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A 2023 overview of French in-space chemical propulsion activities supported by CNES - 10^{th} EUCASS - 9th CEAS

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Abstract
This paper presents an overview of the ongoing research activities carried out on in-space chemical propulsion in France, with the strong support of the French Space Agency CNES. To cope with REACH legislation (Registration, Evaluation, Authorisation and Restriction of Chemicals) the technical roadmap includes mainly activities on green propulsion technologies, that have been investigated by propulsion industry and research centers for more than two decades. A state of the art of the current world-wide, green, in-space propulsion solutions is presented. Advantages and drawbacks of the proposed solutions are highlighted and a brief performance comparison is reported. The CNES supported research activities in the field of green propulsion are presented; in particular, those that have as their main goal the replacement of hydrazine. In addition, the strong research effort put on the search of novel, cheaper and more performing propellants and associated technologies is highlighted. This would, eventually, lead to new chemical propulsion system solutions expanding applications and reducing overall mission cost.

1. Introduction

The European regulation on chemicals (REACH) threatens the use of hydrazine because of its highly carcinogenic and toxic effects. This is a primary concern for the space industry, where hydrazine and its derivatives are widely used in storable monoproellant and bipropellant propulsion systems. Hydrazine could be prioritized for inclusion in Annex XIV of REACH at any time, prohibiting it's use after a certain sun-set date. Common position of the European Space Industry is to try to exempt the propellant related use of hydrazine and its derivates (MMH, UDMH) from this legislation. However, developing innovative and possibly more performing propellants for in space applications would broaden mission possibilities compatible with chemical propulsion systems. Alternative low-hazard, low-toxicity, environmentally friendly propellants need to be developed. The latter shall not require the special handling protocols and strict safety measures requested during handling of hydrazine and its derivatives. This would lead to reduction of costs related to transportation, storage, handling of the propellant and reduction of on ground operations timeline, avoiding as much as possible the expensive and time-consuming procedures specific to hydrazine handling and refueling. Performances as the specific impulse (Isp) and operational constraints like its storability properties are difficulty met by other propellants, thus reducing the number of possible alternatives. To replace hydrazine different industries, space agencies, research teams and facilities have been involved in various programs such as the Europeans Green Advanced Space Propulsion (GRASP), the Pulsed Chemical Rocket with Green High Performance Propellants (PulCheR), Replacement of hydrazine for orbital and launcher propulsion systems (RHEFORM) and European Fuel Blend Development (EUFBD) projects as well as the Green Propellant Infusion Mission (GPIM) technology demonstrator project initiated by NASA. These projects led to the development of different green propellant solutions and thrusters. Furthermore, thanks to the heritage of these projects, many startups started developing green propulsion solutions for the Nanosat and CubeSat families.

2. State of the art of green in-space propulsion

The most investigated green propellant solutions for hydrazine replacement can be divided in four main categories: Energetic ionic liquids, Hydrogen Peroxide based solutions, Nitrous oxide based solutions, and Water-based propulsion. Both monopropellants and bipropellants applications are investigated in this section.

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Ionic liquids are liquid salts mixed with solvents and water to control the combustion chamber temperature. Regulating the propellant mixture allows to regulate the performance in terms of specific impulse (Isp) and adiabatic flame temperature. They feature lower vapor pressure than hydrazine and lower freezing points, usually characterized by the glass transition temperature. Their low decomposition rate during storage makes them suitable for long-lifetime missions. Finally, ionic liquid propellants feature lower toxicity and higher densities with respect to conventional toxic monopropellants. In this frame, Hydroxylammonium nitrate (HAN) based and Ammonium Dinitramide (ADN) based monopropellants have been widely investigated [1]. Comparison of some ionic liquid based existing propellants is reported in Table 1.

	Hydrazine	HAN AF-M315E	HAN SHP163	ADN LMP-103S
Freezing point/Glass transition [K]	275	193	243	266
Density [g/cm^3]	1.0	1.47	1.40	1.23
Theoretical Specific Impulse [sec]	239	266	276	252
Density specific impulse [g/cm^{3}s]	239	390	386	312
Adiabatic flame temperature [K]	1170	2166	2401	1873

Table 1: Green propellants comparison [1].

In the US, the Air Force developed the HAN based AF-M315E. Space proven technology based on this propellant is available from Aerojet Rocketdyne and Busek. In Japan, Mitsubishi Heacy industries, JAXA and Japan Space Systems developed the HAN based SHP163. In Europe, ADN based LMP-103S technology has been mainly developed by Bradford-ECAPS and space-proven thrusters are available.
The drawbacks, when compared to hydrazine based propulsion systems, are the higher preheating power required by the catalytic bed, incapability of performing cold starts and the higher temperature achieved inside the thruster, which limits the lifetime of the catalytic bed and thruster due to exposure to wide thermal cycles. This results in reducing the maximum achievable propellant throughput.
Refractory and oxidizing environment resistant alloys are often employed for the nozzle and combustion chamber increasing the cost of the propulsion subsystem. The increased manufacturing and propellant costs are, however, mitigated by the less expensive propellant handling and loading operations.
Other considerations such as the pyrotechnic class of the propellant, impact sensitivity and electrostatic discharge detonation have to be taken into account during mixture selection to avoid formulations which are not safe to handle/transport.

Hydrogen Peroxide, H2O2, is employed both as monopropellant, thanks to its exothermic decomposition capability, or as oxidizer in bipropellant propulsion systems. Hydrogen Peroxide based applications feature propellant stability issues in time. Concentration loss, due to liberation of oxygen and water, has to be taken into account. This is a concern for missions where long term storage is required. Decomposition reduces propellant concentration and therefore deliverable Isp. In addition, once the system is sealed, the released oxygen leads to overpressure inside the propellant tank that has to be managed. Advantages of H2O2 is the relatively high density (density at 98% concentration 1.43 g/cm3) and lower handling cost: handling procedures are less complex than in the case of hydrazine based propellants due to the lower toxicity of the propellant. Thermal management of Hydrogen Peroxide based propulsion subsystems is not straight forward. As it will be discussed in the following sections, temperature increase in the tank has an impact on the H2O2 concentration loss, thus limiting mission lifetime.
As hydrazine, a H2O2 monopellant thruster is capable of firing without pre-heating the catalyst bed. Propellant decomposition reaches a temperature of 1222 K and specific impulses of 98% HTP (High Test Peroxide) of 186 sec have been recorded [1]. In bipropellant systems, especially with hydrocarbons such as ethanol, HTP can reach Isp > 325 sec with a combustion temperature of 2752 K. This makes H2O2 very appealing when multi mode (monopropellant and bipropellant) propulsion systems are required. In addition, H2O2 based bipropellant configurations can also be developed without the need of an ignition system: hypergolic couples of propellant or additives that allow hypergolicity can be selected. Finally, for some couples such as ethanol and H2O2, hypergolic propulsion systems can be developed exploiting a first monopropellant decomposition stage for H2O2. The decomposed hot gases would then mix with ethanol and ignite.
H2O2 monopropellant based systems are also suitable for launcher Roll and Attitude Control Systems [RACS] applications. Nammo (Norway), for example, is developing a H2O2 monopropellant thruster for future upper stages of the Vega class launchers. The system features an Isp of 160 sec in steady state firing and 130 sec in pulse mode firing, at a Thrust level of 220 N [3].
The moderate decomposition temperatures of H2O2 allows to build thrusters using stainless steel alloys such as AISI

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310S [2], reducing thruster cost. Further limitation of H2O2 based monopropellant systems is the achievable propellant throughput. For a 1 N class thruster, typical propellant throughputs are in the 10 kg range. A fifth when compared to hydrazine monopropellant counterparts. Research on novel and more performant catlyst beds for H2O2 decomposition is ongoing in order to fill this gap.

Nitrous oxide (N2O) is a stable liquid oxidizer. It can be also used as monopropellant exploiting the exothermic decomposition into nitrogen and oxygen. Catalysis can be obtained by metals such as Fe, Cr, Ni and oxides Fe2O3, Cr2O3[1]. Thermal decomposition is reached when temperatures overcome 800 K. At ambient temperature and pressure nitrous oxide is in gaseous state but there are pressure and temperature ranges where it remains liquid and suitable as storable propellant. It does not face decomposition during storage as Hydrogen Peroxide.
An advantage of nitrous oxide is that it is a self-pressurizing liquid, i.e. tank pressure remains theoretically constant during firings. This last behaviour actually depends on firing duration and propellant mass flow rate because the propellant expansion may reduce the tank temperature if a proper thermal control technique is not implemented. The latter, is particularly important to achieve constant performances: variation of tank temperature implies variation of tank pressure which has to be accounted for in the design. The risk is to have low vapor pressures at low temperatures with annexed reduction of the combustion chamber pressure and propellant mass flow rate.
At 293 K the saturated vapor pressure is 5.2 MPa. At these conditions the storage density is 0.745 g/cm3. It is compatible with common tank materials including metals, plastics and composite materials. Concerning performances, N2O has a 15% lower Isp with respect to hydrazine, but has better performances with respect to Hydrogen Peroxide monopropellant systems. As H2O2, nitrous oxide can be used in multi mode propulsion systems as monopropellant and oxidizer.
Monopropellant blends of N2O and fuels (nitrous oxide fuel blends), have been investigated in the 2000s to target specific impulses greater than 300 seconds. However, major risks concerning propellant detonation prevented from further developments. Wider investigations have been performed on N2O based bipropellant technologies, which are safer to handle. Dawn Aerospace has developed bipropellant thrusters based on N2O and C3H6 (propene). Two of them are space proven. The B20 (20 N class thruster Isp=285 sec) and the B1 (1 N class thruster Isp=285 sec) thruster [4].

The last category of green propellant alternatives to hydrazine consists in water based propulsion solutions. The latter can be divided into two sub-categories: electrolysis based and electrothermal based.
Water Electrolysis Propulsion is a system where gaseous oxygen and hydrogen are produced via electrolysis from pure water and burnt in a bipropellant thruster configuration. These systems are capable of firing at Isp>300 sec [5]. Although this high performance, the technology features some disadvantages. In order to consume the entire amount of propellant stored on board, thrusters shall be designed to handle stoichiometric combustion of Hydrogen and Oxygen. Therefore, combustion chamber cooling systems or high temperature resistant materials have to be implemented. In addition, specific technology bricks such as a space grade electrolyser (working in 0g environment) need to be developed. In conclusion, subsystem architecture (tanks for oxygen, hydrogen, water, electrolyser, thruster and associated valves) is more complex than traditional hydrazine based system, implying an increase in the propulsion subsystem dry-mass. However, for missions where several kNs of total impulse are required, the reduced propellant mass consumption of this system (50% higher Isp than hydrazine monopropellant systems) overcomes the augmented dry mass, with a reduction of the final propulsion subsystem wet mass.
Water electrothermal thrusters vaporize liquid water and overheat the produced steam in a resistojet configuration. Specif impulses range from 100 to 140 sec depending on nozzle expansion ratio and water vapor super-heating temperature. Bradford Space (Netherlands) and Pale Blue (Japan) have developed space proven this technology.
Water electrothermal systems have components which are common with typical cold gas propulsion subsytems and allow some mN thrust level with a lower power consumption when compared to Hall Effect Thrusters or Gridded Ion Engines used in Electric Propulsion. Their higher Thrust to Electric Power Consumption ratio, combined with the non-toxic propellant status and their versatility in thrust level makes this technology appealing for cubesat and smallsat applications.

3. CNES activities on green in-space liquid propulsion

In-space chemical propulsion activities at CNES are currently focused on the selection of innovative, REACH compliant, propellants. Several activities financed by the R&D national programs are ongoing on this subject with the aim of finding a green monopropellant or bipropellant couple capable of outperforming hydrazine in terms of specific impulse, retaining reactivity. The latter, is an important parameter for space applications where chemical propulsion susbsytems are involved. Indeed, Chemical propulsion systems are the only technology capable of addressing missions where

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capability of performing agile maneuvers such as collision-avoidance and active deorbitation are required. In addition, as the global satellite market evolves, major attention is put on those elements that could give rise to additional requirements on satellite platforms and associated propulsion subsystems. Ongoing studies on in-orbit servicing missions have shown the interest in developing agile propulsion for docking and proximity operation capabilities. To allow accurate pulse mode operation with high thrust repeatability and short thruster rise and decay time, combustion/decomposition reactivity parameters of propellant couples are investigated in a study performed by ICARE (CNRS). Major effort is put on the research of hypergolic couples for bipropellant systems characterized by low ignition delay times. The latter typically features higher specific impulse than monopropellant systems and are safer to handle: no storage of premixed oxidizer and fuel is involved.

Other activities with industrial partners are focused on the study of Hydrogen Peroxide based applications for in-space propulsion. Several critical points rise when operating H2O2 based systems. Namely, the incompatibility of hydrogen peroxide with standard propulsion system components (ex. incompatibility with materials such as titanium), and the intrinsic concentration loss that has to be mitigated if long satellite life-time missions are addressed (> 5 years). Long term compatibility of Hydrogen Peroxide is investigated, in literature, by retrieving two parameters: the Active Oxygen Loss (AOL) and a term called the Stability. Common test to retrieve AOL involves placing the material in a gas flask with the addition of H2O2. The flask is then exposed at 339 K for 1 week. This is a type of an accelerated exposure test which allows to retrieve long term compatibility conditions of 1 year at 293 K. Materials in common literature have been then divided in compatibility classes according to these tests: Class 1 (the best material choice for long term exposure) to a Class 4 material. The latter is unsuitable for Hydrogen Peroxide exposure and could actually be employed for its catalytic decomposition.
Many factors can impact the long term compatibility of Hydrogen Peroxide with a given material: pH, Hydrogen Peroxide nominal concentration, Hydrogen Peroxide purity, stabilizers, storage temperature and pressure, tank surface to volume ratio, tank surface passivation or coating [6]. In this section, some system-level reflections on H2O2 based propulsion are reported.
Specific Impulse of Hydrogen Peroxide based propulsion subsystem increases as concentration increases. Therefore, for satellite applications, hydrogen peroxide concentrations > 87.5% are foreseen. High performing concentrations (above 95%) imply higher risks of hypergolic reactions, thus impacting system safety and corresponding handling. In addition, procedures to synthesize high concentration H2O2 are more complex, impacting the final propellant cost. Finally, the propellant grade influences the long-term compatibility of the system. A proper tradeoff taking into account all these effects should be addressed to select the proper Hydrogen Peroxide concentration.
Proper material selection and surface treatments are a key factor to improve H2O2 storability and limit propellant decomposition in time. Materials are typically subject to chemical passivation and surface polishing to decrease the AOL. Mission duration of several years are considered possible when aluminum alloys AA6000-AA1000 series are employed. The latter, seem to be the candidate material for most of the propulsion susbsystem components since measurements of AOL<0.4% are available in literature [6]. However, the use of aluminum alloys hinders an increase in the propulsion subsystem dry mass: space-graded aluminum alloys feature lower strength to weight ratios when compared to conventional titanium alloys (which are not compatible for H2O2 long storage applications). Thus the usefulness of H2O2 based solutions on large satellite platforms where large quantity of propellant is required (high tank mass) has yet to be assessed via proper trade-offs with other green propulsion solutions (ex. hypergolic green bipropellants, water propulsion).
The decomposition of Hydrogen Peroxide, and therefore its storability, is dependent on the surface to volume ratio of the system containing the Hydrogen Peroxide. In general when the surface to volume ratio decreases, the storability improves. Spherical shaped tanks are therefore preferred with respect to toroidal or cylindrical shaped tanks. However, tank accommodation on the satellite shall be compatible with other satellite components and payload. If storage of the propellant in several spherical tanks is required, considerations of storing Hydrogen Peroxide in a single cylindrical or toroidal tank should be taken into account to limit this factor.
Temperature and pressure effects on Hydrogen Peroxide AOL are being studied with the aim of finding optimal storage conditions. Other factors such as radiation environment impact on AOL have to be taken into account.
Preliminary long-term stability results have shown that H2O2 based solutions belonging to the 1-22 N for LEO satellite application are considered possible and appealing for global satellite market. Targeted mission lifetime is 5 years. The outcome of future developments of these propulsion systems could also be extended to kick stage/launcher RCS motors. In the latter application, however, it is remarked that the requirements on long-term storage are in the order of 6 months. Therefore, outcome of tradeoffs involving material and propellant grade selection could be different.
A final remark involves H2O2 bipropellant applications. Studies on hypergolic compounds/additives have been proposed to ensure propellant reactivity compatible with in-orbit servicing applications (high thrust repeatability and thruster reactivity). Further activities to cover the subject are previewed with laboratories and industrial partners.

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The aim of the upper mentioned activities is to have an alternative propellant at the end of 2024 and start the development of an associated propulsion system. Some applications make require novel combustion chamber materials to avoid implementation of cooling systems. CNES is supporting, under an R&D contract with ONERA, the development of an Ultra High Temperature (UHT) resistant material able to withstand flame temperatures of 3200 K and thrust chamber associated mechanical loads. The proposed solution is a functionally graded material with a variation in composition between a ceramic (high melting temperature) and metal (good mechanical strength). Steady state firing tests have been performed to assess thermomechanical response of the material. Further tests are ongoing.

Concerning tanks, CNES is supporting an R&D program with Stirweld, focused on the development of friction stir welded aluminum tanks. Despite an increase of the tanks dry mass, the final design could be of interest to several applications. The activity is now focused on the development of a demisable tank (complete disintegration during re-entry) for electric propulsion applications. The final result, could however be extended to Hydrogen Peroxide based propulsion after selection of proper alluminum alloys and surface passivation techniques.

4. Cold gas microproulsion

In the last decade a growth in the number of nano satellites launched in orbit has been observed. To comply with space debris mitigation (involving deorbitation and collision-avoidance manoeuvres), it is preferable to equip these platforms with properly designed propulsion subsystems.
The design is non-trivial: the requirements in terms of ΔV to perform these maneuvers is difficult to satisfy due to constraints on maximum volume and mass dedicated to the propulsion subsystem. In typical Cubesat missions (<16U), the volume allocated to the propulsion subsystem is in the range 0.5-2 U. In addition, particular missions such as interplanetary exploration mission, or missions where high pointing accuracy is needed, may require propulsion subsystems capable of providing multiple degree of freedom maneuvering capabilities to the satellite.
A multi degree of freedom propulsion subsystem is characterized by multiple nozzles, which position and thrust direction are accurately studied to provide capabilities of providing ΔV and torques along more than one satellite main axis. Thanks to these systems the satellite would be able to perform reaction wheel desaturation, orbit change and correction and collision avoidance.
Cold gas propulsion technology is a valuable candidate to provide these capabilities. Thanks to developments in additive manufacturing and the availability of electronic micro valves, several actors have developed their cold gas propulsion solutions: VACCO and Rubicon (USA), T4i (Italy) and GomSpace (Denmark).
To maximize propellant storage, and achievable ΔV, biphasic gases such as butane and hydrofluorocarbons (R236fa, R134a) are employed. These are stored under saturated liquid conditions and feature liquid densities that can overcome 1 kg/m^3. These gases also feature relatively low saturation pressures. The high storage density and the low saturation pressure allow to maximise the ratio between the deliverable total impulse and the propulsion subsystem dry mass. The latter is strongly influenced by the storage pressure of the propellant, which has a direct impact on the thickness and weight of the tank.

At CNES, development of a cold gas micro propulsion system for cubesat applications is ongoing. Preliminary thrust measurements employing nitrogen and helium are foreseen in 2024. Tests will address functionality and performance of the propulsion system during continuous and pulse mode operation. The preliminary system architecture, reported in Fig. 1 involves a tank with associated pressure sensor and fill and drain valve, a latch valve, pressure regulator and 4 thrusters. Due to requirements in terms of volumetric constrains, activation cycles (>100.000) and MIB (<500 uNs) each thruster is controlled by a miniature solenoid valve.

The propulsion unit fits in 1U and target thrust levels are between 1 and 10 mN. Theoretical performance associated to the different propellants considered is presented in 2. Butane has not been considered in the propellant selection since it is flammable and handling/testing would require additional safety procedures. Reference tank of 300 ml at 300 bar MEOP is considered for comparison. Industrial partners have ongoing developments in composite overwrapped pressure vessel tanks targeting this level of pressure for cubesat applications. For comparison, the ΔV in Table 2 is computed on a satellite with 6 kg dry mass. The system architecture will evolve to a version 2.0 for adaptation to the use of hydrofluorocarbons by including a phase-change stage.

As shown in Table 2 the highest achievable ΔV are provvided by biphasic gases thanks to liquid phase storage. Nitrogen provides a ΔV of 11.2 m/s which could be sufficient for missions where minor orbit correction maneuvres are required.

Cold gas propulsion systems feature low ΔV when compared to other propulsion solutions. Limitation is due

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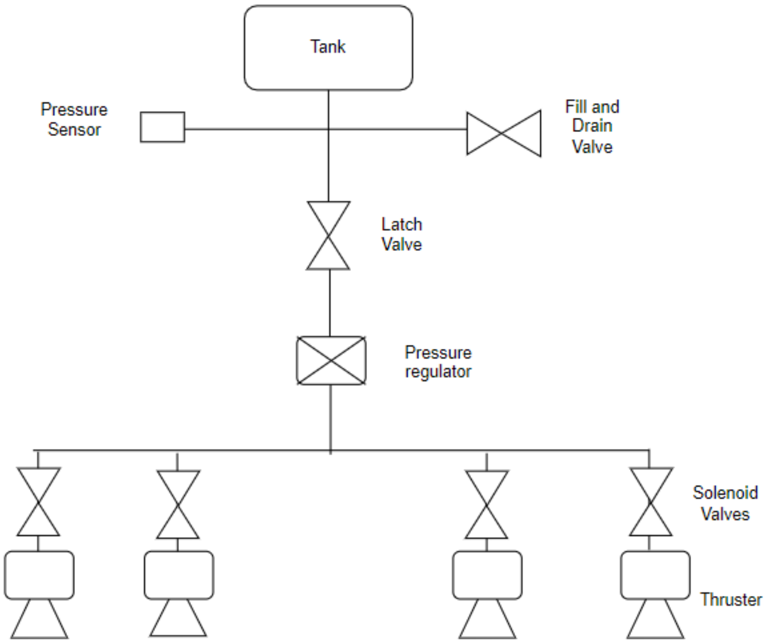

Figure 1: CNES cold gas micropropulsion subsystem scheme

	Nitrogen	Helium	R236fa	R134a
Theoretical Vacuum Specific Impulse [sec]	70	179	40	48
Molar mass [kg/kmol]	28	4	152	102
Density @293K and saturation pressure[g/cm^3]	-	-	1.381 @ 13.2 bar	1.280 @ 5.8 bar
Density @293K and MEOP [g/cm^3]	0.33	0.043	-	-
ΔV [m/s]	11.2	3.8	26.1	29.2

Table 2: Cold gas technology, propellants comparison

to either the low Isp or the low amount of propellant that can be stored inside the tanks (limitation to MEOP and security factors). To overcome these limitation, CNES is supporting developments of a water based resistojet concept at ICARE (CNRS), allowing a two-fold total impulse respect to off-the-shelf dual phase based cold gas propulsion systems. Performance and functional tests on a lab scale model are foreseen for Q1 2024.

5. Conclusions

Observing the increasing number of satellite electrical propulsion subsystems, chemical propulsion will most likely address those applications where agile maneuvers or high thrust are required. These include capability to perform collision avoidance, active deorbitation, proximity operations and interplanetary exploration (ADCS purposes). State of the art chemical propulsion is based on hydrazine. Less toxic (green) propulsion alternatives need to be developed to comply with European regulations. Different green propulsion alternatives are available as commercial off the shelf components or are currently under development. All of these alternatives feature a lower toxicity when compared to hydrazine based propellants. This additionally implies a reduction in mission cost and timeline due to the lower hazards during propellant loading and handling. However, each solution features some disadvantages that have to be taken into account and mitigated at system level. For each satellite mission a proper tradeoff taking into account required ΔV, propulsion subsystem dry mass and lifetime has to be performed to retain the optimal green propulsion solution.
CNES is supporting several activities financed by R&D programs to tackle with hypergolic green propulsion solutions and Hydrogen Peroxide based propulsion systems. Considerations at system level such as material compatibility, propellant lifetime, thrust accuracy and thruster reactivity are taken into account. In addition, cold gas propulsion systems for cubesat applications are under development.

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