Reaction Propagation in Fumed Silica Gelled HAN-Based Propellants

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1 Introduction

Hydroxylamine nitrate (HAN)-based monopropellants have emerged as promising alternatives to conventional hydrazine-based propellants due to their higher specific impulse, lower toxicity, and improved storability. Among these, SHP163, a HAN-based formulation, has been developed to achieve stable and efficient combustion for space propulsion applications [1,2]. However, one of the major challenges associated with HAN-based monopropellants is their highly nonlinear burning behavior, particularly in the low pressure range (< 3 MPa). This instability poses a significant risk in space propulsion system design and operation.

Previous studies have shown that modifying the composition of HAN-based propellants can influence their combustion characteristics. For instance, Amrousse et al. [3] demonstrated that adding methanol to HAN solutions reduces the burning rate, while Katsumi reported that methanol lowers the boiling point, thereby extending the low burning rate regime over a wider pressure range, albeit without fully eliminating the burning rate surge [2]. More recently, Ferguson & Shafirovich [4] proposed that gelling HAN/methanol/water solutions using polyacrylamide (PAM) effectively linearize the burning rate's pressure dependence at relatively high pressures (5-30 MPa). In addition to improved combustion behavior, gelled propellants offer advantages in safety, operating flexibility, and storage stability [5].

Building upon our previous work on the combustion behavior of HAN-water gels [6], the present effort further examines the influence of gelling SHP163 with hydrophilic fumed silica on its burning rate. Fumed silica is widely used in gel propellants due to its ability to alter viscosity and rheological properties through hydrogen bonding interactions with liquid components [7]. Our prior research demonstrated that HAN-water gels exhibit a more linear burning rate in the sub-3MPa pressure range, indicating that gelation can stabilize reaction and reduce burning rate fluctuations in HAN-based monopropellants. However, the impact gelling SHP163 with fumed silica on the decomposition behavior remains largely unexplored.

This study investigates the burning rate of SHP163 gelled with fumed silica under different pressures in argon. Using a high-pressure chamber with optical access, the self-sustained combustion behavior is analyzed through high-speed imaging to determine the linear burning rate. By understanding how fumed silica affects the combustion characteristics of SHP163, this work aims to provide valuable insights into the feasibility of gelled HAN-based propellants for propulsion applications.

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2 Experimental Setup and Methodology

To investigate the effect of gelling agent concentration on the combustion behavior of SHP163, the weight ratios of gelling agent to propellant were varied as 1:14, 1:19, 1:24, 1:29, and 1:39, corresponding to fumed silica concentrations of 6.67, 5.00, 4.00, 3.33, and 2.50 wt.%, respectively. The composition for the gel formulations are summarized in Table 1. High-purity HAN solution in SHP163 was synthesis in-house via a low temperature titration process. Purities of the ingredients are 99.999% for nitric acid, hydroxyl amine, ammonia nitrate were 99.999%, and 99.9% for methanol.

Table 1: Compositions of tested SHP163 gels

Propellant	Propellant Gellant Ratio	HAN (wt.%)	Methanol (wt.%)	Ammonium Nitrate (wt.%)	H_2O (wt.%)	Cab-O-Sil m5 (wt.%)
SG-01	14	68.69	15.21	3.64	5.79	6.67
SG-02	19	69.92	15.49	3.70	5.89	5
SG-03	24	70.66	15.65	3.74	5.95	4
SG-04	29	71.15	15.76	3.77	5.99	3.33
SG-05	39	71.76	15.89	3.80	6.05	2.5

The preparation of SHP163 gel follows a controlled mixing process to minimize methanol evaporation. First, SHP163 is weighed and placed into a sample bottle, while the required amount of hydrophilic fumed silica (Cab-o-Sil ® m-5) is weighed separately. To prevent excessive methanol vaporization, the beaker containing the mixture is placed in a jacketed cooling bath maintained at 4°C. SHP163 is then added to the beaker and stirred at 1500 rpm for five minutes using a 30 mm prize-leaf Teflon stirring rod. A lid is placed over the beaker during stirring to further reduce methanol loss. After mixing, the solution rapidly transformed into a gelled state, forming SHP163 gel.

Since the gelled propellant exhibits shear thinning non-Newtonian behavior, its viscosity cannot be accurately measured using a viscometer. Instead, a rheometer (Anton Paar MCR302) equipped with a 25 mm plate rotor with temperature control was used to characterize the shear-dependent viscosity over a shear rate range of 1–1000 s^{-1}. The viscosity measurements are presented in Fig. 1, demonstrating that all formulations successfully gelled, with viscosity increasing as the gelling agent concentration increased.

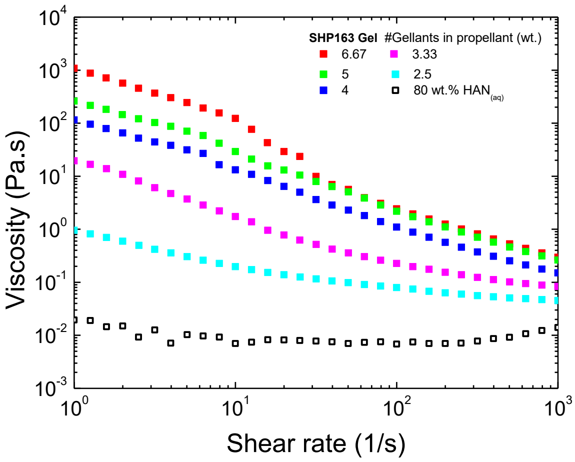

Figure 1: Variation of SHP163 gel viscosity with shear rate

(a) (b)

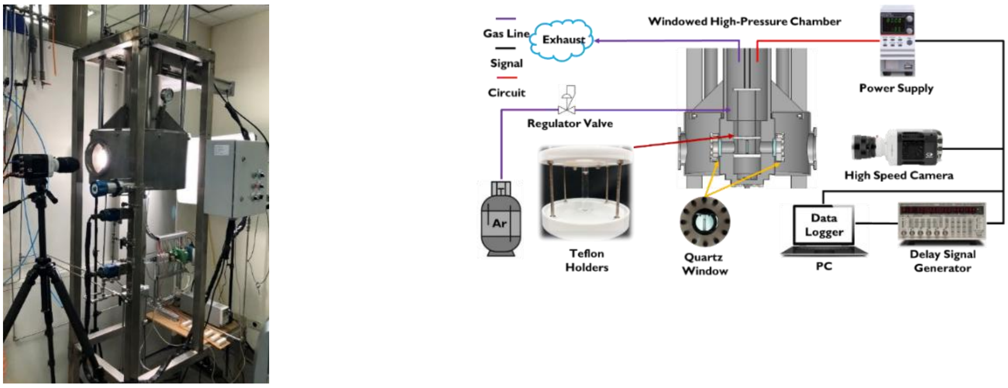

Figure 2. (a) The high-pressure chamber with optical access, and (b) schematic diagram of strand burner test setup.

The combustion tests were conducted using a strand burner in a high-pressure vessel with optical access, shown in Figure 2. The gel propellant is loaded into a glass test tube with an inner diameter of 4.5 mm and a height of 50 mm. The test tube is secured on a Teflon support within the chamber, and a 35 SWG nickel-chromium ignition coil is positioned at the gel surface for ignition. The chamber is pressurized with argon gas to the target pressure, and electrical heating of the ignition coil initiates combustion. A high-speed camera (MiroLab 310, Vision Research) records the regression of the propellant surface to determine the burning rate.

To systematically track the interface position, high-speed images are processed using a custom Python-based OpenCV program developed in-house. The image processing workflow involves grayscale conversion, Canny edge detection to identify the test tube boundary, and extraction of the interface position along the central axis at each time step. This approach ensures consistent and accurate surface tracking across all test cases. The linear burning rate (r_b) is then determined by fitting a linear fit to the interface position over time, with the slope representing the burning rate.

The relationship between burning rate and pressure was analyzed using St. Robert's Law, given by:

$$r_b = \alpha P^n$$

where α is an empirical constant, P is the ambient pressure, and n is the pressure exponent, which characterizes the sensitivity of the burning rate to pressure changes. By plotting the burning rate data on a logarithmic diagram and performing linear fit, the slope of the fitted line provides the pressure exponent n. This analysis allows for a quantitative understanding of the burning rate behavior under varying pressure conditions with the experimental data.

3 Results and Discussion

The reaction propagation behavior of SHP163 gels in a strand burner was investigated under various ambient argon pressures using a nickel-chromium wire ignition coil to initiate self-sustained decomposition. Figure 3 shows a time-sequence visualization of the reaction front propagation in SG-02 (5 wt.% Cab-O-Sil gelled SHP163) in 0.6 MPa argon environment. The images, captured at 500 fps with an exposure time of 800 μs, demonstrate a smooth and steady regression of the liquid surface, indicating stable burning behavior with minimal fluctuations throughout the process. It is worth noting that, unlike the liquid propellant, the gelled propellant exhibited a significantly shorter ignition delay, with reaction propagation initiating almost immediately after ignition.

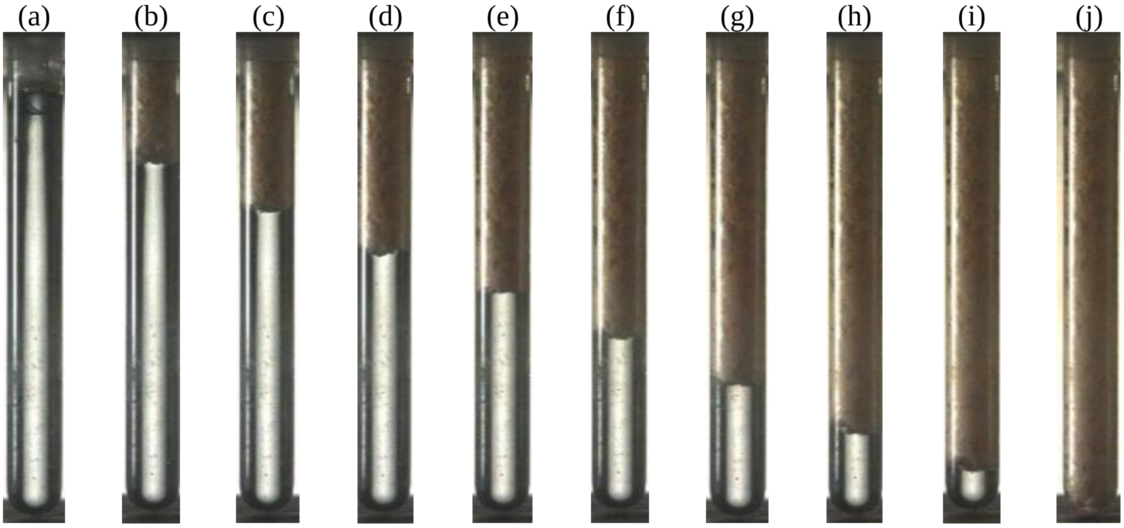

Figure 3: Regression of the SG-02 SHP163 gel strand in 0.6 MPa argon. (a) 0 sec after heating wire was activated, and the interframing time between (c)-(j) are 5.2 sec.

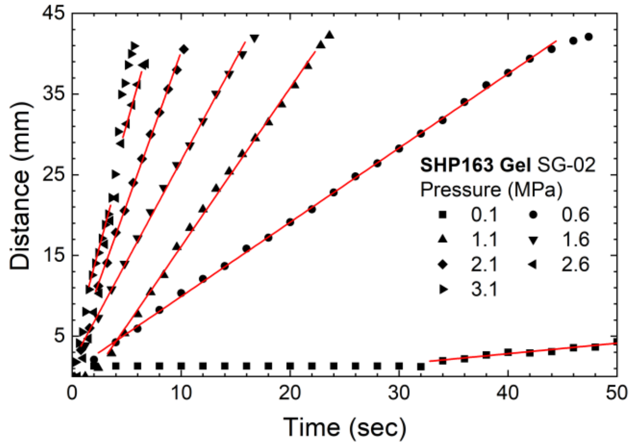

Figure 4: Relationship between the interface position and time during the reaction propagation of SHP163 gel under different pressures.

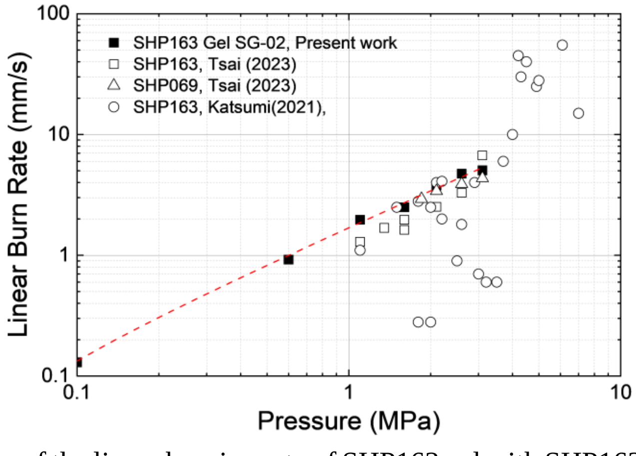

Figure 5. Comparison of the linear burning rate of SHP163 gel with SHP163 and SHP069 liquid formulations from prior studies.

The relationship between the reaction front position and time, extracted via image processing, is presented in Fig. 4. A clear trend is observed where the burning rate increases with pressure, as evidenced by a steeper regression of the propellant surface at higher pressures. The linear nature of these plots confirms a well-defined burning rate behavior across the tested pressure range. At 0.1 MPa, the reaction propagation is slow and barely sustained, whereas at 3.1 MPa, the reaction front advances significantly faster. Repeated tests under identical conditions yielded consistent results, confirming the reproducibility of the measurements.

The measured burning rates of SHP163 gel are compared with values for liquid SHP163, SHP069 in the literature [2,7], as shown in Fig. 5. Notably, SG-02 exhibits a burning rate comparable to that of liquid SHP163 between 1.1 and 3.1 MPa. However, a key difference is that the gelled formulation sustains self-sustained combustion even at atmospheric pressure, whereas liquid SHP163 requires a minimum pressure of 1.1 MPa to maintain continuous burning. The pressure exponent for the SHP163 gel (SG-02) was determined to be 1.09 over the range of 0.1–3.1 MPa, whereas liquid SHP163 exhibited a higher exponent of 1.5 in the 1.1–3.1 MPa range, indicating stronger pressure sensitivity in its liquid state.

The result suggests that gelation significantly influences the low-pressure combustion characteristics, potentially due to the role of fumed silica in modifying thermal transport within the reaction zone. Since fumed silica has a much lower specific heat compared to other propellant components, it is hypothesized that it enhances thermal convection from the reaction zone into the unreacted gel, thereby sustaining combustion at lower pressures. The fitted burning rate curves also indicate that SHP163 gel maintains a linear pressure dependence across the range studied.

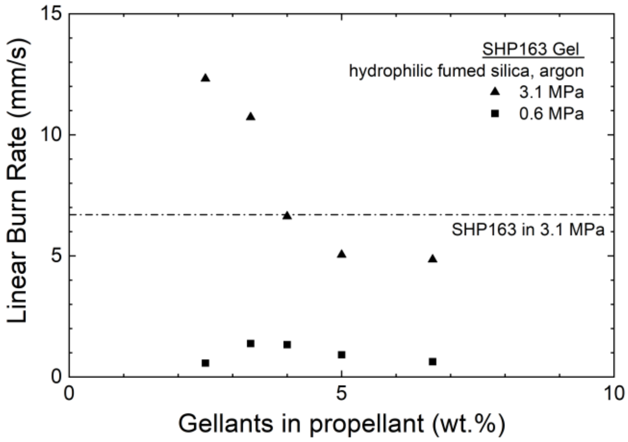

Figure 6. Effects of fumed silica concentration on the linear burning rates of SHP163 gel at 0.6 MPa and 3.1 MPa.

Figure 6 further explores the influence of gelling agent concentration on the burning rate at both 0.6 MPa and 3.1 MPa. At 3.1 MPa, the burning rate of SHP163 gel decreases with increasing gellant concentration. At lower gellant concentrations, fumed silica appears to enhance combustion by generating localized hot spots, owing to its low specific heat relative to the other propellant components. These hot spots are actively transported into the unreacted gel by the boiling interface, thereby facilitating reaction propagation, a mechanism that is not feasible in liquid SHP163. This effect is particularly noticeable when the fumed silica concentration is below 5 wt.%, where the burning rate of gelled SHP163 exceeds that of its liquid counterpart.

However, at higher gellant concentrations, the burning rate declines as the effects of increased heat absorption by the unreactive fumed silica along with the reduced fraction of reactive propellant content outweigh the enhancement from thermal transport. At 0.6 MPa, the burning rate initially increases with rising gellant content, reaching a peak around 5 wt.%, and then declines. Notably, liquid SHP163 fails to sustain decomposition at this pressure, underscoring the critical role of fumed silica in enabling low-pressure reaction. Although catalytic effect of SiO_2 on HAN decomposition has been proposed[9], fumed silica is generally considered inert and our thermogravimetric tests offer little evidence of chemical catalysis. Instead, the primary influence of fumed silica appears to be thermal: at lower concentrations, the formation and transport of hot spots by the particles promote decomposition, whereas at higher concentrations, the increased heat absorption and dilution of reactive material lead to a reduction in burning rate.

4 Conclusions

This study examined the reaction propagation characteristics of SHP163 gel over a range of pressures relevant to space propulsion applications. The successful gelation of SHP163 using hydrophilic fumed silica (Cab-O-Sil m5) as a gelling agent produced a monopropellant with shear-thinning rheological behavior. The experiments demonstrated a linear dependence of the burning rate on ambient pressure within the range of 0.1–3.1 MPa, effectively mitigating the instability observed in liquid SHP163 over this pressure range. Notably, the gel formulation sustained self-sustained combustion down to atmospheric pressure, whereas liquid SHP163 required a minimum pressure of 1.1 MPa for continuous burning.

At low gellant concentrations, fumed silica enhances thermal transport, likely by generating localized hot spots that accelerate reaction propagation. However, at higher concentrations, increased heat absorption and a reduced fraction of reactive content result in a slower burning rate. While the exact role of fumed silica in combustion remains to be fully understood, these findings provide insight into its impact on the thermal behavior of SHP163 and highlight the importance of optimizing gellant concentration to balance reactivity and stability in HAN-based monopropellant formulations.

Acknowledgements

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