HAN/HN-Based Monopropellant Thrusters

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HAN-based monopropellant has been anticipated to be an alternative to hydrazine currently used for space propulsion application. They are very favorable in potentially higher performance, significantly less toxic, and environmentally harmless compared with hydrazine. The practical use of HAN-based monopropellant has not been achieved so far due to the lack of reliable ignition technology with Ir catalysts and because of its complicated combustion mechanism and its high detonability. This paper presents the development and hot firing test results of a mixture of HAN/HN/TEAN/H_2O. The HN addition realized a reliable catalytic ignition and combustion characteristics with 1 N - 20 N class thrusters and safety characteristics without detonability.

1. Introduction

Monopropellants based on hydroxyl ammonium nitrate (HAN; $NH_2OH \cdot HNO_3$) are being studied in Japan and overseas as potentially effective alternatives to those based on hydrazine, which is currently being used as a fuel for thruster.[(1)-(4)] Such propellants would be significantly less toxic than those based on hydrazine, and they are expected to reduce both the environmental burden and the costs of their manufacturing, handling, and operation at launch sites. Technical and safety problems have been experienced with HAN-based monopropellants, however, in that they have inferior ignition and response characteristics to those based on hydrazine and have high detonability, which resulted in a serious explosion[(5)] at a HAN raw material manufacturing plant.

IHI Aerospace Co., Ltd. (hereinafter called IA), which has built up many years of experience in handling HAN in the course of its studies on higher energy solid propellants, had been developing HAN-based monopropellant propulsion systems with the priority given to achieving safety and less toxicity under the guidelines listed in **Table 1**. Eventually, IA prototyped and tested a monopropellant based on a blend of HAN and hydrazine nitrate (HN), and were able to confirm that it offered a high degree of safety and had no detonability or self-sustaining combustion characteristics. IA also confirmed through hot firing tests conducted by using a catalyst currently used for hydrazine thrusters that this monopropellant has reliable ignition and combustion characteristics as well as high response characteristics.

2. Development of a HAN/HN-based monopropellant

Since a HAN-based monopropellant was first developed by the U. S. Navy for use as a liquid gun propellant, many attempts have been made to apply this type of propellant to space propulsion applications both here in Japan and abroad. This type of monopropellant, typified by LP1846, originally consisted of three compositions: HAN, which acts as a high-energy oxidizer; triethanol ammonium nitrate (TEAN; $N(C_2H_4OH)_3(HNO_3)$), which acts as the fuel; and water, which, acting as a solvent for these solid nitrates, controls viscosity, combustion temperature, and sensitivity. This mixed aqueous solution has the following characteristics: ① little toxic vapor is generated, ② no combustion occurs at 0.1 MPa, ③ high density, ④ high

Table 1 HAN/HN-based thruster development guideline

Item	Priority	Target	Remarks
Low toxicity	1	Can be handled in the same way as ordinary strong-acid chemicals	This target can be achieved by using less-toxic additives.
Safety	2	Has no detonability or self-sustaining combustion characteristics	As the fuel content increases, detonability becomes more pronounced and the fuel speed rises.
Performance	3	Has higher density specific impulse than hydrazine	As the fuel content increases, specific impulse improves.
Development period Development cost Minimization	4	Is interchangeable with existing hydrazine thruster systems Accepts hydrazine compatible materials Has a flame temperature that can be used in existing thrusters	As the fuel constituent becomes larger, the flame temperature rises, which means that heat-resistant metals or other such materials must be used, resulting in higher costs and extended delivery deadlines.

performance, and ⑤ low solidifying point. In addition, this type of monopropellant is expected to offer better usability in low temperature environments, and is easily available in Japan at reduced costs. Given this, HAN-based monopropellants are attracting attention as a potential alternative to those based on hydrazine.

The simplest and most reliable technique for igniting a monopropellant is catalytic ignition, in which the decomposition and reaction of the monopropellant exposed to a catalyst starts quickly without any need for an external ignition device. To overcome the poor ignition and response characteristics of HAN-based monopropellants, the authors decided to blend HAN with HN ($N_2H_4 \cdot HNO_3$), which bears a hydrazinium group and acts as an oxidizer, by using an iridium (Ir) catalyst for hydrazine thrusters. First, they conducted open cup test, which confirmed that adding HN contributed to a significant reduction in the reaction time with the Ir catalyst. After that, they began developing HAN/HN-based monopropellants. HN has been satisfactorily used as a reducer and a stabilizer for HAN, and a HAN/HN mix has been used as a reducer for plutonium and uranium in nuclear fuel processing cycles.(6)

However, as has been reported in existing literature, if 75% or more of the HAN/HN mix is made up of HN, it exhibits high detonability.(7) To address this issue, the authors evaluated its safety and various other characteristics in composition designing.

3. Characteristics of HAN/HN-based monopropellants

3.1 Physical properties

HAN/HN-based monopropellants have a density of 1.4 to 1.5 g/cm^3, which is much higher than the density of 1.0 g/cm^3 that those based on hydrazine have. This improves the density specific impulse and enables a reduction in the weight of the fuel tanks and other structures to be achieved. The solidifying point is as low as −35°C, which improves usability in low temperature environments. Their viscosity is slightly higher than that of those based on hydrazine but, depending on their composition, this is not so high as to make it impossible to supply these monopropellants.

3.2 Toxicity

Hydrazine is highly toxic and evaporates easily. When handling it, therefore, self-contained atmospheric protective ensemble (SCAPE) suits and the air supply devices for them need to be used, and special operation personnel and medical personnel need to be employed. What is more, the performance of any other work in parallel with hydrazine loading is prohibited. This reduces the work efficiency of launch site operations.

To evaluate the toxicity of HAN/HN-based monopropellants, the authors measured the amounts of toxic vapor they generated and evaluated the obtained measurements using the following hazard index.(7) Their findings revealed that the monopropellant's toxicity is as low as about 1/10 000 of that of hydrazine and 1/600 of methanol.

$$\text{HAZARD INDEX (mmHg/PPM)} = \frac{\text{Vapor pressure (mmHg at 25°C)}}{\text{LC50 (PPM 4H)}}$$

LC50 : Lethal dose of 50% in tests on animals

Given the above, the authors believe that HAN/HN-based monopropellants can be handled with gloves, goggles, simplified masks, and other protective gear similar to that used for handling ordinary chemicals.

3.3 Detonability

The authors conducted a test using a 28-mm steel pipe in accordance with JIS standards to check for detonability resulting from changes in the composition of the HAN/HN-based monopropellant. To evaluate the monopropellant's detonation propagation in stainless steel pipes, the authors used pipes with a length of 200 mm, an outer diameter of 34 mm, and an inner diameter of 27.6 mm (giving a pipe thickness of 3.2 mm). Each pipe was filled with a HAN/HN-based monopropellant specimen and then detonated using a No. 6 blasting cap attached to the pipe's rubber plug, after which observations were taken of how the steel pipe broke. This test can be considered to apply a stronger impact than that which would be expected under actual operating conditions, but the authors adopted this evaluation method to err on the side of caution.

The authors judged specimens to be detonable if they caused the steel pipes to break along their entire length (complete explosion) or to break up to halfway along their length (incomplete explosion). If the blasting cap swelled to some degree but the steel pipe did not break at all, the authors judged the specimen to be non-detonable. To confirm repeatability, three runs of the test were conducted for each specimen, non-detonable compositions were identified, and a safety map was prepared. **Figure 1** shows the detonation area and the calculated performance values. It indicates that the area close to the stoichiometric ratio is the detonation area. For HAN/HN-based monopropellants used in hot firing tests, the authors decided to adopt either fuel-rich compositions with a high content of TEAN as the fuel constituent or oxidizer-rich compositions with reduced amounts of fuel constituents, thus avoiding the stoichiometric ratio.

3.4 Self-sustaining combustion characteristics

HAN-based monopropellants undergo a rapid reaction in thermal and pressure load environments, and this reaction can suddenly retrograde as a result of the temperature rise caused by heat transfer. This could cause supply pipes and even fuel tanks to detonate. HN has been successfully used as a stabilizer for HAN, which acts as a reducer, in nuclear-related reprocessing processes,(6) so it is expected to prove effective in inhibiting such detonations. The authors conducted a liquid bridge (diameter: 8 mm) hot firing test using thermal ignition in a viewable chamber and verified the effect of HN on the burning rate. **Figure 2** shows the burning rate of the HAN/HN-based monopropellant compared with the results for other compositions. HN-free compositions exhibited very high burning rates within

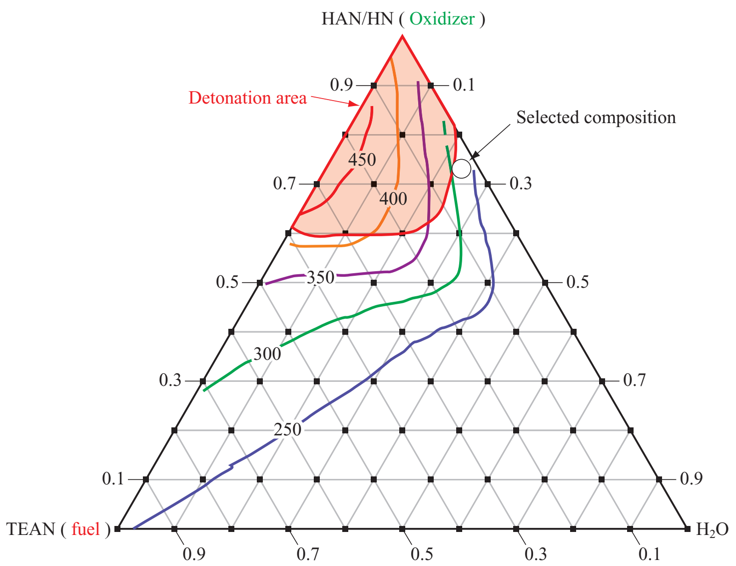
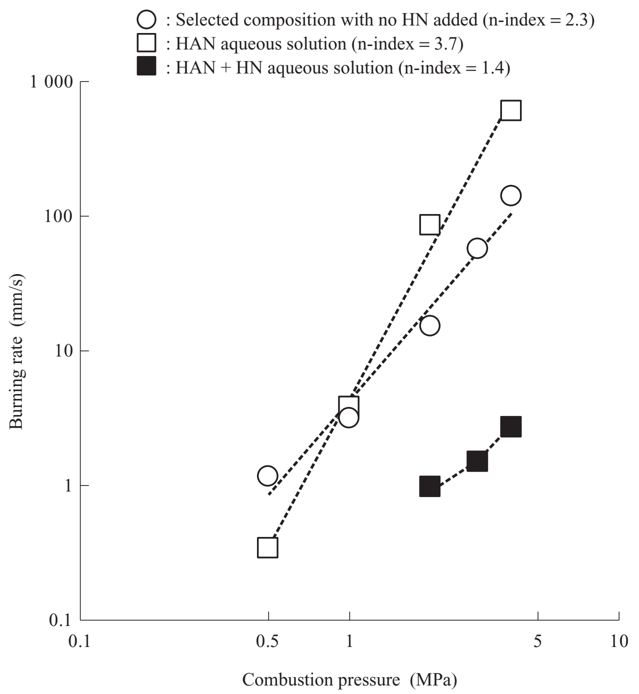


Fig. 1 HAN/HN-based monopropellant composition with ρISP and detonation area



(Note) Indicates the selected HAN/HN-based composition with no plot (with no self-sustaining combustion characteristics)

Fig. 2 Burning rate of HAN/HN-based monopropellant

a range of one to several hundreds of millimeters per second under a pressure of 4 MPa, while the HN mixed monopropellant composed of four compositions had no self-sustaining combustion even under a pressure of 7 MPa, which is the upper limit for the equipment used. This indicates a high degree of safety for this monopropellant. However, increasing the content of water, which acts as a solvent, was not effective in inhibiting self-sustaining combustion. These results indicate that the addition of HN is an effective means of inhibiting self-sustaining combustion.

3.5 Theoretical performance

The authors estimated the performance of HAN-based monopropellants using a chemical equilibrium program (NASA-CEA) under conditions in which the chamber pressure was 1 MPa and the nozzle area ratio was 100 (see **Fig. 1**). To avoid the stoichiometric ratio as mentioned above, they selected an oxidizer-rich composition. The theoretical vacuum Isp of 202 seconds is lower than 237 seconds, which is the calculated value for hydrazine under the same conditions. However, the density is estimated to be 1.4 to 1.5 g/cm^3, which is much higher than that of hydrazine (1.0 g/cm^3), which means that the density specific impulse of this composition is more than 20% higher than that of hydrazine. Consequently, propellant based on this composition can achieve the required total thrust if it can be loaded into existing tanks.

4. Hot firing test using a 1 N thruster and selection of a propellant composition

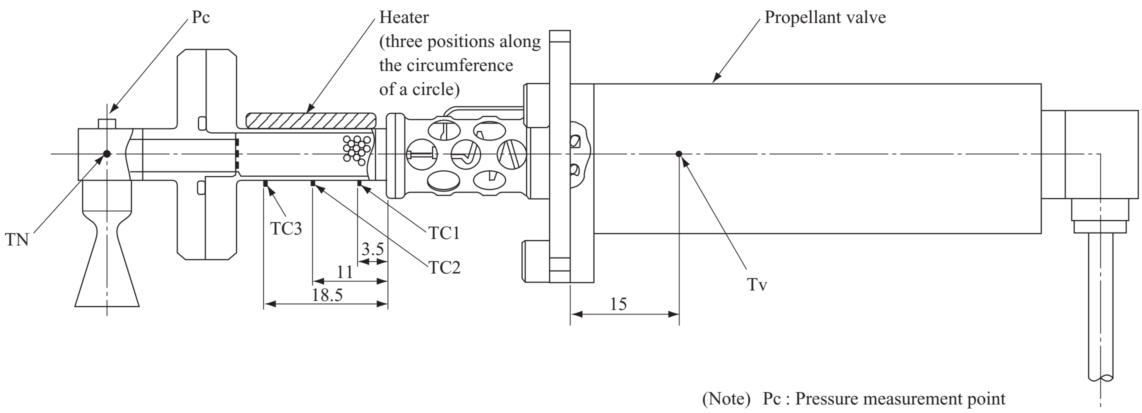
4.1 Outline of hot firing test

The authors conducted a hot firing test for HAN/HN-based monopropellants by using a 1 N thruster with the same specifications as a hydrazine thruster and a propellant valve. As the thrust was hard to measure, they were only able to measure the pressure and temperature. For the purposes of this test, the authors employed the same process as that used for hydrazine; that is, they preheated a catalyst to 200°C and then conducted the test in pulse mode (0.1-second injection in a 1-second cycle) and continuous mode. **Figure 3** shows an outline of the test equipment.

The authors tested 16 compositions of HAN/HN-based monopropellants, including fuel-rich compositions, oxidizer-rich compositions, oxidizer compositions with no fuel composition, and compositions with a variety of fuel constituents, such as methanol and ethanol.

4.2 Effects of HN reactions

The authors analyzed the compositions of the combustion



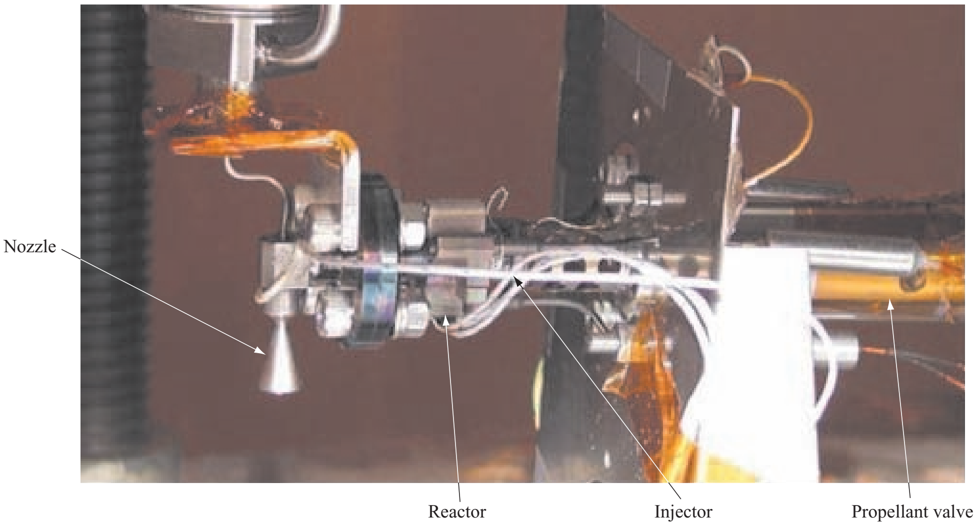


Fig. 3 Setup for 1 N thruster (unit : mm)

product gas, and found that there was no CO_2, which is an indicator of the degree of decomposition and reaction of the fuel constituent, in the composition with no HN added. A large amount of the intermediate product N_2O was generated, however, and NO_2 was generated throughout the combustion. This indicates that the reaction is not completed inside the thruster.

In the composition for which HAN was blended with HN, however, CO_2 was detected throughout the combustion, and the amount of N_2O gradually decreased as the combustion progressed. This indicates that HN accelerates the decomposition process for HAN-based monopropellants.

4.3 Selecting a composition for a HAN/HN-based monopropellant

The detonability of the monopropellant with fuel-rich compositions can be inhibited if the stoichiometric ratio is greater than 20%. In a hot firing test using a composition within this range, however, the rise in the combustion temperature could not be suppressed. This temperature rise damaged the currently-used catalyst, which is considered to be resistant to temperatures of up to 1 100°C, and the slag of TEAN generated a highly-viscous contaminant that clogged the pipes. In addition, the reaction time increased and the response characteristics deteriorated, which is a fatal flaw for thrusters. For these reasons, the authors decided against selecting fuel-rich compositions for use.

The authors also conducted a hot firing test for a composition with a 3-constituent oxidizer and no fuel constituent to serve as representative of oxidizer-rich compositions, and found that this composition offered the best response characteristics and stability, caused no temperature rise that would cause damage to the catalyst, and kept wear to the catalyst to a minimum. These results suggest that this composition holds promise as a fuel for thrusters. However, its specific impulse is about 30% lower than that of hydrazine, and its density specific impulse is also lower than that of hydrazine. Therefore, the authors decided to improve its performance by adding an amount of fuel that would cause no detonation.

Given these considerations, the authors selected a HAN/HN-based monopropellant with the following composition: HAN/HN/TEAN/H_2O = 46/23/6/25 (wt%). **Table 2** shows the characteristics of the selected HAN/HN-based monopropellant. With the exception of the theoretical combustion calculation results, the measurements given in the table are taken from data obtained using actual specimens.

Table 2 Characteristics of HAN/HN-based monopropellants

Composition	Aqueous solution of four constituents: HAN and HN as oxidizers, TEAN as the fuel constituent, and water The first choice was the oxidizer-rich composition.	
Physical properties	Density (g/cm^3) Viscosity (cP) Solidifying point	1.4 6.0 –35°C
Safety	Risk in handling Detonability (shock sensitivity) Self-sustaining combustion characteristics (thermal instability) Risk of detonation in pipes	Low toxicity None None None
Theoretical combustion calculations at 1 MPa Calculation code: NASA-CEA	Adiabatic flame temperature (°C) Specific impulse (opening rate of 100) (s) Density specific impulse (opening rate of 100) Ratio of specific heat	1 052 202 295 1.24
Availability	Domestic procurement Cost	Available Low
Thruster performance	Response characteristics Stability Decomposition (combustion gas analysis)	Good Good Close to chemical equilibrium

4.4 Combustion characteristics of the selected composition with a 1 N thruster

The authors conducted a hot firing test for the selected composition and found that it had good response characteristics for 0.1-second pulses and satisfied the required response time for the Reaction Control System (RCS) for H-IIA rockets. It also exhibited stable combustion and temperature in continuous mode. The temperature values measured on the outer circumference of the thruster converged at around 600°C, indicating that this composition can be used under temperature conditions similar to those for hydrazine.

Figure 4 shows the results of a hot firing test with a 1 N thruster in continuous mode. A comparison of the observed pulse characteristics with those observed for hydrazine in the same thruster indicates that there is little pressure variation in continuous mode and that the response characteristics are also good, which is an important pulse characteristic.

5. Evaluation of a prototype 20 N thruster

5.1 20 N thruster characteristics

As the first step in making a larger thruster, the authors designed, prototyped, and tested a thruster with a lateral shower injector that injects a fuel laterally by employing the same design concept as that used for IA's existing hydrazine 20 N thruster. The authors used a propellant valve designed for hydrazine, which is a value similar to a flight product. **Figure 5** shows a photograph of the test equipment. Using an initial catalyst temperature of 250°C, the authors measured the pressure, thrust and surface temperature.

5.2 Pulse response characteristics

The authors checked the characteristics of the thruster with pulse mode set to 0.1-second injections conducted in 1-second cycles, as was done for the 1 N thruster. **Figure 6** shows the results. The response characteristics were better

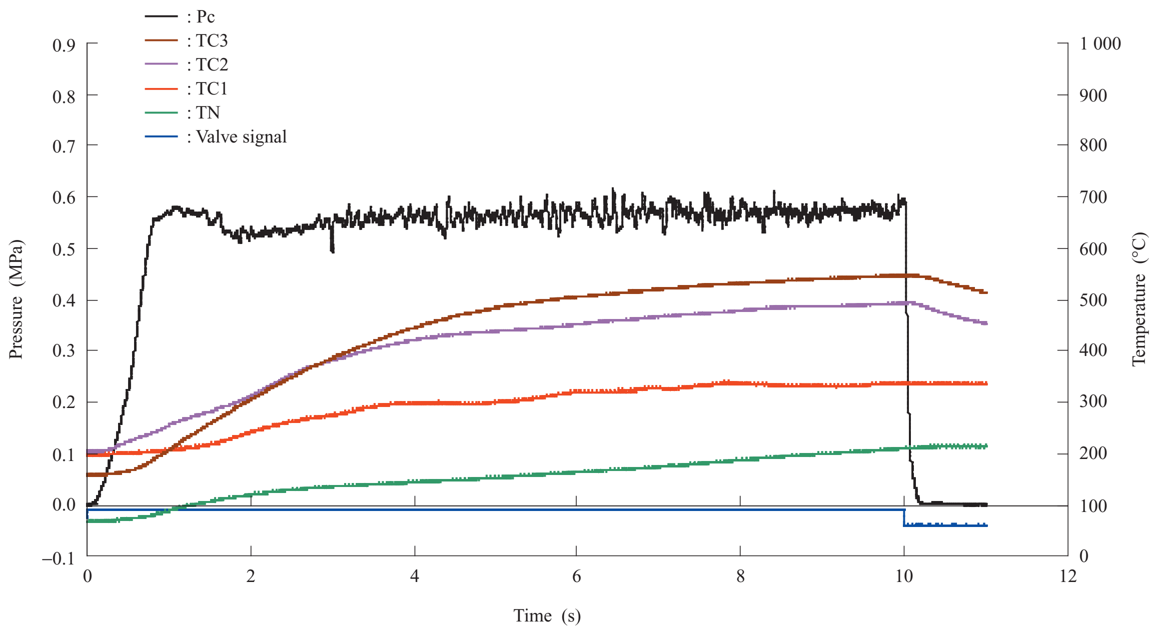


Fig. 4 Results of hot firing test for 1 N thruster in continuous mode

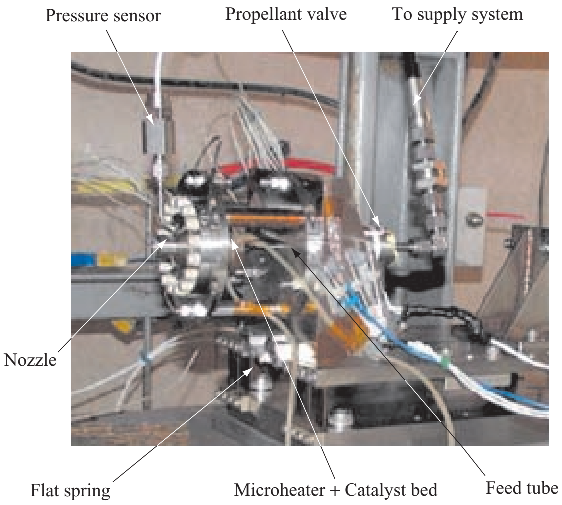


Fig. 5 Setup for 20 N thruster

than those for the 1 N thruster. The response time was about 1/3 that of the 1 N thruster, while the rise time, which is the time that elapses from when the valve is opened (i.e. the solenoid valve turns on) to the time when the pressure reaches 80% of the maximum pressure, was 26 ms. The decay time, which is the time that elapses from when the valve is closed (i.e. the solenoid valve turns off) to the time when the pressure reaches 20% of the maximum pressure, was 19 ms.

5.3 Continuous mode test results

Following the tests conducted in pulse mode, the authors conducted tests in continuous mode by using a 130-second continuous injection, which is almost equal to the maximum gas jet injection time that occurs in actual operations of the M-V-1 to M-V-3 rockets. **Figure 7** shows the test results. The authors confirmed that the ignition and combustion were stable and that steady state was reached at surface temperatures of 900°C and lower. The C* efficiency was 86%, and the authors plan to further improve this by

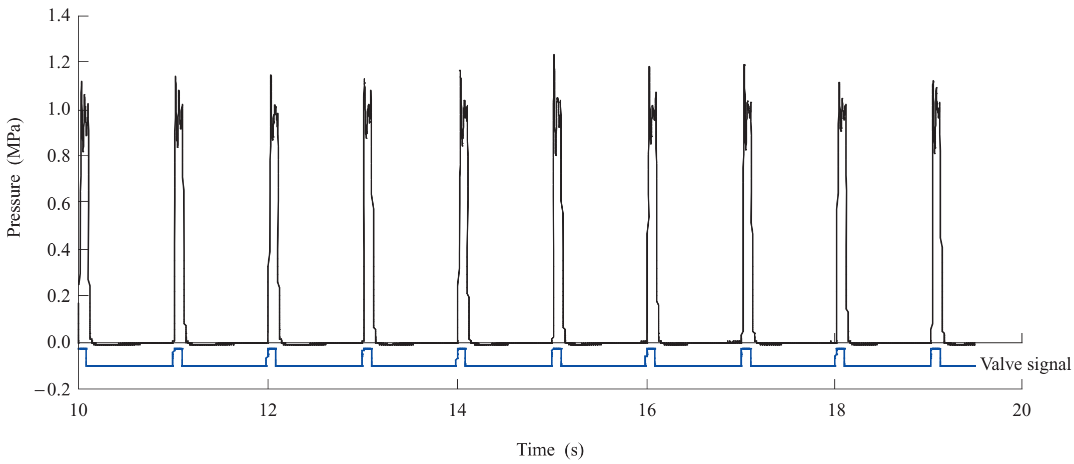


Fig. 6 Results of hot firing test for 20 N thruster in pulse mode

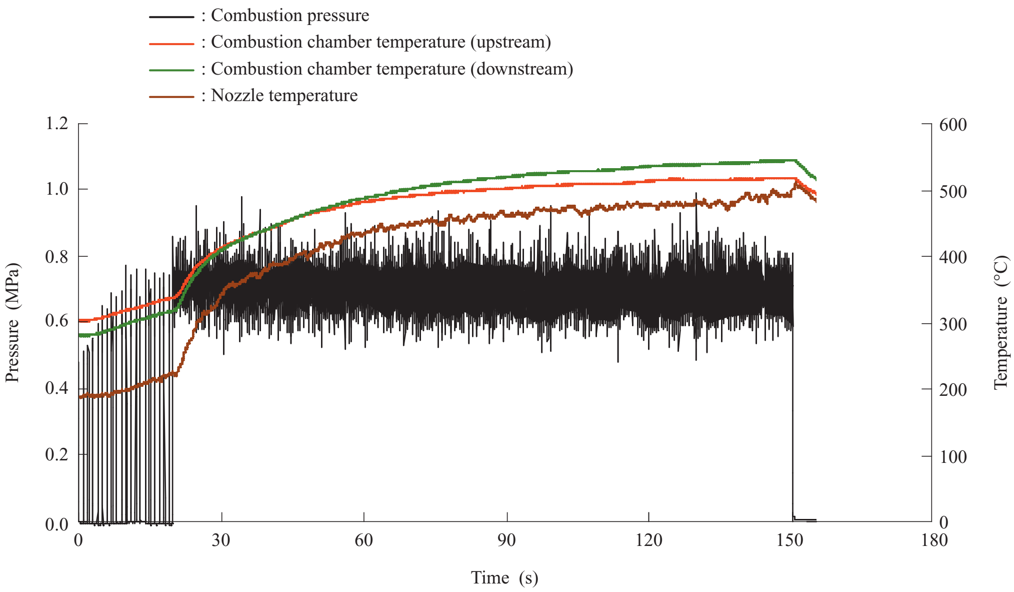


Fig. 7 Results of hot firing test for 20 N thruster in continuous mode

modifying the design of the injector and the catalyst bed. The authors also confirmed that the effective value for the density specific impulse calculated from the measured thrust values was about 10% higher than that for hydrazine.

The catalyst wear rate with respect to the total flow rate for the propellant was 6% for fine particles and 2% for coarse particles. The catalyst experienced greater wear than is the case for the currently-used hydrazine. Going forward, the authors plan to reduce wear on the catalyst by creating an optimum design for the injector and catalyst bed that will reduce the load placed on the catalyst and improving the catalyst charge method.

6. Conclusion

In successfully prototyping a HAN/HN-based monopropellant with the following features, the authors succeeded in creating a less-toxic monopropellant that may prove to be an alternative to propellants based on hydrazine.

(1) A propellant based on a blend of HAN and HN has a composition that allows for safe storage and operation and exhibits no detonability or no self-sustaining combustion characteristics.
(2) This type of monopropellant has the potential to increase density and effective specific impulse by more than 10% compared to a monopropellant based on hydrazine.
(3) The solidifying point of this monopropellant is about 35°C lower than that of a monopropellant based on hydrazine, demonstrating the potential to improve usability in low temperature environments.
(4) A propellant based on a blend of HAN and HN has response characteristics almost equivalent to those of one based on hydrazine.
(5) The results of hot firing tests using 1 N and 20 N thrusters indicate that this monopropellant has stable ignition and combustion characteristics.

For practical applications, the authors plan to proceed with studies of the following subjects.

(1) The optimum design for the injector and the catalyst bed to increase the life of the catalyst.
(2) Confirmation of service life by long duration hot firing tests.

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