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Advanced Hybrid Solid Fuels

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Enabling hybrid rocket propulsion to compete with solid and liquid propulsion is the target of the renewed international interest in hybrid rockets.
From the performances standpoint, conventional hybrids may compete with conventional liquids such as LOX Kerosene and could be much better than solids but they have 2 major drawbacks;

- A low burning rate of current solid fuels represents the main one to overcome for successful operations of hybrid propulsion on large scale.
- Combustion problems with a low combustion efficiency, instabilities and a high level of residuals (difficult mastering of the combustion with a multiport motor)

Moreover, to be really attractive, new formulations have to bring a decisive advantage with a much higher specific impulse. nevertheless these new formulations have to keep the 3 major ones of hybrids; a safe operating mode due to a very high level of mechanical properties, a cheap manufacturing process due to a pure fuel solid grain and the capability to be stopped on demand.
Some formulations appears really attractive with a high burning rate and a good combustion with or without a large increase of the specific impulse
The present paper describes the efforts, by a joint team of investigators, to reach this objective by promoting the use of novel energetic ingredients in hybrid solid fuels and will give an example of application.
A variety of new formulations was tested keeping in mind that both combustion behavior and mechanical properties of solid fuel grains are important for applications. Thus, a systematic experimental investigation was planned to determine the relevant properties of several candidate formulations. For this purpose, a micro-sized hybrid rocket motor test bench was implemented for quasi-steady solid grain regression rate measurements, CO_2 laser for radiative primer charge ignition, and exhaust gases dump system. The solid grain is shaped as a traditional fuel cylinder with one central perforation. Air or mixtures of oxygen and nitrogen, injected at the head-end of the motor, were used as gaseous oxidizer. This apparatus allows, on a relative scale, a quick classification of fuel regression rates and their sensitivity to operating conditions.

Three main directions were explored for developing advanced solid fuel compositions. The first one resorts to nano-sized energetic particles cast in HTPB solid fuel grains. The second direction resorts to fuels characterized by the presence of a liquid surface, resulting in droplets entrainment. Paraffin-based fuels were investigated revealing, for the investigated compositions, severe structural problems due to poor mechanical properties. The third investigated direction specifically addresses to metal hydrides compositions. In particular magnesium and aluminum hydrides formulations were analyzed, showing increases in the solid fuel regression rates depending on the hydride mass fraction.
The incorporation of metal hydride in HTPB-based fuel induces also an energetic increase. For aluminum hydride, the expected specific impulse (vacuum, $\varepsilon = 40$) augmentation is 32 s

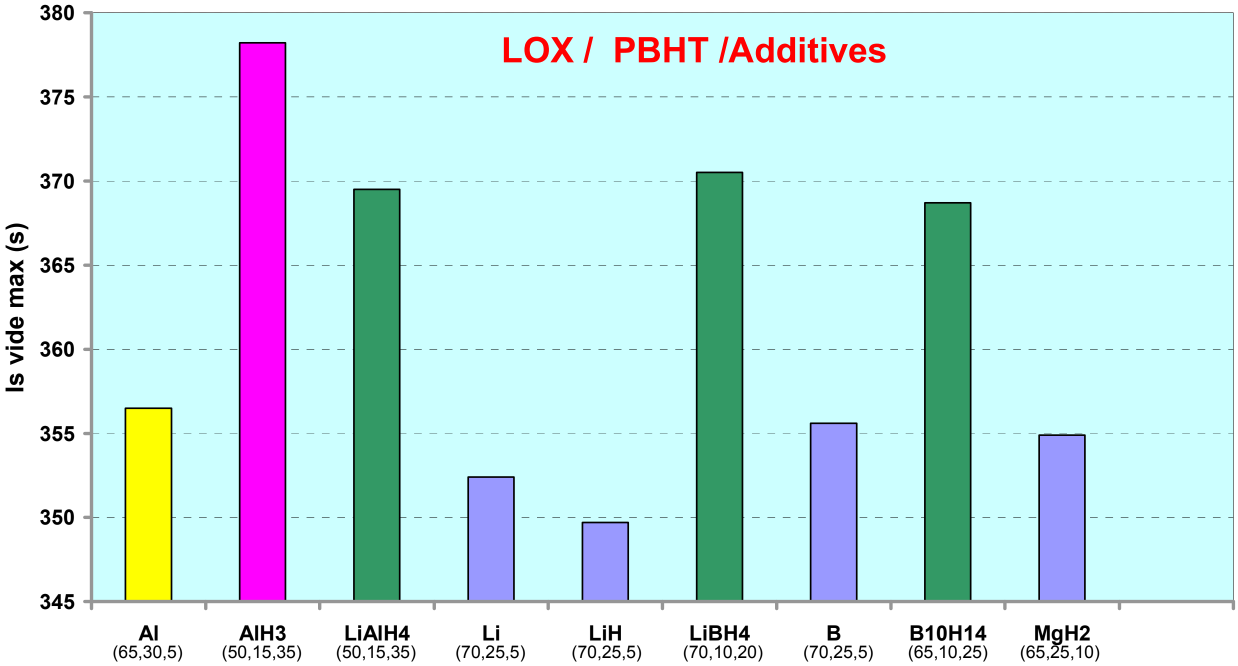

Fig1.: Comparison of the effects of additives on Isv max

INTRODUCTION

Among the chemical propulsive systems, hybrid rocket engines show some appealing advantages with respect to both solid and liquid rockets. Hybrid propulsion offers on-off capability, lower development cost, greater safety, and improved reliability. In addition, hybrid rockets have a lower environmental impact and a lower probability of motor failure due to the nature of hybrids combustion insensitive to the cracks and solid fuel grains, which may have better mechanical properties than the corresponding solid propellant grains (the grain is made of a pure binder or of a binder with a low load factor).
Yet an important drawback is represented by the low mass burning rate of the conventional solid fuels. Hence a larger burning surface is required for a given thrust with respect to solid rocket motors. So, hybrid grain need a large number of ports, the associated solutions (e.g. wagon wheels) magnifies the design complexity and costs; the requirement will be to be able to come back to a single port configuration to be accepted for propulsion systems

Currently adopted solid fuels are thermosetting polymers (e.g. derived from HTPB curing), thermoplastic materials (e.g. polyethylene) or non polymerizable ones as paraffin (initially proposed at Stanford University)., but associated with LOX they are never better than its liquid challenger : LOX Methane even if hey are theoretically but better then the solid

Propellant		Mixture Ratio	Equivalent Density [kg/m^3]	Isv Th (Pc 7MPa, Σ=40)
Solid (AP/Al/HTPB)		68/18/14	1750	315
Hybrid (LOx / HTPB)		72/28	1060	354
Liquid Bi Propellants	NTO/MMH	2.37	1200	341
	H2O2/RP1	7.0	1320	314
	Lox/RP1	2.77	1030	358
	Lox/CH4	3.45	830	369

Table1; LOX/HTPB vs competitors

So the new hybrid family has to both to increase the burning rate (such as to be able to design a simple grain configuration) with a hybrid combination offering an attractive specific impulse (with a structural ratio better than the liquid)

THE NEW FAMILY

Looking to the additives ever tested or envisaged in the past the only products than can provide a Hybrid with an high level of specific impulse are the Hydrides : Alane (AlH3) with 32s more than LOX HTPB, LAH (LiAlH4), LiBH4, B10H14 can be considered as good candidates. The effect on the global density is also always positive; these additive being denser than the binder alone (HTPB or Wax)

Alane is the more energetic and it have been studied and used for solid propellant , so it have been produced in a stable crystal phase and its compatibility with the others product used to realize the grain studied ; It is the more attractive ; Today it is a strategic product for Russia , that apparently uses Alane for some of its solid motors; USA , China and France have the manufacturing into study

	A	B	C
LOX	50	57	55
R45HT	15	23	23
AlH3	35		22
MgH2		20	
Density (g/cm3)	1.188	1.115	1.128
Conditions P =7MPa Epsilon=40			
T (K)	4044	3617	3903
Is vacuum (s)	378.7	354.2	373.7
IsvRho (s.g/cm3)	449.9	395.1	421.5

Table 2: Some results

Use of Hydride have 2 other advantages:

- **Including crystalline loads** increase the **roughness surface** being vaporized and ejected–The turbulence is augmented all along the grain improving the combustion and reducing the instabilities risks
- **The hot gases composition changes and becomes much less erosive**

moles/100g	LOX-CH4	SOLID	Wax	Wax MgH2
H	0.161	0.156	0.035	0.016
H2	0.398	1.136	0.074	2.955
OH	0.359	0.024	0.278	0.000
H2O	2.112	0.035	1.255	0.005
O	0.085	0.002	0.076	
O2	0.178	0.000	0.506	
CO	0.824	0.847	0.455	1.404
CO2	0.562	0.032	0.961	0.000
N2		0.288		
AL2O3		0.337		
HCl		0.467		
MGO				1.090

Table 3: Combustion gases comparison

Speaking of Isv performance, , the combustion law being of the type r_b=A.G^n (A the burning surface and G the mass flux), the mixture ratio (O/F)will evolve along the combustion time , a loss depending of the grain and of the thrust law requirement has to be evaluated for a given project

REGRESSION RATE INCREASE

In the past the major work done to study the regression rate enhancement was done on Oxygen combinations (e.g. HTPB, Polyethylene)
For a civilian Launch Vehicle, LOX have no competitor; it is the more energetic one that is not toxic (as Fluor or ClF3 are)
Acting on the solid grain, there are some effective

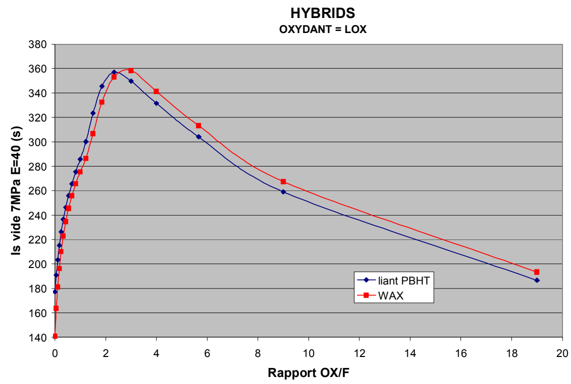

Fig 2 : Isv evolution vs O/F (Wax and HTPB)

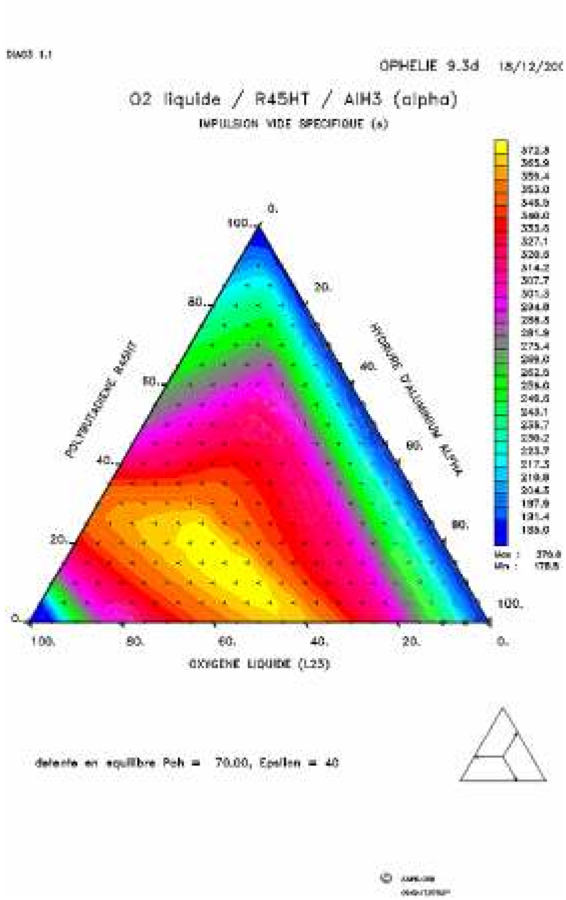

Fig.3: Ternary Diagram for HTPB/Alane/LOX

but forbidden solutions such as:

- addition of an oxidizer or nitro organic compound
- use of an energetic binder (except in a small amount)

The requirements to may use light classical facilities to produce a grain classified out of the class 1 is mandatory to keep the cost advantage of hybrids and to be able to easily demonstrate that the shutting off the oxidizer flow terminate the combustion.

In the new proposed family, the fact to use a hydride, the only ways to adjust the regression rate will be:

- to select the binder or a blend of binders:

- to use conventional ballistic additives

The hydrid itself will have an effect on the regression rate resulting of the particles ejection due to the hydrogen outgasing, nevertheless it cannot be enough. On some HTPB/Hybrid tests, the literature show a small increase, but Alane has a higher combustion temperature and the effect would be amplified

Choice of the binder

For many years HTPB was a likely candidate for hybrid motors for ETO applications: the overall reaction with oxygen is taken as:

$C_4H_6 + 11/2\ O_2 \rightarrow 3\ H_2O_2 + 4\ CO_2 + 6.8$ Kcal/g.

HTPB has a high endothermic heat of ablation, the pyrolised fuel vapor is transported to the flame zone by convection and diffusion, where it mixes with the oxidizer and burns, but the fuel flux due to the pyrolisis stops some of the heat transfer to the surface which is the cause of a low regression rate [ ]. Waxes used in Hybrids are a mixture of n-Alkanes (non polymeric saturated Hydrocarbons) and as DCPD or PE doesn't contain oxygen, it is well able to encapsulate reactive loading, with a better ratio carbon/ hydrogen. Its performance associated to LOx is better than DCPD and equivalent to HTPB, so Wax could be an ideal candidate to replace HTPB. The major advantage on HTPB is to have a basic regression rate (without any additives) greater in a ratio 2.5-3.5 [].

THE TEST FACILITIES OF SPLab

In this context, Space Propulsion Laboratory (SPLab) of Politecnico di Milano developed a microsized testing facility for hybrid combustion investigations This experimental rig includes a pressurized test chamber capable of pressure up to 30 bar, an oxidizer line, and a video acquisition system for quasi-steady rate measurement of solid fuel regression. A CO2 laser is used for the primer charge ignition; the dump system of burnt gases provides chamber pressure regulation by means of automatically driven exhaust valves; a thermalex changer is applied to exhaust piping. An overall sketch of the hybrid test facility is shown in Figure 4. The major objective of this facility is to quickly assess the comparative influence of the operating parameters on the solid grain regression rate. Main testing conditions (fuel grain composition, oxidizer flow rate, and chamber pressure) can easily be changed. Fuel grain samples are manufactured at SPLab and can be enriched with a variety of high-energy ingredients, ranging from uncoated or coated nano-aluminium powders to metal hydrides. Examples are given in Fig. 5

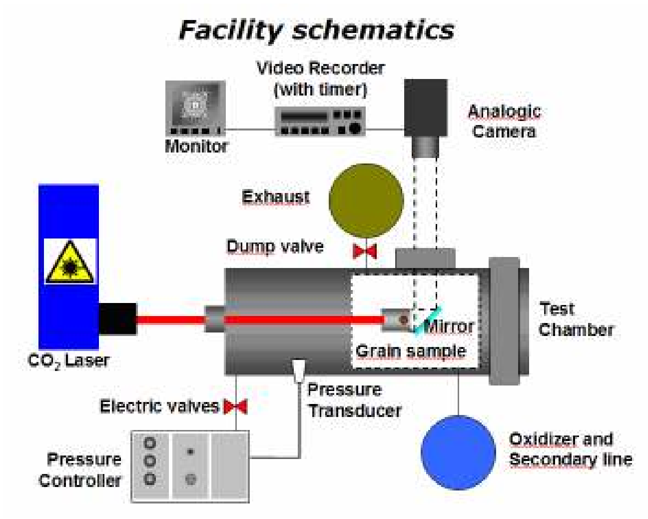

Fig. 4 Overall sketch of the hybrid test facility.

Fig. 5 Test samples

A single port grain is normally considered for the sample geometry. The central perforation is produced by a mandrel and can be easily modified according to needs. Other perforation geometries can easily be tested, thus allowing evaluating their influence on ballistic properties.

Testing Facility Description

The grain is accommodated in a cylindrical iron case mounted in a pressurized chamber. The fuel shell is ignited and the regression is monitored by means of a video recording device. In this phase of the investigation the hybrid testing facility was operated with different gaseous oxidizers up to 13 bar and with a solid fuel grain featuring a single circular port. The ignition system is based on an aluminized solid propellant primer charge, positioned between the frontal surface of the grain and the preburning chamber; this location allows to uniformly heat the “inner leading edge” of the grain and its internal surface. The primer charge is ignited by a CO2 laser source located outside of the chamber. The beam is driven to the primer charge with a set of mirrors, lenses and windows.

The video system is based on an analog camera (Xybion SVC-09, 25 fps); this component was chosen because of the long burning times. A timing device and monitor complete the video

setup. For each test, the corresponding video recording is processed using the proprietary software package *Hydra* entirely developed at SPLab and able to follow the advancement of the regressing surface in time. After some digital filtering of the signal, the test regression rate is obtained.
This is a very-low cost and efficient method of measurement of the regression rate

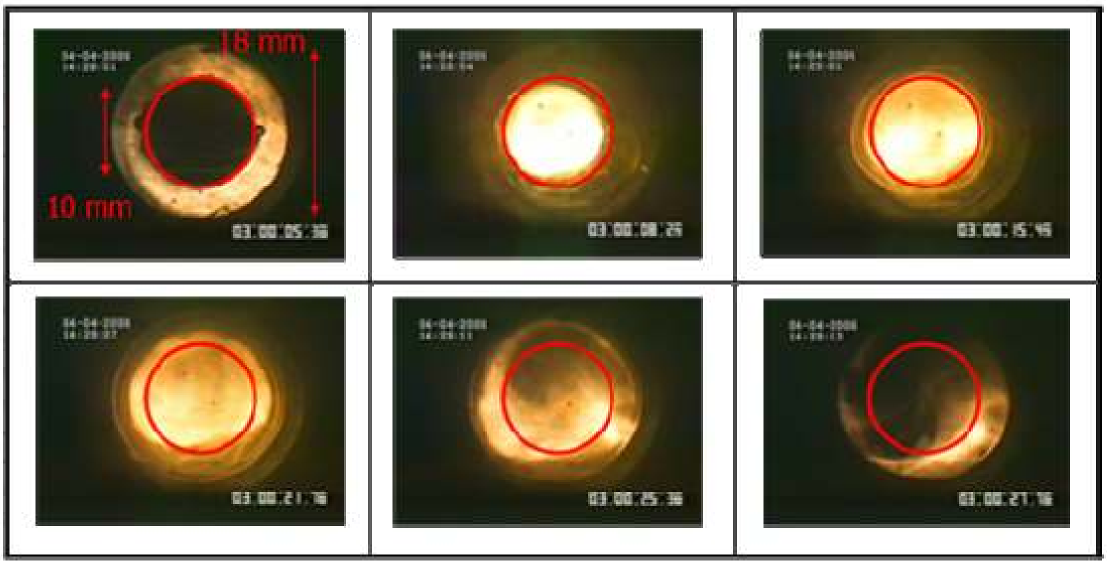

Figure 6: Video-recording frames of a typical burning test

IGNITION DELAY

The ignition delay of hybrid formulations was investigated in the experimental setup sketched in Fig. 7.

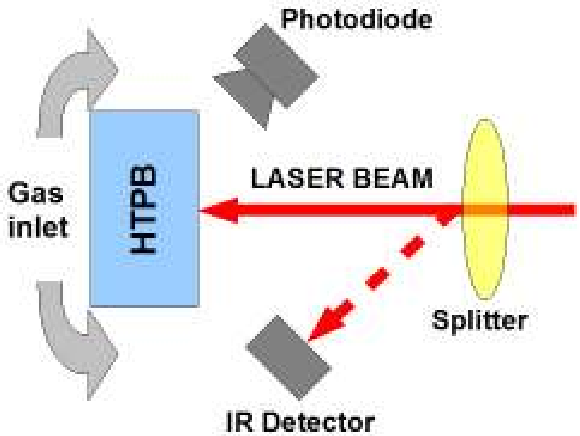

Figure 7: Setup for the ignition delay measurement

The HTPB sample is placed in a combustion chamber filled with an oxidizing gas mixture. A continuous gas inlet from the rear side of the sample is controlled by a flow meter. The ignition delay is evaluated as the time lag between the laser impingement on the sample and the beginning of flame spreading. The laser beam is detected by an infrared detector combined with a beam splitter, while the flame onset is detected by a photodiode sensible to visible light.

The experimental setup allows testing different operating conditions such as pressure, oxidizing mixture or radiant flux.

RADIANT ENERGY EMISSION

The radiant energy emitted by a variety of HTPB solid fuels, including HTPB/paraffin-based fuels, burned in a gaseous 50% O_2 + 50% N_2 oxidizing mixture, was measured by means of a micro-calorimeter. Thermal radiation effects in hybrid combustion were investigated in 1991, by Estey et al. showing that thermal radiation improved correlations for metal added solid fuels, whereas for nonmetallized hydrocarbon fuels convective heat transfer correlations gave better results. Strand et al., in 1994, in contrast to Estey's results, found that radiation from soot greatly affected the pure HTPB regression rate. This is only one example to show that questions still exist about the extent of radiant heat flux in hybrid motors, especially considering modern solid hybrid fuels.

Fig.8: Views of the combustion chamber and of experimental set-up

The solid fuel grain samples used were rectangular (15 x 22 x 4 mm) to allow combustion in a turbulent boundary layer with heat and mass transfer. Samples were arranged in a rectangular cross section chamber (32 x 24 mm, 100 mm long); lateral windows allowed visualizing the combustion process. The fuel sample was ignited using a hot wire; the pressure was kept constant during the test due to an automatic pressure control system. The radiant energy, emitted during the combustion process, was measured by means of a micro-calorimeter, put on the top of the chamber. Details of the experimental set-up are shown in Figures 7, and a sketch of the lay-out in Figure 8.

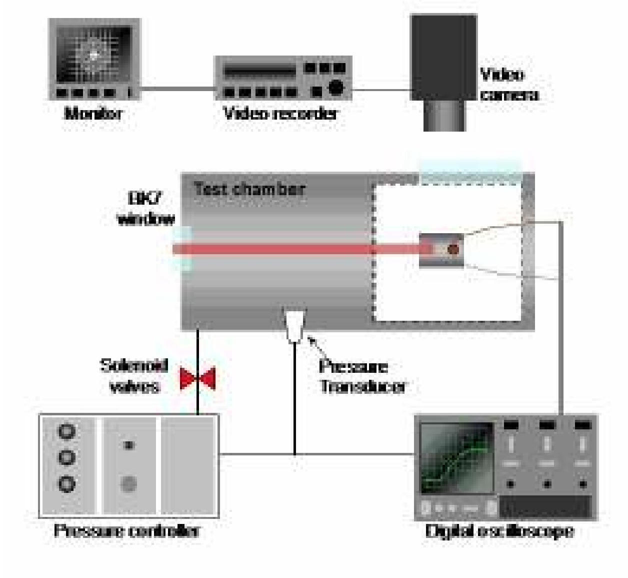

Figure 9: Schematic of the experimental set-up

Radiant energy

Radiant energy measurement

The radiant energy flux sensor used in this work is a "home made" improved version of Zenin's micro-calorimeter. The sensor is manufactured and calibrated at SPLab. The sensitive element consists in a thin copper disk (0.3 mm) with a micro-thermocouple welded on the back surface. The calorimeter thickness is small enough to have a low thermal inertia, allowing dynamic radiant flux measurements over most of the burning time of the solid fuel. The calorimeter temperature rise is sufficiently small to make radiation energy losses negligible as compared to the measured heat flux. This is essential to ensure a good accuracy because radiant losses are not taken into account in the sensor model. To avoid heating or cooling of the calorimeter, due to convective and conductive energy exchange, the copper disk is put into a thick Plexiglas housing, with its blackened surface facing a cylindrical ZnSe window. The window allows most of the radiation to pass through, heating up the disk, but prevents the combustion gases from reaching the calorimeter. Conduction through the Plexiglas housing, in which the calorimeter is perfectly sealed, is negligible.

Results and Discussion

Detailed results on pure HTPB fuel and HTPB loaded with micro- aluminum are shown in [6]; amazingly these results shown a pressure dependence of the regression rate

Several tests were performed on Hydrides using these facilities; they confirms a strong potentiality of Hydrides to accelerate the combustion taking into account that the best fuel is a 30/70 ratio HTPB/Alane

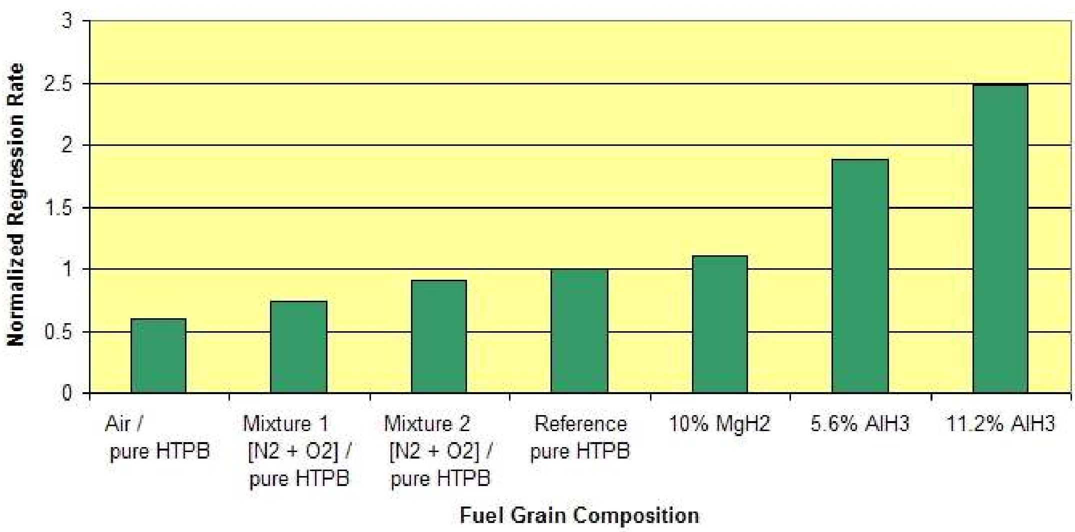

Fig. 10: Effect of Hydrides on the regression Rate

FUTURE WORK

The work will focus on investigating::

- Follow on the work made on HTPB loaded with Alane and different Hydrides
- the effects of additives in HTPB-Hydrides on burning behaviors, to investigate ways of tuning the regression rate
- the general behavior with hydrides of paraffin-based fuels, a new important effect being expected.

REFERENCES

[1]Altman, D. (2003) Highlights in Hybrid Rocket History, 8-IWCP "Rocket Propulsion: Present and Future", De Luca, L.T. (ed.), Grafiche g.s.s., Bergamo, Italy, paper No. 07.

[2] Kuo, K.K. (2007) Fundamentals of Hybrid Rocket Combustion and Propulsion, AIAA Progress in Astronautics and Aeronautics, Vol. 218, Chiaverini, M.J. (ed.), AIAA, Inc., New York, NY.

[3]Chiaverini, M.J., Kuo, K.K., Peretz, A., and Harting, G.C. (2001) Regression Rate and Heat-Transfer Correlations for Hybrid Rocket Combustion, *Journal of Propulsion and Power, Vol. 17, No. 1, pp. 99-110*..

[4] 8-IWPC-Rocket Propulsion: present and future –Pozzuoli, Italy-June 2002- Evaluation of AlH3 for Propellant Application- May Chan and Curtis E. Johnson- NAVAIR Weapons Div., China Lake

[5]AIAA-2004-3823-LOX/HTPB/AlH3 Hybrid Propulsion for Launch Vehicle Boosters M.Calabro The Inner Arch,

[5]Chiaverini M.J., Kuo K.K., Peretz A., Harting G.C., "Regression rate and heat transfer correlations for HTPB/GOX combustion in a hybrid rocket motor", AIAA Paper No 98-3185, 1998.

[6] 7-ISICP Advances In Hybrid Propulsion. Galfetti, L.T. DeLuca, et al, *SPLab, Politecnico di Milano,*