelated topics.

3. DETAILED ROADMAP

Our technical roadmap is divided in four main topics: i) monopropellant, ii) ultra-high temperature material (UHTM), iii) ignition and iv) thruster (Fig. 1). Each domain is crucial in itself since it contributes to the completion of the project, which consists in a fully representative UHTM thruster demonstrator using our green monopropellant.

3.1 Monopropellant development

The green row in Fig.1 depicts the monopropellant development flowchart from the early fundamental research up to the final approval dossier. The first four years (2012-2015) were dedicated to a thorough scientific survey and to theoretical computations over tens

¹ [European Regulation for] Registration, Evaluation, Authorization and Restriction of Chemicals.

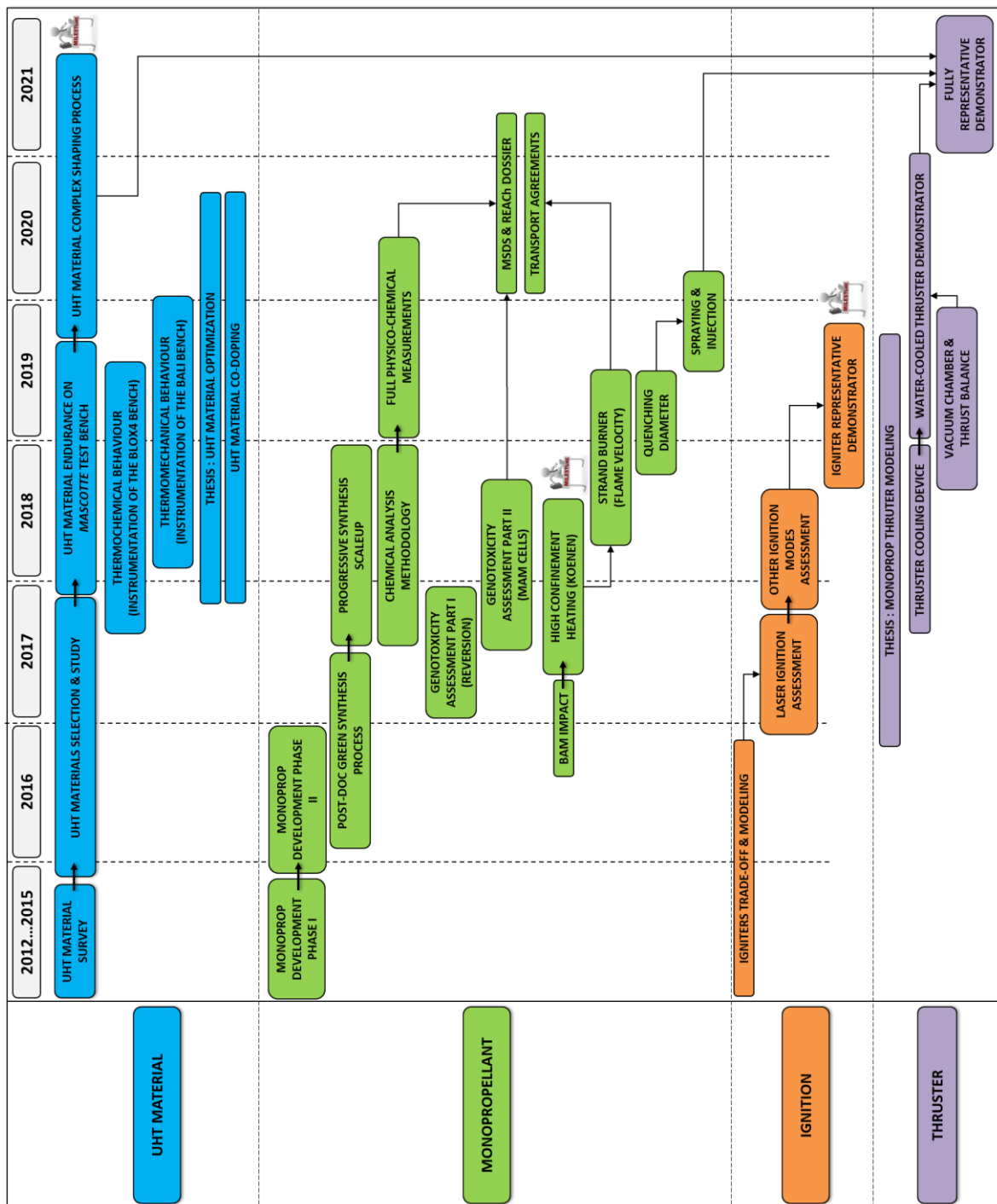


Figure 1. Roadmap of the CNES “High Performance Green Monopropellant”

of advanced energetic materials. This preliminary phase led to the selection of about 20 energetic salts that have been synthesized at small-scale and characterized (2016). In parallel, intense brainstorming was dedicated to green chemistry in all its aspects: reactants toxicity and eco-toxicity, involvement of solvents, number of elementary steps, number of post-processing steps and use of green indicators. It also resulted in the identification of green chemistry processes having the ability to be scaled-up (2016-2017).

The monopropellant activities also address the toxicity issue. Genotoxicity tests are carried out on the final short-list salts to assess their CMR potential (2017-2018). It includes bacterial reverse mutation (Ames tests, OCDE n°471), mammalian cell gene mutation (OCDE n°490) and micronucleus (OCDE n°487). Tests are all performed *in vitro* so as not to involve live animals. Combining those three tests will give a clear and high confidence status of the mutagenic potential of our salts. Tests are carried out following GLP (good laboratory

practices) in order to be recoverable in a REACH dossier.

Pyrotechnic characterization is also mandatory in a propellant development plan (2017-2018). Our goal is to obtain a monopropellant formulation demonstrating very low sensitivity towards all external aggressive stimuli. An iterative approach has been adopted to tune monopropellant composition and make it desensitized while maintaining high Isp. The two most critical tests are the BAM fall hammer (impact test) and the high-confinement heating (Koenen test).

Further combustion characterizations include combustion rate and flame quenching diameter determination as a function of both external pressure and fresh monopropellant temperature. Besides, both droplet regression followed by high speed camera and reaction calorimetry are used to develop a specific combustion kinetic model. Spraying and injection will finally be experimentally tackled with in a series of granulometry tests. All these tests give us a deep understanding of the propellant behavior and important key data for the thruster design.

3.2 UHT material development

Due to the high temperature entailed by the combustion of our monopropellant, new Ultra High Temperature Material (UHTM) must be developed and qualified. The blue row in Fig.1 gives an overview of the UHTM development flowchart. In the very same way as for the propellant, the program started with a scientific survey which led to a pre-selection of satisfying materials and manufacturing processes (2014-2015). It also made an inventory of technical locks to be solved to reach our goal.

Following this pre-selection, a first experimental phase has been scheduled (2015-2017) and was intended to obtain the first samples by additive manufacturing. This "appropriation" phase provided relevant data on the behavior of the material powders during both deposition and post-processing. There is indeed a powerful interplay between the process parameters and the samples final properties (porosity, cohesion, homogeneity, etc.). Dilatometry (measurement of the thermal expansion coefficient) and thermal load traction were also carried out.

This first phase ended in a series of lessons learnt which allowed us optimizing the process from a microstructural point of view.

The next step (2017-2019) was built on the previous achievements to conduct an endurance campaign in two distinct phases: i) static oxidative test on the ONERA BLOx4 test bench

and ii) dynamic oxidative tests on the ONERA Mascotte bench.

3.2.1 BLOx4 test bench

The BLOx4 bench (Fig.2) allows the study of material samples oxidation process in representative static and pressurized atmosphere (H_2O , Ar, N_2 , H_2 , CO_2 , air, etc.) up to 4 bar abs [1]. Thermal flux is deposited by a high power continuous CO_2 laser beam (2kW). Temperature is monitored by two monochromatic pyrometers both on bottom and top faces. In its current configuration, the BLOx4 can heat up samples up to 2800K during 3000s. Tests are still on course in the frame of optimization loop.

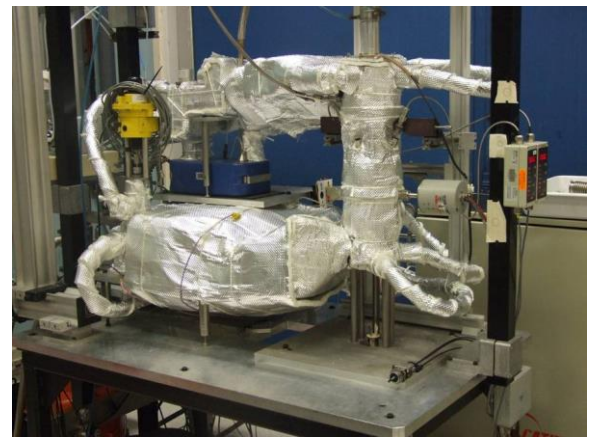


Figure 2. ONERA's BLOx4 bench

3.2.2 Mascotte test bench

The Mascotte bench constitutes a large facility in itself [2]. Its biggest part is dedicated to the management of the oxidizer (GOx or LOx), the fuel (GH_2 or CH_4) and the servitude fluids (He , N_2 , LN_2 , H_2O). The core of the facility is the "reactor box" of which several versions were developed to answer very specific fields of research (e.g. atomization-combustion, new propellants assessment, overexpanded nozzles, ignition, high frequency instabilities, etc.). In our case, Mascotte uses the "Bhp-HrM" version (high pressure-high mixing ratio box) (Fig.3). Endurance campaign is forecast mid-2018 and will last about 18 months including an optimization loop.

Whether for the BLOx4 tests or the Mascotte campaign, a series of thorough comparative analysis is carried out on samples before and after each test, such as X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (MET).

Last but not least, a final step has been scheduled (2019-2020) to focus on the manufacturing of complex shape parts. The

additive manufacturing process must be optimized to obtain a high quality thruster (deposits homogeneity, absence of singularity, dimensional quality, etc.).

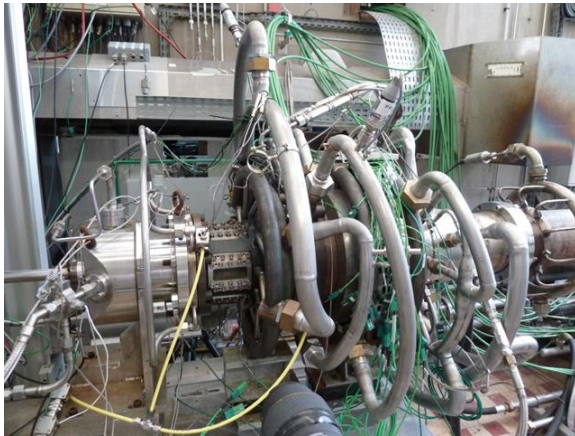


Figure 3. Bhp-Hrm box mounted on the ONERA's Mascotte bench

3.3 Ignition study

3.3.1 Getting rid of catalyst

In contrast to the operating principle of conventional monopropellant thrusters, our concept no longer lies on catalytic decomposition of the fuel, but on an external ignition device. This choice is based on the following observation: propelling performance along with the lifespan of current engines are strongly limited by the use of a catalytic bed, which is the most vulnerable part on the thruster. Indeed, catalyst grains are subjected to harsh thermal and mechanical cycles, leading to many ageing routes: erosion, sintering, chemical deactivation, fouling, etc. [3]. As a consequence, specific impulse gradually decreases throughout orbital mission. It is not uncommon to observe, under certain operating conditions, a full destruction of the catalytic bed structure, leading to an inoperative engine. It is therefore obvious that increasing I_{sp} – and thus combustion temperature – will only accelerate the catalyst deterioration.

Despite this fact, a lot of work is still ongoing on high temperature catalyst and also monolithic catalyst with the ambition to try to reduce those effects. Monoliths structures, based on foams, were for example assessed both for LMP-103S and AF-M315E monopropellants application [4]. Monoliths obtained by additive manufacturing are also currently studied, especially in the framework of the H2020 Rheform Project [5].

Those two technical improvements are noteworthy, but enhance only to a limited extent

catalyst active phase aging, since it is still subjected to a strong thermal cycling sensitivity.

3.3.2 Alternative ignition concepts

All this to conclude that, if we are keen to improve monopropellant thruster performance, a rather wise solution is to initiate chemical reaction by another means.

Such is our strategy, as detailed in Fig.1 (orange row). A comprehensive trade-off has been carried out over the period 2012-2016, based on technical specifications both at thruster and spacecraft levels (power budget, thermal and mechanical environments, number of maneuvers, etc.). This led to the selection of some promising technologies, such as laser ignition (to name but one) which are now being assessed (2017-2018). The best concept (in terms of experimental efficiency, robustness and ease of integration on the thruster) will be retained for more representative further activities.

3.4 Thruster demonstrators

Demonstrators are part and parcel of the monopropellant roadmap, as depicted in Fig.1 (purple row). Three main steps are scheduled:

- 1) Ignition sub-system demonstrator ;
- 2) Water-cooled thruster demonstrator ;
- 3) UHTM thruster demonstrator with integrated igniter.

This decomposition will allow the separated and progressive study of key technical issues, such as ignition, injection, combustion efficiency, UHTM behavior, etc. to finally converge towards a high representativeness ground thruster.

It was decided to focus on ignition through a specific sub-system demonstrator in order not to complicate its fundamental study by a whole thruster design (that could introduce additional technical issues). This demonstrator is intended to:

- get a proof of concept (*i.e.* transient ignition of our monopropellant in realistic conditions) ;
- identify key design parameters ;
- suggest an optimized architecture.

Water-cooled thruster demonstrator will provide, first of all, the first values of experimental I_{sp} . It will also provide a thermal mapping of the combustion chamber, which is of great interest when designing an optimized thruster. This demonstrator will be composed of removable parts, such as a variable injector head, so as to study many key-parameters (spraying, liquid-

wall interaction, flame location, nozzle shape, etc.).

Finally, a fully representative UHTM thruster will be built using optimized additive manufacturing process and the experimental feedback get on the water-cooled demonstrator. The main objective of this thruster will be to achieve a severe endurance campaign (duty cycling) and reach a TRL 6-7.

3. GREEN MONOPROPELLANT

3.5 What is green?

Green technologies can be defined as an engineering field that relies on a set of continuously evolving techniques and methodologies limiting energy and material consumption, while reducing ecological footprint. Such technologies imply a drastic change in our design, manufacture, use and end-of-life logics.

The “green-way-of-thinking” can be summarized in five points:

- Sustainability: meeting the needs of customers in ways that continue indefinitely into future without damaging or depleting natural resources. In short, meeting present needs without compromising future generations own needs ;
- “Cradle-to-cradle” design: ending the ‘cradle to grave’ design cycle of manufacturing, by creating products or by-products that can be partly or fully reclaimed or re-used ;
- Source reduction: reducing waste and pollution by changing patterns of production and consumption ;
- Innovation: developing alternatives to current technologies that have been demonstrated to damage health and environment ;
- Viability: creating a center of economic activity around technologies and products that benefit the environment, speeding their implementation and creating new careers that truly protect planet.

These precepts can obviously be applied to energetic materials manufacturing. However, to be respected and efficiently used, it is necessary to translate them into pragmatic and quantifiable requirements. TAB 1. gives an overview of the most often encountered “green metrics”, where m and \mathcal{M} stand for mass and molar mass respectively.

One illustration among others of our permanent “green concern” can be found in the prime

importance given to the involvement of satisfying reactants and solvents. Indeed, they shall comply with: i) a favorable REACH status (not CMR), ii) a low acute toxicity, iii) encouraging green metrics and iv) limited cost.

Green metric	Formula
Reaction mass efficiency	$RME = \frac{m_{PROD}}{m_{REAG}}$
Carbon efficiency	$CE = \frac{m_{C,PROD}}{m_{C,REAG}}$
Atom economy	$AE = \frac{\mathcal{M}_{PROD}}{\sum \mathcal{M}_{REAG} + \mathcal{M}_{INTERM}}$
Environmental “E-factor”	$E_F = \frac{m_{WASTE}}{m_{PROD}}$

Table 1. Some “green metrics” used in this study

Ultimately, green synthesis processes are looked for, in order to minimize energy consumption and effluents. To date, we achieved for the first time in the world the synthesis of energetic materials by an aqueous electrochemical process. This high-yield technique is now under patent registration.

3.6 Technical requirements

We provide in Tab.2 a list of the main technical requirements that were stated for our monopropellant. Second column gives the minimum requirements, while third column shows what might be ideal values.

It may be noticed that both density and Isp targets are very high compared to traditional monopropellants. We briefly explain hereafter the reason of such constraints.

The velocity increment ΔV can be approached, when $\frac{V_{prop}}{V_{dry}} \rightarrow 0$, by the equivalent:

$$\Delta V \sim \rho \times I_{SP} \times g_0 \times \frac{V_{prop}}{V_{dry}}$$

where ρ is the propellant density, g_0 the gravity, V_{prop} the propellant volume embarked on the spacecraft and V_{dry} the dry mass of the spacecraft.

It can be easily understood that a higher ΔV increase can be obtained playing both on density and Isp. TAB.3 gives some examples of the gain we can expect for a 1000 kg dry mass spacecraft using 30L of propellant. First row is the typical catalyzed hydrazine configuration, used as a reference. It can be seen that

combining a volumetric mass of 1500 kg.m^{-3} and an I_{sp} of 300 seconds more than doubles ΔV and thus in-orbit autonomy.

Property	At least	Ideal
Density*	1300 kg.m^{-3}	1500 kg.m^{-3}
Freezing point	0°C	-20°C
Dynamic viscosity*	$<10 \text{ mPa.s}$	$<1 \text{ mPa.s}$
Decomposition point	$>140^\circ\text{C}$	$>160^\circ\text{C}$
Vapor pressure*	$<10^{-3} \text{ Pa}$	$<10^{-4} \text{ Pa}$
Impact sensitivity	$>40 \text{ J}$	
Vacuum specific impulse (measured, $P_{ch}=10 \text{ bar}$, $\epsilon=100$)	290 s	$>300\text{s}$
Species content	Only C, H, N, O (no halogens)	
Long term stability	10 years @ 20°C	15 years @ 20°C
* at ambient temperature		

Table 2. Green monopropellant main technical requirements

Density	Specific impulse	Velocity increment	Gain w.r.t Ref.
1000 kg.m^{-3}	210 s	60.9 m.s^{-1}	Ref.
1250 kg.m^{-3}	210 s	75.8 m.s^{-1}	+24.5%
1500 kg.m^{-3}	210 s	90.7 m.s^{-1}	+48.9%
1000 kg.m^{-3}	300 s	87.0 m.s^{-1}	+42.9%
1250 kg.m^{-3}	300 s	108.3 m.s^{-1}	+77.8 %
1500 kg.m^{-3}	300 s	129.5 m.s^{-1}	+112.6%

Table 3. Effect of density and I_{sp} improvement on velocity increment

This is certainly ambitious, but possible and desirable, since propellant capacity is currently the limiting factor of spacecraft lifespan, well before the obsolescence of the on-board equipment.

One of the most relevant propellant physico-chemical properties is certainly freezing point. Freezing point was set at 0°C maximum, so as to be comparable to current hydrazine systems

and thus not to introduce any additional constraint on the spacecraft thermal control system. Nevertheless, our ambition is to fall around -20°C to descope thermal regulation and reduce tank heaters power consumption.

Desirable thermal decomposition point (measured by open cup or calorimetry) must be higher than 140°C , preferentially over 160°C in order to ensure handling safety.

3.7 R&D methodology

Fig. 4 gives an overview of the approach followed to obtain *in fine* several satisfying monopropellant prototypes [6].

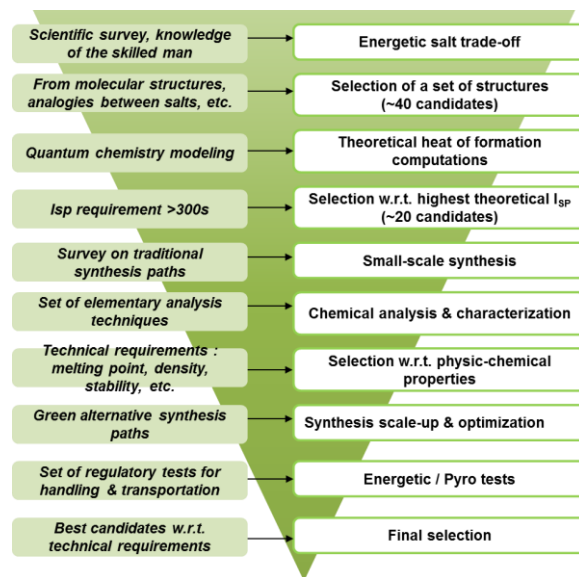


Figure 4. Simplified diagram of the followed R&D methodology

Let's have a brief description of each step mentioned in the preceding diagram:

- Energetic salt trade-off: a large list of salt candidates was built based both on a thorough scientific survey and on the knowledge of the skilled man (*i.e.* structure-property relationship). This list includes rather common formulas, but also advanced structures. Both anion and cation forming the salt were investigated ;
- Selection of a set of structures: based on the preceding survey, a list of about 40 salts has been drawn, many of them having a common core structure (skeleton). Many chemical groups (such as methyl-, nitro-, azido-, -amino, etc.) were chosen with different locations onto the skeletons ;
- Theoretical heat of formation computation: in order to predict specific impulses, standard heats on formation (ΔH_f°) were calculated using the well-known

Gaussian09® quantum chemistry software. Parameters have been optimized to fit experimental values gathered for some salts well described in the literature. Estimated error is about ± 50 kJ/mol ;

- Selection with respect to highest theoretical Isp: theoretical heats of formation were used to estimate potential specific impulse of our candidates. Doing so, only salts demonstrating an Isp over 300 seconds were retained. In order to take into account the uncertainty of the quantum chemistry modeling, Isp were computed using degraded enthalpies of formation: $\Delta H_{f,deg}^{\circ} = \Delta H_f^{\circ} - 50 \text{ kJ/mol}$. Even under such conditions, stupendous Isp values were found ;
- Small-scale synthesis: first syntheses were carried out using traditional methods (*i.e.* ions exchange resin, acid-base reaction, metathesis, etc.) without taking into account neither green markers nor reaction efficiency. The main goal was indeed to obtain effectively each salt with a satisfying purity and structure. This step was also pivotal in order to appraise salts behaviors (stability, handling and storage). Typical quantity was around 5 milligrams. In all, 20 candidates were synthesized, most of them for the very first time in the world ;
- Chemical analysis and characterization: each salt underwent a series of thorough analyses in order i) to establish thermal and chemical properties and ii) to provide a reference on a well-mastered and small batch. Among other characterizations, special emphasis has been placed on NMR (^1H , ^{13}C and ^{14}N), UV and IR spectrometry and ionic chromatography so as to establish a “chemical profile” of each salt. Thermal analysis (both DSC and TGA) were also carried out to complete these profiles ;
- Selection with respect to physic-chemical properties: in order to respect some of the requirements summarized in TAB.2, a selection was carried out anew. This led to a shorten list of 10 salts. Among the most critical properties taken into account, let us mention: melting/freezing point, decomposition temperature and thermal stability (by microcalorimetry) ;
- Synthesis scale-up and optimization: it was decided to launch a synthesis scale-up when a shorten list of 10 salts was reached, this in order not to work on to many synthesis routes in parallel. Scale-up was mandatory in order i) to carry out more salt-consuming tests and ii) to demonstrate our ability to answer commercial demand while ensuring high quality products. Scale-up problematic gave us the opportunity to investigate top-of-the-art green processes and to try “exotic” methods. After many trials and improvements, we finally succeeded in applying to our very specific energetic salts an electrochemical process in aqueous solution. This process can advantageously replace traditional methods, in terms of production rate (today: around 200 grams per week), automation, safety and effluents. Process is now under optimization phase with the goal to reach around 500 grams per week with the same quality ;
- Energetic and pyrotechnical tests: the most critical activities encountered during a propellant development are certainly combustion and pyrotechnical tests. Their objective is to understand the “energetic” behavior of the substance when subjected to various and more or less aggressive stimuli. Those tests are mandatory from a legal point of view (regulation on energetic materials) and for the perfect understanding of the product. Hereafter is a list of the tests carried out to date: open cup and DSC auto-ignition, BAM impact test, Koenen sleeve test (heating under high confinement), strand burner (flame velocity) and finally electrostatic discharge (ESD). All those tests have been carried out both on pure salts and on monopropellant prototypes (blends). Some more specific tests are required so as to submit a complete transport certification file to the French Authorities. These tests are expected to be achieved next year ;
- Final selection: a final selection is forecast for the end of this year, based on the agglomeration of all the data collected through the last year. In particular, pyrotechnical results are of prime interest in our selection process, since we are looking for the most stable formulation.

3.8 Major findings

We found that it is possible to obtain a high energy density liquid blend (*i.e.* monopropellant) demonstrating Isp over 300 seconds while ensuring a very low sensitivity. To achieve this, ternary mixtures have been created. They are composed of an energetic salt, a flegmatizer and water. The flegmatizer is an energetic solvent

providing a low sensitivity to the blend, while keeping high Isp. Water is added to tune viscosity. Fig.5 gives an example of theoretical Isp ternary diagram. Computations were realized based on the following conditions: chamber pressure $P_{ch}=10$ bar abs, expansion ratio $\epsilon=100$, average between frozen and equilibrium flows in the nozzle and use of degraded heat of formation $\Delta H_f^{\circ deg}$.

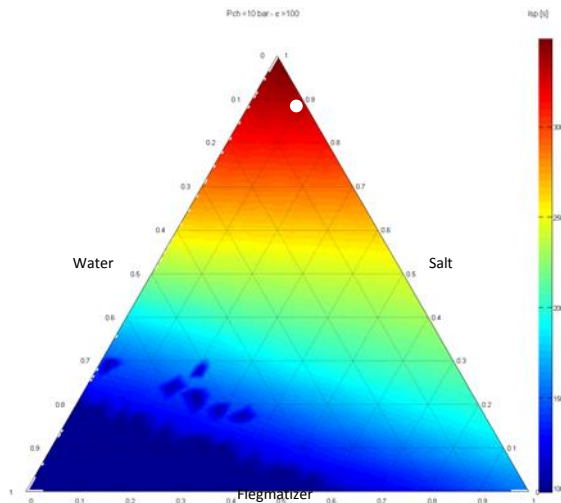


Figure 5. Theoretical specific impulse ternary diagram and composition of one of our monopropellant prototypes (white dot)

Each axis stands for a component mass fraction (between 0 and 1). It can be found that a significant part of the diagram is over 330s, where flegmatizer and water combined fractions can reach up to 20%wt. This is very attractive since it means that there is a comfortable margin with regards to a compromise between desensitization and performance.

Note that theoretical Isp must be corrected by a thruster efficiency to obtain real Isp. Considering a combustion efficiency (η_{c^*}) around 97% for premixed propellants and a nozzle efficiency (η_{nzt}) of about 95%, this leads to a credible real Isp of 300s with appreciable flegmatizer content.

So far, this strategy seems to pay off since it allowed passing BAM impact tests at 40J on three promising monopropellant prototypes (Fig.6). This energy level is very high and corresponds to that of dinitrobenzene (DNB), which is considered as a reference in terms of handling limit.

In the same way, heating under high confinement (known as Koenen sleeve test) led to an exciting outcome: for the three prototypes, no detonation has been noticed (smooth combustion) when using a blowhole of 2 mm diameter, at a heating rate of 3.3 K/s (Fig.7).



Figure 6. BAM fall hammer (OZM Research) used for impact tests carried out on our monopropellant prototypes

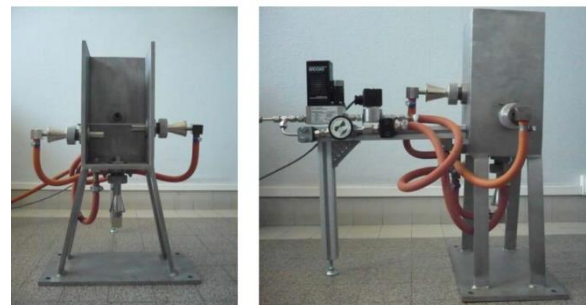


Figure 7. Koenen "sleeve tester" (Reichel und Partner) used for the high-confinement heating of our monopropellant prototypes. Top: rear view of the armored box; bottom: details of the apparatus

Each of these two tests – of great criticality – constituted a potential showstopper in our developments. Their favorable outcome paved the way for many complementary studies, still in progress.

This includes the study of flame velocity. For this, a specific test bench was designed so as to provide both finer visualization and analysis compared to traditional solid propellant stand burner (Fig.8). This bench includes a thermalization circuit that can be plugged to a

thermocryostat, in order to perfectly control initial propellant temperature in the gutter (range [-10,+50]°C). The latter can be inserted in a closed vessel so as to work from primary vacuum up to 20 bar abs. This bench allows us to access the direct observation of the flame structure by high speed camera. Furthermore, the various integrated sensors give us the possibility to construct the flame velocity curve $V_f(P,T)$.

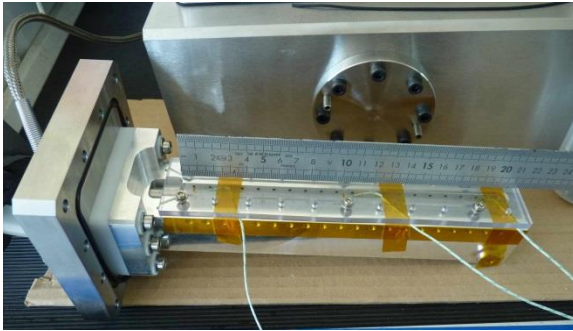


Figure 8. CNES strand burner specifically developed for the study of liquid monopropellant combustion velocity

Bulk propellant combustion study shall be completed by more representative configurations. This is why additional studies are carried out on the GIMLI bench (*Green Ionic Monopropellant Lab-scale Investigation*). This bench, of very great modularity, allows a wide range of analyzes, covering the following areas: injection/atomization process, ignition, flame propagation in sprays or even combustion instabilities. One of the specificities of this bench can be found in its injection system, called MIS (*Microfluidic Injection System*), which is able to reproduce a 1 to 10 Newton thruster operation without any pressurized hardware (Fig.9).

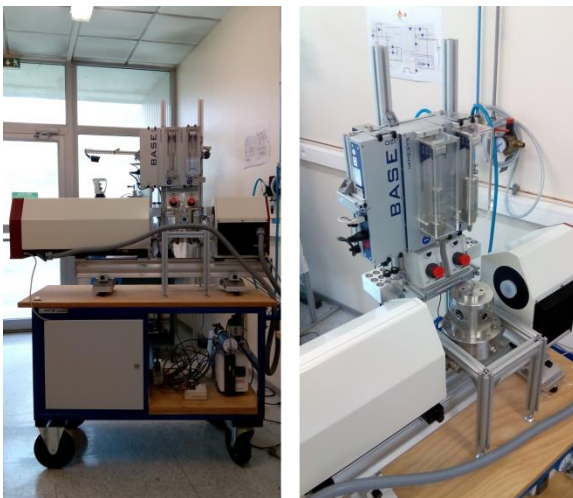


Figure 9. GIMLI test bench equipped with a laser granulometer and the MIS injection system

All those activities allow a deep understanding of monopropellant prototypes, obviously for selection purpose, but also to secure future developments at thruster level.

Many of these results are injected in multi-physics simulation carried out under ONERA's Cedre® computing platform. The ultimate objective is to run a fully representative thruster test case, taking into account injection, ignition, flame propagation and hypersonic gas ejection. To achieve this, the great specificities of liquid premixed propellant shall be taken into account and modeled. For instance, combustion kinetics and propellant droplets regression are two of the main issues to be tackled with [7].

4. ULTRA-HIGH TEMPERATURE MATERIAL

4.1 Origins and approach

As already mentioned in this paper, the adiabatic flame temperature reached by our monopropellant is close to that encountered in biliquid engines (2800-3000K). This is an obvious consequence of the following proportionality:

$$I_{sp} \propto \sqrt{\frac{T_{ad}}{\bar{M}}}$$

where T_{ad} and \bar{M} are the adiabatic combustion temperature and the mean molar mass of the gas products respectively. Since the combustion of CHNO substances generally provides \bar{M} values comprised between 22 and 28 g.mol⁻¹, the best degree of leverage in the race for I_{sp} remains temperature (Fig.10).

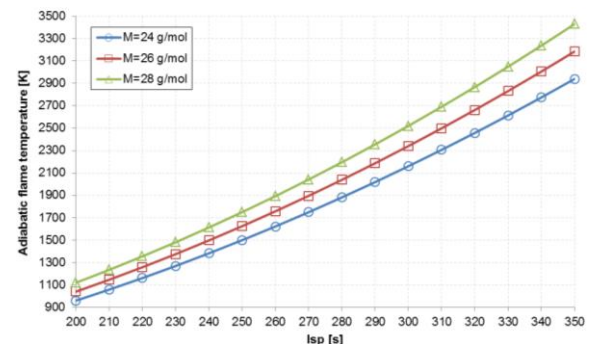


Figure 10. Typical evolution of adiabatic flame temperature with I_{sp} for three gas products mean molar masses

This is why we have adopted the rather bold position to develop a brand new ultra-high temperature material (UHTM) able to withstand 3000K (continuous) in a very oxidative environment. Clearly, there is no such material off-the-shelf, so that a Herculean work plan rapidly imposed itself. Fig.11 gives an overview

of the chosen R&D approach. First of all, a complete technological survey was conducted to appreciate the past and current, wrong or promising, research orientations. This helped us to define the most suited:

- i) material families ;
- ii) manufacturing processes ;
- iii) microstructures

all this through the prism of our own application constraints.

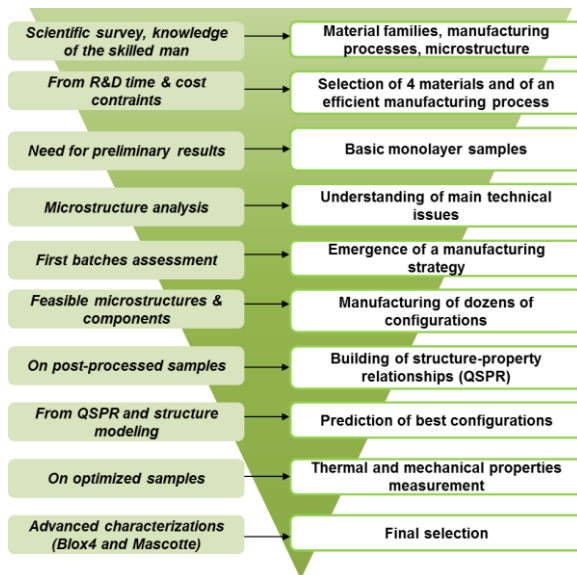


Figure 11. Overview of the MUHT development work plan, from fundamental to experimental studies

4.2 Technical requirements

The UHTM composing the thruster assembly (*i.e.* combustion chamber and nozzle) shall comply with the following requirements:

- Ability to withstand 3000 K (continuous) with a good softening/melting margin ;
- Absolute chemical passivity when subjected to oxidative inner flow (steam and free oxygen) ;
- High resistance towards thermal cycling (thousands of thruster start/stop between 300K and 3000K) ;
- Good thermo-mechanical behavior up to 20 bar abs inner pressure ;
- Excellent dimensional stability (in particular in the nozzle throat region) ;
- Perfect ageing of the microstructure (no cracking/delamination/debonding).

4.3 Major findings

We adopted a trial-error approach, mixing empirical deductions with structure-properties modeling. After many attempts to obtain a homogenous and stable material, we gradually found a way to build a satisfying composite structure.

A great part of our work was dedicated to the understanding and optimization of the additive manufacturing process, in terms of:

- Powders pre-processing: it was found that precursors granulometry and mixing have a major effect on deposition process and microstructure. A huge work was thus dedicated to the mastering of powders shaping ;
- Powders injection: there are many ways of injecting/mixing powders which can produce very dissimilar deposits. Finding the best injection process is a tricky task and can only rely on an empirical iterative approach ;
- Process kinematics: multi-species powders can introduce an additional issue due to the density gap between the precursors. This must be absolutely solved to obtain homogenous layers ;
- Thermal control: additive manufacturing of UHTM obviously requires the process to be performed at high temperature. To ensure uniformity of deposits characteristics, substrate temperature – on which powders are deposited – must be precisely mastered. This requires a deep understanding of heat and mass transfers during the multi-layer building process. Cooling of the substrate by a gas flow can then be optimized to respect a certain temperature window ;
- Complex shapes: once all those critical points mastered, a last step is to jump from rather simple shapes (*i.e.* plates and tubes) to complex parts such as a thruster assembly. To achieve this, important work has to be carried out on process automation, in particular to ensure a perfect overlap of the layers between each pass. This is the point where we are now.

An example of the result of the agglomeration of all these lines of work can be seen on Fig.12.



Figure 12. Example of UHTM sample obtained by additive manufacturing in the frame of this project

The “planar equivalent” of this microstructure was recently subjected to a BLOx4 test campaign and gave very promising results in terms of thermal cycling between ambient and 2700K : i) excellent resistance towards high rate thermal shock, ii) no microstructural cracking and iii) no chemical attack neither oxygen inclusion.

Over 2700K, some defaults are expected to appear during the BLOx4 tests. This is why, in parallel with manufacturing activities, an intense work is still underway on the improvement of the composite functions. More particularly, two issues are currently addressed:

- Increase of structural stability at highest temperatures: it is indeed thought that additional composite doping with Rare Earth species could enhance structural stability, especially under harsh thermal cycling (ambient-3000K) [8] ;
- Reinforcement of the antioxidant barrier: again, use of combined Rare Earth species could generate a synergetic effect to drastically decrease oxygen diffusion through the barrier.

In order to sustain these two research axes, specific samples are designed and tested.

On the one hand, crystalline phase stability is especially assessed by X-ray diffractograms comparison before and after BLOx4 testing.

On the other hand, antioxidant barrier efficiency is evaluated by an ionic conductivity relaxation method [9]. Our objective is there to try as many co-dopants combinations as possible in order to build semi-empirical correlations.

5. CONCLUSION

This paper provided a detailed description of the CNES “High Performance Green Monopropellant” Project taking place between 2016 and 2020.

After a brief reminder of the context – showing how a mid-term alternative to hydrazine could be beneficial –, technical objectives and roadmap have been reviewed. Everyone could appreciate the extent and complexity of the work in progress, whether in the fields of propellant or UHT material.

Last achievements were then presented. The 300 seconds specific impulse target never seemed so credible, while encouraging results were obtained on the UHTM.

Last characterizations are still in progress on monopropellant so as to be in line with applicable regulations. Synthesis scale-up has been validated and keeps going up.

All this leads us to think that the thruster demonstrator will be able, as hoped, to come to fruition in 2021.

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