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Experimental Investigation of Green Hypergolic Propellants for Upper-Stage Propulsion: Drop Test Results and Performance Analysis

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Abstract

To address concerns regarding toxicity inherent in conventional storable bipropellants, the propulsion community is actively exploring "green" alternatives. Hydrogen peroxide (HTP), paired with eco-friendly fuels such as kerosene or ethyl alcohol, is emerging as a promising option due to its potential for cost reduction in space launch, enhanced safety, ease of handling, and favorable density-impulse characteristics. This study investigates the hypergolicity and combustion dynamics of HTP with kerosene doped with organic manganese-based additives, targeting application in a 100 N class upper-stage thruster. The experimental campaign employs 95% and 98% HTP combined with variable catalyst loadings in kerosene to optimize ignition behavior and combustion performance. Drop tests were performed under controlled conditions to characterize ignition delay times (IDT) and post-ignition flame temperatures, supported by high-speed imaging and infrared diagnostics. Two O/F ratios (6.5 and 7.5) were explored to balance stoichiometric efficiency and ignition responsiveness. Comparative evaluation of Mn(II)AA and Mn(III)AA catalysts was conducted across a unified experimental matrix, with Mn(III)AA consistently outperforming Mn(II)AA by enabling faster ignition and higher combustion efficiency. Furthermore, the demonstration of catalytic hypergolicity eliminates the need for a conventional HTP decomposition catalyst bed, simplifying propulsion system architecture and reducing engine mass and cost. These findings provide critical data for the development of next-generation green propulsion systems, contributing to lighter, simpler, and safer thrusters for space applications. This research is an integral part of the EU Horizon Marie Skłodowska-Curie Actions (MSCA) funded initiative GREENLAM project, which aligns with the overarching goals of the EU Horizon initiative, facilitating technological innovation and advancements in the aerospace industry for the benefit of space exploration and satellite deployment.

Keywords: Green Propellants; Hydrogen peroxide (HTP); Kerosene; Hypergolic Ignition; Manganese Catalysts (Mn(II)AA, Mn(III)AA); Ignition Delay Time (IDT)

Acronyms/Abbreviations

fps	Frames per second
HTP	High-Test Peroxide
IDT	Ignition Delay Time
Isp	Specific Impulse
O/F	Oxidizer-to-Fuel mass ratio
RCS	Reaction Control Systems
SCAPE	Self-Contained Atmospheric Protective Ensemble
TRL	Technology Readiness Level
w/w	Weight by weight
wt%	Weight percent

1. Introduction

For decades, the advancement of in-space and upper-stage propulsion has been intrinsically linked to the use of storable hypergolic bipropellants, most notably monomethyl hydrazine (MMH) and nitrogen tetroxide (NTO) [1]. The defining advantage of these propellants is their ability to ignite spontaneously upon contact, which provides unparalleled reliability for engine systems that require multiple restarts for orbital manoeuvring or attitude control [2]. This reliability, however, comes at a significant cost. Hydrazine and its derivatives are acutely toxic, known carcinogens, and pose severe environmental hazards, mandating extensive and costly safety protocols, including the use of SCAPE suits during ground operations [3]. Consequently, increasing global regulatory pressure from frameworks like the European Union's REACH program has created an urgent imperative to develop "green" propulsion alternatives that can match or exceed the performance of legacy systems while drastically reducing operational hazards and life-cycle costs [4].

Among the leading candidates for green propulsion, the combination of HTP and a hydrocarbon fuel like kerosene is particularly promising[5]. HTP, a highly concentrated solution of hydrogen peroxide (typically >87%), is a dense, storable oxidizer whose

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decomposition products are simply water and oxygen, making it environmentally benign. When paired with kerosene, it forms a bipropellant system with a high density-impulse, a critical metric for volume-constrained upper stages, as it allows for smaller and lighter propellant tanks. This combination is not new, having a flight heritage dating back to pioneering rocket programs like the British Black Knight, which demonstrated its fundamental viability [3,6,7].

The primary technical challenge is that HTP and kerosene are not naturally hypergolic. Historically, ignition was achieved using a decomposition catalyst bed, where HTP is first passed through a solid catalyst bed (often silver or manganese oxides) to decompose it into a hot stream of oxygen and steam, into which the kerosene is then injected for autoignition. While effective, this approach requires a heavy, complex catalyst reactor that introduces a significant pressure drop and a potential point of failure [8–10]. A more advanced solution is to dissolve a catalyst directly into the fuel, producing a homogeneous mixture that ignites instantly upon contact with HTP. This approach combines the performance and environmental benefits of HTP/kerosene with the operational simplicity and reliability of a true hypergolic system, while eliminating the need for an external decomposition bed.

Research into fuel-soluble catalysts has highlighted both potential and limitations. Early systems, such as the "Block 0" fuel, required extremely high loadings (approximately 24 wt% manganese acetate tetrahydrate (MAT) in methanol) to achieve hypergolicity, a level that severely compromises fuel energy content and specific impulse. More recent efforts using copper-based catalysts in amine fuels achieved ignition delays below 10 ms but often required high concentrations (~13 wt%) and relied on fuels that are less common and less practical than kerosene [11]. The predominant challenge remains to identify a catalyst that delivers short ignition delay times at low, practical concentrations (<5 wt%) in a widely available, high-performance fuel like kerosene.

This paper addresses that gap by presenting the first direct, side-by-side comparative analysis of Mn(II)AA and Mn(III)AA under an identical and application-relevant experimental matrix spanning catalyst loading, oxidizer concentration, O/F ratio, and temperature. This comparison is not incremental but essential for making informed, data-driven engineering decisions on catalyst selection for next-generation green propulsion systems. The novelty of this work lies in three contributions: *(i)* it systematically evaluates both catalysts at practical loadings in kerosene; *(ii)* it delivers a unified dataset enabling quantitative comparison of ignition delay and flame temperature; and *(iii)* it demonstrates that catalytic hypergolicity achieved in this way eliminates the need for a conventional HTP decomposition bed, thus reducing system complexity, weight, and budget while enhancing sustainability.

By systematically linking ignition kinetics to combustion efficiency across a broad operating matrix, this study provides critical data to advance the TRL of green hypergolic systems. The results directly inform the design of lighter, simpler, and more reliable engines, aligning with the broader goals of reducing mission costs, improving operational safety, and enabling a sustainable transition away from toxic legacy propellants.

2. Experimental Methodology

2.1 Experimental Setup and Procedure

The hypergolic performance of the two catalytic systems was evaluated using a standardized open-air drop test apparatus at ambient pressure, as depicted in Fig. 1. In each test, a precise volume of HTP was dispensed via a syringe pump and impinged vertically onto a quiescent pool of catalyst-doped kerosene held in a borosilicate glass bottle. The catalyst-fuel mixtures were prepared by dissolving a specific weight percentage of either Mn(II)AA or Mn(III)AA into kerosene. The comparative analysis was conducted over the matrix of conditions justified above. Ignition events were recorded with a high-speed camera (Photron FASTCAM NOVA S6) at 6400 fps. The IDT was defined as the time interval between the first physical contact of the HTP droplet with the fuel pool and the first emission of visible light. Post-ignition flame temperatures were measured using a calibrated infrared thermal imaging camera (FLIR A655sc). Each test condition was replicated a minimum of five times to ensure data reliability.

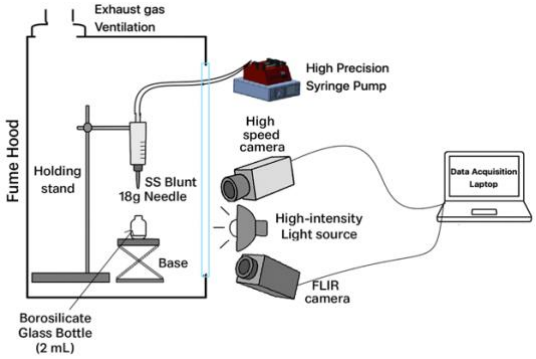


Fig. 1. Schematic illustration of the open-air drop test apparatus

2.2 *Selected Test Parameters*

To ensure a relevant and conclusive comparison, the experimental matrix was strategically defined to reflect conditions pertinent to high-performance upper-stage propulsion. HTP concentrations of 95% and 98% (w/w) were selected because they represent the state-of-the-art for achieving high specific impulse, with 98% HTP being the target for numerous advanced development programs [12]. O/F mass ratios of 6.5 and 7.5 were chosen to explore the critical trade-off between thermodynamic and

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kinetic optima. While thermodynamic calculations for maximum specific impulse often suggest a peak near an O/F of 6.5-7.0, comprehensive experimental data consistently show that ignition kinetics are most favorable at higher, more oxidizer-rich ratios like 7.5, which produce the shortest and most reliable ignition delays [10]. As rapid ignition is a non-negotiable safety requirement for hypergolic systems, evaluating performance at a kinetically favorable O/F is essential. The catalyst loading range of 1.0% to 5.0% (w/w) was selected to map catalytic efficiency from reliable ignition thresholds up to the point of diminishing returns, which prior studies identified as beginning around 5.0 wt% [13]. Finally, an elevated initial temperature of 50°C was chosen for the primary comparison, as preheating is a practical strategy for in-space systems to ensure robust ignition in cold-soak conditions and has been shown to consistently reduce IDTs by 30-40%.

3. Results and Discussion

3.1 IDT Performance and Chemical Interpretation

The comparative IDTs for both catalysts at an elevated initial temperature of 50°C are presented in Table 1. The data explicitly demonstrates that Mn(III)AA is the superior catalyst, yielding substantially shorter IDTs than Mn(II)AA across every comparable condition. This performance advantage is most pronounced under the optimal conditions tested (98% HTP, O/F 7.5, 5.0 wt% catalyst), where Mn(III)AA achieved an IDT of 28 ms, a 38% improvement over the 45 ms recorded for Mn(II)AA.

Table 1. Comparative Ignition Delay Times (IDT in ms) at 50°C

HTP Conc.	O/F Ratio	Catalyst Wt. %	Mn(II)AA IDT (ms)	Mn(III)AA IDT (ms)
98%	7.5	1.0%	No Ignition	43
		2.0%		39
		3.0%	57	35
		4.0%	51	31
		5.0%	45	28
	6.5	1.0%	No Ignition	52
		2.0%		46
		3.0%	65	43
		4.0%	59	39
		5.0%	53	35
95%	7.5	1.0%	No Ignition	47
		2.0%		43
		3.0%	65	41
		4.0%	60	38
		5.0%	55	35
	6.5	1.0%	No Ignition	56
		2.0%		51
		3.0%	70	47
		4.0%	63	42
		5.0%	57	38

For a hypergolic system, where rapid and reliable ignition is a critical safety and performance requirement, this marked reduction in IDT establishes Mn(III)AA as the more effective and desirable catalytic agent [14]. The superior performance of Mn(III)AA can be attributed to the initial oxidation state of the manganese ion. The catalytic decomposition of HTP is initiated via a redox cycle, where a key step is the reaction:

$$H_2O_2 + M^{n+} \rightarrow HO^{\cdot} + M^{(n+1)+} + OH^{-} \quad (1)$$

For Mn(II)AA, the catalyst begins in the Mn(II) state and must first be oxidized to Mn(III) to generate the initial hydroxyl radical. In contrast, Mn(III)AA is already in the higher Mn(III) oxidation state, which may allow it to enter the catalytic cycle more readily or participate in subsequent radical-generating steps more quickly, providing a more direct and faster mechanistic pathway to ignition [15]. This provides a fundamental chemical explanation for the consistently shorter IDTs observed.

Analysis of the parametric trends reveals a consistent behavior for both catalysts. Increasing the catalyst concentration consistently reduces the IDT, though with diminishing returns, particularly beyond 5.0 wt%, as visualized in Figure 2. This suggests a transition from a regime limited by chemical kinetics to one limited by physical processes like mass transport. Similarly, higher HTP concentration (98% vs. 95%) and a more oxidizer-rich O/F ratio (7.5 vs. 6.5) also consistently shorten IDTs. This is attributed to the increased availability of reactive oxygen species upon decomposition, which accelerates the subsequent fuel oxidation and enhances the efficiency of the initial exothermic reactions.

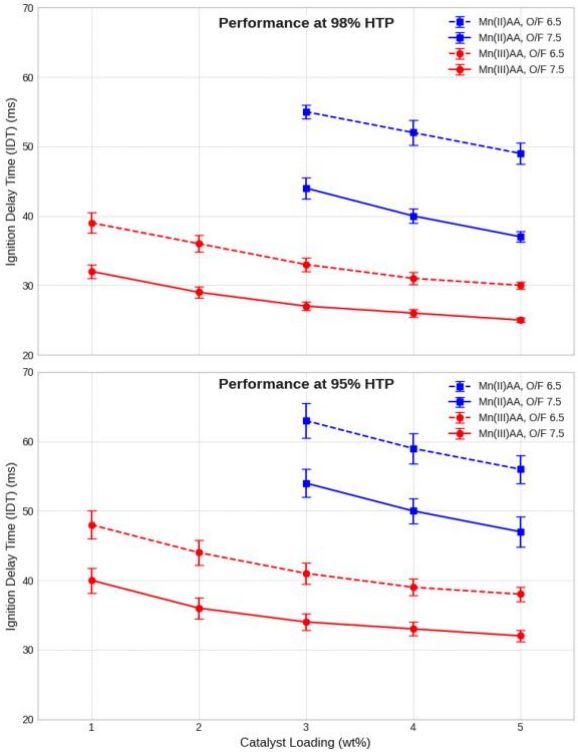


Fig. 2. Comparative IDT vs. Catalyst Loading for Mn(II)AA and Mn(III)AA at 98% and 95% HTP, O/F 6.5 and 7.5, at 50°C. Values reported ±1.7 avg. SD

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3.2 Post-Ignition Flame Temperature and Combustion Efficiency

Post-ignition flame temperature is a critical indicator of combustion efficiency, reflecting the extent to which chemical energy is converted into thermal energy. In propulsion systems, higher combustion temperatures directly correlate with higher I_{sp}, the primary measure of engine efficiency. A catalyst that combines rapid ignition with vigorous and sustained combustion therefore provides clear advantages for maximizing propulsive performance.

High-speed camera images further corroborate these findings. As shown in Fig. 3a and Fig.3b, under optimal Mn(III)AA conditions, ignition rapidly encompasses the vapor phase above the reaction pool, producing a near-volumetric ignition event. This phenomenon ensures more uniform flame propagation, minimizes local quenching, and promotes complete oxidation of the fuel. In contrast, Mn(II)AA cases generally exhibit slower flame kernel expansion, consistent with greater energy dissipation and lower measured flame temperatures.

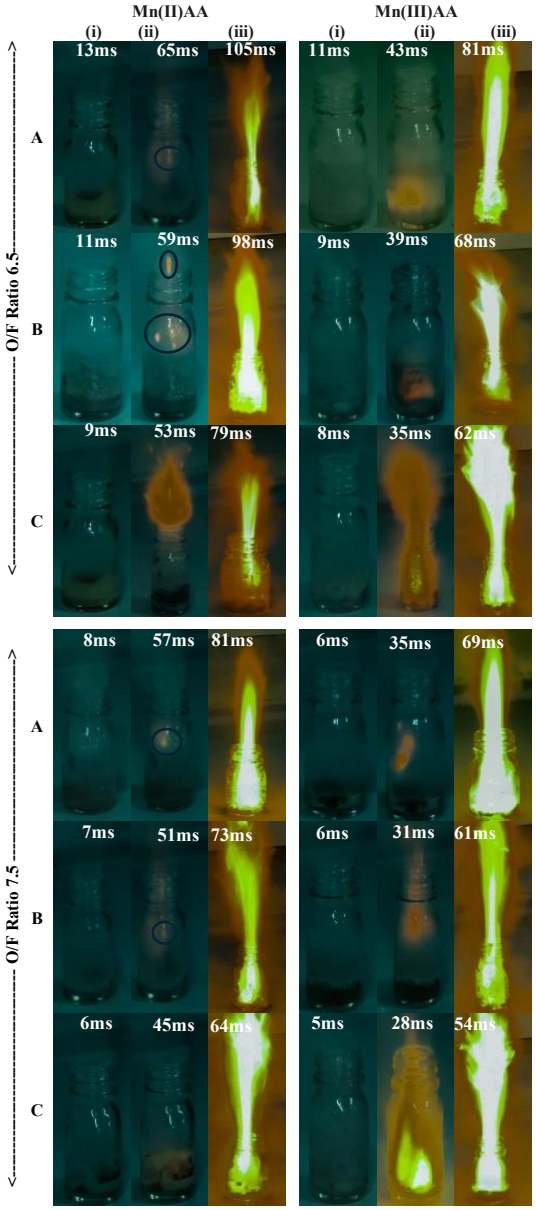


Fig. 3a. High-speed camera 6400fps sequence illustrating the distinct phases of hypergolic ignition for all conditions (98% HTP, Mn(II)AA and Mn(III)AA Catalyst, 50°C), showing (i) HTP Decomposition, (ii) First Light Kernel, and (iii) Peak Combustion. A, B, and C are the catalyst wt% of 3%, 4% and 5% respectively.

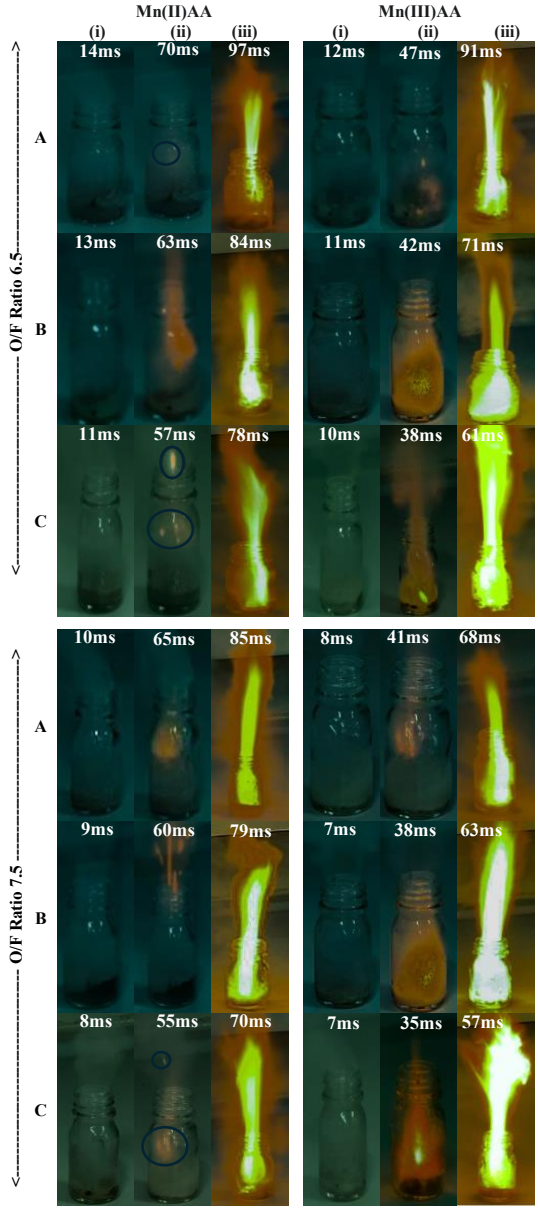


Fig. 3b. High-speed camera 6400fps sequence illustrating the distinct phases of hypergolic ignition for all conditions (95% HTP, Mn(II)AA and Mn(III)AA Catalyst, 50°C), showing (i) HTP Decomposition, (ii) First Light Kernel, and (iii) Peak Combustion. A, B, and C are the catalyst wt% of 3%, 4% and 5% respectively.

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Table 2. Comparative Post-Ignition Flame Temperatures (°C) at 50°C

HTP Conc.	O/F Ratio	Catalyst Wt. %	Mn(II)AA Flame Temp (°C)	Mn(III)AA Flame Temp (°C)
98%	7.5	2.0%	No Ignition	1075 ± 12
		3.0%	1080 ± 12	1110 ± 11
		4.0%	1150 ± 10	1180 ± 9
		5.0%	1210 ± 9	1240 ± 8
	6.5	2.0%	No Ignition	1020 ± 13
		3.0%	1016 ± 13	1046 ± 12
		4.0%	1067 ± 12	1097 ± 11
		5.0%	1119 ± 10	1149 ± 9
95%	7.5	2.0%	No Ignition	1035 ± 13
		3.0%	1040 ± 13	1070 ± 12
		4.0%	1110 ± 11	1140 ± 10
		5.0%	1160 ± 9	1190 ± 8
	6.5	2.0%	No Ignition	980 ± 14
		3.0%	977 ± 14	1007 ± 13
		4.0%	1031 ± 13	1061 ± 12
		5.0%	1085 ± 11	1115 ± 10

Table 2 summarises the peak flame temperatures achieved with Mn(II)AA and Mn(III)AA across the experimental matrix at 50 °C. To further visualize the combustion process, representative thermal heat maps of the flame plumes were extracted from the IR camera data for both catalysts under selected conditions (Fig. 4a and 4b.). These maps provide spatially resolved temperature distributions, highlighting differences in flame structure and completeness of combustion between Mn(II)AA and Mn(III)AA. Reported flame temperatures are radiometrically corrected with an assumed emissivity of 0.90, consistent with literature for hydrocarbon/HTP flames. A ±20 °C uncertainty reflects sensitivity to emissivity variation (0.85–0.95).

The results strongly reinforce the IDT analysis. In every condition tested, Mn(III)AA not only ignited more rapidly but also sustained higher peak flame temperatures than Mn(II)AA. At the optimal condition of 98% HTP and O/F = 7.5 with 5.0 wt% catalyst, Mn(III)AA reached 1240 °C, approximately 30 °C higher than Mn(II)AA under identical conditions. This consistent temperature gain highlights the link between ignition kinetics and combustion thermodynamics. Shorter IDTs accelerate the onset of exothermic reactions, reducing the time window for heat losses to the liquid pool, the vessel walls, and ambient surroundings. As a result, the Mn(III)AA system retains more of the released energy within the flame zone, yielding temperatures closer to the theoretical adiabatic limit and indicating more efficient combustion.

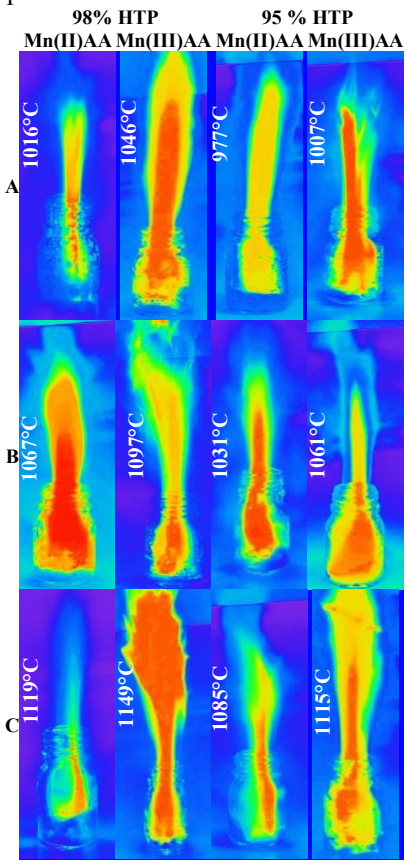


Fig. 4a. Infrared heat maps of flame plumes for Mn(II)AA and Mn(III)AA catalysts for HTP 95% and 98%, O/F = 6.5, T = 50 °C. Here, A, B, and C are the catalyst wt% of 3%, 4% and 5% respectively

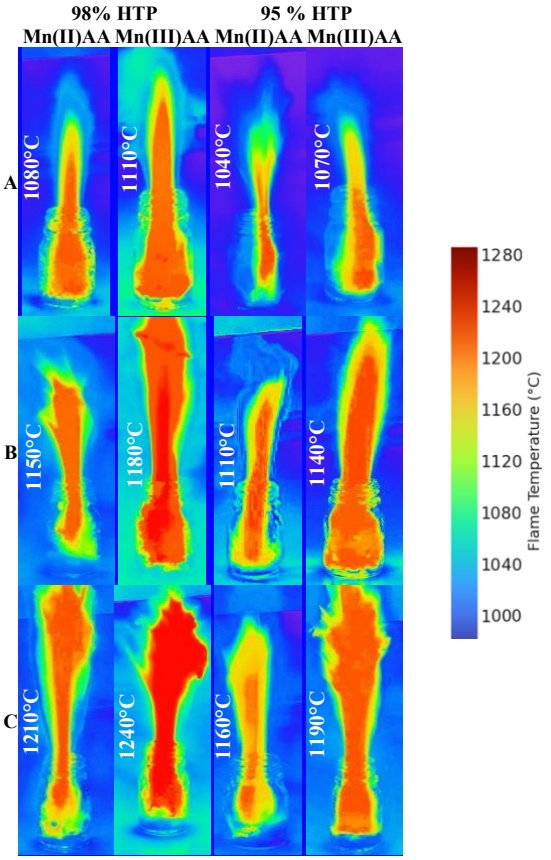


Fig. 4b. Infrared heat maps of flame plumes for Mn(II)AA and Mn(III)AA catalysts for HTP 95% and 98%, O/F = 7.5, T = 50 °C. Here, A, B, and C are the catalyst wt% of 3%, 4% and 5% respectively

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As shown in Fig. 4 (a and b), flames produced with Mn(III)AA exhibit broader, more uniform high-temperature zones compared to Mn(II)AA, which displays narrower and more heterogeneous profiles. This difference aligns with the higher peak flame temperatures in Table 2 and supports the conclusion that Mn(III)AA promotes more complete combustion. The spatial uniformity of the Mn(III)AA flames also reflects the near-volumetric ignition captured in the high-speed images (Fig. 3a and 3b), reinforcing the synergy between rapid ignition kinetics and efficient energy release.

Taken together, the higher flame temperatures, faster energy release, and volumetric ignition dynamics provide compelling evidence that Mn(III)AA enables a more efficient and energetically complete combustion process than Mn(II)AA. This powerful synergy between rapid ignition kinetics and enhanced thermal output establishes Mn(III)AA as the superior candidate for high-performance propulsion applications where both responsiveness and efficiency are mission-critical.

4. Applications, System-Level Impact, and Mission Trade-Offs

4.1 Sustainability and Safety Imperative

The motivation for this research is fundamentally rooted in the need for sustainability and enhanced safety in space operations. Legacy hypergolic propellants like MMH/NTO are highly effective but are also extremely toxic, carcinogenic, and environmentally hazardous [1]. Their handling necessitates costly and complex safety measures, including full-body SCAPE suits, which significantly increases ground processing time and mission life-cycle costs [16]. The HTP/kerosene system catalyzed by Mn(III)AA represents a paradigm shift. HTP and kerosene are common industrial chemicals with well-established and significantly safer handling protocols [17]. The primary decomposition products of HTP are non-toxic water and oxygen, eliminating the long-term environmental hazards associated with hydrazine-based spills [18]. This transition to a green propellant system drastically reduces risks to personnel and the environment. This, in turn, yields substantial economic benefits by simplifying ground operations, reducing specialized infrastructure requirements, and shortening launch campaign timelines, contributing to more sustainable and cost-effective space missions.

4.2 Mission Applicability Framework

The selection of a propulsion system for an upper stage is a complex, system-level trade-off between performance, mass, cost, and reliability. To translate the experimental findings into actionable engineering guidance, the catalyst performance is mapped onto representative mission contexts using a Mission Applicability Matrix (Table 3). This framework evaluates ignition responsiveness, repeatability, combustion efficiency, and system-level hardware implications, enabling rational trade-offs between Mn(II)AA and Mn(III)AA depending on mission requirements.

Table 3. Mission Applicability Matrix

Mission Context	Key Requirements	Mn(II)AA Performance	Mn(III)AA Performance	Engineering Implications
Upper-Stage Main Engines	High reliability, maximum *Isp*	Provides reliable ignition at moderate loadings but lower flame temperatures	Faster ignition and consistently higher flame temperatures → marginal but valuable *Isp* gain	Mn(III)AA preferred when payload maximization is critical; Mn(II)AA viable as alternative
Reaction Control Systems (RCS)	Minimal latency, high repeatability, precise impulse delivery	Moderate IDTs (tens of ms), less responsive	~38% shorter IDTs and more repeatable ignition	Mn(III)AA strongly favored for RCS where precision and responsiveness are essential
Cost-Constrained Missions	Adequate ignition, low cost, robustness	Meets baseline obligations; low material cost, supply-chain maturity	Higher performance but potentially higher cost	Mn(II)AA pragmatic choice where cost dominates

This trade-off analysis demonstrates that while Mn(III)AA is the technically superior catalyst, the optimal choice is mission dependent. For high-performance applications like interplanetary upper stages or precision RCS, the enhanced kinetics and efficiency of Mn(III)AA are critical. For more routine or cost-sensitive missions, the reliable and well characterized performance of Mn(II)AA makes it a strong and practical contender. This framework provides a clear, data-driven path for engineers to select the most appropriate catalyst, balancing cutting-edge performance with system-level practicalities.

4.3 System-Level Benefits

Beyond mission-specific trade-offs, a broader system-level advantage emerges. The use of fuel-soluble catalysts eliminates the need for a dedicated HTP decomposition catalyst bed. This hardware simplification reduces engine mass, cuts recurring costs, improves reliability by removing a failure-prone subsystem, and simplifies propellant feed architecture [9]. Coupled with the non-threatening decomposition products of HTP, the result is a propulsion approach that aligns performance with sustainability, offering a practical, scalable pathway to replace toxic legacy hypergols with environmentally responsible alternatives for future space transportation.

5. Conclusions

This comparative experimental investigation has provided a quantitative assessment of Mn(II)AA and

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Mn(III)AA as fuel-soluble catalysts for green HTP/Kerosene hypergolic propulsion. The analysis, conducted across an expanded range of relevant operational parameters, yields clear and decisive conclusions:

1. Mn(III)AA is the superior catalyst, consistently demonstrating significantly shorter IDTs (up to 38% faster) and higher post-ignition flame temperatures compared to Mn(II)AA under all identical conditions. This is attributed to its higher initial oxidation state, which provides a more direct pathway for initiating HTP decomposition.
2. Optimal performance for both catalysts is achieved with high HTP concentrations (98%), a kinetically favorable O/F ratio (7.5), and a catalyst loading of approximately 5.0 wt%, beyond which diminishing returns are observed.
3. The performance demonstrated by the Mn(III)AA-catalyzed system confirms its viability for upper-stage applications. It enables the development of simpler, lighter, and more reliable engines by eliminating complex ignition hardware, directly contributing to reduced costs, weight savings, and enhanced safety.
4. This technology provides a sustainable and high-performance alternative to toxic legacy propellants, aligning with the global imperative for greener and more cost-effective space missions.

Based on these findings, Mn(III) acetylacetonate is recommended as the prime candidate for further development and hot-fire testing in a representative engine environment. This technology, as advanced by the GREENLAM project, represents a significant step toward the realization of safer, more cost-effective, and high-performance green propulsion systems for future space missions.

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