

Ammonium dinitramide-based Energetic Ionic Liquid Propellant as a replacement to Hydrazine

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Abstract— The monopropellant Hydrazine is frequently used today in industries like aviation and the military, however, it has a reputation for being highly toxic for humans and arduous for transportation. Hence, this study will explore and discuss a new alternative of a 'green' propellant; Ammonium dinitramide (ADN) based Energetic Ionic Liquid Propellant (EILP). This paper will explore the current uses of ADN, through studying its chemical and physical composition of the mixture and how it can help organizations optimise performances in their aerospace models. Furthermore, whilst discussing on how organisations can implement this mixture, this study will introduce the use of High Performance Green Propulsion (HPGP) thrusters, developed by SNSB (Swedish National Space Board). Current studies by organisations like FOI and EURENCO show that the chemical and physical composition of this form of EILP will be superior the current monopropellant of Hydrazine, as ADN covers and caters to Hydrazine's disadvantages like non-toxicity and can be stored safely for a long time at room temperatures.

Index Terms— Energetic Ionic Liquid, Green propellant, Ammonium Dinitramide, rocket propulsion, non-toxic propellant, future space mission, Hydrazine

1 INTRODUCTION

Energetic ionic liquids are materials that not only execute high performances but are exceptionally great for the environment and humans. To organisations like NASA or SpaceX where their main goal is to work with the humans' needs of having a non-toxic environment whilst exploring further into the universe, their current use of propellants and propellant systems are contradicting to their goals. For four decades, the monopropellant hydrazine has been used dominantly in 85% of various spacecraft made. However, this inorganic propellant is highly toxic, exceedingly expensive, and will explode in the presence of oxygen and heat (making transportation of the propellant arduous).

The first use of hydrazine dates back to 1977 (Voyager 1) and carried two types of fuels; hydrazine and plutonium-238 dioxide, which NASA estimates that the Voyagers' fuel efficiency is upwards of 30,000 miles per gallon of hydrazine. The positive of the monopropellant is; it's quite stable and does not go under any long term chemical changes. It can last under an unlimited time in a clean tank. Yet the negatives of hydrazine outweigh the positives. Hydrazine is a clear liquid that has an appearance and behaviour similar to water. They have similar freezing points, surface tension, density, and viscosity. Essentially, Hydrazine in the thrusters of a rocket dissociates and expands in the presences of a catalyst and heat, providing the thrust needed to move the satellite. Given this, hydrazine will burn if given the opportunity. In fact, in the

presence of oxygen or conventional air, a catalyst that could include just a spec of rust in the container, and a small amount of heat, hydrazine will spontaneously explode. Hence, these characteristics make it desirable as a fuel for satellites as it can ignite easily without further complicated steps, but dangerous to the humans who are around it. Besides being highly and easily combustible, it is extremely toxic, caustic, and probably carcinogenic. Therefore, making the move to a greener propellant is crucial now more than ever.

Looking at the replacement, which in this study, is Ammonium Dinitramide based EILP does not has not been utilised in major missions at the current time. JAXA and Japan Carlit Co., Ltd. developed solvent-free monopropellants, which contain ADN, monomethylammonium nitrate (MMAN), and Urea. Even though, these mixtures a solid at room temperature, the mixture of powders becomes liquid because of the freezing point depression. Essentially, Ionic liquid (IL) is defined as salt whose freezing point is below 373K. Hence, IL is a liquid which contains only ions. Furthermore the mixture does not have a solvent and its flame temperature is relatively high, so, transporting this fuel is far easier to hydrazine.

This study will also include how ADN can be used in organisations through the help of High Performance Green Propulsion (HPGP) thrusters. HPGP propellant contain 60-65% of ADN, 15-20% of Methanol, 3-6% Ammonia (fuel) and a water

as a solvent. Essentially these thrusters have improved performances with better stability of fuel and Higher Specific Impulse and Density Impulse. They also have increased safety with less toxic, Non-Carcinogenic, and Environmentally Benign. This overall reduces the cost as well as there is simplified handling and transportation, and reduced cost for fueling operations. [1]

2 PROPERTIES AND FUNCTION OF HYDRAZINE

An important factor when considering replacing a frequently used product with a newer invention is to highlight both of its properties and function to understand and bring a fair conclusion as to whether it is viable to replace the product.

2.1 Properties

Hydrazine (N₂H₄) is a molecule that is a strong base, looks very similar to water, and has an odour of ammonia. Hydrazine can be often called Diamine or Diazane or Nitrogen hydride and is an azane and dangerously unstable. Each subunit of H₂N-N is pyramidal and the N-N bond distance is about 1.45 Å. This molecule is often known to be unusual as anhydrous hydrazine will not explode, but the vapours will make explosive mixtures with air. Other properties of N₂H₄ are that it is colourless, highly polar, and is completely miscible in water. It has a boiling point of 114 °C and has a melting point of 2 °C (Figure 1). [2]

	Hydrazine
Density (g/cm ³)	1.0037
Specific Impulse ^b (s)	230
T _{min} ° (°C)	2.01
Temp. in Chamber (°C)	1120
Thermal expansion coefficient (1/K)	9.538*10 ⁻⁴
Viscosity (cP, mPas)	0.913
Heat Capacity (J/gK)	3.0778

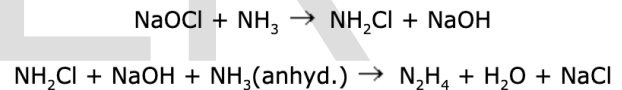
Figure 1- Properties of hydrazine. a) All properties at 25 C. Hydrazine data from Schmidt (Schmidt, 2001)

2.2 Discovery

Hydrazine was first invented in 1889 by a German chemist named Theodor Curtius, however, his method of developing the organic molecule was rather inefficient. Hence, over the

coming years, scientists and chemists found industrial routes to produce N₂H₄ like using the Olin-Raschig process which was developed by another German chemist, Friedrich Raschig in 1907. Essentially in this process, bleach or sodium hypochlorite is mixed with ammonia at 5 °C to form sodium hydroxide and chloramine. This produced mixture is immediately added to anhydrous ammonia under pressure and at 130 °C to produce hydrazine and water, plus salt as a waste product as shown in Figure 2.

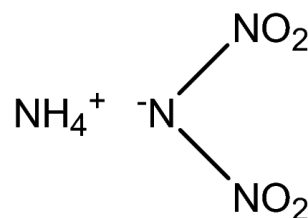
After this efficient production, many found value in the compound as it was cheap and versatile in terms of uses; from rocket propellants to power stations and car airbags. However, during World War 2, the Germans were the first to identify Hydrazine's value as rocket fuel. They invested in large production factories to produce and increased the output of the fuel from a few tons to about 150 tons per month. Immediately after the war, Germany started to gain recognition for the progress it had made from producing hydrazine and that it had a potential price of 70 cents per pound at large tonnage levels, the aviation and aerospace industry boomed. But as predicted, the demand for the organic molecule grew higher as there were so many more uses of it, the industry started placing high prices. The price per pound of anhydrous hydrazine (95% of N₂H₄ minimum) was about \$9.00.



2.3 Function and Implementation

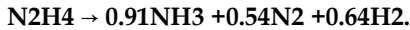
Figure 2- Production of hydrazine using the Olin-Raschig process which was developed by another German chemist, Friedrich Raschig in 1907.

Hydrazine as a monopropellant is often used in a catalytic decomposition engine. Essentially, there is no necessitate for complicated mixing with oxidisers because hydrazine decomposition is fairly energetic due to its high reactivity and instability, and the catalyst provides simple hypergolic ignition.

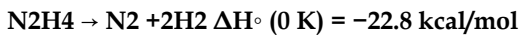
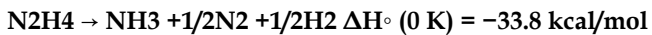


As there was no need for complicated steps, the importance of hydrazine is a great deal of experimental research on both gas phase and catalysed decomposition rates. A number of the reactions considered below are also relevant to the Haber's process

for producing ammonia from N₂ and H₂, but the focus of the current report is on the decomposition reactions leading to small molecules. The catalytic decomposition usually occurs in the presence of Iridium (the catalyst) to produce a mixture of H₂, N₂, and NH₃. The decomposition reaction at 983 K produces the following product ratio



The stoichiometry is considered to arise from two product channels: [3]



3 PROPERTIES AND FUNCTION OF ADN

3.1 Properties

Typically, Ammonium-Dinitramide (ADN) is a solid white salt/crystal containing both the ammonia cation (NH₄⁺) and the dinitramide anion [N(NO₂)₂]⁻. It has a high oxygen balance (OB) of 25.8%, a melting point of 93 degrees Celsius, and a decomposition temperature of 150 degrees Celsius. ADN is a hygroscopic crystal which dissolves easily in water and other polar solvents, but not in non-polar solvents. At 25.0 °C, the critical relative humidity (CRH) for ADN is 55.2 percent. In the solid state, ADN has a density of 1.81 g/cm³. It has a molar volume of 74.08 g/mol and a density of 1.675 g/cm³ in the liquid state at 25.0 °C. Furthermore, because ADN is a water-soluble ionic salt, one of the best methods for analysing ADN crystals is UV-Visible spectrometry. Two peaks at 214 and 284 nm were identified in the UV spectra of ADN. The absorption maximum at 214 nm is linked to the increased energy $\sigma\text{-}\sigma^*$ transition, while the absorption maximum at 284 nm is due to the characteristics of the $\text{-N(NO}_2\text{)-}$ ion due to the low energy $n\text{-}\pi^*$ transition. [4]

3.2 Discovery

Figure 3- Structure of ADN. Image from semanticscholar.org "7 Green Propellants Based on Ammonium Dinitramide (ADN)"

Half a century ago, the former USSR developed ADN secretly in the middle of the cold war, as a goal to produce smokeless propellants for their tactical-rocket/missiles. However, the ammonia like compound was first introduced to the public in 1993 by Bottaro. J. C. Bottaro applied for a patent that was granted to SRI (Stanford Research Institute) in 1993 for this subject matter of making green propellants, which was when the first synthesis of ADN was performed. However, later that year, LNPO Soyuz released a paper at the AIAA Conference in the United States in 1993 claiming that, what is now accepted as being the origin of ADN in the former USSR (Union of Soviet Socialist Republics). At the Fraunhofer-ICT Conference in Germany in 1994, Tartakovsky and Lukyanov (1994) reaffirmed ADN's Soviet origins. It is now widely accepted that ADN was initially synthesised in the Soviet Union in the early 1970s. Meanwhile, the Soviet Union's economy deteriorated over that decade, resulting in the end of the Cold War in the late 1980s. As events unfolded, ADN experts relocated to other countries to aid local engineers.

In 1996, the Swedish Defense Research Agency (FOI) developed a new one-step technique, and one year later, in 1997, Bofors opened a plant and began producing ADN using the same FOI technology. Later that, Eurochem made ADN samples available for purchase, motivating engineers all across the world to continue to work on the innovation. ADN was desired by NASA/GRC (National Aeronautics and Space Administration/ Glenn Research Center) for solid rocket boosters. Regardless of the fact that NASA began exploring ADN in the 1990s, they ended shortly after caused by a lack of funding supported by AFOSR (Air Force Office of Scientific Research), and later due to the recession in the American space programme over the last two decades. However, in December 2008, they expressed interest in purchasing parts from FOI in order to manufacture ADN for the new ARES rocket, which would be intended to replace the Space Shuttle. ADN research is also underway in a number of nations, including Japan, India, China, and, most recently, Brazil's AQI-IAE (Chemical Division - Institute of Aeronautics and Space). [5]

3.3 Function and Implementation

The molecular structure of Ammonium dinitramide (ADN)

[NH₄N(NO₂)₂]. is primarily composed of nitrogen (N), oxygen (O), and hydrogen (H). As a result, ADN combustion products are environmentally friendly. Moreover, the presence of the dinitramide anion [N(NO₂)₂-] results in increased density, the heat of creation, oxygen balance, and oxygen content. At low pressure, ADN burns without releasing any light, creating abundant white vapours which condense as a fine white powder inside the tube and on the bomb's cold surfaces. Small "flamelets" erupted from the local reaction sites as the pressure increased. The gases become nearly clear above 1–2 MPa, a brilliant flame develops, and the condensed products of combustion are not visible.

Some organisations may reach to add paraffin to the crystal ADN, which changes the low-pressure deflagration limit (LPDL) limit from 0.2 MPa to 0.02 MPa. Similarly, a mixture of ADN with 0.2 percent paraffin pressed into 7 mm plexiglass tubes could keep burning at air pressure even at temperatures as low as 77 K. The influence of a modest amount of paraffin on the ADN burning rate characteristics could be explained by the fact that paraffin appears to be a more easily oxidisable alternative fuel than NH₃. Another alternative to paraffin is halocarbon oil (which is not an oxidisable fuel) and SiO₂ (which is non-combustible) also helps to lower the LPDL limit, although soot (which stabilises combustion) does not. As a result, it was determined that the LPDL limit for ADN is linked to physical rather than chemical factors.

ADN combustion produces a substantial exothermic condensed-phase heat release (approximately 50 kcal/mol) at lower pressures (less than 20 atm). At low pressures, the temperature gradient on the surface of ADN is also modest, therefore heat feedback from the gas phase is negligible in the first area of combustion. Hence, a scientist Sinditskii, claimed that the first zone of combustion is controlled by condensed phase breakdown, with the gas phase flame having little or no influence. Condensed-phase material, such as liquid droplets, is disseminated into the gas phases and decomposes there due



to the fast burning rate. For compounds where condensed phase breakdown dominates combustion process, dispersion of condensed materials was observed. The temperature of ADN dissociation rises as pressure rises, as does the energy required for dissociation. However, in this region, the condensed phase heat release does not increase with pressure, and the gas phase still

plays a minor role. As a result, the amount of energy required to heat and evaporate the condensed phase materials is decreasing.

The temperature rises after the ADN droplets dissociate, forming the initial flame. This flame depicts the reaction of ammonia oxidation by nitric acid breakdown products, such as OH and NO₂. However, because N₂O and NO remain partially unreacted in the flame, the temperature of the zone does not match to the whole heat release. Only the second flame, which was practically visible at 10 MPa, completes the combustion reaction, while it could also be noticed at lower pressures and at greater standoff distances. Figure 4 shows a schematic illustration of the ADN flame structure. [4]

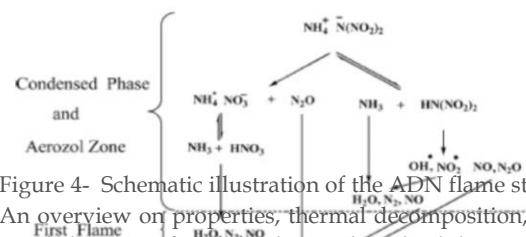


Figure 4- Schematic illustration of the ADN flame structure. From An overview on properties, thermal decomposition, and combustion behaviour of ADN and ADN-based solid propellants - Scientific Figure on ResearchGate. Available in: https://www.researchgate.net/figure/Schematic-representation-of-ADN-flame-structure-39_fig1_324111093 [accessed 6 Jul, 2021]

3.4 Motor Testing

This segment of the research is referring to FOI's paper on "Green Propellants Based on Ammonium Dinitramide (ADN)". This is where rocket motor firings were performed to verify the calculated specific impulse. As shown in Fig. 5, three 3 kg case bonded grains were cast in steel cartridges. An HTPB-based liner was employed. After casting, some little machining was required. The propellant was simple to manufacture and had a smooth finish. The motor is shown in Figure 6 firing. The observed pressure is shown in red in Fig. 7 as a function of time. [6]

Fig. 5 - Case bonded 3 kg ADN/GAP (70/30) grain cartridges for motor testing. From FOI's paper on "Green Propellants Based on Ammonium Dinitramide (ADN)"



Fig. 6 - Test firing of ADN/GAP rocket motor. From FOI's paper on "Green Propellants Based on Ammonium Dinitramide (ADN)"

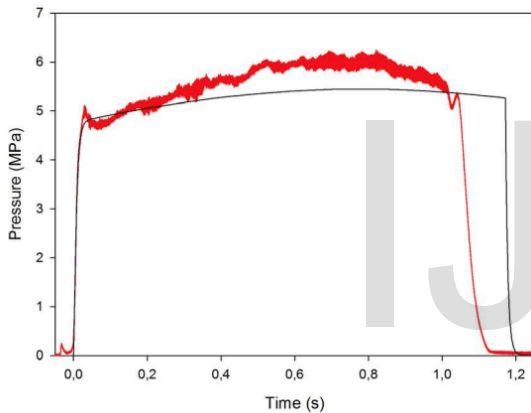


Fig. 7 - Combustion pressure as a function of time. Red curve experimental, black curve calculated. From FOI's paper on "Green Propellants Based on Ammonium Dinitramide (ADN)"

4 ENERGETIC IONIC LIQUIDS

As in this study, we are looking at Ammonium Dinitramide (ADN) based Energetic Ionic Liquids, it is crucial to look at the act of Energetic Ionic Liquids (EIL) as a monopropellant. Karl Christe proposed the use of EILs for monopropellant applications for the first time in 1998. Since then, a few efforts

have been made to create 20 alternative EILs that could operate as monopropellants. The targeted monopropellants, also known as self-oxidising EILs, pair cationic fuel partners with an oxygen-rich anionic oxidiser, eliminating the need for external strong oxidants. This lowers the cost of using hazardous and corrosive oxidisers while also making monopropellants appropriate for simple green applications.

The majority of known EILs have a low oxygen concentration, which causes them to perform worse than standard energetic materials. Even EILs with modest anions, such as nitrates, perchlorates, and dinitramides, do not have enough oxygen to completely oxidise their corresponding cations; thus, EILs must be used in conjunction with powerful oxidisers. Because CO₂ primarily dissociates into CO and O₂ at increased temperatures (Boudouard equilibrium), oxidising the carbon content to CO rather than CO₂ may provide the optimum performance, in addition to low molecular weight exhaust gas products.

5 INTRODUCING HPGP THRUSTERS

An Ammonium dinitramide fuel that was developed by the ECAPS is called LMP-103S. It's a storable ADN-based monopropellant blend with a density impulse up to 30% higher than hydrazine. The propellant is a premixed bi-propellant with a high energy content and low sensitivity. LMP-103S is a propellant with a mixture of ADN, water, methanol and ammonia. Due to the low toxicity and environmental friendliness of LMP-103S, no SCAPE operations are necessary during propellant handling. In limited quantities, LMP-103S is also permitted for air cargo shipment. The pursuit of authorisation for the air transport of fuelled spacecraft is still continuing. The Advance Concept Engine (ACE) program was started to investigate the possibilities for designing future engines for launch vehicles (i.e., roll and altitude control), spacecraft apogee engines, and lander engines employing low-hazard propellants. Figures 8 and 9 show a simplified comparison of current storable space propulsion thruster performance (mono- and bipropellant) and predicted performance for HPGP thrusters (using LMP-103 and 103S monopropellants) as demonstrated in the ECAPS paper "EXPANDING THE ADN-BASED MONOPROPELLANT THRUSTER FAMILY."

The usual delivered vacuum-specific impulse for MMH/MON (bipropellant), hydrazine (monopropellant), LMP-103, and LMP-103S is shown in Figure 8. (monopropellants at different thrust levels).

The typically delivered density impulse for

MMH/MON (bipropellant), hydrazine (monopropellant), LMP-103, and LMP-103S is shown in Figure 9. (monopropellants at different thrust levels). [7]

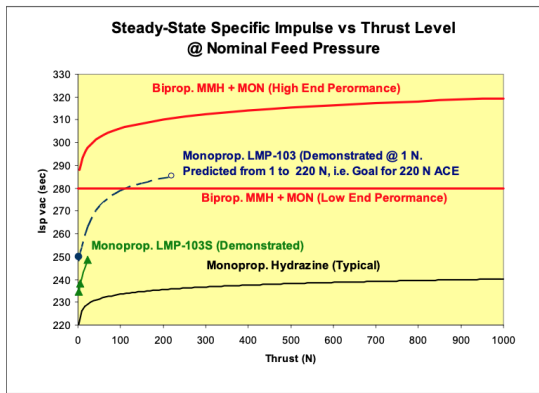


Fig. 8 - vacuum-specific impulse for MMH/MON (bipropellant), hydrazine (monopropellant), LMP-103, and LMP-103S. From ECAPS's paper on "Expanding the ADN- based monopropellant thruster family"

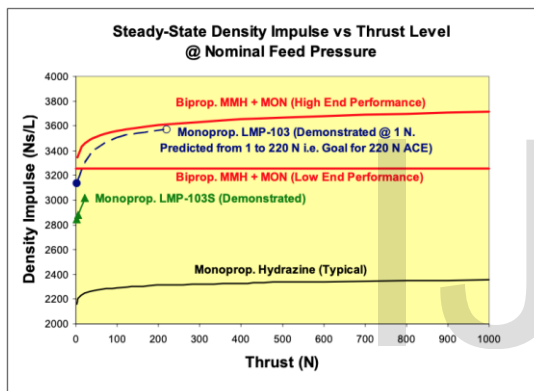


Fig. 9 - density impulse for MMH/MON (biprop. From ECAPS's paper on "Expanding the ADN- based monopropellant thruster family"

5.1 Implementation of HPGP and ADN in missions

On PRISMA, the HPGP technology will be demonstrated for the first time in space (to reach TRL 7). PRISMA is comprised of two LEO satellites. The primary goal is to show that automated unit flight and rendezvous manoeuvres are achievable. The ECAPS HPGP system will have a delta-V capability of roughly 60 m/s. PRISMA was set to launch from Yazny (Russia) in late 2009 on a Dnepr launch vehicle. The PRISMA HPGP subsystem operates in blow-down mode and utilises a conventional monopropellant architecture. One diaphragm-

type propellant tank with a capacity of 4.5 L (5.6 kg), two service valves, one pressure transducer, one system filter, one isolation latch valve, and two 1 N HPGP monopropellant thrusters cover up the propulsion subsystem. All of the fluid components are "Commercial-Off-The-Shelf" (COTS) hydrazine components. Since 1999, ECAPS has produced and tested more than 50 thrusters that use ADN-based propellants. Figure 10 summarises the steady-state specific impulse and density impulse at MEOP (Maximum Expected Operating Pressure) for the various HPGP thrusters.

Thrust Level	Propellant	I_{sp} (Ns/kg)	Density Impulse (Ns/L)	Status
0.5 N	LMP-103S	2210* (~225 sec)	2730	TRL 5
1 N	LMP-103S	2310* (~235 sec)	2860	TRL 6
5 N	LMP-103S	2340* (~238 sec)	2900	TRL 4
22 N	LMP-103S	2445* (~249 sec)	3030	TRL 4
50 N	LMP-103	2515** (~256 sec)	3120	TRL 2
220 N	LMP-103	2800** (~285 sec)	3580	TRL 2

* Delivered steady-state vacuum specific impulse at MEOP
** Predicted steady-state vacuum specific impulse at MEOP

5.2

Fig.10 - From ECAPS's paper on "Expanding the ADN- based monopropellant thruster family"

The ACE concept

ACE is a 220N test engine designed to demonstrate significantly higher thrust and performance for ADN-based storable liquid propulsion systems. The ACE engine's aim is to demonstrate higher thrust rates with a specific impulse and density impulse that are equivalent to storable propellant bipropellant engines. As a step between the 22 N HPGP thruster and the 220 N ACE, a 50 N test engine is being constructed by the ECAPS.

The ACE has the following design features and aims for operating in steady-state and pulse mode (ECAPS PAGE 6)

- Multi-fuel capability
- Dual-mode
- Throttling Capability
- Increased performance Increased thrust level (> 100 N)
- Modular design

Higher combustion temperatures are intended to enhance the particular impulse. Formulations based on ADN have been

identified for improved performance. A three-year R&D initiative began to improve the high-temperature resistant catalyst life in order to sustain even higher temperatures, has been launched with the goal of enabling future thruster designs for improved performance. The work is funded by the National Space Research Program, and ECAPS leads a Swedish consortium (NRFP). [7]

same tank, fewer co-manifest challenges like a reduced physical risk to other satellites, parallel processing at the launch site, and more launch opportunities.



Fig.11 - A 22N, 50N, and 220 N HPGP thrusters From ECAPS's paper on "Expanding the ADN- based monopropellant thruster family"

6 CONCLUSION

In this study, we have reviewed the regularly used toxic monopropellant Hydrazine, as rocket fuel in comparison with the new replacement of the compound Ammonium-Dinitramide (ADN). To conclude, ADN is a compound of interest to the rocket community as well as the community of energetic materials. Furthermore, because ADN may be used in both solid and liquid - fueled rockets, there is a strong incentive to continue research on it. There is also intensive research on this compound through organisations like NASA or SpaceX, because as analysed, Hydrazine is highly reactive and demanding in terms of storage, which ends up costing companies in large amounts. So far, the HPGP thrusters with the use of LMP-103S propellant have only been utilised in smaller satellites like PRISMA as fuel for manoeuvring the satellite. However, the downside is that ADN has not been used as a launch fuel as it requires lots of careful handling when it comes to the thermal decomposition of the fuel as the rates of decomposition due to the temperature of this compound are high. But the HPGP thrusters can cater to various positives such as lower mission costs due to; longer mission lifetime with the

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