



## Research paper / Praca doświadczalna

# Investigation of hypergolic ignition of a kerosene-based fuel with high test peroxide as an oxidizer *Badania zapłonu hipergolicznego paliwa na bazie nafty z wysokostezonym nadtleniem wodoru w charakterze utleniacza*

Łukasz Mezyk<sup>\*</sup>), Tomasz Łobodziec

*Warsaw University of Technology, Faculty of Power and Aeronautical Engineering, Institute of Heat Engineering, Nowowiejska 21/25, 00-665 Warsaw, Poland*

*\* E-mail: lukasz.mezyk@pw.edu.pl*

### ORCID Information:

Mezyk Ł.: 0000-0002-2297-5672

**Abstract:** *This paper investigates the development and experimental characterization of a novel green hypergolic propellant system based on High Test Peroxide (HTP) and a modified kerosene fuel. To address the toxicity and handling risks associated with hydrazine-based bipropellants, a ternary fuel blend consisting of aviation kerosene (Jet A-1), pyridine, and a manganese-based catalytic promoter was developed. The study evaluates three formulation strategies: alcohol-based emulsions, commercial cobalt-based additives, and a pyridine-based solution. Experimental validation was conducted using a high-speed photographic drop test apparatus (2000 fps) to determine the Ignition Delay Time (IDT) and ignition probability. Results indicate that alcohol-based emulsions suffer from poor long-term stability, while high-concentration commercial additives significantly increase fuel viscosity, hindering atomization. The optimized formulation, comprising 80% pyridine and 20% Jet A-1 with 2.5% manganese acetate tetrahydrate (MAT), demonstrated superior performance with a mean IDT of 32.6 ms and high reproducibility ( $\sigma = 3.71$  ms). Statistical analysis further revealed a synergistic effect where moderate kerosene loading (10-30%) accelerates ignition kinetics compared to pure pyridine. Theoretical performance analysis using NASA CEA indicates that the 20% Jet A-1 blend offers a favorable compromise between specific impulse, handling safety, and economic feasibility. However, aging tests highlight a performance degradation over time due to catalyst precipitation, identifying long-term chemical stabilization as a critical area for future research.*

**Streszczenie:** *W niniejszym artykule przedstawiono proces opracowania i charakterystyki eksperymentalnej nowego, ekologicznego układu materiałów pędnych o zapłonie hipergolicznym, opartego na nadtlenu wodoru o wysokim stężeniu (HTP) oraz modyfikowanym paliwie naftowym. W celu wyeliminowania toksyczności i zagrożeń operacyjnych związanych z dwuskładnikowymi materiałami pędnymi na bazie hydrazyny, opracowano trójskładnikowa mieszankę paliwową składającą się z nafty lotniczej (Jet A-1), pirydyny oraz katalizatora manganowego. W ramach*

badan oceniono trzy strategie formułacji: emulsje alkoholowe, komercyjne dodatki na bazie kobaltu oraz roztwory na bazie pirydyny. Walidacje eksperymentalna przeprowadzono z wykorzystaniem stanowiska do testów kroplowych z szybka kamera (2000 kl./s) w celu wyznaczenia czasu opróżnienia zapłonu (IDT) oraz prawdopodobieństwa zapłonu. Wyniki wskazują, że emulsje alkoholowe wykazują niską stabilność długoterminową, natomiast wysoko stężone dodatki komercyjne drastycznie zwiększają lepkość paliwa, utrudniając atomizację. Zoptymalizowana mieszanka, zawierająca 80% pirydyny i 20% Jet A-1 z dodatkiem 2,5% octanu tetrahydratu manganu(II), wykazała najlepsze parametry eksploatacyjne ze średnim czasem IDT wynoszącym 32,6 ms i wysoką powtarzalnością ( $ff = 3,71$  ms). Analiza statystyczna wykazała efekt synergiczny, w którym umiarkowana zawartość nafty (10-30%) przyspiesza kinetykę zapłonu w porównaniu z czystą pirydyną. Teoretyczna analiza osiągnięć przy użyciu kodu NASA CEA wskazuje, że mieszanka z 20% zawartością Jet A-1 stanowi korzystny kompromis między impulsem właściwym, bezpieczeństwem obsługi a aspektami ekonomicznymi. Niemniej jednak, testy starzeniowe ujawniły degradację parametrów w czasie w wyniku precypitacji katalizatora, co wskazuje na konieczność dalszych badań nad długoterminową stabilizacją chemiczną układu.

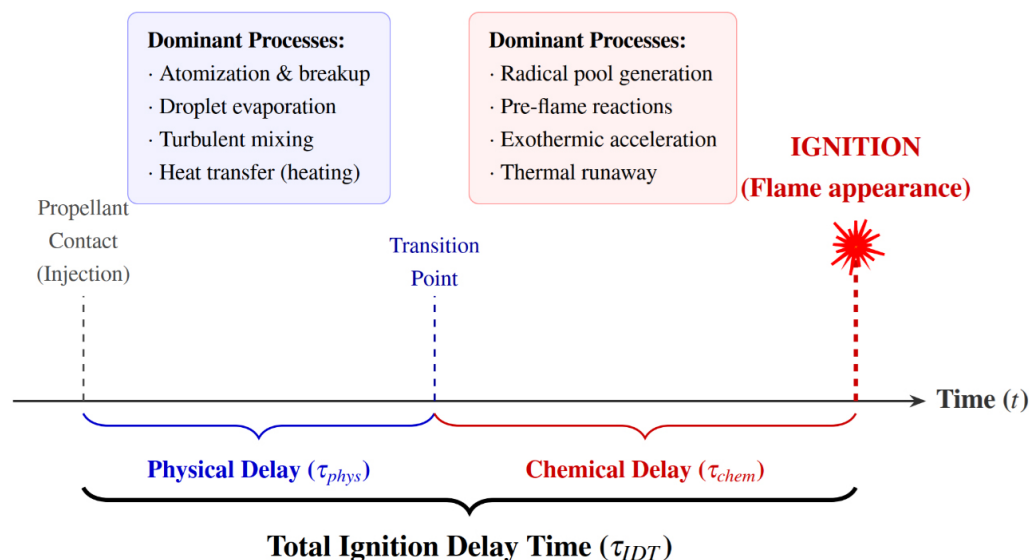
**Keywords:** green propellant, hypergolic ignition, high test peroxide, HTP, ignition delay time, IDT, Jet A-1, rocket propulsion

**Słowa kluczowe:** ekologiczne materiały pędne, zapłon hipergoliczny, wysokostężony nadtlenek wodoru, HTP, czas opróżnienia zapłonu, IDT, Jet A-1, napędy raketowy

## 1. Introduction

Classical combustion processes generally require an initiation source to overcome the activation energy barrier and sustain flame propagation. The kinetics of this process are governed by ambient conditions (temperature, pressure), the physico-chemical properties of the reactants, and their state of aggregation. While conventional propulsion systems rely on forced ignition via external stimuli such as spark plugs, pyrotechnic charges, or resonance heating, hypergolic ignition represents a distinct phenomenon. By definition, hypergolicity is a form of auto-ignition occurring spontaneously upon the contact of a fuel and oxidizer, eliminating the need for an external ignition system.

A critical parameter characterizing hypergolic systems is the Ignition Delay Time (IDT). Defined as the time interval between the initial contact of propellants and the onset of a self-sustaining flame, IDT is a composite of physical and chemical processes. Physical delay ( $T_{\text{phys}}$ ) encompasses atomization, mixing, and evaporation, governed by properties such as viscosity and surface tension. Chemical delay ( $T_{\text{chem}}$ ) refers to the time required for pre-flame generation of radicals and exothermic acceleration. To better illustrate the temporal sequence of these phenomena, a schematic representation of the ignition process is provided in Figure 1.



**Figure 1.** Schematic representation of the ignition delay phases in a hypergolic system (based on the concept presented in [1])

In rocket propulsion, particularly in Reaction Control Systems (RCS) and orbital manoeuvring, minimized IDT is essential for precise impulse delivery (minimum impulse bit) and operational reliability. Historically, this has been achieved using hydrazine and its derivatives (e.g., monomethyl hydrazine – MMH, unsymmetrical dimethylhydrazine – UDMH) paired with nitrogen tetroxide (NTO) delivering IDTs of the level of several milliseconds [2-6]. Despite their mature technology, hydrazine based fuels are carcinogenic and highly toxic, incurring high handling costs and environmental risks. This has led to strict legislative restrictions, such as the inclusion of hydrazine in the European Chemicals Agency – Registration, Evaluation, Authorization of Chemicals in the European Union (ECHA REACH Regulation) candidate list [7] accelerating the search for so called green propellants [8, 9].

High Test Peroxide (HTP) – highly concentrated hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) – has emerged as a leading alternative oxidizer. It is non-cryogenic, relatively safe to store, and decomposes into benign products: superheated steam and oxygen. Although HTP offers a slightly lower specific impulse ( $I_{sp}$ ) compared to NTO, its significantly higher density ( $1.44 \text{ g/cm}^3$  for 98% concentration [10]) results in a competitive density impulse, allowing for compact tankage [11]. Since HTP is not naturally hypergolic with standard hydrocarbons, it requires an alternative approach.

There are two primary methods of igniting a hydrocarbon-HTP mixture: homogeneous and heterogeneous catalytic ignition. In both cases, the ignition of kerosene vapours occurs due to the elevated temperature resulting from the catalytic decomposition of hydrogen peroxide. The difference between the methods lies in the manner in which HTP decomposition is induced. The former involves adding the catalyst directly to the fuel [12, 13]; therefore, it requires no separate support carrier. The latter employs a catalytic bed to induce partial decomposition of the peroxide before it enters the combustion chamber [14-18], where fuel injection takes place, followed by the standard combustion of the mixture.

This study represents the initial phase of research focused on rendering aviation kerosene (Jet A-1) hypergolic with HTP. Kerosene is stable, widely available, and non-toxic compared to hydrazine. Creating a hypergolic Jet A-1/HTP pair via chemical promotion combines the safety and economic benefits of hydrocarbons with the operational simplicity of hypergolic engines.

## 2. Materials and methods

### 2.1. Materials

The oxidizer used in this study was HTP with a concentration of 98%, obtained from Jakusz SpaceTech Ltd. (Szymbark, Poland). The HTP was stored in passivated high-density polyethylene (HDPE) containers at a temperature of 4°C prior to testing. The fuel formulations were based on aviation kerosene Jet A-1, supplied by ORLEN S.A. (Płock, Poland), utilized without further purification. Pyridine (pure grade) was purchased from Pol-Aura (Morąg, Poland) and served as the polar solvent carrier. The catalytic agent, manganese(II) acetate tetrahydrate (MAT), was of analytical grade and was also supplied by Pol-Aura (Morąg, Poland). For the comparative phases of the study (Phase 1 and Phase 2), the following auxiliary chemicals were used:

- Surfactants: Tween 80 (supplied by Pol-Aura (Morąg, Poland)), Triton X-100 and Span 80 (supplied by Sigma-Aldrich (Steinheim, Germany)).
- Commercial additives: cobalt neodecanoate solution (referenced as COMCAT), obtained from Comar Chemicals (Pty) Ltd (Cape Town, South Africa).

### 2.2. Experimental Apparatus

#### 2.2.1. Fuel Preparation Setup

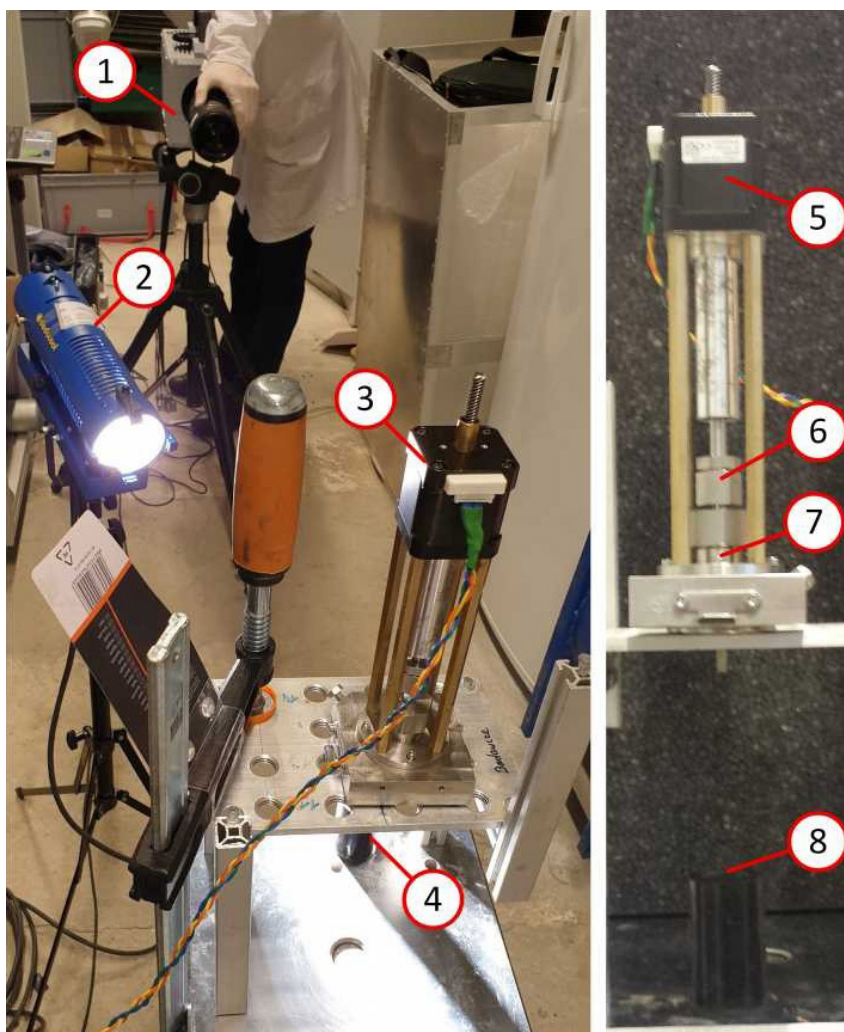
The fuel preparation station employed in this study comprised an analytical electronic balance Radwag AS 310.R2 with a precision of 0.1 mg, dual magnetic stirring units (WIGO MS 11 HS and WIGO MS 21), and digital timers for process control. This setup was utilized to evaluate both the chemical miscibility of the components and the stability of the resulting emulsions, as shown in Figure 2. The synthesis followed a strict gravimetric protocol described in subsequent sections.



**Figure 2.** Fuel preparation and mixing station: 1 – precise scale, 2 – electromagnetic stirrers, 3 – timers

### 2.2.2. IDT measurement setup

The experimental validation of hypergolic properties was conducted using a dedicated drop test apparatus consisting of a high-speed camera Photron FASTCAM SA 1.1 (2000 fps), a specialized Dedotec Dedocool CoolT3 lighting system and an automated oxidizer dosing head. The dosing head, driven by a precision linear actuator Nanotec LGA421L18-B-UKGI-063, dispensed hydrogen peroxide droplets with a reproducible mass of approximately 0.06 g from a height of 85 mm. The impact velocity was calculated theoretically as  $v = \sqrt{gh} \ll 1.29$  m/s. The setup is depicted in Figure 3.



**Figure 3.** Hypergolicity testing station: 1 – high-speed camera, 2 – lighting, 3 – oxidizer injection mechanism, 4 – test area, 5 – linear actuator drive, 6 – syringe piston holder, 7 – oxidizer container (syringe), 8 – fuel seat (contact area)

The testing procedure involved depositing a fixed fuel volume of 35 dm<sup>3</sup> onto the test stand. A computer-controlled signal triggered the camera recording and the dosing head simultaneously. The IDT was determined from the footage with a resolution of 0.5 ms. For each formulation, 5 to 10 trials were conducted.

## 2.3. Fuel formulation and optimization

The primary objective was to identify a stable, hypergolic mixture of aviation kerosene (Jet A-1) and HTP using accessible chemical agents. The selection process involved a systematic screening of carrier solvents, catalysts, and stabilization methods.

### 2.3.1. Phase 1: Alcohol-based carriers and emulsification attempts

Initial screening focused on polar solvents (methanol, ethanol, isopropanol) capable of dissolving inorganic manganese-based catalysts. While manganese acetate tetrahydrate (MAT) exhibited favorable solubility in alcohols, these solutions were immiscible with kerosene. To stabilize the heterogeneous mixture, the hydrophilic-lipophilic balance (HLB) methodology was applied using two distinct surfactant systems.

#### System 1: Span 80 / Triton X-100 screening

A low-resolution screening was conducted with HLB increments of 1.0-2.0. Based on visual stability assessments summarized in Table 1, the operational window was narrowed to 4.3-5.0. Subsequent high-resolution optimization indicated that an HLB value of 4.5 yielded the best results for this system, yet the stability remained temporary.

**Table 1.** Summary of the initial HLB screening for Methanol-Kerosene emulsions (System 1)

HLB Range	Surfactant System	Observation
HLB < 4.0	Span 80	Rapid phase separation into distinct layers.
4.3 < HLB < 5.0	Span 80 / Triton X-100	Increased stability window. Milky emulsion formed.
HLB > 6.0	Triton X-100 dominated	Immediate destabilization.

#### System 2: Span 80 / Tween 80 and phase inversion

To investigate the influence of surfactant chemistry, a second series utilizing Span 80 and Tween 80 (HLB = 15) was conducted. While chemically less stable, this system revealed a critical density-driven phenomenon dependent on the HLB value:

- For HLB  $\leq$  6.0: The dispersed kerosene phase settled to the bottom (higher density than the matrix).
- For HLB  $\geq$  7.0: The dispersed phase rose to the surface (lower density than the matrix).

This observation indicated a density matching point in the range of 6.0-7.0. Optimization tests confirmed that at HLB = 6.5, gravitational separation was minimized, resulting in the most physically stable emulsion among all tested alcohol-based samples.

**Conclusion of Phase 1:** Despite the density optimization at HLB 6.5, alcohol-based emulsions proved unsuitable for long-term storage due to eventual phase separation (coalescence).

### 2.3.2. Phase 2: Investigation of commercial catalytic additives

Parallel to emulsification efforts, a commercial cobalt neodecanoate solution (hereinafter referred to as COMCAT) was investigated. According to the Safety Data Sheet, the mixture consists of neodecanoic acid (40-60%), cobalt carbonate (20-40%), and solvent naphtha.

**Miscibility vs. rheology:** Miscibility tests demonstrated that COMCAT exhibits unlimited miscibility with Jet A-1, forming homogeneous, dark-blue solutions without surfactants. However, a critical limitation was identified during preliminary testing. As the catalyst concentration increased, the viscosity of the fuel mixture increased drastically, resulting in a syrup-like consistency. While catalytic decomposition of HTP was observed, no hypergolic ignition was achieved. This failure was attributed to mass transfer limitations; the elevated viscosity fundamentally inhibited rapid interfacial mixing between the propellant phases, creating a transport barrier which prevented the formation of a reactive ignition kernel. Consequently, this approach was discontinued.

### 2.3.3. Phase 3: Development of the pyridine-based system

Following the failures of Phases 1 and 2, the research focused on Pyridine. As a heterocyclic aromatic compound, Pyridine was hypothesized to offer superior compatibility with kerosene fractions compared to aliphatic alcohols.

**Miscibility and Solubility Screening:** Visual inspection confirmed that Pyridine and Jet A-1 exhibit unlimited miscibility in all proportions. Solubility tests were then performed for various manganese salts to identify a compatible catalyst:

- Inorganic salts ( $\text{MnF}_3$ ,  $\text{MnSO}_4$ ,  $\text{MnCl}_2$ ): Showed negligible solubility, leaving significant solid residues.
- Organometallic salt (MAT): Dissolved readily in pyridine, forming a clear solution.

**Stability of the Ternary System:** A target formulation was prepared by dissolving 2.5% MAT in Pyridine and blending this solution with Jet A-1 (ratio 80:20). The resulting ternary mixture remained optically clear, homogeneous, and free of sedimentation after 24 h. Crucially, unlike the COMCAT samples, the viscosity of the Pyridine-MAT-Jet A-1 mixture remained low, comparable to pure kerosene, facilitating atomization.

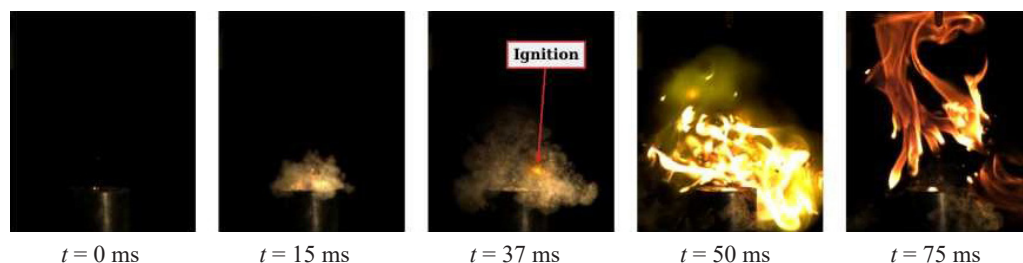
### 2.3.4. Final formulation selection

The Pyridine-based system proved superior to previous attempts by satisfying all physicochemical requirements: thermodynamic stability (unlike emulsions in Phase 1) and low fluid viscosity (unlike commercial additives in Phase 2). Consequently, the mixture consisting of 20% Jet A-1 and 80% Pyridine containing 2.5% MAT was selected as the sole candidate for the hypergolic ignition drop tests.

## 3. Results and discussion

The experimental campaign focused on characterizing the hypergolic ignition performance of the optimized pyridine/Jet A-1/MAT system. The drop tests aimed to determine the IDT, defined as the time interval between the initial contact of the oxidizer droplet (98% HTP) with the fuel surface and the first visible emission of light.

To provide insight into the phenomenological progression of the ignition, high-speed imaging was performed for the optimized fuel blend. Figure 4 presents selected frames from the drop test. Upon contact ( $t = 0$  ms), a brief physical delay is observed, characterized by the intense generation of white vapors (visible at  $t = 15$  ms), indicating rapid exothermic decomposition of the peroxide on the catalyst-laden fuel surface. This pre-ignition phase concludes with the first emission of visible light at  $t = 32$  ms, marking the IDT. Subsequently, the flame propagates violently, achieving a fully developed combustion state within the next 40 ms.

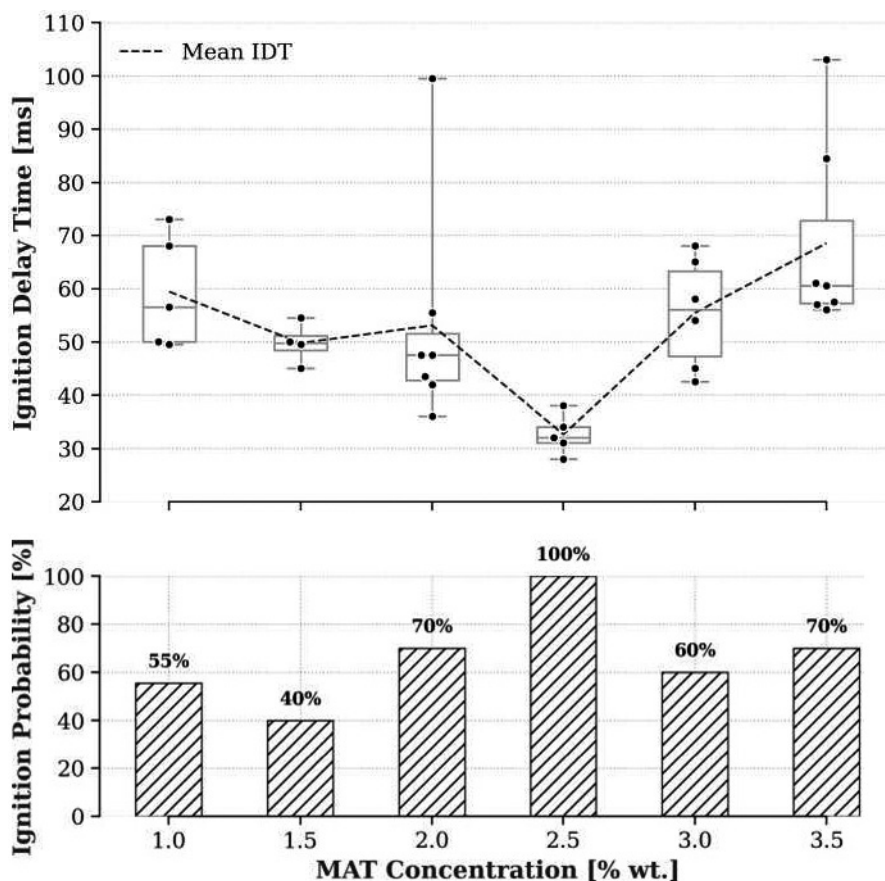


**Figure 4.** Temporal evolution of the hypergolic ignition event recorded via high-speed imaging (2000 fps). The sequence illustrates the critical phases: initial propellant contact, vigorous pre-ignition vaporization ( $t = 15$  ms), and the formation of the ignition kernel followed by flame propagation

### 3.1. Influence of catalyst concentration

The first phase of testing investigated the effect of MAT concentration on the system's reactivity. Samples were prepared with a fixed Jet A-1 content of 20% and varying MAT concentrations ranging from 1.0% to 3.5% (relative to the pyridine mass). Visual observation revealed that catalyst concentrations exceeding 3.0% led to rapid saturation. Crystallization of the catalyst on the vessel walls was observed shortly after preparation, suggesting that the effective concentration of dissolved manganese ions in the bulk liquid reaches a saturation limit, which negatively impacts the ignition reproducibility.

Experimental data indicated a non-linear relationship between catalyst loading and ignition delay. The system exhibited the shortest ignition delays (average  $T_{IDT} \ll 32.6$  ms) at a MAT concentration of 2.5%. Lower concentrations (1.0-1.5%) resulted in significantly longer delays and lower ignition probability, attributed to an insufficient density of active catalytic centers. Conversely, increasing the concentration beyond 3.0% did not improve performance; instead, erratic ignition behavior and increased delays were observed, likely due to the aforementioned crystallization and mixture heterogeneity. The distribution of IDT values as a function of MAT concentration is visualized in Figure 5.

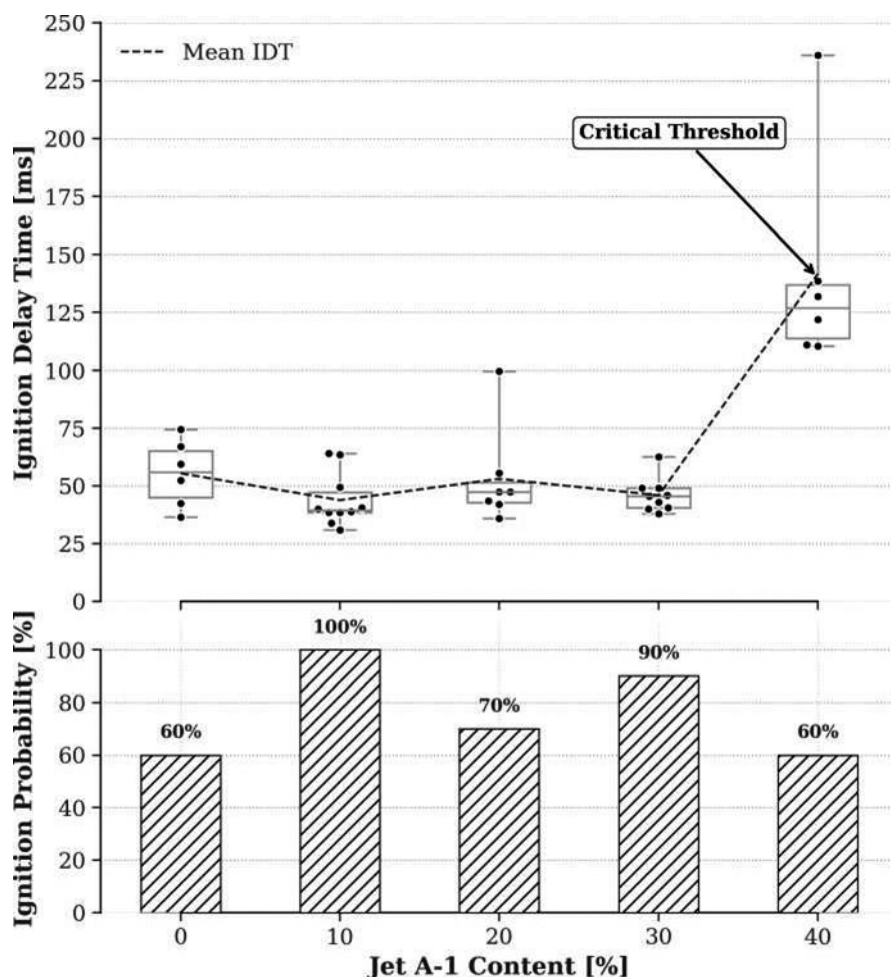


**Figure 5.** Distribution of the IDTs versus MAT catalyst concentration. Individual data points are displayed using a swarm plot technique with white outlines to distinguish overlapping values; the dashed line indicates the trend of the mean values

### 3.2. Influence of fuel content

The second phase examined the role of the energetic fuel component (Jet A-1). Samples were prepared with a fixed MAT concentration of 2.0% and varying Jet A-1 mass fractions from 0% to 40%. A counter-intuitive trend was observed: the addition of kerosene initially improves the ignition performance compared to pure pyridine. Pure pyridine (with catalyst) exhibited an average IDT of roughly 58 ms. The addition of 10-30% Jet A-1 reduced the delay to approximately 44-46 ms. This suggests that kerosene, characterized by higher volatility and distinct flammability limits compared to pyridine, accelerates the gas-phase combustion kinetics once the initial catalytic decomposition of HTP releases sufficient heat.

However, a critical stability threshold was identified at 40% fuel content. Beyond this point, the ignition delay spiked dramatically (avg. > 140 ms), and the process became highly erratic. This transition indicates that high kerosene loading dilutes the polar pyridine phase to a degree where catalyst solubility is compromised, or the contact surface area between the catalyst and the oxidizer is reduced, hindering the initial decomposition reaction. Figure 6 illustrates the impact of fuel content.



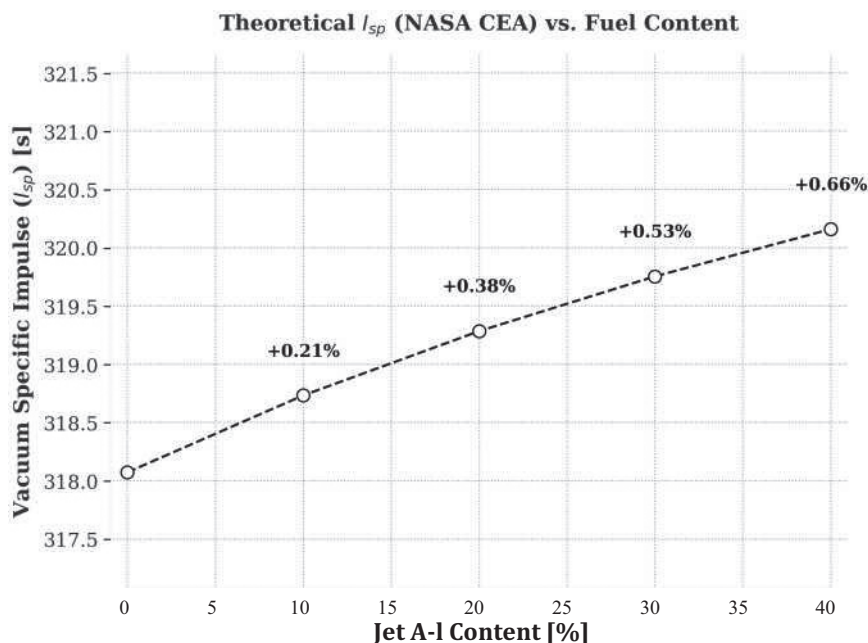
**Figure 6.** Distribution of the IDTimes versus Jet A-1 fuel content. The distinct separation of points at 40% highlights the high variance and loss of stability

### 3.3. Aging and stability analysis

Long-term stability remains a critical parameter for operational fuels. To evaluate this, the optimal formulation (2.5% MAT) was re-tested after a 5-day storage period under laboratory conditions. The aging process resulted in a significant degradation of performance. The average IDT increased from 32.6 ms (fresh) to over 67 ms (aged). This performance drop correlates with the slow precipitation of the organometallic catalyst from the solution. As the active manganese species precipitate, the fuel loses its hypergolic potency, leading to slower and less predictable ignition.

### 3.4. Theoretical performance and trade-off analysis

Beyond the ignition characteristics, the propulsion performance of the proposed blends was evaluated theoretically to justify the inclusion of the hydrocarbon fraction. Figure 7 presents the Vacuum Specific Impulse ( $I_{sp}$ ) calculated using NASA CEA code. The simulation assumes an expansion ratio of  $\epsilon = 40$ , a chamber pressure of 10 bar, and an optimized mixture ratio (MR = 5.0) corresponding to near-stoichiometric conditions for 98% HTP.



**Figure 7.** Theoretical  $I_{sp}$  calculated via NASA CEA code for varying Jet A-1 content (Expansion ratio  $\epsilon = 40$ ,  $P_c = 10$  bar, HTP 98%). The trend indicates a continuous thermodynamic benefit of adding kerosene

Under these ideal assumptions, the addition of Jet A-1 increases the impulse from 318 s to over 320 s. Although this theoretical gain is modest ( $< 1\%$ ), the rationale for blending Jet A-1 into the Pyridine matrix extends beyond thermodynamic performance. The addition of Jet A-1 introduces a complex set of trade-offs between physical properties and operational utility.

#### Operational Benefits:

**1) Economic feasibility:** Replacing a significant fraction (20%) of synthesis-grade pyridine with commodity aviation kerosene drastically reduces the overall propellant cost. This is a critical factor for large-scale propulsion systems where fuel volume is substantial.

**2) Safety and toxicity:** Jet A-1 acts as a diluent, lowering the overall vapor pressure of the mixture compared to pure pyridine. This reduction in volatility enhances handling safety and mitigates the toxicity hazards associated with aromatic solvents, aligning with the objectives of green propulsion.

**3) Thermal stability and lubricity:** Pure aromatic compounds may be prone to polymerization or coking in regenerative cooling channels. The addition of aliphatic hydrocarbons improves the fluid's suitability for active engine cooling and provides better lubricity for turbomachinery components.

However, these benefits are counterbalanced by a penalty in bulk density. Since Jet A-1 ( $\rho \ll 0.80 \text{ g/cm}^3$  [19]) is significantly less dense than Pyridine ( $\rho \ll 0.98 \text{ g/cm}^3$  [20]), the 20% blend exhibits a lower volumetric energy density compared to the pure solvent. Consequently, while the specific impulse per unit mass increases, the density impulse decreases, potentially necessitating slightly larger tankage volumes for a given mission delta-v.

Considering the experimental results (ignition stability) and the theoretical analysis, the 20% Jet A-1 formulation represents an optimal engineering compromise. It maximizes the economic and safety benefits of the hydrocarbon additive without crossing the critical threshold of phase stability or significantly compromising the volumetric efficiency of the propulsion system.

## 4. Statistical analysis

To rigorously evaluate the reliability of the proposed hypergolic system, a statistical analysis of the experimental data was performed. Key statistical descriptors – mean ( $\bar{x}$ ), standard deviation ( $a$ ), minimum, and maximum values – were calculated to assess both the performance and the repeatability of the ignition process.

### 4.1. Catalyst concentration statistics

The statistical summary (Table 3) confirms that the 2.5% MAT concentration offers the best balance between reactivity and repeatability, characterized by the lowest standard deviation ( $a = 3.71$  ms). In contrast, the high variance at 3.5% loading ( $a = 19.16$  ms) quantitatively supports the observation of system instability due to saturation.

**Table 2.** Raw Data Verification: Complete set of IDT measurements [ms] used for Figure 5; NI stands for „no ignition”

MAT concentration [%]	Recorded IDTs [ms]
1.0	NI, 68.0, 49.5, 73.0, NI, 50.0, NI, 56.5, NI, NI
1.5	NI, NI, 54.5, 49.5, 45.0, NI, NI, NI, NI, 50.0
2.0	NI, NI, NI, 42.0, 55.5, 43.5, 36.0, 47.5, 99.5, 47.5
2.5	31.0, 34.0, 28.0, 38.0, 32.0
3.0	45.0, NI, NI, NI, NI, 54.0, 42.5, 58.0, 65.0, 68.0
3.5	103.0, NI, 57.5, 57.0, NI, 60.5, 56.0, 61.0, 84.5, NI

**Table 3.** Statistical summary of IDT [ms] for varying MAT concentrations (fixed 20% Jet A-1)

MAT [%]	Mean ( $\bar{u}$ )	Std. Dev. ( $a$ )	Min	Max	Count
1.0	59.40	10.65	49.5	73.0	5
1.5	49.75	3.88	45.0	54.5	4
2.0	45.33	6.55	36.0	55.5	6
<b>2.5</b>	<b>32.60</b>	<b>3.71</b>	<b>28.0</b>	<b>38.0</b>	<b>5</b>
3.0	55.71	9.47	42.5	68.0	7
3.5	70.33	19.16	56.0	103.0	6

## 4.2. Fuel content statistics

The updated dataset reveals that while 10% and 30% Jet A-1 concentrations offer high reliability (90-100% ignition probability), the pure pyridine solution (0% fuel) and the 20% mixture exhibited reduced consistency, with success rates of 60% and 70%, respectively. Specifically, the 20% Jet A-1 sample, despite having a reasonable median, recorded a significant outlier (99.5 ms) and three non-ignition events, raising the standard deviation to 21.33 ms. This suggests that the optimal stability window is narrower than initially assumed, with the 10% Jet A-1 formulation showing the highest robustness ( $\sigma = 11.51$  ms, 100% success rate). The breakdown of hypergolic reliability at 40% concentration is confirmed by a massive increase in standard deviation ( $\sigma = 47.54$  ms) and a 40% failure rate, as detailed in Table 5.

**Table 4.** Raw Data Verification: Complete set of IDT measurements [ms] used for Figure 6; NI stands for „no ignition”

Jet A-1 Content [%]	Recorded IDTs [ms]
0	36.5, 74.5, NI, 67.0, NI, NI, 59.5, NI, 42.5, 52.5
10	34.0, 38.5, 40.5, 39.0, 49.5, 31.0, 38.5, 40.0, 64.0, 63.5
20	NI, NI, NI, 42.0, 55.5, 43.5, 36.0, 47.5, 99.5, 47.5
30	46.0, 49.0, 62.5, 40.0, 38.0, 49.0, 43.0, 45.5, NI, 40.5
40	122.0, NI, 110.5, 236.0, 138.5, NI, 132.0, 111.0, NI, NI

**Table 5.** Statistical summary of Ignition performance for varying Jet A-1 content (fixed 2.0% MAT); Note the drop in Success Rate at 0%, 20%, and 40%

Jet A-1 [%]	Mean IDT (M) [ms]	Std. Dev. (a) [ms]	Min [ms]	Max [ms]	Success/Total	Prob. [%]
0	55.42	14.65	36.5	74.5	6/10	60
<b>10</b>	<b>43.85</b>	<b>11.51</b>	<b>31.0</b>	<b>64.0</b>	<b>10/10</b>	<b>100</b>
20	53.07	21.33	36.0	99.5	7/10	70
30	45.94	7.33	38.0	62.5	9/10	90
40	141.67	47.54	110.5	236.0	6/10	60

## 4.3. Aging statistics

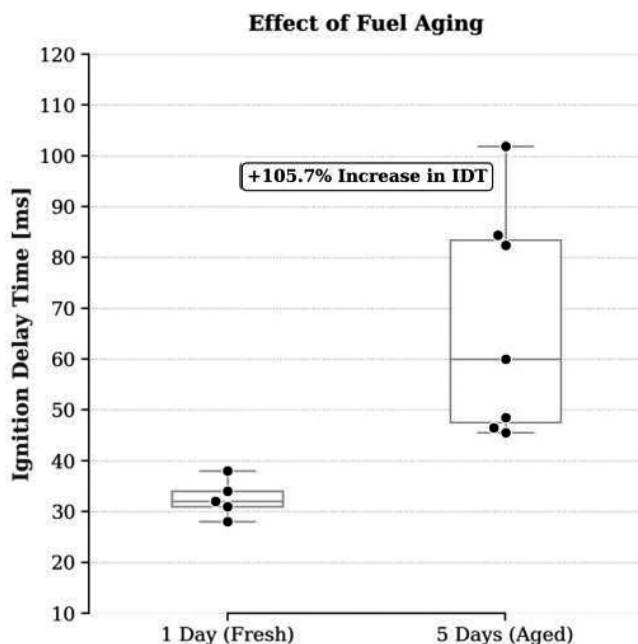
The impact of aging is quantified in Table 7 and Figure 8. The introduction of Non-Ignition (NI) events in the aged samples fundamentally alters the statistical assessment. While fresh samples exhibited 100% reliability with a tight standard deviation ( $\sigma = 3.71$  ms), the aged samples suffered from a significant loss of ignition probability, dropping to 70%. This degradation confirms that catalyst precipitation not only slows down the reaction kinetics (increasing the mean IDT from 32.6 to 67.1 ms) but also renders the system stochastically unpredictable, posing a risk of total ignition failure.

**Table 6.** Raw Data Verification: Complete set of IDT measurements [ms] used for statistical analysis; NI stands for „no ignition”

Storage Condition	Recorded Ignition Delay Times [ms]
Fresh (1 Day)	31.0, 34.0, 28.0, 38.0, 32.0
Aged (5 Days)	48.5, 60.0, 84.5, NI, 45.5, 46.5, NI, 82.5, 102.0, NI

**Table 7.** Comparison of statistical performance for fresh vs. aged samples (2.5% MAT)

Storage Time	Mean IDT (M) [ms]	Std. Dev. (ff) [ms]	Min [ms]	Max [ms]	Success/Total	Prob. [%]
1 Day	32.60	3.71	28.0	38.0	5/5	100
5 Days	67.07	22.53	45.5	102.0	7/10	70



**Figure 8.** Impact of storage duration on the mean IDT. The error bars (standard deviation) for the aged samples are calculated based solely on successful ignition events, excluding NI

## 5. Conclusions

The study successfully demonstrated the feasibility of creating a hypergolic bipropellant system using 98% High Test Peroxide and a kerosene-based fuel blend. Based on the experimental results and physicochemical analysis, the following conclusions are drawn:

- ◆ **Optimal formulation:** The most effective fuel composition consists of 80% Pyridine and 20% Jet A-1, doped with 2.5% MAT. This mixture yields a repeatable ignition delay time of approximately 32.6 ms with high consistency ( $\sigma = 3.71$  ms), meeting the requirements for rapid-response propulsion systems.
- ◆ **Role of rheology and mixing:** The failure of commercial cobalt-based additives (COMCAT) highlighted the critical role of fuel rheology. It was demonstrated that excessive viscosity creates a transport barrier that inhibits rapid interfacial mixing between the propellant phases, preventing the formation of a reactive ignition kernel even when catalytic decomposition is present.
- ◆ **Synergistic effect of Jet A-1:** Aviation kerosene acts as more than a passive energetic diluent. Its presence in the range of 10-30% actively optimizes the ignition delay compared to pure pyridine. However, exceeding a 30% mass fraction leads to a breakdown in hypergolicity due to the dilution of the polar catalyst carrier and a subsequent reduction in effective catalyst-oxidizer contact area.
- ◆ **Stability and storage:** While the pyridine-based system solves the viscosity issues of traditional emulsions, the long-term chemical stability remains a challenge. Catalyst precipitation observed over a 5-day period significantly degrades the IDT and reduces ignition probability, indicating that future research should focus on the development of more robust organometallic stabilizers or alternative aromatic carriers.
- ◆ **Operational viability:** The proposed Jet A-1/pyridine/MAT system represents a promising “green” alternative to hydrazine derivatives, consistent with recent trends in gel and amine-based fuels [8, 9]. It combines low fluid viscosity, which is essential for efficient atomization, with the economic and safety benefits of standard aviation fuels, provided the propellant is utilized shortly after preparation [8].

## Acknowledgments

This work was supported by the Warsaw University of Technology within the framework of Dean's Grant 2019.

## References

- [1] Rarata G., Surmacz P. Hypergolic Ignition of Stabilized Hydrogen Peroxide with Catalytically Promoted Hydrocarbons. (in Polish) *Prace Instytutu Lotnictwa* **2011**, 12(221): 173-181.
- [2] Rupe J.H. *The Liquid-Phase Mixing of a Pair of Impinging Streams*. California Institute of Technology, Progress Report No. 20-195, **1953**; [https://archive.org/details/nasa\\_techdoc\\_19650072428](https://archive.org/details/nasa_techdoc_19650072428) [retrieved 01.12.2025].
- [3] Zung L.B., White J.R. *Combustion Process of Impinging Hypergolic Propellants*. National Aeronautics and Space Administration. NASA Contractor Repr, NASA- CR-1704, Washington, DC, **1971**; <https://ntrs.nasa.gov/citations/19710017393> [retrieved -01.12.2025].
- [4] Houseman J., Lee A. Popping Phenomena with the Hydrazine Nitrogen-Tetroxide Propellant System. *J. Spacecr. Rockets* **1972**, 9(9): 678-682; <https://doi.org/10.2514/3.61775>.
- [5] Catoire L., Chaumeix N., Paillard C. Chemical Kinetic Model for Monomethylhydrazine/Nitrogen Tetroxide Gas Phase Combustion and Hypergolic Ignition. *J. Propuls. Power* **2004**, 20(1): 87-92; <https://doi.org/10.2514/1.9234>.
- [6] Frank I., Hammerl A., Klapotke T.M., Nonnenberg C., Zewen H. Processes During the Hypergolic Ignition Between Monomethylhydrazine (MMH) and Dinitrogen Tetroxide (N<sub>2</sub>O<sub>4</sub>) in Rocket Engines. *Propellants Explos. Pyrotech.* **2005**, 30(1): 44-52; <https://doi.org/10.1002/prep.200400084>.
- [7] European Chemicals Agency. *Substance Infocard: Hydrazine (EC number: 206-114-9)*. ECHA; <https://echa.europa.eu/substance-information/-/substanceinfo/100.005.560> [retrieved 05.12.2025].
- [8] Goldin R., Nath S., Lewkowitz J.K., Natan B. Hypergolic Ignition of a Kerosene-Based Gel Fuel with Hydrogen Peroxide in Rocket Motors. *IJEMCP* **2024**, 23(2): 67-78; <https://doi.org/10.1615/IntJEnergeticMaterialsChemProp.2023051032>.
- [9] Mota F.A.S., Fei L., Tang Ch., Huang Z., Costa F.S. Hypergolic Ignition Behaviours of Green Propellants with Hydrogen Peroxide: The TMEDA/DMEA System. *Fuel* **2023**, 336: paper 127086; <https://doi.org/10.1016/j.fuel.2022.127086>.
- [10] Rarata G., Surmacz P. Hydrogen Peroxide 98% HTP-Class - Alternativr for Hydrazine. (in Polish) *Prace Instytutu Lotnictwa* **2014**, 1(234): 25-38.
- [11] Okniński A., Surmacz P., Sobczak K., Florczuk W., Cieslinski D., Gorgeri A., Bartkowiak B., Kublik D., Ranachowski M., Gut Z., Parzybut A., Kasztankiewicz A., Mazurek J., Valencia F. Bel A., Herbertz K., Underhill D., Schneider, Flock A. Development of Green Bipropellant Thrusters and Engines Using 98% Hydrogen Peroxide as Oxidizer. *Aerospace* **2025**, 12: paper 879; <https://www.mdpi.com/2226-4310/12/10/879>.
- [12] Yuan T., Chen Y.T., Huang B. Semi-Hypergolic Kerosene/Hydrogen Peroxide Fuel System and its Auto-Ignition Injector Design. *Proc. 51<sup>st</sup> AIAA/SAE/ASEE Joint Propulsion Conf.* Coronado, FL, **2015**, paper 3847; eISBN: 978-1-62410-321-6.
- [13] Schiebl M., Woschnak A., Krejci D., Winter F., Scharlemann C. Modeling of Jet A1-H<sub>2</sub>O<sub>2</sub> Autoignition in a Microrocket Combustion Chamber. *J. Propuls. Power* **2013**, 29(2): 385-395; <https://doi.org/10.2514/1.B34643>.
- [14] Han S., Cai G., Yu N., Jiao B., Li J., Di S. Experimental and Simulation Investigation on Partially Catalyzed Ignition Process of Hydrogen Peroxide/Kerosene in a Lab-Scale Rocket Engine. *Acta Astronautica* **2025**, 233: 138-154; <https://doi.org/10.1016/j.actaastro.2025.04.029>.
- [15] Kang H., Lee E., Moon Y., Kwon S. Development of 500-N Scale Green Hypergolic Bipropellant Thruster Using Hydrogen Peroxide as an Oxidizer. *Proc. 51<sup>st</sup> AIAA/SAE/ASEE Joint Propulsion Conf.*

Orlando, FL, **2015**, paper 4062; <https://doi.org/10.2514/6.2015-4062>.

- [16] Han S., Cai G., Zeng Z., Yu N. Effect of H<sub>2</sub>O<sub>2</sub> Concentration and Catalytic Ratio on the Autoignition Characteristics of RP-3 Kerosene under Catalytic Ignition Engine-Like Conditions. *Proc. 73<sup>rd</sup> Int. Astronautical Congress, IAC*, Paris, France, **2022**, paper 71232.
- [17] Li S., Wei X. Ignition Delay Characteristics of Kerosene with Decomposed Hydrogen Peroxide. *J. Propuls. Power* **2016**, 32(2): 431-438; <https://doi.org/10.2514/1.B35723>.
- [18] Sisco J., Mok J.S., Anderson W.E. Ignition Studies of Hydrogen Peroxide and Kerosene Fuel. *Proc. 41<sup>st</sup> AIAA Aerospace Sciences Meeting and Exhibit.*, Reno, NV, **2003**, paper 831; <https://doi.org/10.2514/6.2003-831>.
- [19] Edwards T. Liquid Fuels and Propellants for Aerospace Propulsion: 1903-2003. *J. Propul. Power* **2003**, 19(6): 1089-1107; <https://doi.org/10.2514/2.6946>.
- [20] *CRC Handbook of Chemistry and Physics*. 85<sup>th</sup> ed. (Lide D.R. Ed.), Boca Raton London New York Washington, DC: CRC Press, **2004**.

Received: December 16, 2025

Revised: December 30, 2025

First published on line: December 30, 2025