Hydroxyl Ammonium Nitrate (HAN) based Propellants for the Next Generation Launch Vehicles – A Review

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Abstract - Hydroxyl Ammonium Nitrate (HAN) based propellants are the future propellants for the launch vehicles of rockets. These HAN based liquid mono propellants are the replacement of Hydrazine Toxic components. These hydroxyl ammonium nitrates (HAN) are known to be the Green Propellants. It is because of its significant features when compared to conventional fuels. Recent studies showed that the performance of these HAN fuels is providing more flexibility to the environment. In order to make it into a usable form, the green propellants must be mixed with the stable hot catalyst, to make it stable. These fuels are utilized in the launch of the Space X heavy falcon, Green Propellant Infusion Mission (GPIM). And, it showed that the 50% higher performance compared to the traditional propellants. This paper insight concerning future propellants. By utilizing the green propellants, the usage of hydrazine based mono propellants is reduced.

Key Words: Green Propellants, Cube SAT propulsion, Future Propellants, Rocket Engine, HAN mono propellants, Hydrazine Mono propellants.

1. INTRODUCTION

For many years hydrazine has been used as monopropellants for launch vehicles due to its toxicity and high vapor pressure increases the costs. Whenever dealing with hydrazine monopropellant a special protective Equipment has been used because of its toxicity nature. To overcome these types of difficulties and toxicity a new propellant named "Green" propellants has come into the picture. Even though the green propellants has been introduced the catalyst, which is used for hydrazine monopropellant cannot be applied for green propellants. Because those type of catalyst has capable to generate high flame temperature and even contains oxidizers. The catalyst which is used for hydrazine monopropellant doesn't tolerate high temperature when used as a catalyst in green propellants (Shindo et al. 2017) Green opropellant technologies expand their capabilities beyond what has been achieved with current conventional propellants like hydrazine. It doesn't mean that hydrazine monopropellant will produce less performance and efficiency when a green propellant came into the current scenario.

Hydrazine monopropellants have excellent track records for the past six decades and behind the success of thousands of space missions, hydrazine plays a key role in propulsions. But, quickly recognized that true greenness lies not in the safety improvement besides lowering cost and simplification of propellant handling. Generally, these green propellants may have low vapor pressure so, that there will be no risk of inhalation while handling with propellants. (Sackheim and Masse 2014)

The decomposition of Hydrazine under catalytic reaction generates hot gases in the nozzle. We know decomposition of hydrazine is an exothermic reaction and it can elevate up to 1000 oC. The decomposition of Hydrazine gives heat and energy when it comes into contact with the catalyst then the generation of gases will take place to run the turbines. The decomposition of hydrazine will be described according to the following reactions:

$3N_2H_4$ (I) 4 NH_3 (g) + N_2 (g) (1)

2 NH_3 (g) N_2 (g) + 3 H_2 (g) (2)

3 N_2H_4 (I) $2NH_3$ (g) + 2 N_2 (g) +3 H_2 (g) (3)

The first two reactions are common and the obtained ammonia in the first reaction further decomposed to nitrogen and hydrogen. (Amrousse et al. 2017)

2. GREEN PROPULSION

The monopropellant which is the replacement of hydrogen ad must be chemically and thermally stable for long term usage. The monopropellant which is going to replace must be easily decomposable and contain good combustion properties, not only combustion properties but also should contain higher specific impulse (Isp) why because specific

Impulse determines the performance/Efficiency rate of rocket engines. Both the materials Hydroxylammonium nitrate (HAN) and Ammonium dinitrate (ADN: NH4. N(NO2)2) are unstable and potentially Explosive. To limit the explosion potential both the materials are used in a concentrated aqueous solution. In complex applications, methanol is added o the solution to get maximum performance these types of performance will have low vapor pressure as well as low risk of Inhalation while handling. (Amrousse et al. 2017)

The liquid form of HAN based monopropellant was prepared by Hosoya company (Tokyo). The composition is as follows:

(HAN/AN/H2O/ CH_3oH)

HAN - 73.6 wt. %

AN - 3.9 wt. % (Ammonium Nitrate)

H2O - 6.2 wt. %

CH_3OH - 16.3 wt. % (Methanol)

To minimize the freezing point of monopropellants AN is added to the HAN solution. However, to control the burning rate of monopropellants methanol is used. (Amrousse et al. 2015).

3. IMPACT OF GREEN PROPULSION

The target of green propulsions is to reduce the cost, complexity, and also environmental pollution;

1. Low Toxicity.

   Low risk of inhalation.

   Easy to handle non-toxic fluids.

   Parallel operations will be done.

2. Low pollution Impact.

   Environmental pollution will be controlled.

   Reduction in space pollution.

   Reduction in Environmental hazards.

3. Higher performance.

   Better than conventional monopropellants.

   Higher specific Impulse (Isp).

4. Low cost.

   Due to less in toxicity requirement cost will be reduced.

   Transport costs will be reduced. (D. Haeseler 1393)

4. PROPULSION SYSTEM OF CUBESAT

CubeSats are the small satellites having 10*10*10 cm cube (1U). These CubeSat programs provide access to space for small payloads. The specific standards for CubeSats help to reduce costs. CubeSat comes in several sizes, which are based on standard CubeSat "unit "referred to as 1U. It's a 10cm Cube that has a mass of approximately 1 to 1.33 kg and it has a high-speed communication link and characterizes an earth observation imager. CubeSat Satellite is made up of Aluminum 6061-T6. It contains all standard commercial off-the-shelf materials, Electrical components, and solar cells. The battery storage consists of a Lithium-ion battery with over. The poly picosatellite Orbital Deployer (P-POD) is Cal poly's standardized

CubeSat deployment system. This P-POD is capable of carrying three CubeSat Satellite and serves as an interface between CubeSat and Launch Vehicle. The P-POD is a rectangular box with a door and a spring mechanism. CubeSat slides along a series of rails while ejecting into Orbit.

4.1 GREEN PROPELLANT FOR CUBESAT

Some of the properties of green propellants are opposed to hydrazine because of low volatility at atmospheric pressures and low vapor pressure compared to hydrazine. Mostly two non-toxic monopropellants are discussed here, the one Hydroxylammonium nitrate (HAN) and the other ammonium dinitramide (AND) based propellants. These two propellants have more thrust, performance, and higher density than hydrazine. Getting higher specific impulse when burnt at high temperature. Non-toxic monopropellants can't ignite below 250oC, which means that a satellite with non-toxic monopropellant requires three times the preheat power than conventional monopropellant i.e hydrazine.

HAN Based AF-M315E is a propellant developed by the Air force research laboratory (AFRL) in 1998. However, a mission called Green propulsion infusion mission (GPIM) has been planed hence, there will not be any flight heritage for AF-M315E. Both HAN and ADN-based monopropellants contain a specific impulse of about 250s.compared to hydrazine HAN and ADN possess a 50% and 30% increase in specific impulse density. (Tummala and Dutta 2017)

4.2 PROPULSION SYSTEM PERFORMANCE

There are many ways for comparing performances for example Thruster efficiency, Specific Impulse, total Impulse, Impulse Density. While discussing monopropellants Combustion Efficiency plays a key role. Whenever the propellant is burned the chemical bond breaks and energy will be generated with an increase of propellant temperature. The energy released is then accelerated to produce thrust through the nozzle.

The chemical energy that is used for chemical propulsions creates difficulty while launching CubeSat as a secondary payload due to limits of pyrotechnics and stored chemical energy. (@20 Performmannnce of HAN.pdf n.d.)

For all the space missions commonly used chemical propulsion is Hydrazine monopropellants. This is because of the smooth propellant delivery system besides high specific impulse (Isp). Having more toxic propellant is highly expensive and safety requirements are necessary while handling hydrazine monopropellant. Hydrazine has capable of auto-combustion at room temperature and pressure. To go towards less toxic, low-cost build, launch, and flight operations a concept called "Green propulsions" has come into the picture. It replaces Hydrazine monopropellant and developed into propulsions systems for CubeSats. The chemical combustion propulsion system including Green propellants, hydrazine, monopropellants, and bipropellants are as follows

Table 1- Summary of chemical propulsion systems

Product	Thrust	Isp	Size
MPS-130/ HANBased	1N	244S	1U
BGT-5X/ ANNBased	0.5N	220-225 s	1U
BGT-1X/ HANBased	0.1N	214s	---
MPS-120/ Hydrazine	1N	225s	1 U
Hydros/ Water	0.25-0.6 N	258s	0.5 – 1U

The modular propulsion system of CubeSat from Aerojet is a system that targets the small spacecraft Aerojet has decided to adopt MPS for HAN Based propellants. (Lemmer 2017)

4.3 EXAMPLE OF HAN BASED MONOPROPELLANT SYSTEM.

BGT-5X has a 0.5N thruster and it is packaged with a microvalve, propellant tank into a 1U volume. To heat the catalyst for chemical reaction the system requires 15W of power. And also they have developed a CubeSat subsystem that contains four 0.1N thrusters which operate on ADN based propellant

ECAPS has partnered with VACCO offers a thruster that operates on a blended mixture of AND called "LMP-103S". so, this thruster used in the mission named "Lunar Flash flight mission".This HAN based monopropellant has been used in "Green propellant Infusion mission "which is a NASA technology demonstrator project tests less toxic and higher performance. This mission is launched onboard a SpaceX Falcon Heavy rocket in 2019 June 25th. This entire program costs $45 million. It offers nearly 50% higher performance for a given propellant tank compared to Hydrazine monopropellant. The propellant, nozzle, valves are being manufactured by the Air force research laboratory(AFRL). The new AF-M315E fuel is 45% denser than hydrazine which means more fuel can be stored in containers of the same volume. (Amrousse et al. 2015)

5. CATALYTIC DECOMPOSITION

The catalyst which is used for decomposition needs to be preheated at a definite temperature.

HAN based mixtures;

i) HAN-TEAN-H2O (7 HAN FOR 1 TEAN ,20WT% OF WATER).

ii) HAN-H2O (17WT-% OF WATER).

iii) HAN-GLYCINE-H2O (9 HAN FOR 4 GLYCINE, 20 WT- % OF WATER).

iv)HAN-UREA H2O (3 HAN FOR 2 UREA, 20WT-% OF WATER.)

HAN - (NH3OH)(NO3); GLYCINE – H2NCH2CO2H

TEAN – [HN(C2H4OH)3](NO3) ;

UREA – (H2N)2CO

5.1 CATALYSTS.

Catalysts for HAN Based monopropellants are as follows;

1. Platinum, Rhodium, and palladium supported catalysts.
2. To get more stability at high temperatures various types of supports are being prepared using the sol-gel process.

5.2 DECOMPOSITION OF HAN-BASED MONOPROPELLANTS.

The parameters that we going to discuss are mentioned below;

- Catalyst will be fixed either in Initial Temp. or Increased Temperature modes.
- Catalyst Sample nature.
- The fuel nature in the Propellant blend.

INITIAL OR INCREASED TEMPERATURE MODE

The tests were performed on HAN–TEAN – H2O Mixture also called (LGP-Liquid Gun Propellant 1846). Decomposition may be done in two ways one in thermal decomposition (no catalyst) and catalytic decomposition on catalyst B4151.

Basically, thermal decomposition starts at 117oC for the first trial, but according to our conditions the observed pressure value is lower than the calculated value, this seems that the decomposition into gaseous products is not completed fully. In fact, inside the reactor, a yellow-brownish carbonaceous residue was present due to the polymerization reaction of C2H4 fragments of TEAN. This seems to affect the next upcoming trails because of a decrease in onset temperature and a slight increase in pressure.

Therefore, thermal decomposition will be done in two ways without a catalyst. One is giving gaseous products as input and the other is leading to condensed polymerization products. To confirm the results that are obtained with the batch reactor the decomposition of LGP 1846 was investigated by differential thermal analysis (DTA) by following the below conditions.

i) 30 min isotherm at 30 oC.

ii)Temp slope 10 K min-1.

iii)Quartz Crucible.

iv)Argon flow.

After thermal decomposition the onset temperatures, support alone (sample 4151), and catalyst (support + active phase) are as follows; (Rachel Elorirdi 2003)

Table 2

No catalyst	Sample 4151	Sample B4151
128 ^{o} C	105 ^{o} C	75 ^{o} C

The data we obtained sees good with the results obtained in the batch reactor. After several experiments, we observed the decomposition of LGP 1846 is very sensitive to the rate of temperature increase.

After doing several experiments in a batch reactor will raise the following points;

- ✓ On decreasing onset temperature shows a catalytic effect on LGP 1846decoposition.
- ✓ The percentage of yield is never reached 100%
- ✓ It is observed that By decreasing the onset temperature there will be a catalytic effect by carbonaceous residue.

UNIFORM TEMPERATURE MODE.

Initially, the catalyst sample (A1151) was preheated at 92 oC with the injection of 50 microliter of LGP (at 20 oC) leads the first decrease in catalyst temperature 10 oC due to the vaporization of water of the monopropellant.

According to the formation of water vapor, during the same time, the pressure increases slowly with a rate of 0.29mbar/s. then observed that there is a long ignition delay(49s).

The ignition delay is much shorter (0.6s) when the catalyst temperature is 130 oC and the rate observed is twice the previous value (152 bar/s). The different sample results for both temperatures are listed below;

Table3- The Pressure increase in bar after injection 50uL LGP at 90oC and 130^{o} C

T.catalyst /^{o}C	A1151	F1151	B4151	A4151 (Oxidised)	C4151
90	154	147	175	151	162
130	223	269	290	260	366

COMPARISON OF HAN BASED PROPELLANTS.

To obtain differences between the propellants four propellants have bee checked with the same catalyst support 4151. The catalyst is preheated at 130oC and propellant volume is injected to 50uL. The temperature and pressure reached peaks due to the first injection for HAN-water and HAN-TEAN – water propellants have been observed a peak pressure value while the slopes are 124 and 74 bar/s.

we also observed a curved pressure and low decomposition rate with the addition of glycine and urea.

Poor results are obtained from we addition of glycine and urea as a fuel and it shows long ignition delay. The reaction rate for glycine and urea is very low i.e 6bar/s for glycine and 1 to 2 bar/s for urea

Finally, it is decided that the HAN-Glycine-water propellant is not suitable for high performance after checking micro thruster with high initial temperature as it shows slow ignition ad melting of the catalyst (In this case shell 405 catalysts).

To determine the catalytic decomposition batch reactor is very important for the ignition of monopropellants to good combustion without degradation at very high temperatures. (Rachel Elorirdi 2003)

6. 1N THRUSTER HOT FIRING TEST.

6.1 PROCEDURE FOR HOT FIRING TEST.

Using a 1N thruster hot firing test is conducted for HAN/HN Based monopropellant with the same specifications of Hydrazine thruster. As we know that taking measures for thrust is difficult only temperature and pressure will able to measure. The thruster test conducted for HAN/HN-based monopropellant is the same as that of a test conducted by the Hydrazine monopropellant, The catalyst used for the hot firing test is preheated to 200oC, and pulse mode test is conducted(0.1-second injection in a 1-second cycle) and continuous mode.

The tests were done for a total of 16 compositions of HAN/HN- based monopropellant, including fuel-rich, oxidizer rich, with no fuel, and a variety of fuel compositions such as methanol and ethanol.

6.2 RESULTS FOR HN REACTIONS.

After the test, it is concluded that the reaction is completed inside the thruster since because a huge amount of N2O is generated as an intermediate product through which NO2 was generated for the entire reaction.

For composition in which HAN was blended with HN, it observes that CO2 was identified throughout the combustion besides that amount of N2O was decreased gradually. This reaction tells that HN provides a boost to the decomposition process for HAN-based monopropellants.

6.3 COMPOSITION CONSIDERATION FOR HA/HN BASED MONOPROPELLANTS.

After performing all the tests it some of the points are concluded that the specific impulse is 30% lower than Hydrazine besides the density of specific volume is also lower than that of Hydrazine. By considering all these points authors have decided to increase the performance by adding the amount of fuel that doesn't cause any detonation.

Taking all these considerations the authors selected HAN/HN based propellant composition is as follows;

HAN/HN/TEAN/H2O = 46/23/6/25 (wt%)

The below table indicates the characteristics of HAN/HN-based monopropellants.

Table4-Characteristics of HAN/HN Based monopropellant

Composition	Aqueous solution of four constituents: HAN and HN as oxidizers, TEAN as fuel, and water First choice was oxidizer rich composition	
Physical	Density (g/cm^3)	14

properties	Viscosity (cP)	6.0
	Solidifying point	- 35 °C
Safety	Risk in handling	Low toxicity
	Detonability	None
	Thermal instability	None
	Risk of detonation in pipes	None
Availability	Domestic procurement	Available
	Cost	Low
Thruster performance	Response characteristics	Good
	Stability	Good
	Decomposition	Close to chemical equilibrium

7. INVESTIGATION OF GREEN PROPELLANTS ON MODEL K100E THRUSTER.

The Model contains a heater for a warm-up and a combustion chamber and the entire chamber is made from refractory metal with a special coating. To observe the thermal state of model thermocouples are installed.

For measuring the pressure a capillary tube is attached to the combustion chamber and firing tests will be conducted in air.

7.1 FIRING TEST RESULTS.

The model is tested in air at normal Environmental conditions by firing both in impulse and continuous operating modes.

After testing it is clear that the time for the thrusters to reach up to a particular model doesn't exceed 0.3s. during start-up, inlet pressure is observed which is explained by a pressure drop protective valve installed in front of the thruster. (Goza 2017)

During testing, it states that the inlet pressure is directly proportional to the pressure in the combustion chamber, which states that the thruster is working stably. While performing the test the time to reach particular mode for all ranges of inlet pressure was not exceeded more than 0.3s.

The maximum consumed time for model K100E was 1500 start-ups with 1.5 kg of fuel. from all these, it is clear that because of testing at atmospheric conditions the thruster failure takes place. To get better performance additional protective screen was installed on the thruster to test the model in continuous mode. During testing the temperature of the external surface of the combustion chamber was exceeded 1300 oC, at the same time temperature in the combustion chamber exceeded 1800 oC.

7.2 Conclusion for K100E Laboratory Model.

The capability of the K100E model on green propellant both in impulse and the continuous mode was observed. Initially, the thruster was started at temperature 350 to 390oC and the time to reach a particular mode does not exceed more than 0.3sec after the time effect was not more than 0.6sec. During the thruster testing, the firing operation is limited by the materials of Design Elements.

8. Satellite Platforms.

Whenever designing a propulsion system for a satellite most require non-toxic, technical feasibility, and low cost. Most of the satellite designers must consider advanced technology and minimizing the risk factors.

The Selection of propulsion technology is done during the early stages of the design and combination of the thrust, specific impulse, and performance. The specific impulse values for different propellants types are mentioned below; (Gohardani et al. 2014)

Table5- Isp of different types of propellants.

Propellant Type	Specific Impulse (Isp)
Cold gas propellants	30 – 150
Liquid monopropellants	150 – 290
Liquid bipropellants	290 – 360
Exotic Propellants	460 – 10,000

The below table explains high-performance electric propulsion (HPEP) compared to other electric propulsion has mentioned along with specific impulse and specific power (KW/N)

Table6- HPEP features compared to other electric thruster Tech.

Common thrusters	Electric Isp	Specific power
Arcjet	520	7
HPEP	1000-3000	8–18
HET	1600	17
HEMPT	2500	34
Ion thruster	3000	30

9. Conclusions.

This paper describes the development of HAN-based monopropellants for next-generation launch vehicles by developing HAN-based monopropellants that will accelerate the commercial application to small satellites. The Latest trends in thrusters are also discussed for further improved performance by conducting several Experiments and tests.

After several experiments the effects of green propellants are listed out here;

i) Lower the cost of operation.

ii) Increase in flexibility.

iii) Increase performance.

iv) Safely space and ground storable.

v) Higher specific impulse than commercial monopropellants like Hydrazine.

vi) Cheap and high potential to decrease the cost for large quantities in production

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