Innovative Formulations for Solid and Hybrid Rocket Propulsion

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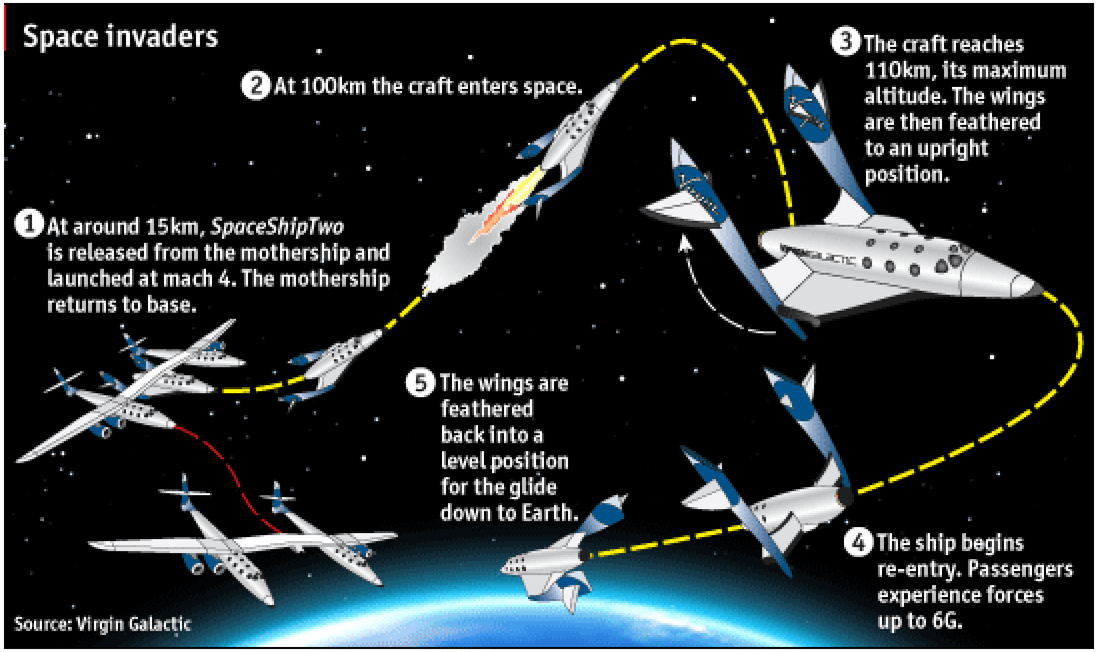
Plan of Presentation - Overall

➔ General Introduction to Rocket Propulsion

- Basic Concepts and Definitions
- Solid Rocket Motors (SRM)
- Solid Rocket Propellants (SRP)
- Metallized Formulations
- Nanosized Metals
- Solid Fuels for Hybrid Propulsion
- Conclusions and Future Developments

Introduction Propulsion 1

- Propulsion is the applied science that studies and designs those devices, called engines/motors/thrusters, capable to modify the motion of a body (for example, start a motion, change velocity and/or direction, stop a motion in progress).
- In a broad sense, propulsion also studies the associated operating modes (such as trajectory optimization).
- Aerospace propulsion specifically studies and implements applications for both the aeronautical domain (that is, with altitudes limited by the presence of an atmosphere) and the space domain (that is, in vacuum).
- Conventionally, 100 km altitude is the accepted boundary aero/space.

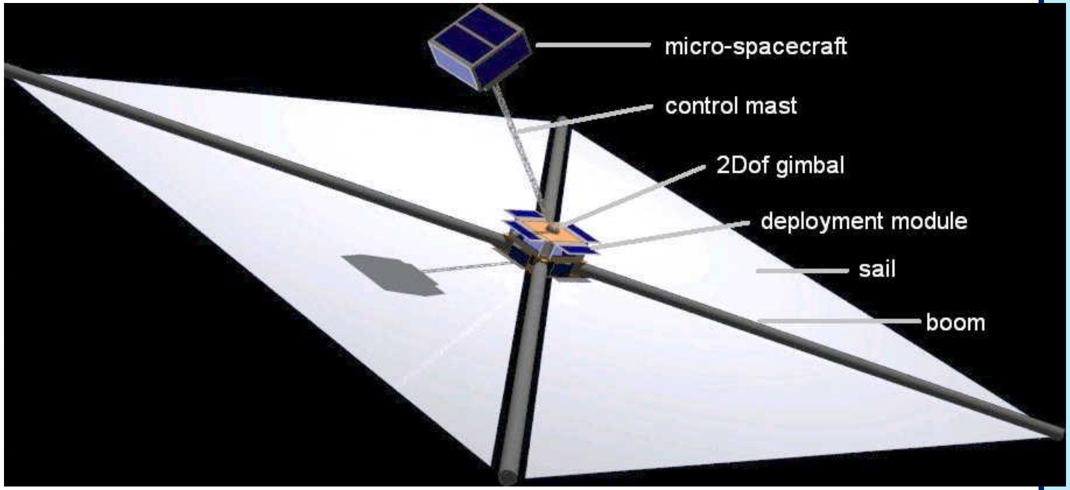


Introduction Propulsion 2

- Jet propulsion is a particular but widespread propulsion technique based on the principle of momentum conservation: expulsion of matter in a given direction (action) causes a thrust (reaction) in the same direction but opposite sign.
- Propellant (or expellant) is the matter that constitutes the exhaust jet.
- While the exhaust jet is mainly or totally in the gaseous state (gasdynamic nozzles suffer in the presence of condensed phase), the propellant stored in the tank(s) is commonly in the liquid or solid state (to save volume and inert mass, as for all flying objects).
- According to the specific propulsive device, the exhaust jet - in addition to mass – involves a variety of further effects: thermal (high or low temperature), chemical (reactive or inert), electrical (charged or neutral), visibility, pollution, radioactivity, and so on.

Introduction Propulsion 3a

- Propellantless propulsion is of particular interest **for space navigation** (specific impulse more important than thrust); for example: solar sails.
- **Solar sails** offer a wide range of applications for high-energy low-cost missions in space propulsion with low-thrust and no propellant. Sails are accelerated in space by reflecting solar photons off large mirroring surfaces, thereby transforming the momentum of photons into a propulsive force.



Fully deployed 20 m × 20 m solar sail at DLR-Cologne

DLR design for a free-flying three-axis stabilized sailcraft with deployed control mast

Introduction 4

- Propulsion in general is not a basic science, but resorts to concepts and notions of chemistry, thermodynamics, heat transfer, radiation, mechanics, gasdynamics, electromagnetism, and possibly nuclear physics.

- Difficulties that are faced in the theoretical studies and practical realizations are due to the needed integration of very different topics and the extreme values of operating conditions:

- pressures ranging from vacuum up to o(100) di atm
- temperatures from o(10) K up to o(10, 000) K
- operation times variable from fractions of second to weeks (even years, in the case of satellites or interplanetary probes)
- gasdynamics from subsonic to supersonic and maybe hypersonic
- multiphase reactive turbulent compressible flows
- cryogenic hydraulics,
- intense heat transfer also of radiant nature
- and so on.

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- Short History
- Basic Architecture and Figures of Merit
- Solid Rocket Propellants (SP)
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- Nanosized Metals
- Motor Performance

NASA State of the Art for Space Exploration

TRL = Technology Readiness Level

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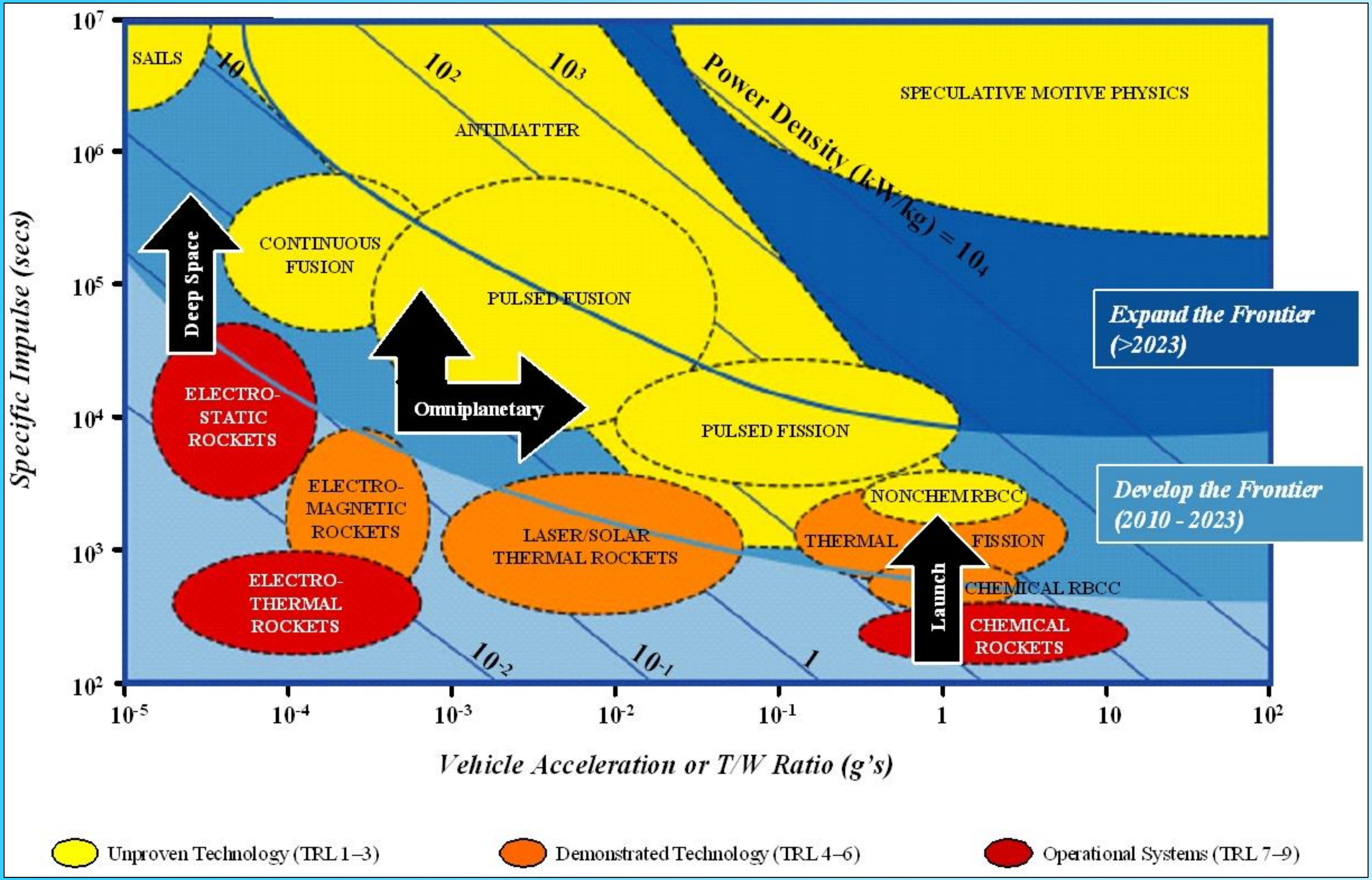


The European Space Launchers Family

Ariane-5 up 4,000 - 19,500 kg

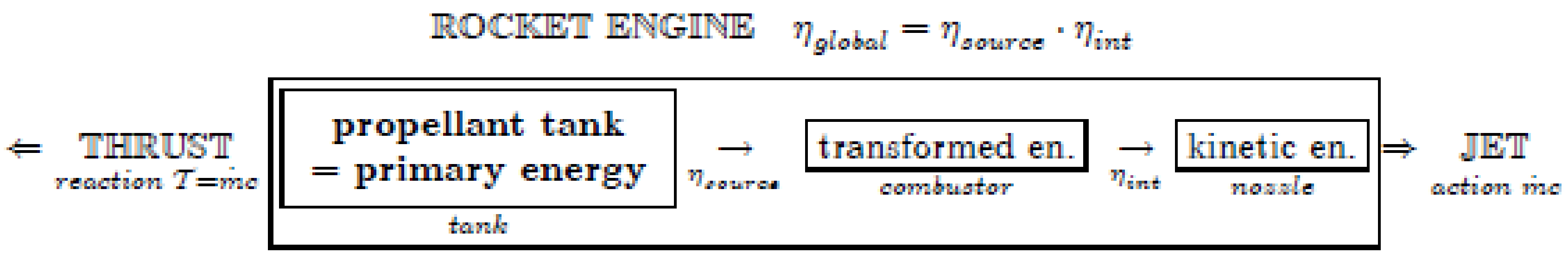
Soyuz 1,500 - 4,900 kg

Vega 50 - 1,500 (2,500 next) kg

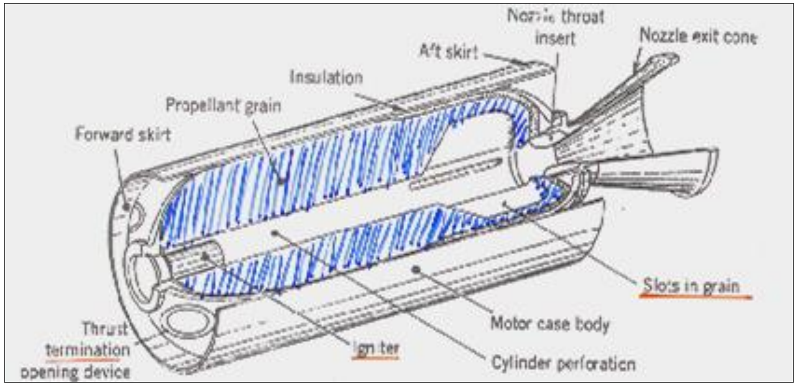
Energetics 1a

- From an energetic viewpoint, all **jet engines** (whether of rocket or airbreathing kind) can conceptually be portrayed as indicated in the following sketch.

- A typical, but not exclusive, configuration for thermochemical propulsion includes a **propellant**/energy **tank**, propellant combustor/energy **converter**, propellant **accelerator**.



(a) Conceptual sketch of *propellant* jet propulsion.



SOLID ROCKET PROPULSION

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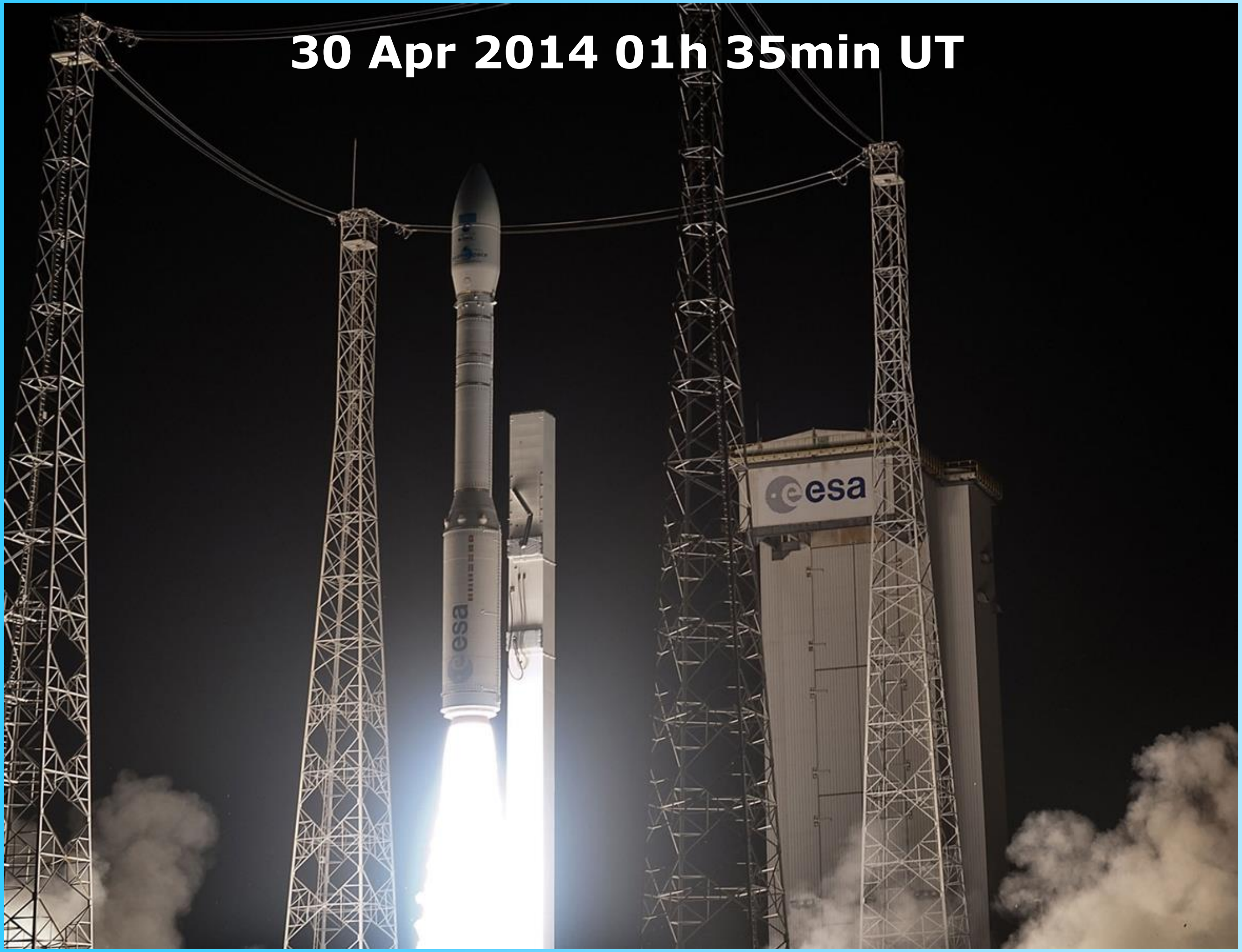

ADVANTAGES:

- High Thrust Density
- Readiness/Storability
- Manufacturing
- Cost
- **High TRL**

DISADVANTAGES:

- Short firing time
- No ON/OFF capability
- **Modest I_s**

HYBRID ROCKET PROPULSION

ADVANTAGES:

- Low Cost
- Safety and Low Impact
- ON/OFF and Throttling
- **Possible High I_s**

DISADVANTAGES:

- Low Regression Rate
- Poor Combustion Efficiency
- Time-varying Performance (?)
- **Low TRL**

FLOX/HTPB + Li with 11 perforations fuel grain showed I_s= 380 s for ε = 40.

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Main Features SP vs. HP

- Solid propulsion SP is a mature technology much used for a variety of civil and military applications.

➔ ***SRM provide prompt and storable large thrust in a compact, simple, reliable, and low-cost unit. High TRL.***

- Hybrid Propulsion HP is a promising technology in principle useful for a variety of civil and military applications.

➔ ***HRE may provide large thrust featuring low-cost and a good operation flexibility. Low TRL.***

- Thanks to some specific features (large thrust density, use readiness, long time storability, simplicity of operations …), SP will still be used for decades, especially for military missions.
- Follow Up: a wide body of literature available, but sensitive data not public.
- Purpose: offer a general survey of the current status and point out innovative solid or hybrid rocket formulations.

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State-of-the-Art

Current state of the art in chemical rocket propulsion.

45 contributions by outstanding international investigators:

- from 13 countries
- essentially experimental work
- introductory chapter

New oxidizers
New fuels
New binders
New additives of various kinds

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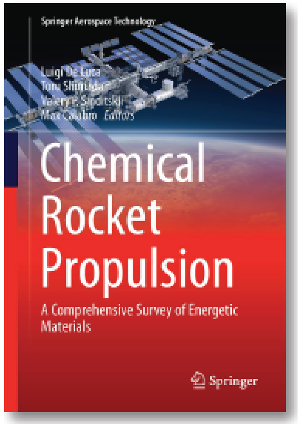

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L.T. De Luca, T. Shimada, V.P. Sinditskii, M. Calabro (Eds.)

Chemical Rocket Propulsion

A Comprehensive Survey of Energetic Materials

Series: Springer Aerospace Technology

- Brings together topics that are currently scattered across the literature, saving the reader time
- Presents research from across the world, including from Russian and Chinese teams whose work is not usually available
- Gives new research results in chemical propulsion

Developed and expanded from the work presented at the New Energetic Materials and Propulsion Techniques for Space Exploration workshop in June 2014, this book contains new scientific results, up-to-date reviews, and inspiring perspectives in a number of areas related to the energetic aspects of chemical rocket propulsion. This collection covers the entire life of energetic materials from their conceptual formulation to practical manufacturing; it includes coverage of theoretical and experimental ballistics, performance properties, as well as laboratory-scale and full system-scale, handling, hazards, environment, ageing, and disposal.

Chemical Rocket Propulsion is a unique work, where a selection of accomplished experts from the pioneering era of space propulsion and current technologists from the most advanced international laboratories discuss the future of chemical rocket propulsion for access to, and exploration of, space. It will be of interest to both postgraduate and final-year undergraduate students in aerospace engineering, and practicing aeronautical engineers and designers, especially those with an interest in propulsion, as well as researchers in energetic materials.

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Part III Metals as Energetic Fuels for Chemical Propulsion

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Part IV Solid Rocket Propulsion

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Part VI Hybrid Rocket Propulsion

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Once Upon A Time In China

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Solid rocket propulsion fortuitously stems from alchemist activities in China dating as early as 220 BC ca. Drugs made from minerals and metallic substances were considered more effective than the herbal ones. Black powder, or something similar, was a mixture of saltpeter (KNO_3), sulfur and charcoal - in various proportions - initially studied for medical reasons (elixir, longevity, immortality). The search for elixirs of immortality failed (being actually poisonous), but a new weapon was instead discovered.

Chinese soldier launches fire-arrow

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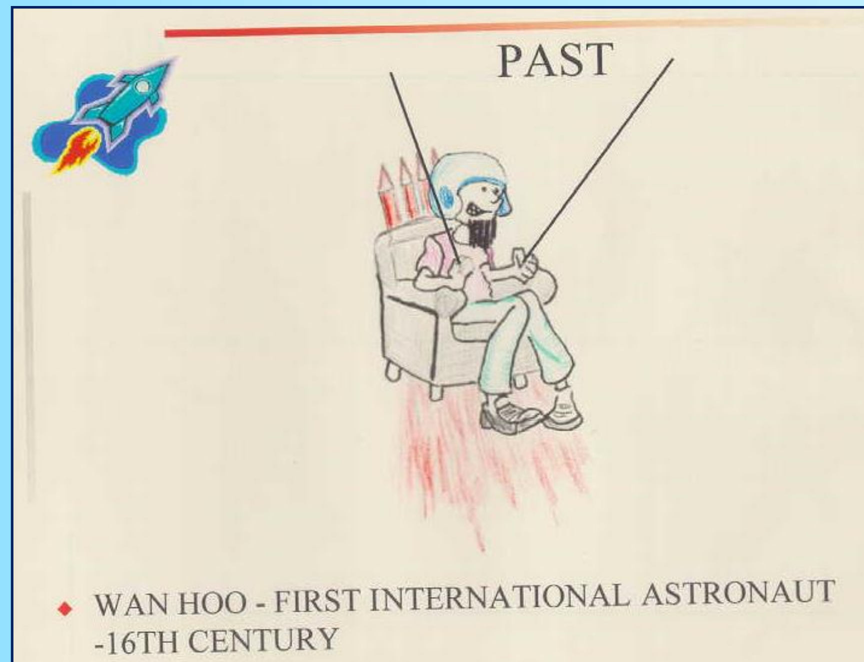
Once Upon A Time In China…

Wan Hoo or Wan Pu, circa 1500, a legendary mandarin
47 rockets (KNO3+S+charcoal in bamboo canes)

Wàn Hǔ (萬虎 or 萬戶) (d. ca. 1500) was a minor Chinese official of the Ming dynasty who attempted to become the world's first recorded astronaut. The crater Wan-Hoo on the far side of the Moon is named after him.



Courtesy of Civil Air Patrol showing characters from ancient Taoism; standing person is in Song Dynasty official suit.

History – Modern Times

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Von Karman (center) between Summerfield (left) and Malina (right), CalTech, USA, 1936-1944

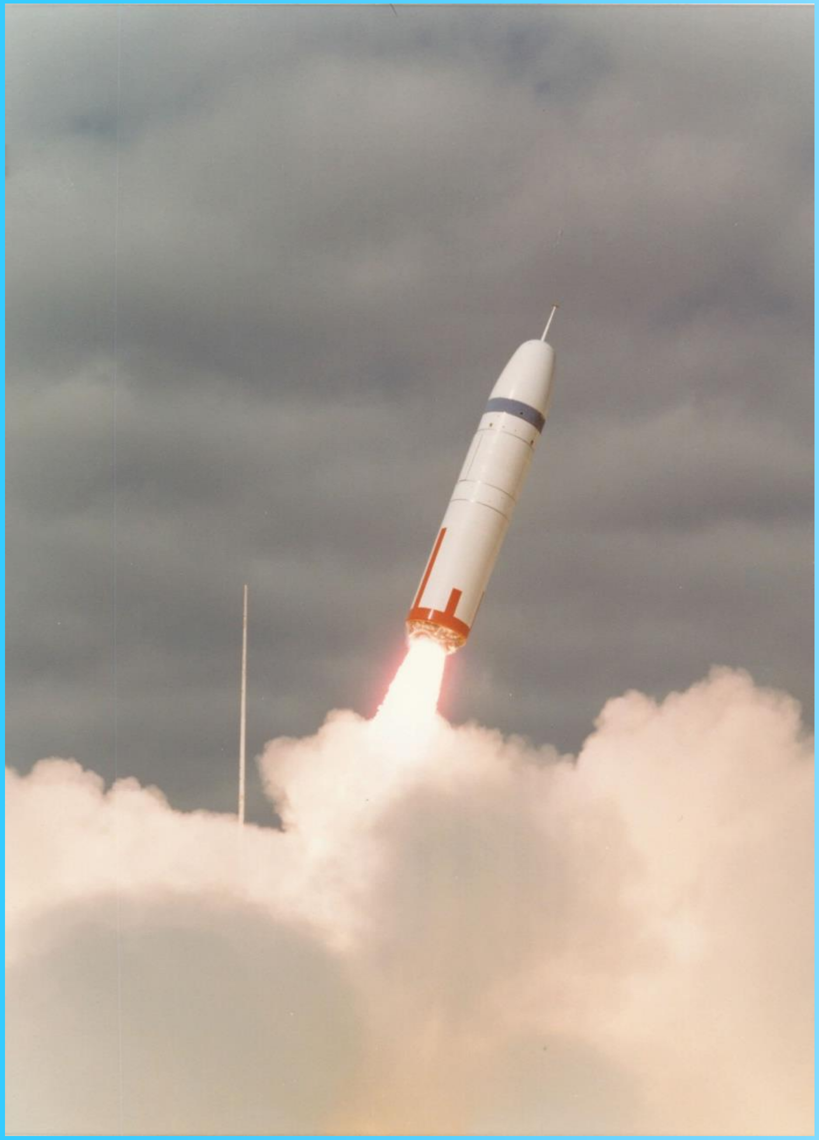
First composite castable solid rocket propellant by J. Parsons at GALCIT: $KClO_4$ + asphalt, June 1942, JATO

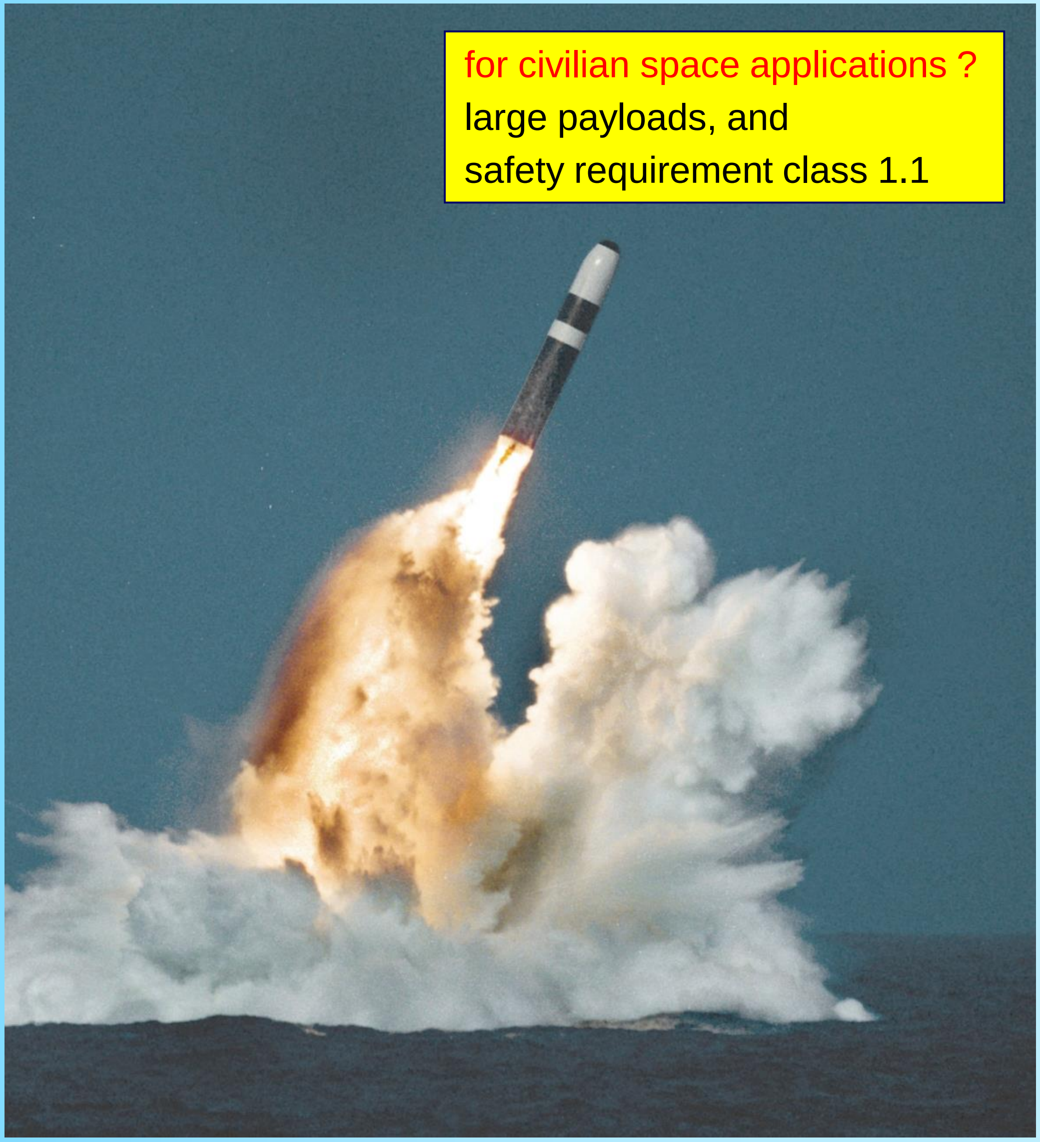
AP first used 1948 at Aerojet operational 1960 Polaris A1

Al powder tested for many years
ok lab only in 1955 @ Atlantic Research
ok motor firing 1956 @ Aerojet.

MOST PERFORMING SOLID ROCKET PROPELLANTS

Left: First launch of *Trident I* on 18 Jan 77 at Cape Canaveral
Right: submarine launch of *Trident II*





Plan of Presentation

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2. Broad overview of space propulsion systems
3. Main Features and Representative Realizations - SRM
4. Short history highlights SRM: Once Upon A Time In China…
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6. Internal Ballistics: Burning rate SRM
7. Flame structure SRM
8. Some movies to understand flame structure and combustion efficiency
9. Aggregation & Agglomeration
10. Metals and nanosized metals
11. Future propellants/expellants
12. Current innovative solid propellants – 2 EEC Programs
13. Hybrid propellant hopes - HRE
14. Actual motor performance – SRM & HRE

Future 1

Several families of HEDM propellants were identified, such as formulations based on high-nitrogen compounds, octanitrocubane $C_8(NO_2)_8$, metallic hydrogen, atomic radicals, metastable helium, and so on.

Metallic hydrogen is a theoretically dense energetic material (not yet produced on earth). The TRL level is not at level 1 as the characteristics are based on theoretical calculations. The estimated density at ambient conditions is 7 g/cm^3, 10 times LH2. Above a critical temperature, possibly 1000 K, metallic hydrogen will become unstable and recombine to the molecular phase, releasing the energy of recombination, 216 MJ/kg (for reference: LH2/LOx in the SSME releases 10 MJ/kg, RP1/LOx releases 6 MJ/kg). Ongoing experiments are using diamond anvil cells and short pulse laser technologies to follow the hydrogen melt line toward the conditions for the metallic state. Expected I_s values are in the 500-2000 s range.

The challenges in implementing are: upgrading existing experimental equipment is required for synthesis and characterization of small quantities of metallic hydrogen. Also, scaling up production by many orders of magnitude is required. Engine components must be developed that are compatible with metallic hydrogen. Test engines must be developed to verify expected operations and performance with a variety of diluents and mixture ratios. Potentially, there is a need for tankage that operates at several thousands MPa of pressure.

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Future 2

High-energy oxidizers such as fluorinated compounds include fluorides such as ClF3, ClF5, and OF2. These oxidizers were tested in the 1980s under the Strategic Defense Initiative (SDI). Flight testing was planned for hydrazine/ClF5.

Atomic Boron /Carbon /Hydrogen propellant have been investigated for many decades. Atomic hydrogen, boron, and carbon fuels are very high energy density, free-radical propellants. These atoms have been trapped in solid cryogens (neon, etc.) at 0.2 to 2 mass %. Atomic hydrogen may deliver an $I_s \approx 600$ to 1,500 s. There has been great progress in the improvement of atom storage density over the last several decades. Laboratory studies have demonstrated 0.2 and 2 mass % atomic hydrogen in a solid hydrogen matrix. If the atom storage were to reach 10–15 mass %, which would produce $I_s \approx 600 – 750$ s. The storage of atoms at 10, 15, or 50 mass % is needed for effective propulsion.

High-nitrogen compounds (N4, N5+, N5-, N8, etc.) are potentially the most powerful chemical explosives created in history. Work was conducted on N5+ and N5- in USA (AFOSR HEDM Program) and Sweden (N5-). Gram quantities of the (N5+) ionic salt were produced in the laboratory. Theoretical studies have shown that these materials may have in-space propulsion applications.

Future 3

Most of the previous HEDM are still **far from being practically usable in the short range** due to severe difficulties in large scale manufacture, ground processing, personnel safety, handling safety, transportation, prolonged storage, and cost considerations. In particular, these materials are highly shock sensitive.

Presently, there are **no integrated vehicle designs** that can make use of these possible propellants.

Work is continuing worldwide.

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SOLID ROCKET PROPULSION

How to Improve Performance ?

Typical Performance Losses SRM (10% of ideal vacuum $I_s \approx$ 330 s)

- Two phase flow losses (2P, 35% of overall losses, say about 10-13 s)
- Combustion losses (5% of overall losses, say ≤ 5 s)

Two approaches can be taken

- **Evolutionary** (for about 50 years, after Al and HTPB): mitigate performance losses, mainly 2P losses, of current (existing) propulsion systems. But little room left…, Green Programs for Clean Space…
- **Revolutionary long range**: Many new compounds proposed, but they are far from being practically usable in the short range due to a variety of severe difficulties in large scale manufacture, ground processing, personnel safety at different stages, handling and transportation safety, shock sensitivity, prolonged storage, and cost considerations. Work is continuing every day, but presently no integrated vehicle designs make use of these radically new potential propellant ingredients or formulations
- **Revolutionary feasible now**: use viable innovative energetic ingredients or techniques to augment performance and mitigate impact of rocket propulsion systems (Pak, 1993).

The European Approach & Objective

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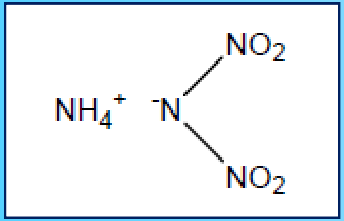
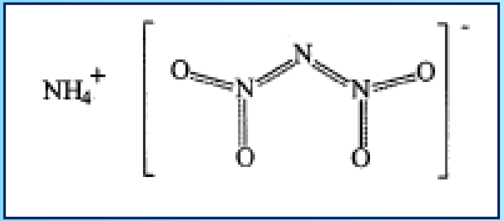
Approach according to Pak [Ref. 14, 1993], a composite metallized propellant using ADN (instead of AP), AlH_3 (instead of Al), and nitrate ester binder offers the highest I_s among all of the currently viable solid rocket propellants.

Objective identify a viable High Specific Impulse and Green Propellant for European launchers and space exploration motors (within the framework of two successive European Projects, called HISP and GRAIL, both coordinated by the Swedish FOI).





By properly combining three inorganic oxidizers all based on the ammonium cation $(NH_4)^+$, the innovative ADN with the two well-known salts AN and AP, a wide range of interesting applications beyond the current limitations appear feasible.

SPLab of PoliMi is in charge of the high-energy metallic fuel (formulation + characterization).

PROBLEMS

- Ballistic properties
- Mechanical properties
- Castability
- Hazards
- Ageing
- Cost …

Solid Propellant Oxidizers: Chemistry

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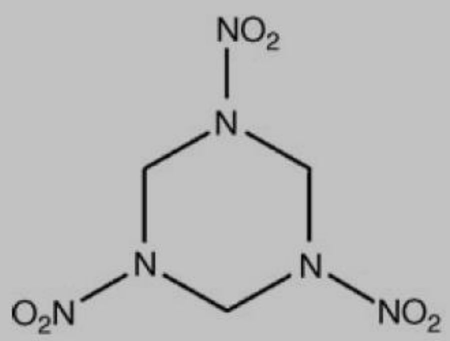
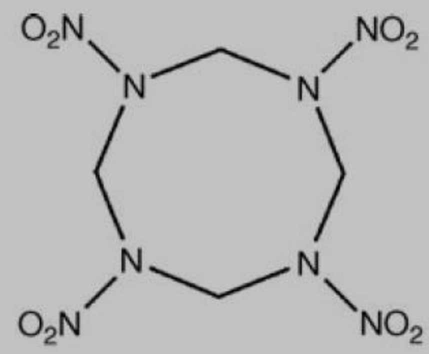
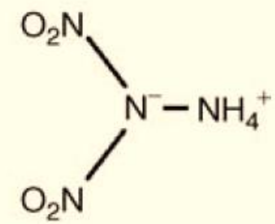


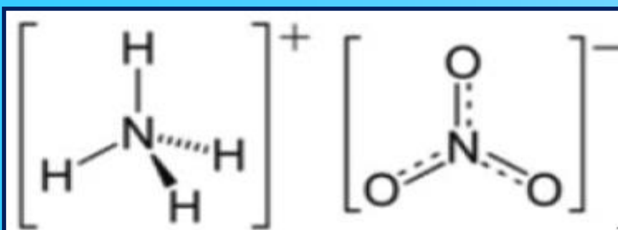
RDX (1899)



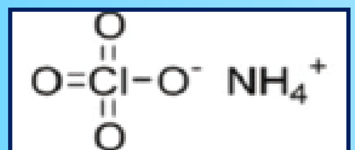
HMX (1943)



ADN (1971)

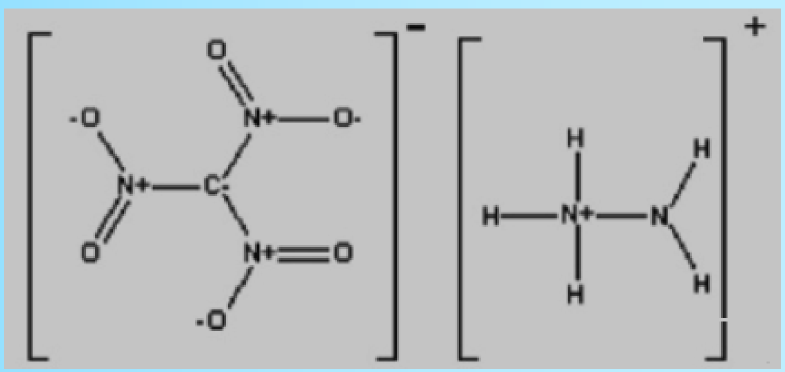


AN (1659)

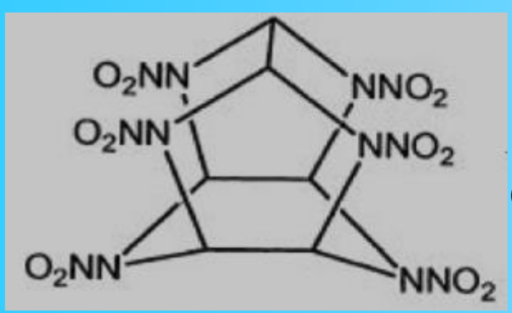


AP (1831)

$N_2H_5^+C(NO_2)_3^-$



HNF (1968)



CL-20 (1987)

… all are monopropellants (containing fuel + oxidizer) capable of self-deflagration …

Some Current Binders/Fuels

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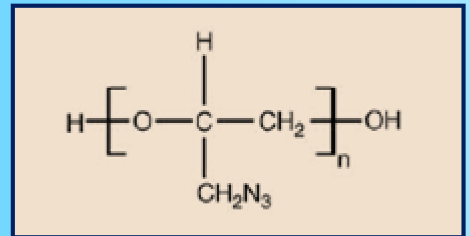
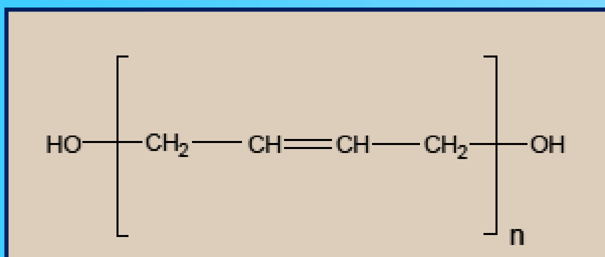


GAP, 1976, 3M and Eurenco (SNPE), T_g = -34 °C

$C_{2n}H_{4n+2}O_{n+1}$



$$H - [O - CH_2 - CH_2]_n - OH$$

HTPB, 1961, R-45T commercialized by ARCO, T_g = -68 °C
HTPB, 2014, R-45M Propulsion Grade™ by MACH I

HTPE

Prepolymers tested for binders in this investigation

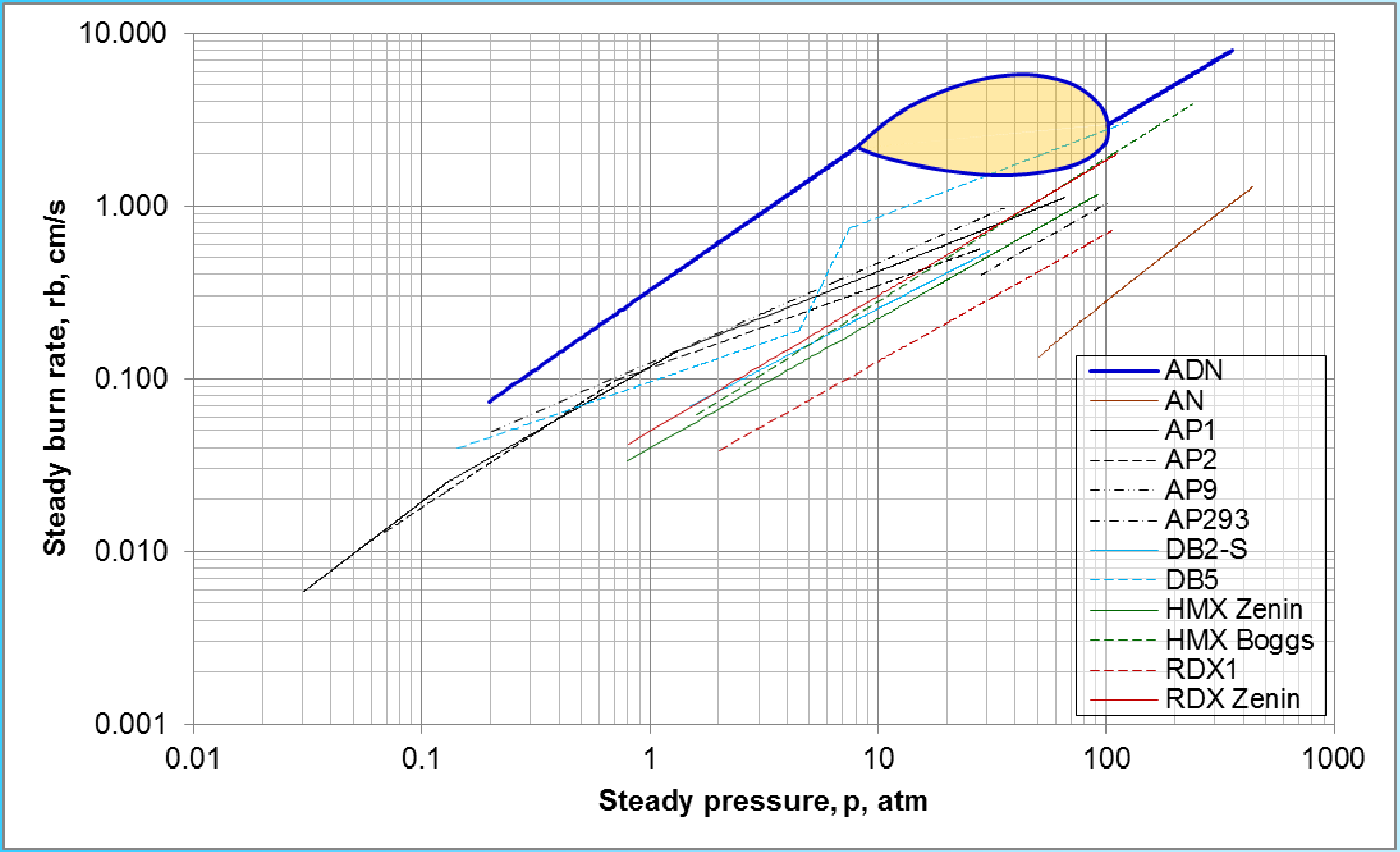
Denomination	Chemical Formula	Oxygen Balance, OB, %	Molar mass, $\mathcal{M}$, g/mole	Density, ρ, g/cm³	ΔH_f, kJ/mole	T_f, K
Desmophen® D2200	$C_{10}H_{16.678}O_{5.267}$	-166.9	221.2	1.18	-976.1	
GAP DIOL	$C_3H_5N_3O$	-121.1	99.1	1.29	+117.2	1570
HTPB-R45T	$C_{10}H_{15.4}O_{0.07}$	-323.8	136.8	0.918	− 62.0	-
HTPE	$C_6H_{12}O_2$	-220.5	116.1	1.04	-485.3	-
PGN	$C_3H_5NO_4$	-60.5	119.1	1.39-1.45	-322.8[30]	1465

ADN PECULIARITIES

AN and AP are both well-known and have been used at all levels for several decades, whereas ADN is a relatively new product.

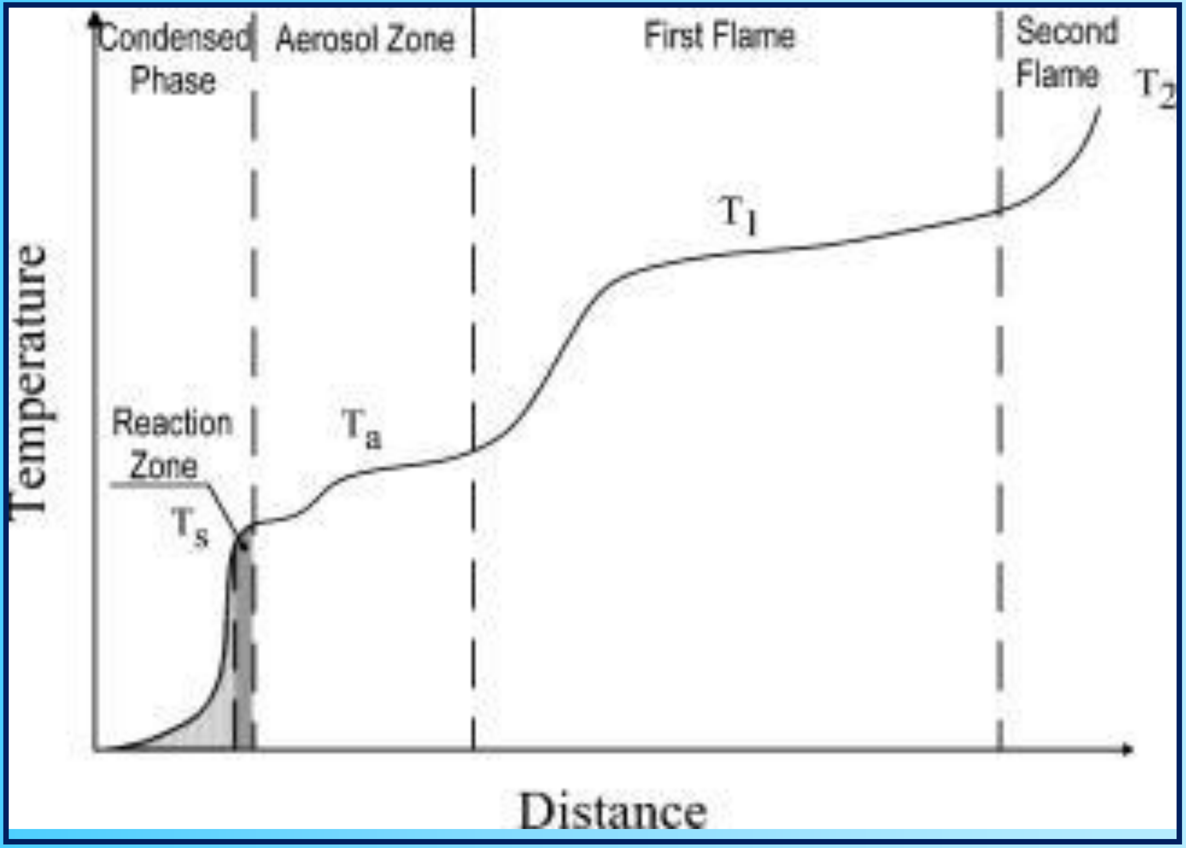
- first synthesized at the Zelinsky Institute of Organic Chemistry in Moscow, Russia, 1971 (and much later at SRI,USA, 1988).
- Unconfirmed: ADN-based SRM are in operational use by Russian ICBM.
- main advantages of ADN as an oxidizer are “superior” performance (I_s), good ballistic properties (high burning rates and possible low pressure sensitivity), low signature, and total environmental respect.
- however, strong sensitivity to humidity (like AN) and initial temperature (like AN) as well as low melting (92-94 °C or 365–367 K) and decomposition (starting at 135 °C or 408 K) temperatures make its field use problematic.
- prilling technique required to overcome difficulties with needle shape.
- ADN also possesses a number of unique properties, such as high condensed phase heat capacity of 0.59 cal/g/K, low surface temperatures, and a low PDL around 2 atm.
- ADN burning as a monopropellant is a quite complex process whose characterization is hindered by a conspicuous data scattering reported by many investigators.

Ballistic Properties: steady r_b



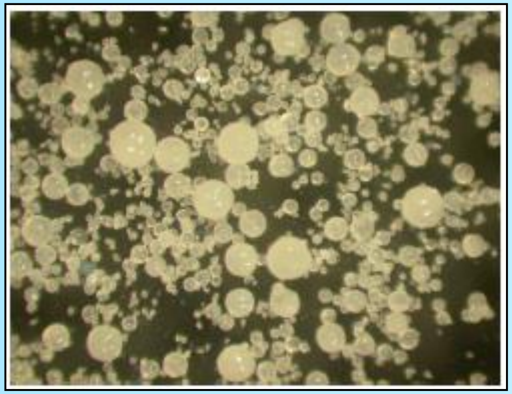
Steady burning rate vs. pressure for a wide range of solid propellant formulations tested at SPLab compared to ADN data from literature.

Flame Structure ADN

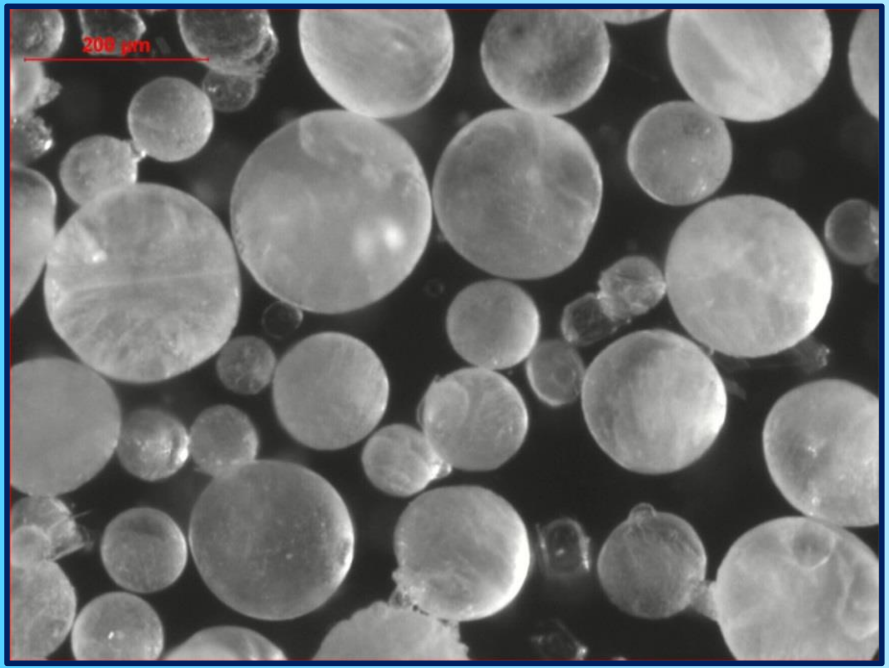


Sketch of ADN multistep flame structure [Sinditskii et al.[21]]. Burning appears flameless below 1 bar, condensed-phase controlled up to 10 bar, unstable up to 100 bar, and collapses to one, luminous, gas-phase controlled zone above 100 bar.

ADN Prilling at ICT and FOI



Spray prilled ADN (FOI).



Micrograph (reflected light) of prilled ADN; mean particle size 208 µm (ICT).

ADN-Prilling process used at ICT is an emulsion crystallization technology developed at the end of the 1990s (European patent). Achievable particle size range could be enlarged down to 35 µm and up to 320 µm. Typical ADN-prill sizes for reproducible kg-scale productions are: 50 µm fine and 200 µm coarse.

ADN-Prilling process used at FOI is based on crystallization after molten ADN spray through a nozzle.

SPLab Current Metallic Fuels

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µAl powders (Avio ⇦ UK)

- typically in the range 15 to 45 µm, density 2.7 g cm^{-3}, active Al >99%, spherical shape;
- BET surface ≈ 0.10 m^2/g and T_{ign} > 1000 K.

nAl powders (STK by EEW)

- typically in the range 50 to 100 nm (at most 150 nm) , density ≈ 2.5 g cm^{-3}, active Al ≈ 70-90%; ESD hazard;
- BET surface 7 to 16 m^2/g (clustering and increase of propellant viscosity) and T_{ign} ≅ 770 to 950 K.

chem-actAl powders (FOI)

- based on Valimet H3 µAl (2.73 g cm^{-3} density and 3 µm size), but details undisclosed;
- BET surface 2 to 3 m^2/g and T_{ign} ≅ 860 to 905 K.

mec-actAl powders (SPLab)

- based on Avio µAl from Alpoco, but details undisclosed;

amAl powders (ESA)

- details undisclosed.

More undefined ingredients may be tested provided by international manufacturers …

Stabilized AlH_3 (TNO, U. Poitiers)

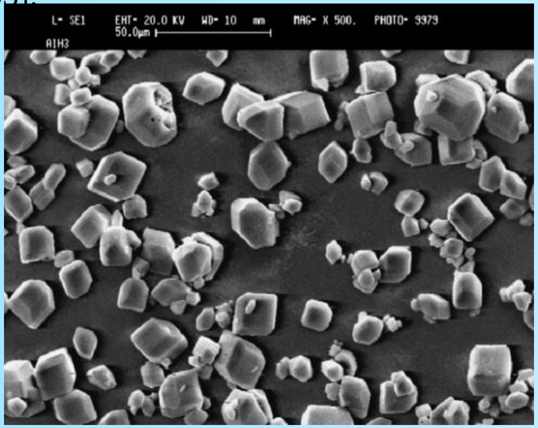
- big crystals 1-20 µm size of irregular structure, low density (1.477 g cm^{-3}), 88.2 % (89.9 % theoretical) active Al;
- decomposition temperature of 179.7 °C, about 20 °C higher than usual [ICT 2003];
- outstanding storage stability (superior to common µAl powders);
- marginal handling stability, poor under ESD, T_{ign} = 614 K.

Other Metal Hydrides (Chemetal, commercial)

- $LiAlH_4$ (T_{ign}= 398 K , density = 0.917 g cm^{-3});
- Li_3AlH_6 (T_{ign}= 451 K , density = 1.130 g cm^{-3});
- MgH_2 (T_{ign}= 835 K , density = 1.450 g cm^{-3}); …

Mg_xB_y composite metal (MACH-I)

- particle size essentially in the range 1-20 µm;
- B purity 90 or 95%;
- Mg coating ranging from 10 to 60%;
- ignition temperature T_{ign} reduced to 835-950 K.



SEM showing 1–20 µm size particles AlH_3

Representative Fuel Characterization Tests

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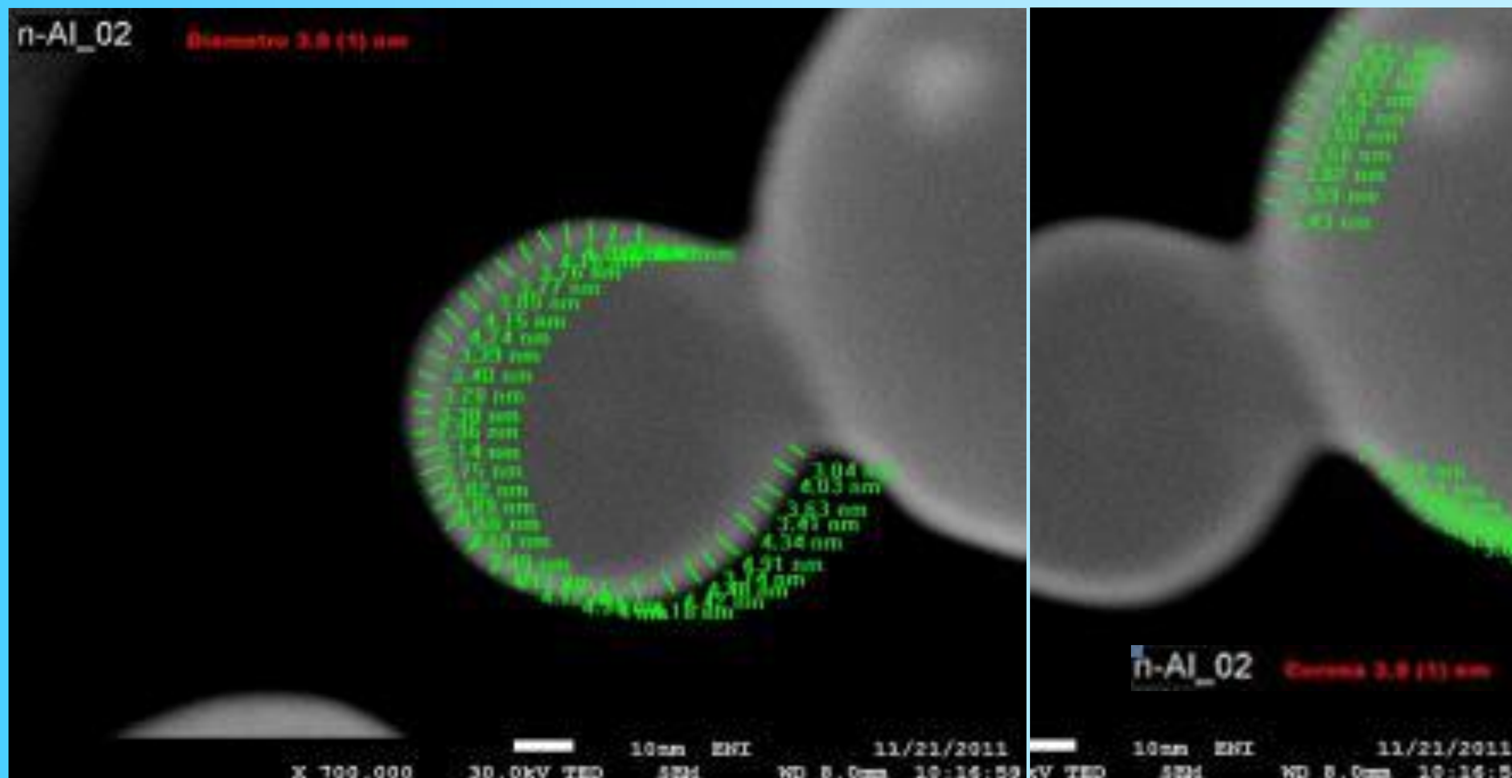
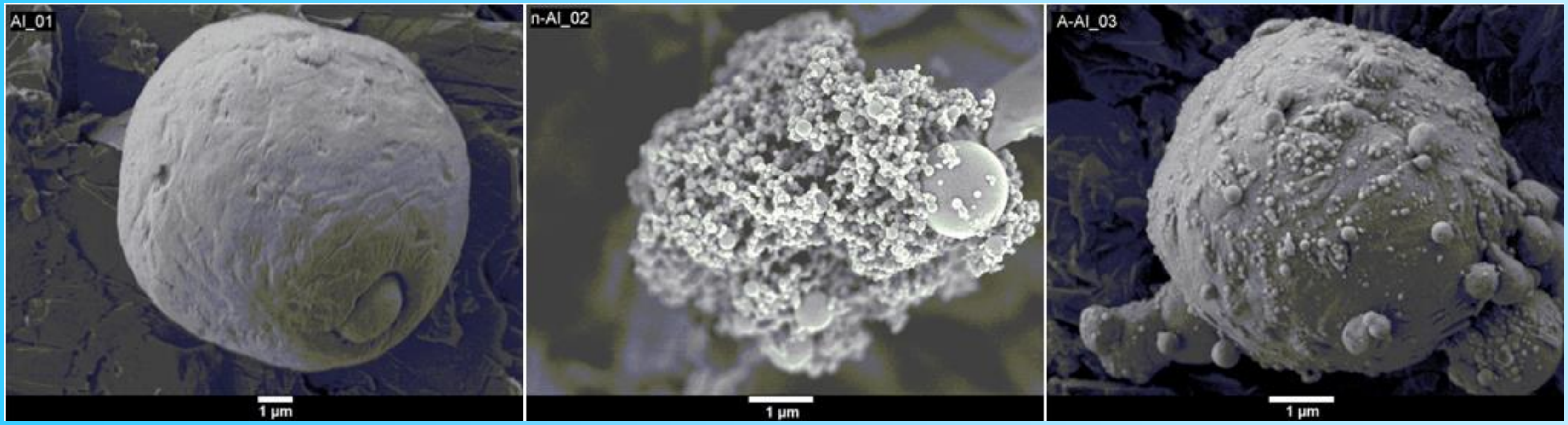
- SEM
- TEM
- XRD
- XPS
- BET
- Size (Malvern)
- Purity
- Compatibility HTPB
- Compatibility GAP-ADN
- T ignition
- TGA (air)
- TGA (O_2)

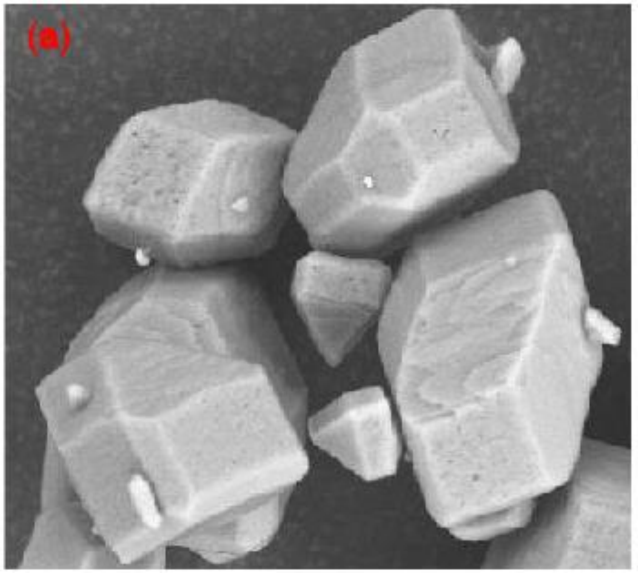


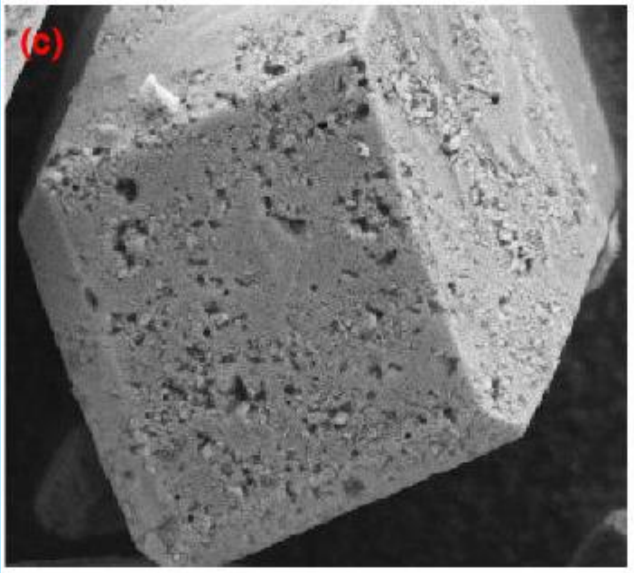
Example: Transmission Electron Detector (TED) imaging for n-Al02 reporting measurements of external oxide layer thickness covering active Al. Green are local values, red average values (3.8–3.9 nm).

Representative SEM Images



Representative SEM images for each tested family of metallic fuel: (a) µAl-05b, (b) nAl-01i, (c) chem-actAl-19c.



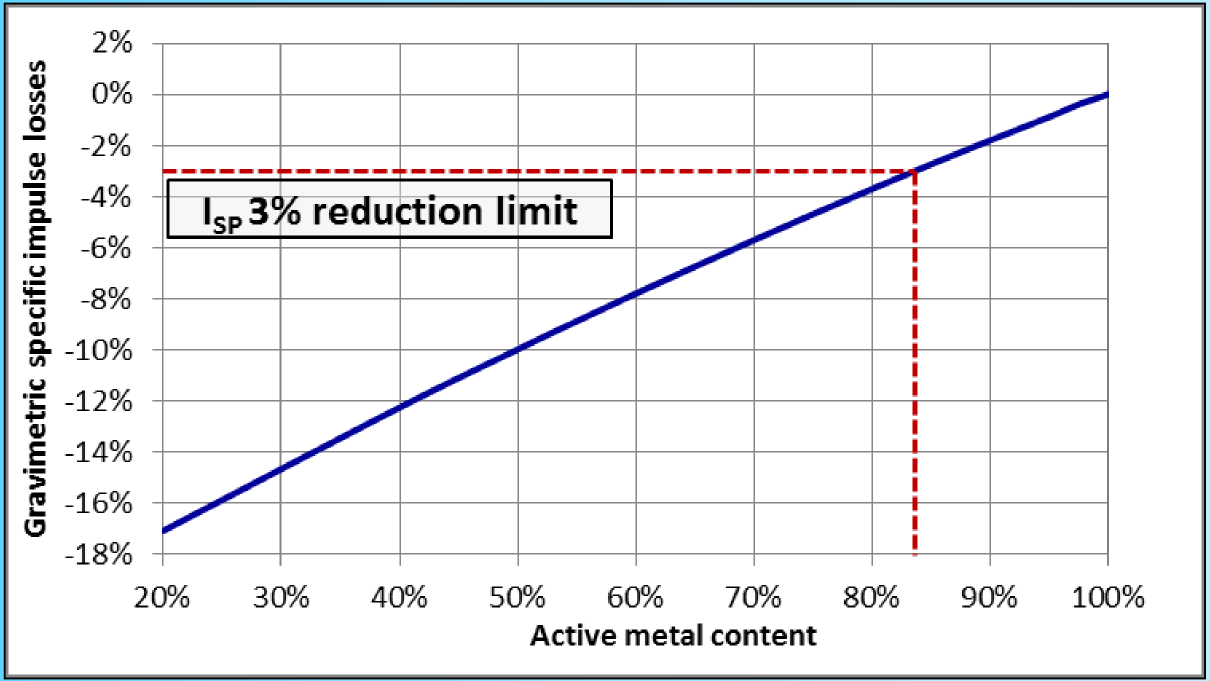


(a) AlH_3 crystals before pyrolysis test at ICT; (c) porous structure after decomposition at 400 °C (ICT testing).

Metallic Fuels: μAl vs. nAl

The well-known technology of nano metal powders successful in many fields overall not yet ready for rocket propulsion (good for increase of r_b not I_s, effective for dynamic burning) for a series of drawbacks including:

- clustering of particles [1, Ch. 27];
- decreased active metal content (I_s reduction) ➔ not less than 85% ➔ avoid too small particle size;
- dependence on passivation technique;
- ESD, impact, and friction hazards;
- possible catalytic effects on propellant curing;
- increased viscosity of the propellant;
- ageing of particles;
- and increased cost.



Compensating effects of decreased 2P flow losses (delivered I_s increase) vs. decreased active metal content (I_s reduction), when using nAl as high-energy fuel.

Accumulation & Aggregation & Agglomeration

AP/HTPB/Al

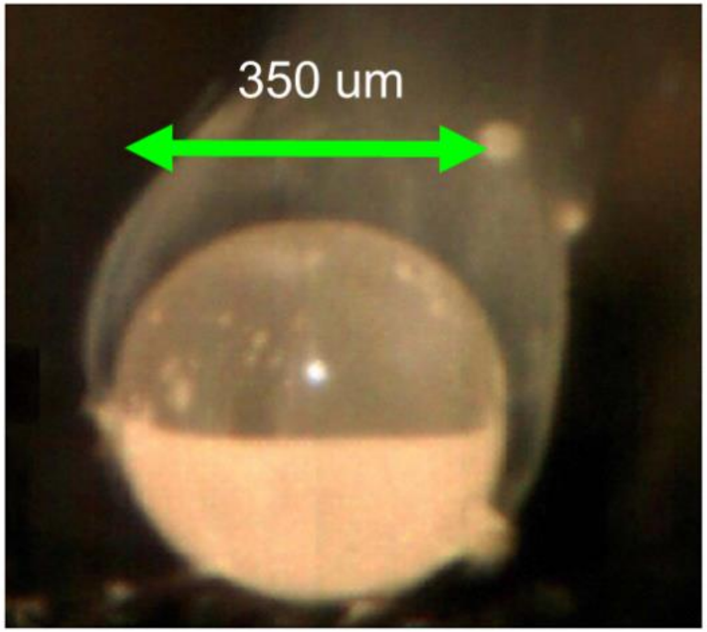
Transition from surface accumulate (skeleton layer) first to aggregates (partial oxidation) and then to agglomerates (burning spheres) for µAl particle clusters. [Video SPLab: AP/HTPB/µAl industrial propellant microstructure].

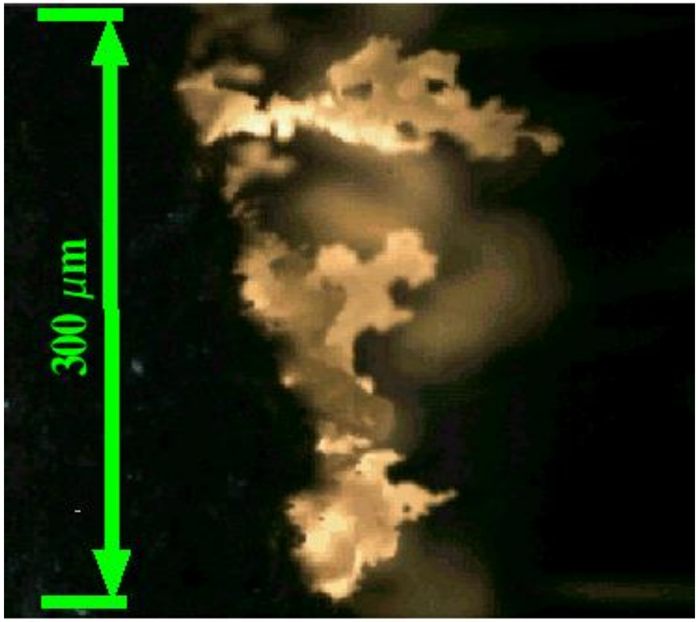
Agglomeration vs. Aggregation

- Accumulate (or skeleton layer) is the material stacking up on the burning surface; its nature is tightly related to tested energetic material.
- Aggregation = partial (or final) oxidation step characterized by CCP of irregular shape, often seen as intermediate between accumulates and agglomerates. It implies high temperatures.
- Agglomeration = final oxidation step characterized by spherical drops of liquid metal in combustion, starting from aggregates (seen as precursors of agglomerates). It implies and actually need high temperatures for inflammation.
- Agglomeration always implies a loss of the initial particle individuality, while aggregation may keep some reminiscence of it.
- Clustering = assembling of particles before combustion, during manufacture and storage, typical of nAl powders. It implies ambient temperatures.
- Cohesion (or adhesion) = "a portion of a substance cleaving together in a thick nondescript mass".
- Coagulation = "viscous lump of a portion of liquid" (from Merriam-Webster Dictionary).

Agglomeration vs. Aggregation

Al size effect in AP/HTPB matrix



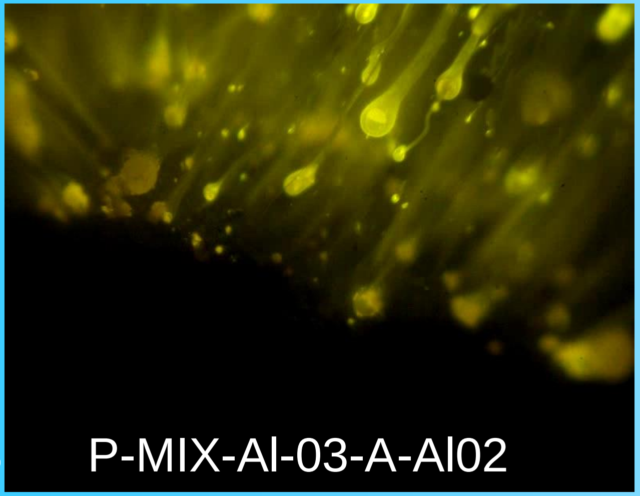


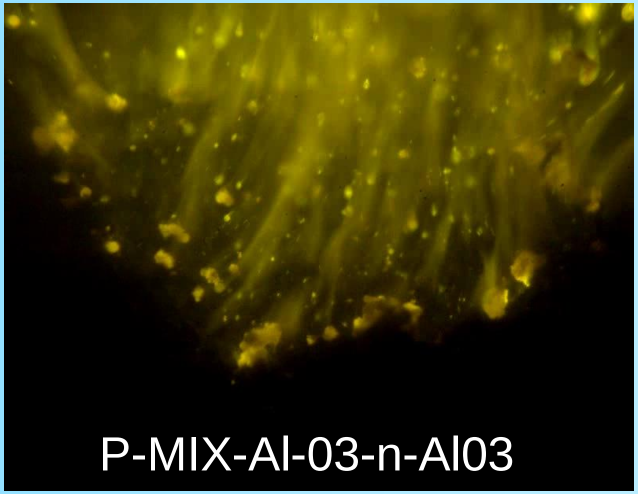
Left - Magnified view of a single spherical agglomerate of μAl in combustion *above* propellant surface following inflammation of aggregates (filaments or filigrees) *at* the propellant surface, with loss of the initial particle individuality.
Right – Oxidized metal flakes emerging from the burning surface of a 0.15 μm nAl propellant tested at 10 bar, with flakes replicating the 3D nAl distribution in the propellant matrix.

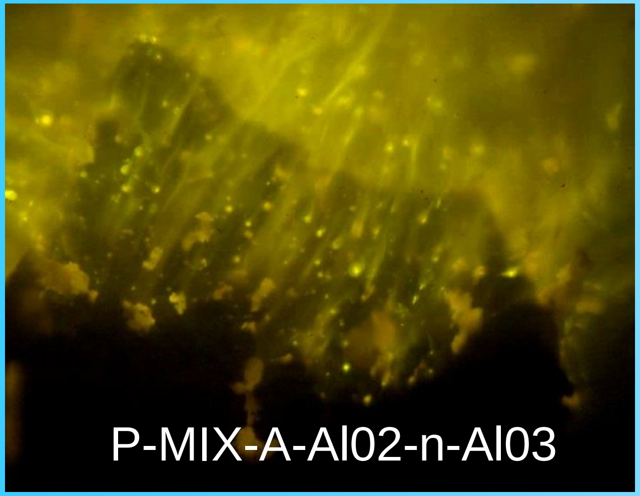
➔ nAl particles imply larger SSA and reactivity, higher r_b, effects slope ?, less agglomeration, unchanged ideal I_s, increased delivered I_s.

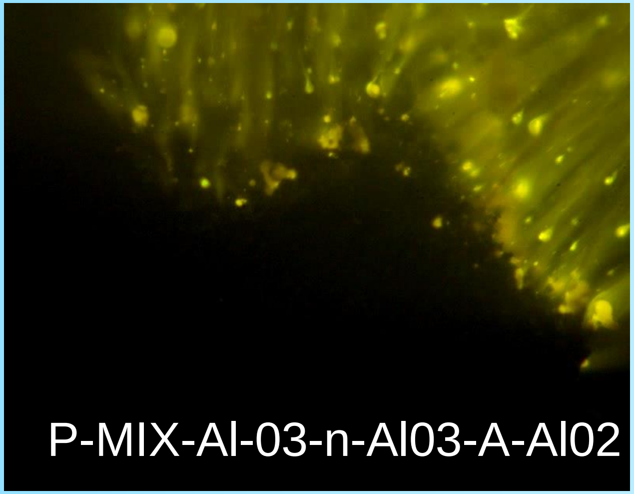
Visualizations: Multimodal Fuels

Al-03









Burning waves visualizations with digital high speed color camera

L.T. DeLuca, L. Galfetti, F. Cozzi, G. Colombo, M. Galeotta, P. Taiariol

PHOTRON LIMITED
2001-2002

High-Speed Movies: Standard Al

- Show Movie [01b] SP booster Ariane5 @10 bar

  close-up view above surface micron-sized Al

- Show Movie [02] SP booster Ariane5 @10 bar

  detailed view at surface micron-sized Al

- Show Movie [03] same formulation with Alex™ @10 bar

  overall view above surface nano-sized Al

- Show Movie [04] same formulation with Alex™ @10 bar

  detailed view at surface nano-sized Al

State-of-the-Art SRM (2014)

Current state of the art of solid propellants is based on AP/HTPB/μAl.

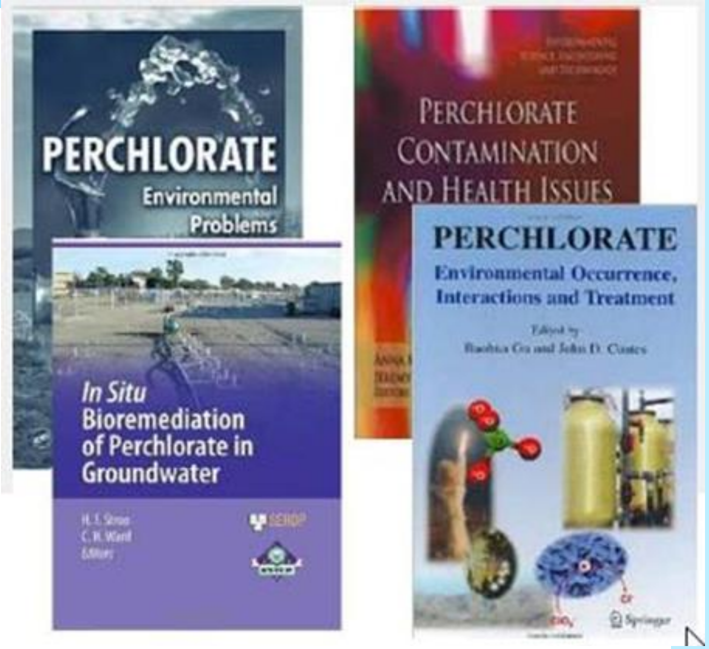
AP is an outstanding solid oxidizer (a “miracle of nature”), but

- Ozone layer depletion
- Acid rains
- Thyroid gland interference

New solid oxidizer?

Replace AP with a mixture of the two green oxidizers:

- Ammonium Dinitramide (ADN)
- Ammonium Nitrate (AN)



GRAIL (Green Advanced High Energy Propellants for Launchers) project was funded by the European Union’s Horizon 2020 research and innovation program, as continuation of HISP (High performance solid propellants for In-Space Propulsion) project already funded in the framework of the FP7 program.

HISP duration was of 3 years (2011-2013), www.hisp-fp7.eu

GRAIL duration again of 3 years (2015-2017), www.grail-h2020.eu

RECOMMENDATIONS FUTURE WORK

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- For the near future, formulations including dual-oxidizers based on ADN, such as (ADN+AN) or (ADN+AP), in conjunction with a dual-metallic fuel based on μAl, such as (μAl+nAl) or (μAl+AlH_3), bound by a suitable active or inert binder, are expected to advance the state-of-the-art of solid rocket propellants.

- However, the quite peculiar properties of ADN require a careful design and implementation of the propellant formulation. Most investigations so far accomplished did not fully exploit the unusual dependence of ADN ballistic properties on particle size. Appropriate burning rate modifiers or coolants may be needed to fully control the propellant internal ballistic properties.

- At this time, in view of the already available experimental results described, the mixture (ADN+AP) seems easier to master than (ADN+AN).

- Overall, when dealing with ADN, it is the binder system still demanding a decisive effort to manufacture well-behaved formulations; other critical areas area the implementation of a suitable phase-stabilizer for AN (PSAN obtained by KNO3 was compatible with ADN but not if obtained by NiO [30]) and bonding agent for the propellant (HX-880, also known as BHEGA, is compatible with AP but not with ADN [1, Ch. 32]).

- At any rate, the mechanical and hazard properties of the resulting formulations have to be closely monitored and possibly improved. Target is class 1.3 for hazard rating.

Background Hybrid Propulsion

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- Hybrid rocket engines are an attractive "new" option (low TRL) for a range of applications including minilaunchers (CNES Perseus), boosters (ASI), upper stage propulsion (PF7 Orphée), lander systems (PF7 Spartan), private human space access (IAA), active space debris removal (IAA), in-space navigation …
- Application of HRE based on H_2O_2 + rubber to cruise stages of light-weight launch vehicles, boosters and interorbital towing vehicles, as well as to launching boosters of LV with cruise oxygen LRE of various classes is economically justified; few years of good stay in space expected (KeRC).
  - Higher I_s than SP and monopropellant LP
  - Simpler system and lower development cost than bipropellant LP
  - High throttleability
  - High versatility
  - On-off capability
  - Safety
  - Commandable cut once desired ΔV is reached (ADR)
  - Low regression rates suitable to avoid excessive accelerations (ADR)

- Enhance combustion efficiency and regression rate.
  - Low regression rate overcome by fuel formulation and multiport grain
  - High O/F mitigate negative effects of low regression rates
  - Excessive engine L/D ratio overcome by technological advances (see LM)
  - Ad-hoc geometries of injector/grain (single swirl ➔ 3X, double coaxial swirl ➔ 6X, vortex flow pancake ➔ reduced L/D, CAMUI ➔ …) can sensibly help …

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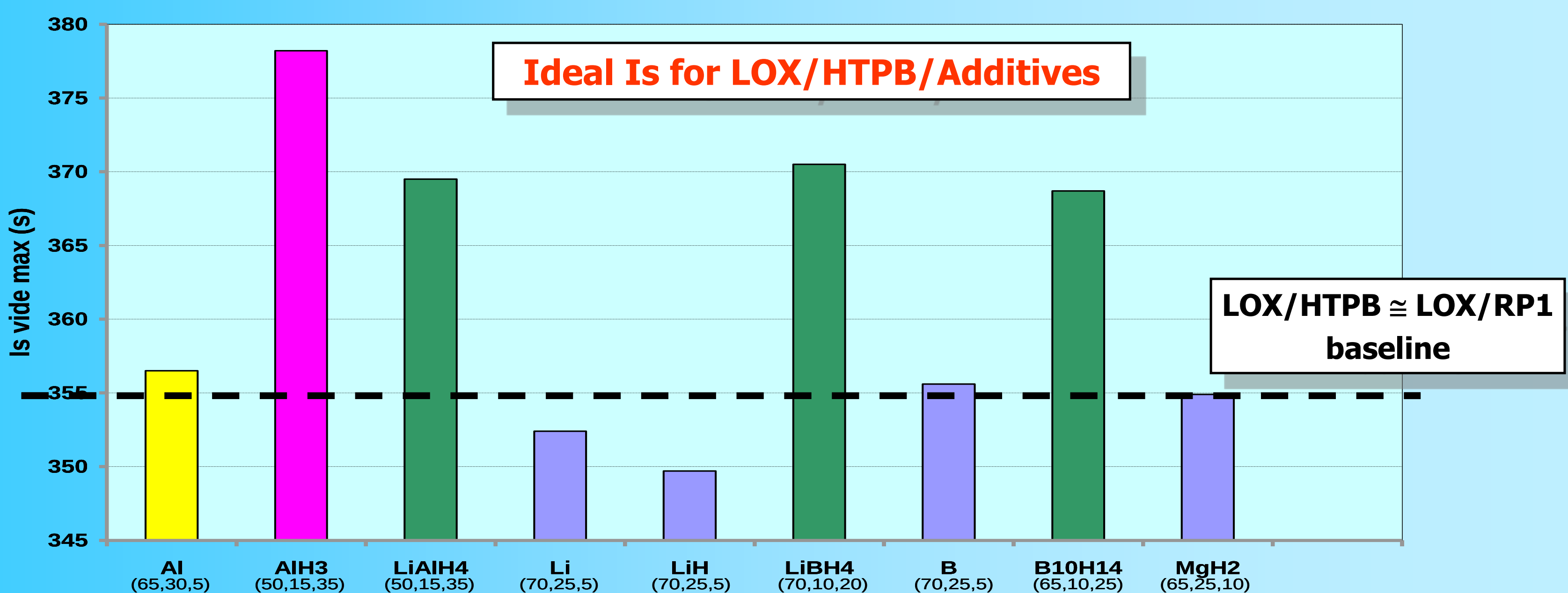
Hybrid Propulsion Performance (courtesy of Mr. Calabro)

Propellant		Mixture Ratio	Density kg/m³	Isv (ideal) 7 MPa, ε=40
Solid AP/Al/HTPB		68/18/14	1750	315
Hybrid LOX/HTPB		72/28	1060	354
Liquid Bi Propellant	NTO/MMH	2.37	1200	341
	H_2O_2/RP1	7.0	1320	314
	LOX/RP1	2.77	1030	358 ←
	LOX/CH_4	3.45	830	369



Al has no effect on ideal I_s, whether µAl or nAl. Same for B.

2D-Radial Burner

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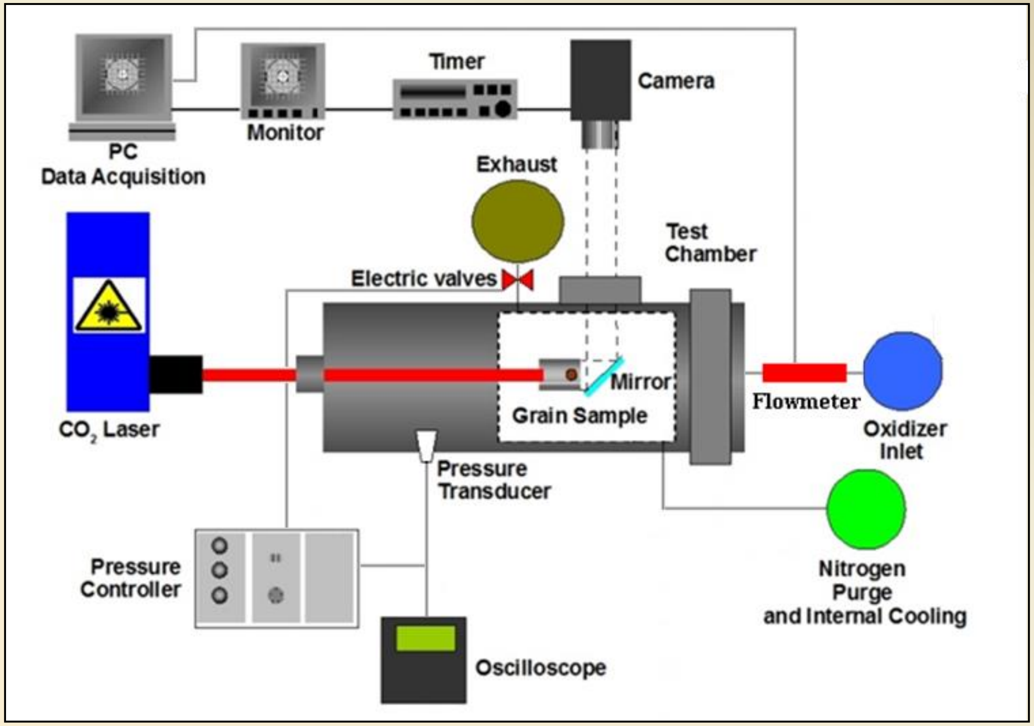

- Combustion chamber: stainless steel operating pressure up to 30 bar
- Injection of gaseous oxidizer and/or nitrogen for purge & cooling
- Oxidizer flux up to about G_{ox} = 400 kg/m^{2}s (250 Nlpm)
- Controlled combustion pressure and oxidizer flow rate (separate)
- Laser ignition of primer charge
- Video camera with mirror allowing unique view of regressing central port
- Digital data acquisition
- Hybrid strand burner to test new high-energy ingredients

2D-Radial Burner: Some Tested Samples

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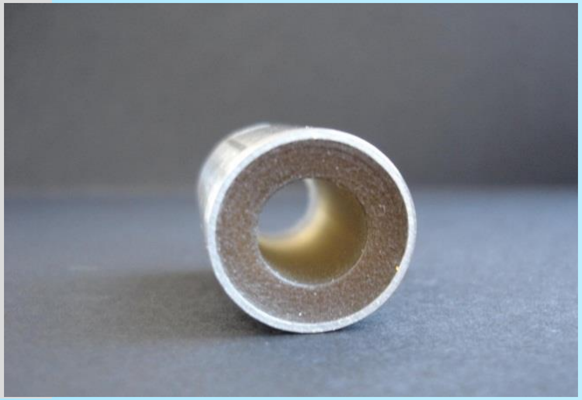
- INTRODUCTION
- HISTORY
- PROPELLANT
- 2D RADIAL
- VISUALIZATION
- **BALLISTICS**
- REGRESSION
- SURFACE
- UNSTEADY
- PERFORMANCE
- MECHANICS
- DISPERSION
- IMPACT
- CONCLUSIONS

HTPB

HTPB + AlH_3



HTPB + AP

HTPB + MgH_2

HTPB/c NAMMO

HTPB + nAl

2D-Radial Burner: burning visualization

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Example 1: **pure HTPB**
pressure: 10 bar; oxidizer: 100% O_2 @ 70 Nlpm

Regression HTPB in GOX: Pressure Effect

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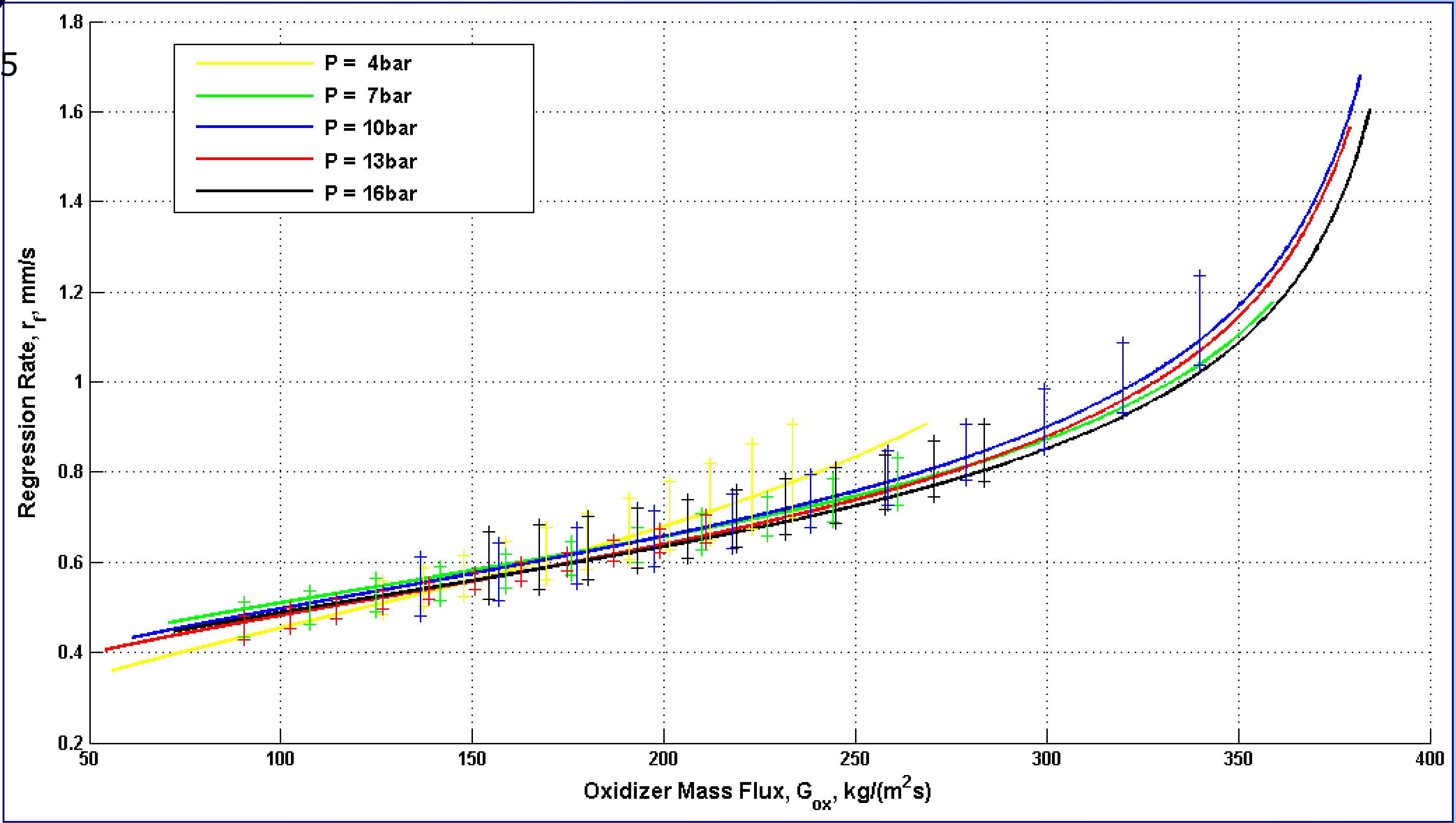

- Operating conditions: 4-16 bar and 210 Nlpm pure oxygen flow rate
- Complete set of ensemble average curves of r_f vs. G_{ox}
- Linear regression rate essentially independent of pressure (at most, slightly decreasing)
- Confirmed also for HRE in the range of p_c = 24 to 44 bar [Risha 2003]
- Constant power law regression rate (Marxman) not valid, it should be seen as an approximation.

Journal of Propulsion and Power, 2012, under press

Solid Fuel Regression Rate Modeling for Hybrid Rockets

F.M. Favarò, W.A. Sirignano, M. Manzoni, and L.T. DeLuca

Regression HTPB in GOX: Industrial Check

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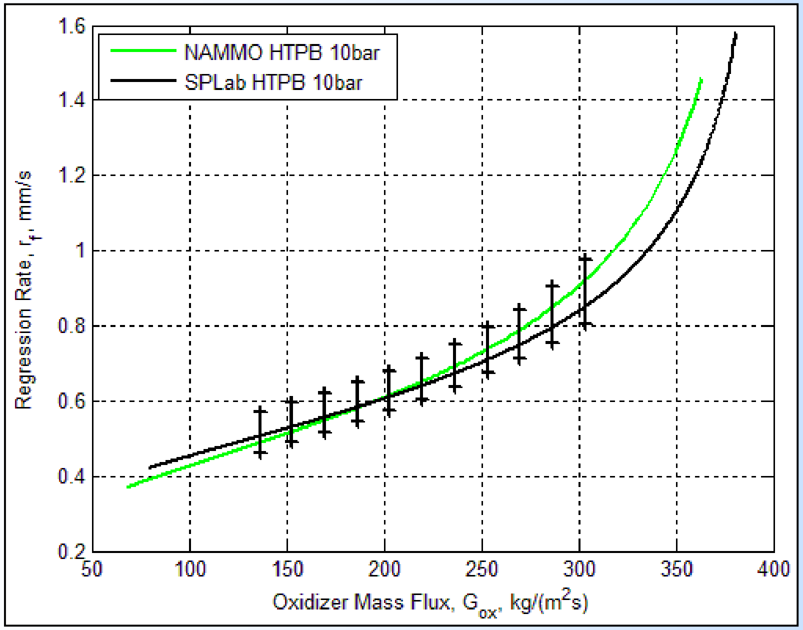
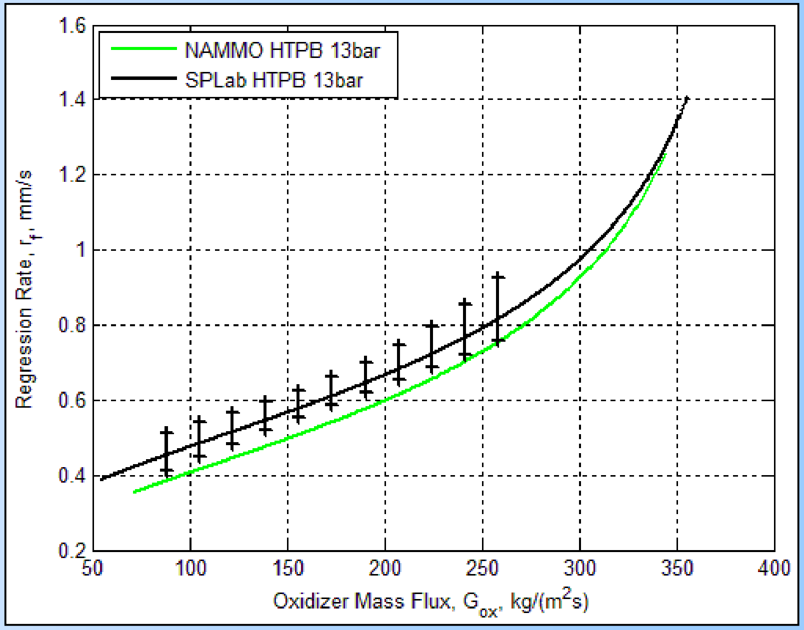
Comparing SPLab and industrial (NAMMO) samples of pure HTPB





Comparing instantaneous regression rates of pure HTPB burning under GOX at 10 bar (left) and 13 bar (right) for SPLab and industrial formulations, under 210 Nlpm pure O_2 flow rate.

Regression HTPB + nAl in GOX

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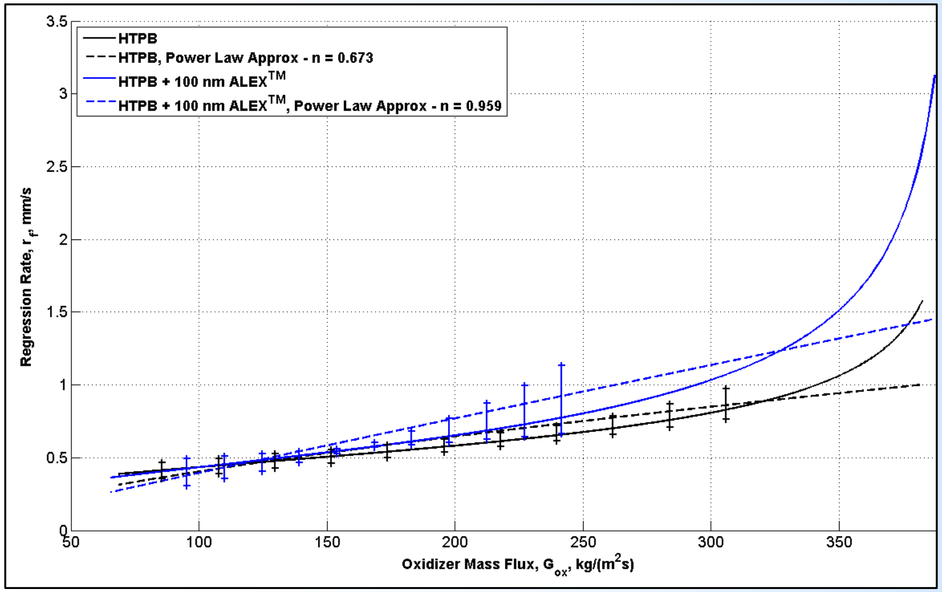
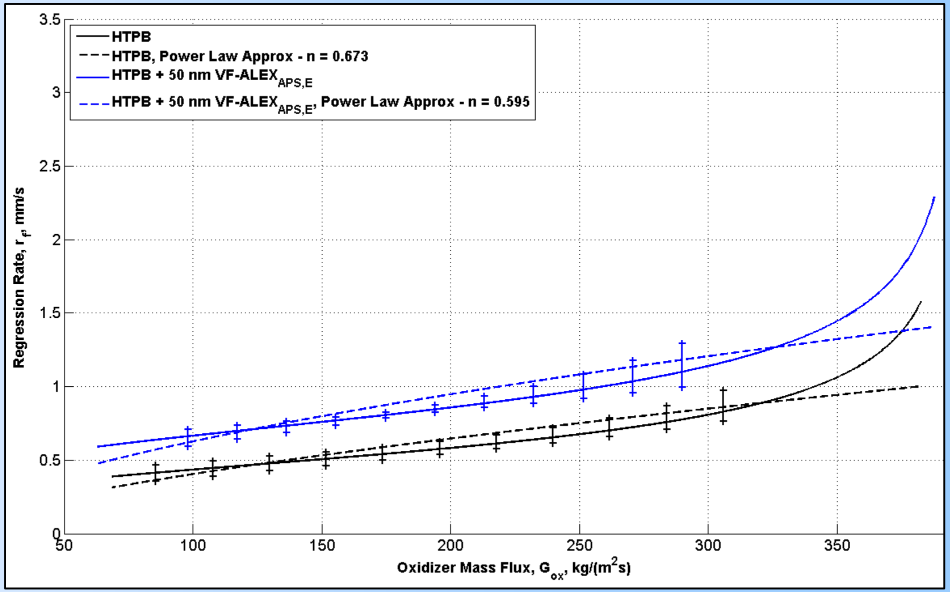
- Operating conditions: 10 bar and 210 Nlpm pure oxygen flow rate
- Complete set of ensemble averages curves for a wide range of loaded HTPB
- For all tests, under high oxidizer mass flux, initial regression rates are in excess wrt power-law approximation (constant power law not valid)





Ensemble instantaneous regression rate of loaded HTPB + 100 nm ALEX (left) and + 50 nm VF-ALEX$_{APS,E}$ (right) each compared to pure HTPB.
Only fluoroelastomer coatings yield nearly constant increase of regression rate.

Hybrid Propulsion 2D Radial Burner

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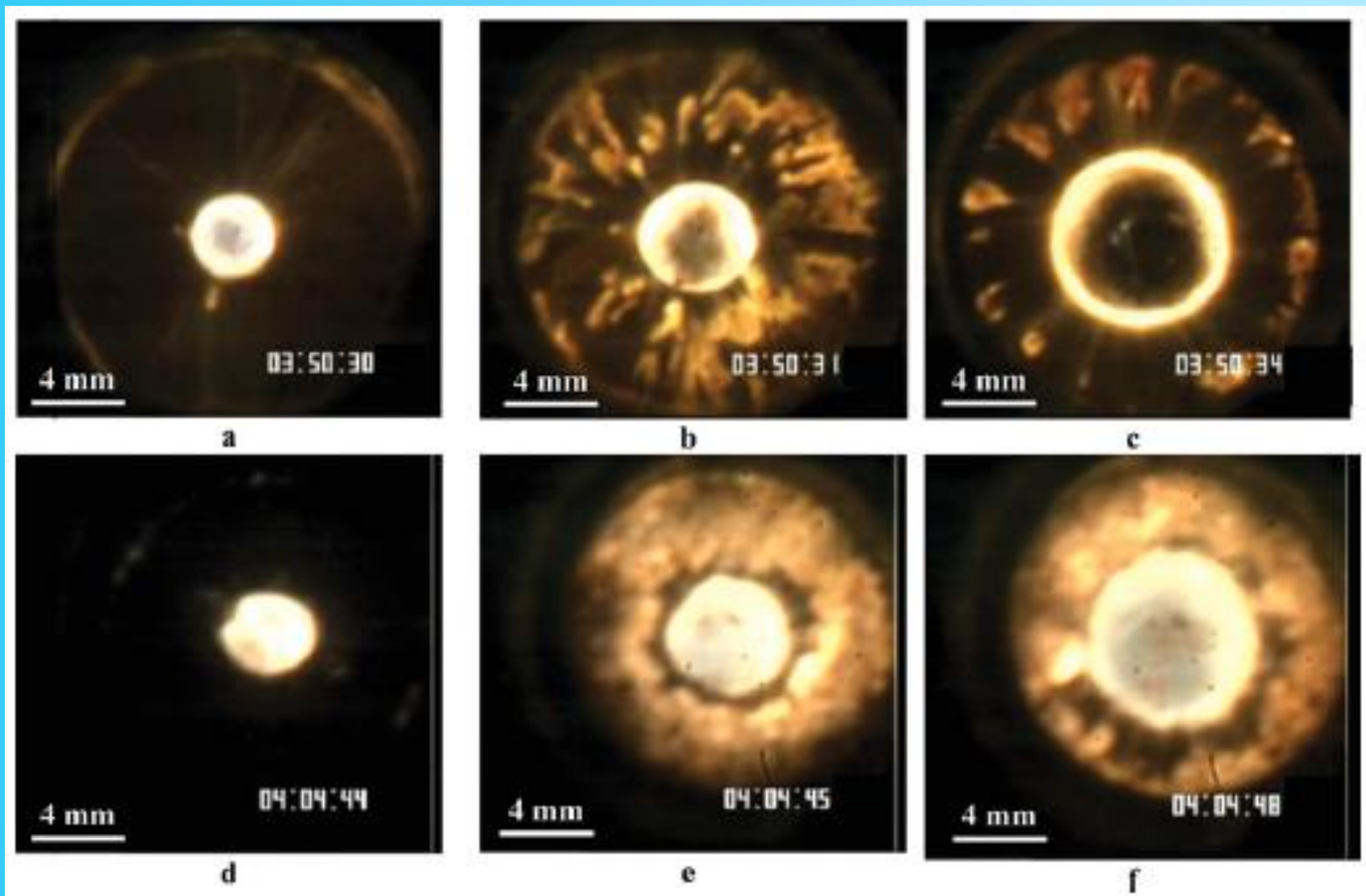

← **pure HTPB**

← **HTPB+nAl**

Sample frames of HTPB burning tests under GOX: pure HTPB (a: t_{ign}; b: t_{ign} + 1 s; c: t_{ign} + 4 s) and nAl-loaded HTPB (d: t_{ign}; e: t_{ign} + 1 s; f: t_{ign} + 4 s).

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Summary Hybrid Propulsion

AUGMENTING SOLID FUELS

While μAl does not contribute to specific impulse, hydrides (AlH_3, $LiAlH_4$, MgH_2) and other metals (nAl or Mg_xB_y) promote regression rate, mitigate nozzle erosion and soot formation, and may increase density.

- AlH_3 (1.476 g/cm^3) and $LiAlH_4$ (0.917 g/cm^3) outstanding I_s increase, but $LiAlH_4$ suffers low density
- $B_{10}H_{14}$ (0.94 g/cm^3) outstanding I_s and regression rate (in 92% H_2O_2) increase, modest density
- F-coated nAl ($\rho \cong 2.520$ g/cm^3) helps to reduce I_s losses, increases density and regression rates
- Mg_xB_y (1.450 g/cm^3) can sensibly increase regression rate, but no I_s increase
- Note limited compatibility of hydrides with HTPB

BURNING SOLID FUELS

Large-scale operations need advanced fuels combining good handling, mechanical, and ballistic properties:

- instantaneous regression does not obey standard constant power law even under ss
- deeper understanding of flame structure for soot formation
- VFP pancake design promising for ADR

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- Tomsk Polytechnic University (Russia, nano powders supplier)
- APT (Russia, nano powders supplier)
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- Donegani (Italy, lab analyses of ingredients)

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- FOI, Sweden for providing actAl samples;
- ICT, Germany for providing PSAN samples;
- STK, Russia for providing nAl samples;
- MACH I, USA for providing Mg_xB_y samples; and
- ENI Donegani Institute, Novara, Italy in performing advanced powder analyses

The authors finally wish to thank the many SPLab students and coworkers who made possible this presentation with their daily research contributions.