Article

Monoethanolamine-Based Fuels Hypergolic with Rocket-Grade Hydrogen Peroxide

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Abstract: The object of this work is to study the ignition performances of promising catalytically promoted amino-based green fuels to be used in combination with rocket-grade hydrogen peroxide. The main hypergolic parameter, the ignition delay time, was experimentally determined with an automated drop test setup. Additionally, the kinematic viscosity was experimentally measured, while the CEA2 software was used to determine the ideal rocket performances of the propellants. Three inorganic copper salts were selected as catalysts to be used in combination with monoethanolamine in concentrations ranging from 0.5 wt% to 20 wt%. Then, N,N-dimethylethylenediamine was introduced as part of a blend with monoethanolamine to target the high viscosity and low gravimetric specific impulse of the fuel for the pure monoethanolamine case. Due to the reduced monoethanolamine and low additive content, some formulations were observed to be characterized by gravimetric specific impulse higher than 320 s, and kinematic viscosity lower than 5 cSt while retaining ignition delay times shorter than 30 ms with 98 wt% HTP. Finally, the addition of ethanol to the blend was preliminarily investigated to improve the additive solubility. The effects on the ignition delay time were found to depend on the concentration ratio of the two amines.

Keywords: green propellants; ethanol; hypergolicity; hydrogen peroxide; monoethanolamine; N,N-dimethylethylenediamine

1. Introduction

Currently, many chemical propulsion systems for in-space applications make use of hypergolic bipropellant couples. Indeed, the use of hypergolic reactants (i.e., capable of reliably igniting upon contact without the need for an external ignition source) is highly desirable, as it allows for simpler engine design. The quality of a hypergolic system is often quantified in terms of the Ignition Delay Time (IDT) of the oxidizer–fuel couple employed. The IDT is defined as the time elapsed between the first contact of the two propellants and the ignition, revealed by the first light emission. Hence, better solutions show low IDTs. Conventionally, the threshold value to consider a reaction hypergolic has been set to 100 ms [1]. Low IDTs are sought as they may allow for shorter (hence lighter) combustion chambers, reduce the risk of a hard start, and increase the responsiveness of the entire propulsive system. Such advantages explain why hypergolic systems have found wide applications as attitude and orbital control systems (AOCSs) throughout history, including in Gemini and Apollo spacecraft, the Space Shuttle [2], and, most recently, in SpaceX space capsules [3].

Current systems achieve hypergolicity employing hydrazine or one of its derivatives (i.e., monomethylhydrazine, MMH, or unsymmetrical dimethylhydrazine, UDMH) as fuel and one among nitrogen tetroxide (NTO), red fume nitric acid (RFNA), white fume nitric acid (WFNA), and mixed oxides of nitrogen (MON) as oxidizer. All these substances are universally known for their acute toxicity and corrosiveness. Such drawbacks are the reason why academies and companies are researching so-called green alternatives, despite

the long heritage and the high performances offered by current solutions. Hydrazine and its derivatives have become quite notorious due to the extremely stringent regulation put in place for occupational safety [4]. The National Institute for Occupational Safety and Health (NIOSH) mandates maximum permissible exposure limits (evaluated on a time-weighted average 8 h work shift) equal to 0.001 ppm for hydrazine and its derivatives [5], well below the odor threshold of such substances, which is reportedly $2 \div 5$ ppm [6]. Due to the reported mutagenic properties of these substances, the European Chemical Agency has listed them as Substances of Very High Concern (SVHC) since 2011 [7].

Several liquid propellants have been reviewed in the open literature to assess their health and environmental hazards, handling and safety requirements, and the resulting performances to evaluate their suitability for conventional storable bipropellant replacements [8–13]. Among the potential oxidizers, much interest has arisen around high-concentration aqueous solutions of hydrogen peroxide, also known as High Test Peroxide (HTP). When compared with NTO or nitric acid, despite a lower oxygen yield during combustion, it is considerably less harmful, has a low vapor pressure, and is more compatible with many materials commonly used in manufacture [14]. However, the number of substances that are reportedly hypergolic with HTP is limited [15]. Hence, it is common practice to use additives to improve the reactivity of the fuel. Depending on the reaction mechanism, two classes can be identified: catalytic and reactive additives. The former ones catalyze the oxidizer dissociation, which causes ignition once the auto-ignition temperature (AIT) of the fuel is reached, while the latter ones directly react with the oxidizer exothermically. It is reported that the second class typically imparts lower IDTs [16,17]. However, the most promising one, sodium tetrahydroborate, was reported for suspected reproduction toxicity in the framework of the Classification, Labelling, and Packaging (CLP) regulation to ECHA and could potentially be soon included in the SVHC list.

The present paper reports the results of the investigation on hypergolic bipropellants carried out at the Space Propulsion Laboratory of Politecnico di Milano. In particular, different fuel formulations based on monoethanolamine (MEA), N,N-dimethylethylenediamine (DMEDA), and copper-based catalytic additives were produced to assess their hypergolic character with 98 wt% and 87.5 wt% HTP and preliminarily assess the possibility of replacing traditional hypergols. Analyses were carried out with the underlying aim of investigating only non-SVHC substances nor substances being considered for inclusion in this list. Additionally, experiments to determine the kinematic viscosity of the fuels were carried out together with the theoretical evaluation of density and vacuum gravimetric specific impulse of the bipropellant couples.

Section 2 highlights the state of the art of hypergolic fuels with HTP based on amines, while the substances and diagnostic methods are presented in Sections 3 and 4. Section 5 reports and discusses the results of the conducted tests, before conclusions are drawn in Section 6.

2. Background

In recent years, many investigations have been carried out on the ignition capabilities of catalytically promoted fuels. Despite the often relevant differences in the fuel formulations, the most active catalysts with HTP were found to belong to an identifiable group: the organic and inorganic salts of transition metals, such as manganese, cobalt, copper, and iron [18]. The catalytic activity of such salts can, in principle, impart hypergolicity to any fuel, provided that its amount is sufficient. As a consequence, to achieve reasonably low IDTs ($\approx$20 ms), large additive fractions are often needed, as demonstrated by Frolik et al. [19]. However, large additive fractions (>10 wt%) lead to an increase in the fuel viscosity and a decrease in the gravimetric specific impulse, while demanding dedicated studies on long-term storability. It is therefore clear that any study shall be focused on the development of formulations employing as little metal catalyst as possible. Consequently, ensuring that other components within the fuel mix can react energetically with the oxidizer is of utmost importance.

Chemical compounds belonging to the amine family have been repeatedly identified as promising elements to be part of a hypergolic fuel composition [18,20]. As shown in

Table 1, primary amines are known to react strongly with HTP even without the addition of catalysts, making them a good starting point for the development of highly reactive fuels. Although non-primary amines are not reportedly hypergolic with HTP, they have been successfully used as part of hypergolic blends. They have been used either as (i) promoter (i.e., enhancing the catalytic capability of the metallic cation [21] in polar fuels) or as (ii) co-solvent, allowing the mixing of the polar salt in non-polar fuels (depending on the nature of the -R group) [22–24].

Table 1. Reactions of hydrogen peroxide with amines [25].

Primary Amines		
$RNH_2 + H_2O_2$	$\rightarrow$	Vigorous peroxide decomposition; reaction difficult to control; no products isolated.
Secondary Amines		
$R_2NH + H_2O_2$	$\rightarrow$	R_2NOH Hydroxylamine
Tertiary Amines		
$R_3N + H_2O_2$	$\rightarrow$	R_3NO Amineoxide

The high reactivity of primary amines with HTP was observed in the screening study performed by Melof and Grubelich [15]. In particular, the authors observed that primary amines such as monoethanolamine (MEA), diethylenetriamine, and ethylenediamine reacted with 90% HTP. Additionally, they reported that the addition of only 1% in mass of copper (II) chloride ($CuCl_2$) gave "instantaneous" ignition in a drop test. The use of MEA was further investigated by Ak et al. [26], and Florczuk and Rarata [1]. Despite slight differences in the results, the high reactivity of this amine and the viability of using a small fraction of copper-based additives were confirmed, as ignitions within 40 ms were consistently recorded.

Regrettably, despite being highly reactive, MEA has two considerable drawbacks: a high freezing point of about 10 °C and a high viscosity [27], which prevent it from being a substitute candidate for hydrazine derivates. As demonstrated by Melof and Grubelich [15], a viable way to improve both parameters is to blend MEA with an alcohol. This choice appears further justified by the fact that alcohols are generally cheap, stable on storage, and offer better combustion performances (in terms of gravimetric specific impulse) than MEA. Despite not having disclosed the IDT, they reported that formulations with furfuryl alcohol ignited faster than those without it for the same catalyst amount. The idea of a blend was further investigated by Maschio et al. [28] via DOE. An optimal formulation, capable of igniting in less than 16 ms with 90% HTP, was determined using as fuel components MEA, ethanol, and copper (II) nitrate trihydrate.

In both cited studies, however, the MEA fraction in the blend was high, 47.5 wt% and 61 wt%, respectively. It is straightforward that, as the only virtue of MEA is its high reactivity with HTP, ideal blends should include as little MEA as possible. Finally, Mota et al. [29] successfully investigated the possibility of blending two amines to better leverage the higher reactivity of this molecule class than ethanol. They eventually determined the possibility of achieving ignitions in as little as 12 ms with a blend consisting of N,N,N'N'-tetramethylethylenediamine (TMEDA), dimethylaminoethanol (DMEA), and ethanol, with only 1 wt% of copper (II) chloride dihydrate additive.

3. Substances and Materials

3.1. Fuels

MEA (Thermo Scientific, Waltham, MA, USA, CAS N.: 141-43-5) was selected as the baseline fuel by virtue of its availability, low toxicity, and its reportedly high reactivity with the oxidizer of choice (i.e., HTP). As seen in Section 2, several studies have already been conducted

with it, thus offering an appropriate basis for comparison of the fuel performances. Additionally, working first with MEA allowed us to build upon the obtained results for the development of better formulations targeting specifically the most significant drawbacks of MEA-based fuels.

Table 2 reports the result of the comparison of the ideal rocket performances of the MEA/HTP couple with those of conventional hypergols. For this purpose, the NASA CEA2 software (vers. 05-21-04) [30] was employed, assuming (i) combustion chamber pressure of 20 bar, (ii) expansion ratio equal to 100, (iii) Bray model for nozzle expansion, and (iv) pure substances. Although the gravimetric vacuum specific impulse obtainable with the simple combination MEA/HTP is lower than those of conventionally used hypergols, the volumetric specific impulse is approximately 2% larger than the one of the couple MMH/NTO. This leads to non-negligible advantages in the case of volume-restricted applications such as compact satellites. Additionally, the corresponding predicted temperature in the combustion chamber is considerably lower, simplifying its design.

Table 2. Peak performance values and relative oxidizer-to-fuel mass flow ratio (O/F) for the selected fuels.

Propellant	$I_{s,vac}$ [s]	O/F	I_v [s·g/cm^3]	T_c [K]
MMH/NTO	336.9	1.8	391.7	3224.3
UDMH/NTO	333.6	2.2	380.0	3252.5
UDMH/WFNA	312.8	2.8	374.3	2938.5
MEA/HTP (98%)	304.2	3.6	401.0	2553.8

Obtained with NASA CEA2 code.

Additionally, the toxicity assessments of MEA and hydrazine are reported in Table 3. In particular, the "Time-Weighted Average Threshold Limit Value" (TLV-TWA), the "Permissible Exposure Limit" (PEL), and the "Immediately Dangerous to Life and Health" (IDLH), values published, respectively, by the American Conference of Government Industrial Hygienists (ACGIH), the Occupational Safety and Health Administration (OSHA), and the National Institute of Occupational Safety and Health (NIOSH), are reported for comparison purposes along with the hazard statements in the framework of the "Globally Harmonized System of Classification and Labeling of Chemicals (GHS)" and the health prioritization according to the NFPA 704 of the U.S. National Fire Protection Association (NFPA). It can be noticed that MEA shows a significantly decreased acute toxicity with respect to hydrazine and a larger TLV-TWA, even though the difference in the threshold limit values is strongly dependent upon the institute taken as a reference for the analysis of the exposure limitations. Additionally, even though MEA is shown to be harmful to aquatic life (i.e., the H412 hazard statement), the aforementioned environmental hazard is far less critical than in the case of hydrazine. In fact, both acute and long-term effects of the latter chemical are classified as "very toxic". Finally, MEA is not classified among the so-called CMR (i.e., carcinogenic, mutagenic, and repro-toxic) substances, i.e., chemicals having the potential to cause cancer, cell mutation, or to affect reproduction and fertility. Hence, MEA can be considered an appropriate substance to be further explored in the framework of green propulsion.

As shown in Table 4, three drawbacks shall be taken into consideration when dealing with MEA, namely the large viscosity, the high freezing point, and the high AIT. Thus, other amines have been investigated to overcome these disadvantages, targeting a partial or total substitution of MEA. Concerning the kinematic viscosity, a target value of 15 cSt for the final blend was selected. A comparison of the theoretical vacuum specific gravimetric impulse of the candidates (applying the same conditions used for comparison of Table 2) is reported in Figure 1. This allowed the observation that an increment in the gravimetric impulse was to be expected as well with the new amines.

Table 3. MEA toxicity assessment.

	Hazard Statements [a]	NFPA 704 Fire Diamond [b]	OSHA PEL TWA [ppm] [c]	ACGIH TLV TWA [ppm] [d]	IDLH [ppm] [b]
MEA	H302, H312, H332, H314, H318, H335, H412		3	3	30
N_2H_4	H301, H311, H330, H314, H318, H317, H350, H400, H410		1	0.01	50

[a] Thermo Scientific, (Waltham, MA, USA), [b] Cameo Chemicals, (Silver Spring, MD, USA), [c] NIOSH 2022 (Washington, DC, USA), [d] ACGIH 2023 (Sharonville, OH, USA).

Table 4. Relevant properties of selected fuels.

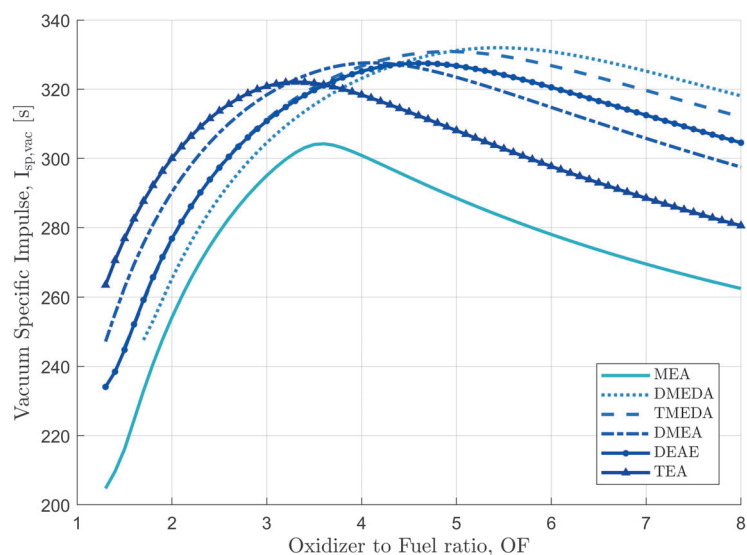| Abbreviation	Formula	Molar Mass [g/mol]	Freezing Point [°C]	AIT [°C]	Density [g/cm^3]	Viscosity [cP]
MEA monoethanolamine	C_2H_7NO	61.08	10	780	1.012	18.7440
DMEDA N,N-dimethyl-ethylenediamine	$C_4H_{12}N_2$	88.15	−70	255	0.814	0.895
TMEDA N,N,N',N'-tetramethyl-ethylenediamine	$C_6H_{16}N_2$	116.21	−55	150	0.772	0.586
ETH ethanol	C_2H_5OH	46.08	−114	365	0.789	1.074

Figure 1. Comparison of the gravimetric vacuum specific impulse of the considered amines with 98% HTP.

The amines (i) N,N-dimethylethylenediamine (DMEDA, Thermo Scientific, CAS N.: 108-00-9), and (ii) N,N,N',N'-tetramethylethylenediamine (TMEDA, Thermo Scientific, CAS N.: 110-18-9) were selected for further investigations in virtue of their physical properties (listed in Table 4) and high theoretical vacuum specific gravimetric impulse.

Despite what was reported by Constantine and Cain [25] on primary amines, ignition tests revealed that DMEDA was not strongly reactive with HTP. Additionally, tests with the selected additives revealed its scarce tendency to create stable solutions. Thus, DMEDA was employed as part of a blend with MEA targeting the improvement of performances offered by the latter, namely impulse and viscosity.

On the other hand, due to the non-polar nature of TMEDA, both the dissolution of the selected catalyst and the blending with MEA failed (thus confirming Mota et al.'s findings [29]). However, given the reportedly excellent catalytic promoter property of this amine with cupric salts [23,24], future studies will be conducted at SPLab employing more compatible salts.

Finally, it is worth noting that another viable way to reduce the fuel AIT, improve salt solubility, and reduce viscosity, while granting the green character of the blend, may be the selection of alcohols. In fact, despite being reportedly not hypergolic with HTP, alcohols are better fuels than amines, cheaper, less viscous, and generally safer to handle. Thus, a preliminary investigation on the use of ethanol (ETH, Sigma Aldrich, (St. Louis, MO, USA), CAS N.: 64-17-5) was carried out, showing interesting results in terms of IDT when added to MEA-DMEDA blends. The toxicity assessment of the considered fuels is reported in Table 5.

Table 5. Fuel toxicity assessment.

	Hazard Statements	NFPA 704 Fire Diamond [a]	OSHA PEL TWA [ppm] [c]	ACGIH TLV TWA [ppm] [d]	IDLH [ppm] [b]
DMEDA	H225, H302, H312, H314, H318 [a]	3 3 1	n/a	n/a	n/a
TMEDA	H225, H302, H322, H314, H318 [a]	3 3 1	n/a	n/a	n/a
ETH	H319, H225 [e]	2 3 0	1000	1000	3300

[a] Thermo Scientific, [b] Cameo Chemicals , [c] NIOSH 2022 , [d] ACGIH 202 , [e] Sigma Aldrich. OSHA PEL TWA, ACGIH TLV TWA and IDLH of DMEDA and TMEDA are not available.

3.2. Additives

Copper (II) nitrate trihydrate (formula: $Cu(NO_3)_2 \cdot 3H_2O$, Thermo Scientific, CAS N.: 10031-43-3), copper (II) chloride anhydrous (formula: $CuCl_2$, Thermo Scientific, CAS N.: 7447-39-4), and copper (II) chloride dihydrate (formula: $CuCl_2 \cdot 2H_2O$, Thermo Scientific, CAS N.: 10125-13-0) have been selected as catalytic additives. The selection of these salts was made on the grounds of their availability, low toxicity, and their reportedly successful use as HTP catalysts. For the sake of brevity, from this point onwards, the three salts will be referred to as CN, CC, and CCH, respectively. Table 6 reports the toxicity assessment of the chosen catalysts (from the toxicity point of view, CC and CCH are identical).

Table 6. Additive toxicity assessment.

	Hazard Statements [a]	NFPA 704 Fire Diamond [a]	OSHA PEL TWA [ppm]	ACGIH TLV TWA [ppm]	IDLH [ppm]
CN copper (II) nitrate trihydrate	H272, H314, H318, H400, H411	3 3 OX	n/a	n/a	n/a
CC/CCH copper (II) chloride anhydrous/dihydrate	H302, H312, H315, H318, H400, H411	2 0 1	n/a	n/a	n/a

[a] Thermo Scientific. OSHA PEL TWA, ACGIH TLV TWA and IDLH are not available.

4. Methodologies

4.1. Fuel Manufacturing

The catalytic additives were dissolved in the liquid phase of the fuel employing a magnetic stirrer (Velp Scientifica ARE (Usmate, Italy)) and an ultrasound washer (ENCO FC10 (Lancenigo, Italy)). The magnetic stirrer was set to 700 rpm at an operating temperature of $\approx$20 °C for 30 min. The ultrasound mixing, lasting 5 min, was performed afterward. Depending on the amount of catalyst, the mixing sequence had to be repeated several times until the complete dissolution of the salt. The full list of produced fuel samples is reported in Table 7.

Table 7. Produced samples.

Batch	Subsets	Formulations
MEA-based	MEA + CN MEA + CC MEA + CCH	[CN]: 1%; 2.5%; 5%; 10%; 20% [CC]: 1%; 2.5%; 5%; 10% [CCH]: 1%; 5%
MEA-DMEDA blends	M:D + CCH 0.5% M:D + CCH 1%	M:D: 20:80; 30:70; 60:40; 50:50; 40:60; 30:70; 20:80 M:D: 20:80; 30:70; 60:40; 50:50; 40:60; 30:70
ETH blends	M:D + CCH 1% + ETH 10%	M:D: 30:70; 50:50; 70:30; 80:20

All concentrations expressed as percentages are intended as mass fractions wt%.

The first fuel batch, made of MEA with CN and CC as additives, consisted initially of 9 samples. The minimum additive concentration was set to 1 wt%, while the maximum was determined experimentally. As the solubility limits of the selected catalysts were not available in the open literature, it was decided to set the maximum additive content to 20 wt% and 10 wt% for CN and CC, respectively, as solubility issues were encountered for larger fractions. Additionally, two samples containing CCH were produced for comparison purposes. For the same concentration, the dissolution of CCH in MEA was observed to be easier than CC.

The second fuel batch, made of MEA-DMEDA blends with CCH as an additive, consisted of 13 samples. The CCH catalyst was selected because of the resulting easier manufacturing process. Additionally, as shown in Section 5.1, it leads to larger IDTs results, thus enabling the better identification of the benefits of the amines blending against the sole MEA formulations. The additive concentration was fixed to 0.5 wt% and 1 wt%, given the observed low solubility in DMEDA, while the MEA-DMEDA ratio ranged from 20:80 to 80:20 and 70:30, respectively, for the two additive contents.

Finally, a third batch consisting of four samples including ethanol was produced to verify the viability of using alcohol to improve the properties of the fuel, such as additive solubility, while retaining the hypergolicity character.

Each batch was produced separately, with the last being produced almost six months after the first. With the exception of some MEA-DMEDA blends, whose details are reported in Section 5.2, no signs of additive deposition, auto-oxidation, or instability were recorded in the days following the production, allowing us to perform the entirety of the characterization and ignition tests. Compatibility and aging studies shall be performed to properly complete the characterization of the fuels in future activities, as eventually, all samples ended up showing signs of aging in the months following the manufacture.

4.2. Theoretical Performances

The theoretical performances of the propellants were estimated using the NASA Chemical Equilibrium with Application (CEA2) software. In particular, the gravimetric vacuum specific impulse ($I_{sv ac}$) and volumetric specific impulse (I_v) were computed. Computations were performed considering (i) pressure in the combustion chamber fixed to 20 bar, (ii) freezing point at the throat (Bray approximation), and (iii) nozzle expansion ratio equal to 100. The figures of merit were computed for different oxidizer-to-fuel mass

flow ratios (O/F), evaluated as the ratio between the oxidizer and fuel mass flow rates. The volumetric specific impulse (I_v) was computed considering the theoretical density (ρ_{th}) of the propellant at the respective O/F obtained with the formula:

$$\rho_{th} = \frac{\rho_{oxidizer} \cdot \rho_{fuel} \cdot (O/F + 1)}{\rho_{oxidizer} + \rho_{fuel}(O/F)} \tag{1}$$

Densities of the substances were retrieved from the literature for a temperature of 25 °C. Any difference with the results reported in [31] is attributable to minor differences in used data (namely the formation enthalpies or density). Finally, for all computations, substances were considered pure and the additives in their anhydrous form.

4.3. Viscosity Measurement

The evaluation of the viscosity of each sample was performed immediately after its production employing a Kpg-Ubbelohde viscosimeter (Schott Gerate GMBH (Mainz, Germany)). Each viscosity test was repeated 5 times employing 15 mL of the sample. The kinematic viscosity measurements have to be considered valid for a temperature of 18 °C.

4.4. Drop Test Setup

Ignition tests were conducted employing a drop test setup developed internally at the Space Propulsion Laboratory (SPLab) of Politecnico di Milano. The IDT was measured by dropping a known quantity of HTP onto a static pool of fuel while recording the reaction with a high-speed camera. Additionally, measurements of the time elapsed between the reactant contact and the beginning of HTP decomposition, known as Time to Vapor Generation (TVG), were carried out. A depiction of the test rig is given in Figure 2.

The test rig consists of a closed constant-volume stainless-steel chamber of cylindrical shape (3), with internal diameter and height of 12.5 cm and 20 cm, respectively. The chamber is optically accessible from one side (1), while the opposite opening acts as a hatch, allowing the fuel sample to be loaded. An inert atmosphere during the tests, along with the evacuation of the combustion gases after the experiments, can be achieved by introducing nitrogen inside the chamber. The system for HTP supply (2) consists of a linear actuator, connected to the plunger of a syringe. The linear actuator (EyPiNS, Hong Kong, China, 10 cm stroke, maximum speed of 1 cm/s) is remotely operated to push the plunger of the syringe (Hamilton Company, (Reno, NV, USA) , model 1002 LT SYR), and, hence, to drop a controlled amount of oxidizer into a glass vial containing the fuel. The oxidizer feeding system is equipped with a manual safety valve, introduced to exclude the oxidizer from the system during the set-up of the test. The IDT is determined through a high-speed imaging technique. The tests are recorded with a Phantom Camera v710 (ViSiON Research (Wayne, NJ, USA)) at 2000 fps. Additionally, HTP droplet impact and ignition may also be recorded utilizing an oscilloscope (4) connected to a miniaturized accelerometer, placed below the glass vial and a load cell to evaluate the mass change during the early phase of the reaction. The control of the setup is managed through an Arduino Due controller. The scheme of the apparatus is given in Figure 3. The implemented drop test setup is characterized by considerable sensor redundancy and valves ensuring safe operations. In case of electronic component malfunctions leading to continuous oxidizer supply or unwanted pressure raising, the operator can manually operate the setup, restoring nominal operating conditions.
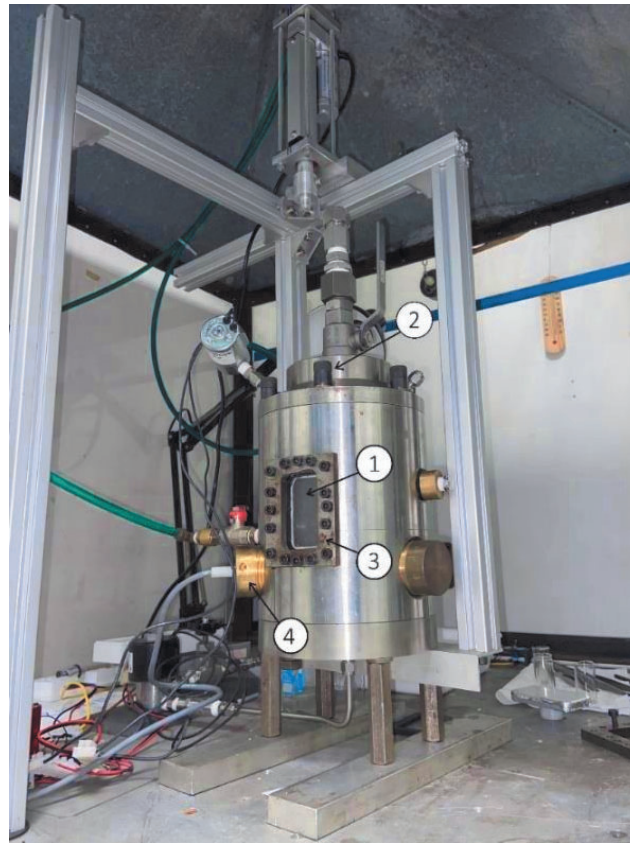
Figure 2. Drop test reaction chamber: (**1**) optical access; (**2**) HTP supply system; (**3**) combustion chamber body; (**4**) sensor connections.
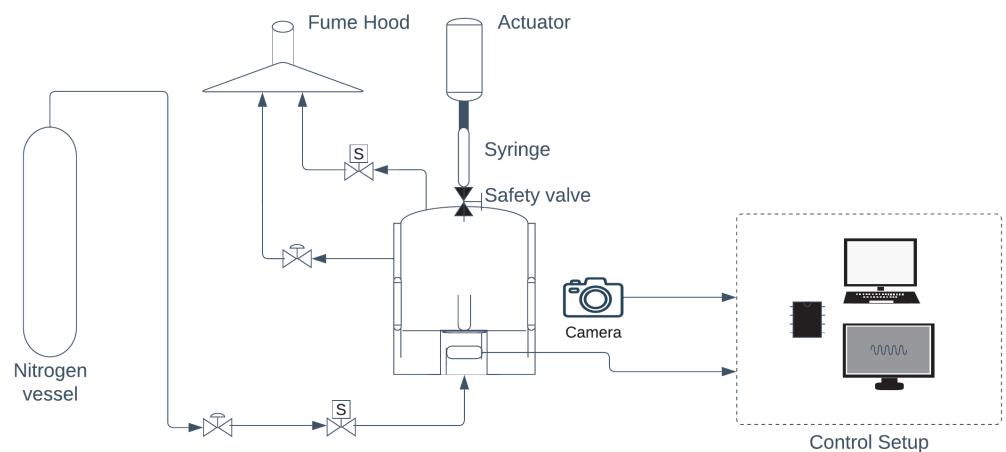

Figure 3. Drop test apparatus scheme.

All tests were conducted at ambient conditions (i.e., P = 1 atm and T ≈ 20 °C). For each test, the fuel quantity was fixed to 100 ± 5 mg, while the oxidizer amount can be evaluated as a function of the HTP concentration and the required actuator displacement. The HTP droplet masses are listed in Table 8. In particular, the tests were carried out employing 98% HTP (JAKUSZ SpaceTech Sp. z o.o. (Szymbark, Poland)) and 87.5% HTP (PROPULSE® 875 by Evonik (Essen, Germany)). Each fuel sample was tested multiple times to properly evaluate the average IDT, TVG, and their corresponding standard deviations.

Table 8. Oxidizer droplet size.

Oxidizer (wt%)	Mass [mg]	
	Avg	Std
HTP 87.5%	63.6	3.4
HTP 98%	67.3	3.5

Drop tests repeated 8 times.

5. Results and Discussion

5.1. Mea-Based Fuels

The results of the evaluation of the theoretical rocket performances of the produced fuels are reported in Table 9. The obtained data on the rocket performances reveal negligible differences in the gravimetric vacuum specific and volumetric specific impulses offered by the two different additives. For a given HTP grade, due to its positive effect on fuel reactivity and high molar mass, the increase in the additive mass fraction causes both a reduction in the maximum gravimetric impulse and in the associated optimal O/F. In particular, the reduction of $I_{s,vac}$ is approximately 2% with 98% HTP for both additives. Being that the density of the oxidizer is larger than that of the fuel, the effects on the volumetric specific impulse of the reduction in both $I_{s,vac}$ and O/F are negative. The resulting reduction in I_v is less than 1%. On the other hand, a reduction in the HTP grade (hence, the reactivity of the oxidizer) leads to a decrease in the $I_{s,vac}$ and an increment in the optimal O/F, with the overall effect of reducing the volumetric specific impulse as well. In particular, the $I_{s,vac}$ and I_v of the fuel MEA + CN 1 wt% decrease, respectively, by 4% and 6%.

Table 9. MEA-based fuel maximum gravimetric vacuum specific impulse, corresponding O/F, and volumetric specific impulse.

Formulation	98% HTP			87.5% HTP		
	$I_{s,vac}$ [s]	O/F	I_v [$s \cdot g/cm^3$]	$I_{s,vac}$ [s]	O/F	I_v [$s \cdot g/cm^3$]
MEA + CN 1 wt%	304.0	3.5	400.5	291.0	4.0	374.7
MEA + CN 2.5 wt%	303.6	3.5	400.9	290.6	3.9	374.4
MEA + CN 5 wt%	302.9	3.4	400.7	290.1	3.8	374.5
MEA + CN 10 wt%	301.4	3.1	399.7	288.9	3.5	374.0
MEA + CN 20 wt%	297.9	2.7	398.7	286.9	3.0	374.6
MEA + CC 1 wt%	303.7	3.5	400.2	290.8	4.0	374.4
MEA + CC 2.5 wt%	303.2	3.5	400.4	290.2	4.0	374.4
MEA + CC 5 wt%	302.1	3.4	399.6	289.2	3.9	373.8
MEA + CC 10 wt%	299.7	3.2	398.1	287.1	3.7	372.6
MEA (reference)	304.2	3.6	401.1	291.2	4.1	375.0

Obtained with NASA CEA2 code set according to Section 4.2.

The results of the experimental characterization of the fuels in terms of TVG, IDT, and kinematic viscosity are reported in Table 10. Broadly speaking, CN-based fuels show better performances and thermophysical properties than CC-based fuels. In particular, apart from the case with 1 wt% of additive, both the viscosity and the IDT are lower. Additionally, two different IDT trends can be identified. Fuels with CN show a rapid IDT decrease with the catalyst content increment from 1 wt% to 5 wt%, reaching a minimum for a concentration close to 10 wt% before slowly increasing. Fuels with CC, on the other hand, show a clearer minimum for a concentration close to 5 wt%. Such trends are the consequence of the two opposite effects that the addition of additive has on the IDT, namely increment in catalytic activity and viscosity. Therefore, the existence of an optimal formulation is to be expected. The steeper IDT increment past the minimum observed with CC can be attributed to the higher viscosity imparted to the fuel by this additive. For both additives, the corresponding

standard deviations appear to be lower for low values of the IDT. This implies that the influence of the mixing process with the oxidizer has less influence when the fuel reactivity reaches an optimum. Among the two subsets, MEA + CN 10 wt% and MEA + CC 5 wt% provide the lowest IDTs. However, the former is characterized by a kinematic viscosity 18% higher than the latter. This downside can be avoided by selecting a slightly lower amount of CN. In fact, MEA + CN 5 wt% grants a viscosity 17% lower than MEA + CC 5 wt% while still retaining low IDTs (i.e., 16.3 ms with 98% HTP and 29.1 ms with 87.5% HTP). Finally, as the two additives allow for achieving similar impulses, the choice of the most suitable composition shall be a trade-off between viscosity, IDT, and impulse, and in more advanced design phases, shall also include rocket sub-system design. The plots of the theoretical density and viscosity are reported in Figure 4. The linear least square method was used to fit the viscosity values.

Table 10. MEA-based fuel experimental campaign results.

Formulation	TVG 98% HTP [ms]		TVG 87.5% HTP [ms]		IDT 98% HTP [ms]		IDT 87.5% HTP [ms]		Viscosity [cSt]	
	Avg	Std	Avg	Std	Avg	Std	Avg	Std	Avg	Std
MEA + CN 1 wt%	7.4	1.1	9.8	1.8	39.8	6.1	91.3	8.2	30.07	0.17
MEA + CN 2.5 wt%	6.0	0.6	6.6	1.0	22.3	3.4	43.9	6.7	34.07	0.36
MEA + CN 5 wt%	4.0	0.5	5.1	0.6	16.4	1.5	29.1	2.7	39.78	0.55
MEA + CN 10 wt%	3.2	0.3	3.9	0.4	16.3	1.3	22.4	2.0	56.74	1.65
MEA + CN 20 wt%	5.7	1.1	4.9	0.3	17.0	3.5	28.5	4.8	119.14	5.68
MEA + CC 1 wt%	5.8	1.2	7.0	1.0	35.3	4.4	56.8	4.8	26.14	0.35
MEA + CC 2.5 wt%	5.1	1.0	5.6	0.9	30.1	1.7	48.3	7.1	35.09	0.41
MEA + CC 5 wt%	3.7	0.3	3.3	0.3	18.5	2.9	27.3	1.8	48.25	0.42
MEA + CC 10 wt%	5.2	1.0	4.2	0.5	28.9	1.2	47.1	6.2	100.71	2.16
MEA + CCH 1 wt%	9.1 *	n/a	17.8 *	n/a	52.8 *	n/a	67.3	6.5	n/a	n/a
MEA + CCH 5 wt%	3.4	0.4	3.9	0.2	19.0	2.0	32.1	3.4	n/a	n/a

* Data extrapolated from average data obtained testing the MEA-DMEDA blends (hence the lack of related standard deviation). Ignition with 98% HTP was tested 6 times, with 87.5% HTP 12 times, MEA + CCH 6 times. No viscosity measurements were carried out for sample with CCH.
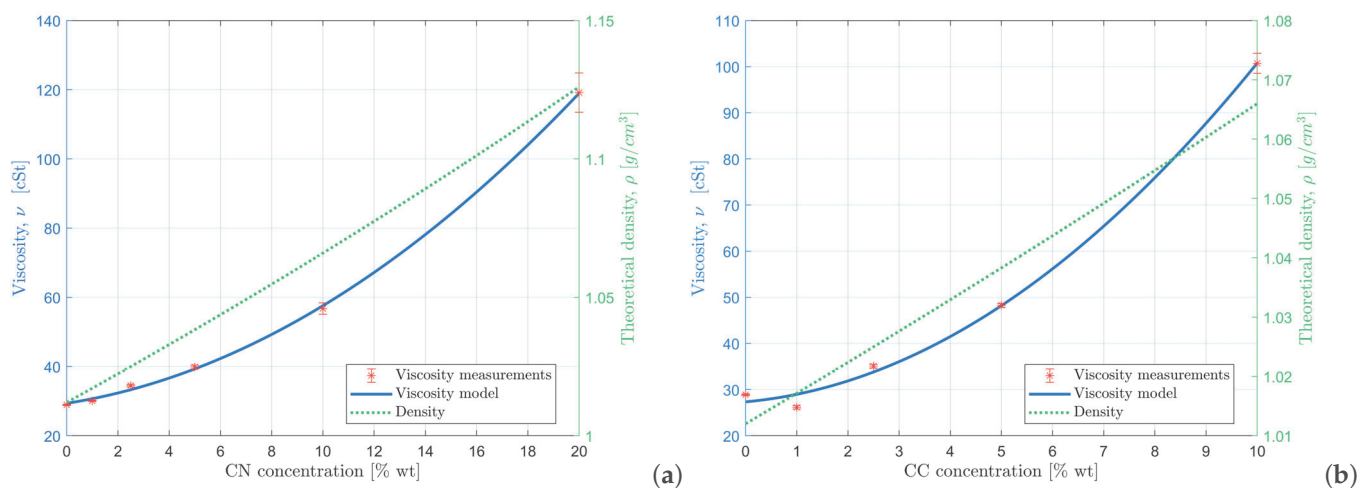

Figure 4. Theoretical density and measured kinematic viscosity of MEA-based fuels: (**a**) MEA + CN (i) theoretical density (green) and (ii) viscosity fitted model $R^2 = 0.9995$ (blue); (**b**) MEA + CC (i) theoretical density (green) and (ii) viscosity fitted model $R^2 = 0.9968$ (blue).

An additional consideration that can be made from Table 10 concerns the behavior of the two different forms of copper chloride. Data relative to the fuel MEA + CCH 1 wt% are extrapolated from MEA-DMEDA blends, as this sample was only tested with 87.5% HTP. As expected, the presence in CCH of two additional moles of water per mole of copper hinders the ignition process by acting as a heat sink, delaying the reaching of the AIT of the fuel. The difference in the TVG and IDT of the two additive forms is found to depend on

its concentration; the larger the amount of catalyst, the lower the difference, in accordance with the lower proportion of water in the fuel.

The influence of HTP grade is shown in detail in Figures 5 and 6, which compare the measured TVG and IDT values and the corresponding fitting of the fuels. The fitting was made using nonlinear least square and linear least square methods, respectively, for CN and CC. The IDT increases with the decrease in the HTP grade because of the larger water quantity acting as a heat sink during the early phase of the reaction. On the contrary, the effect on the TVG is quite contained. Hence, it can be concluded that the presence of water does not affect the onset of the decomposition of hydrogen peroxide, but mostly leads to heat absorption, delaying the auto-ignition.
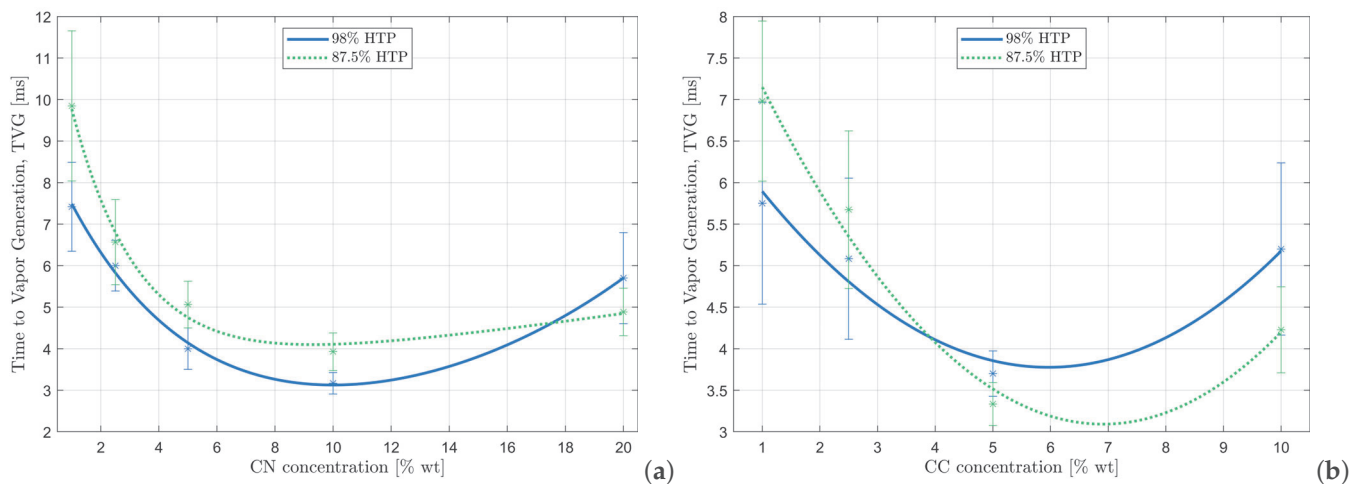

Figure 5. Measurements with relative standard deviations and fitting of TVG versus additive concentration of MEA-based fuels: (**a**) TVG of MEA + CN fuels with (i) 98% HTP, $R^2 = 0.9951$ (blue) and (ii) 87.5%HTP, $R^2 = 0.9910$ (green); (**b**) TVG of MEA + CC fuels with (i) 98% HTP, $R^2 = 0.9466$ (blue) and (ii) 87.5%HTP, $R^2 = 0.9785$ (green).
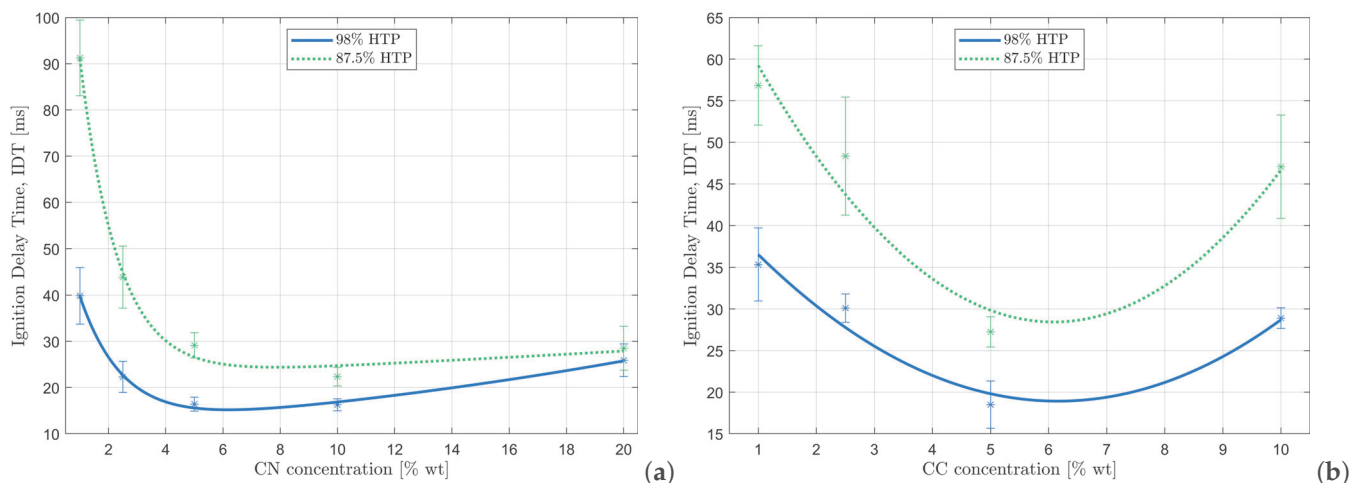

Figure 6. Measurements with relative standard deviations and fitting of IDT versus additive concentration of MEA-based fuels: (**a**) IDT of MEA + CN fuels with (i) 98% HTP, $R^2 = 0.9967$ (blue) and (ii) 87.5%HTP, $R^2 = 0.9957$ (green); (**b**) IDT of MEA + CC fuels with (i) 98% HTP, $R^2 = 0.9424$ (blue) and (ii) 87.5%HTP, $R^2 = 0.9283$ (green).

An example of the ignition sequence is given in Figure 7. The first frame shows the drop of hydrogen peroxide prior to the impact, while the second one highlights the release of vapor once the fuel and oxidizer mixture starts reacting. The third frame shows the ignition and the fourth one the flame propagation.

Given the large additive mass fraction of the fastest igniting formulations, it was deemed necessary to execute a preliminary combustion product analysis to understand potentially negative environmental and propulsive effects. The analysis was based on ideal thermochemistry to have a rough estimation of each product quantity. The analysis was conducted by means of the NASA CEA2 software under the operating conditions defined in Section 4.2, with the difference of having assumed thermodynamic equilibrium conditions at the nozzle. In fact, the Bray assumption is more relevant for performance computation, while the shifting equilibrium condition may give insight into the theoretical equilibrium chemistry behavior, besides allowing a more conservative estimation of the amount of harmful products. The target formulations are those characterized by the largest additive content, i.e., 20 wt% of CN and 10 wt% of CC. For these punctual computations, the O/Fs were set equal to the optimal ones reported in Table 9. The mass fractions of the resulting combustion products are reported in Table 11. Most of the product mass fraction is composed of water, carbon dioxide, and nitrogen ($\approx$97%), while the solid mass fraction is low (below 2% threshold), thus allowing us to neglect in first approximation the two-phase flow effects. Finally, the amount of substances representing health hazards for humans, namely carbon monoxide and hydrochloric acid, was found to be less than 1.5% of the total mass. Hence, the health hazards can be considered minimal for these fuels, especially for those with CN. However, better modeling and live experiments are needed to more accurately determine the computed fractions.
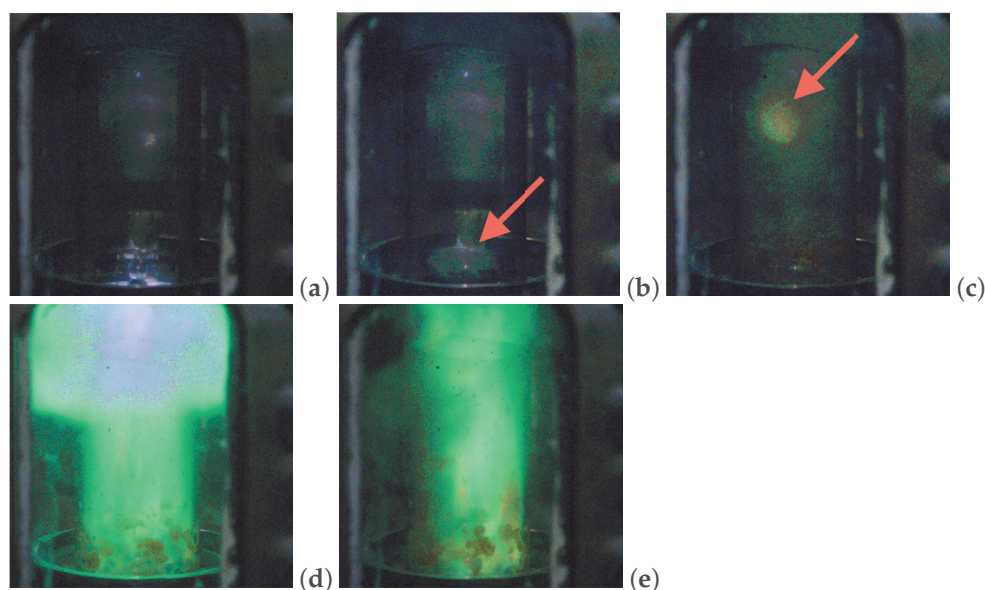

Figure 7. Example ignition sequence of MEA + CN 10 wt% with 98% HTP: (**a**) $t = 0$ ms, contact; (**b**) $t = 3.5$ ms, first vapor generation; (**c**) $t = 14.5$ ms, ignition; (**d**) $t = 17.5$ ms, flame kernel enlargement, (**e**) $t = 23.5$ ms, reaction. Red arrows in (**b**) and (**c**) point, respectively, at the vapor cloud and ignition kernel to help locating them in the pictures.

Table 11. Mass fractions of the combustion products at the exit section for additive-rich formulations and 98% HTP.

Products	MEA + CN 20 wt%	MEA + CC 10 wt%
CO	0.03%	0.06%
CO_2	31.11%	30.79%
Cu	1.83%	1.13%
HCl	-	1.29%
H_2	0.05%	0.13%
H_2O	61.21%	61.69%
N_2	5.77%	4.91%

Obtained with NASA CEA2 code set according to Section 4.2 with the exception of the flow at the nozzle, here considered evolving under thermodynamic equilibrium.

5.2. MEA-DMEDA Fuel Blends

This section deals with the results of the characterization of the fuels produced by blending MEA with DMEDA. The ideal rocket performances of the 13 samples are reported in Table 12. The low additive quantity found in these samples is limited by its low solubility in DMEDA. The consequences on the IDT will be presented afterward. By analyzing the results of the theoretical performance analysis, it is possible to appreciate the increase with respect to the first batch fuels in both gravimetric and volumetric specific impulses, which can be traced to the reduced amount of additive and the reduction in MEA content due to DMEDA addition.

Table 12. MEA-DMEDA blend fuel maximum gravimetric vacuum specific impulse, corresponding O/F and volumetric specific impulse.

Formulation (MEA:DMEDA)	98% HTP			87.5% HTP		
	$I_{s,vac}$ [s]	O/F	I_v [s·g/cm^3]	$I_{s,vac}$ [s]	O/F	I_v [s·g/cm^3]
20:80 + CCH 0.5%	324.9	4.5	415.2	312.5	5.3	392.2
30:70 + CCH 0.5%	322.9	4.4	414.2	310.5	5.2	391.0
60:40 + CCH 0.5%	320.8	4.3	413.0	308.4	5.0	389.2
50:50 + CCH 0.5%	318.5	4.2	411.7	306.1	4.9	387.7
60:40 + CCH 0.5%	316.1	4.1	410.2	303.6	4.7	385.5
70:30 + CCH 0.5%	313.4	4.0	408.5	300.9	4.6	383.7
80:20 + CCH 0.5%	310.6	3.8	405.9	298.0	4.4	381.0
20:80 + CCH 1%	324.7	4.5	415.4	312.3	5.3	392.3
30:70 + CCH 1%	322.7	4.4	414.3	310.3	5.2	391.1
40:60 + CCH 1%	320.6	4.3	413.1	308.2	5.0	389.3
50:50 + CCH 1%	318.3	4.2	411.8	305.9	4.9	387.8
60:40 + CCH 1%	315.9	4.1	410.3	303.5	4.7	385.6
70:30 + CCH 1%	313.3	3.9	407.9	300.7	4.6	383.7

Obtained with NASA CEA2 code set according to Section 4.2.

The results of the experimental characterization of the fuels are reported in Table 13. By comparing these results with those in Table 10, it is possible to notice that the use of DMEDA allowed the production of fuels showing remarkably low kinematic viscosity, which falls within the satisfactory threshold of 15 cSt in all but one case. The theoretical density and viscosity plots are reported in Figure 8. The linear least square method was used to fit the viscosity values.

Table 13. MEA-DMEDA blend fuel experimental campaign results.

Formulation (MEA:DMEDA)	TVG 98% HTP [ms]		TVG 87.5% HTP [ms]		IDT 98% HTP [ms]		IDT 87.5% HTP [ms]		Viscosity [cSt]	
	Avg	Std	Avg	Std	Avg	Std	Avg	Std	Avg	Std
20:80 + CCH 0.5%	4.3	0.3	6.7	0.6	24.1	3.3	159.6	55.8	2.93	0.04
30:70 + CCH 0.5%	5.2	0.7	7.0	1.1	28.7	5.1	158.6	57.5	3.50	0.02
40:60 + CCH 0.5%	6.0	0.9	9.1	2.3	30.8	1.0	195.6 *	80.4 *	4.12	0.02
50:50 + CCH 0.5%	6.0	0.8	10.4	1.9	37.3	6.3	64.8 *	18.0 *	5.94	0.03
60:40 + CCH 0.5%	8.4	1.1	12.2	1.2	47.4	4.9	64.1 *	4.2 *	7.31	0.03
70:30 + CCH 0.5%	8.5	1.3	14.5	1.0	47.2	8.3	134.8 *	35.7 *	11.80	0.08
80:20 + CCH 0.5%	9.8	2.0	16.6	1.6	58.4	8.3	173.3 *	35.7 *	16.94	0.18
20:80 + CCH 1%	3.6	0.4	3.6	0.6	18.4	1.0	27.9	5.8	5.42	0.04
30:70 + CCH 1%	3.7	0.4	4.6	0.6	21.3	0.7	55.1	18.7	5.71	0.04
40:60 + CCH 1%	4.7	0.4	5.1	0.6	24.0	1.9	71.8	23.9	6.46	0.04
50:50 + CCH 1%	5.9	0.9	7.4	1.0	30.3	4.7	60.5 *	7.3 *	7.29	0.09
60:40 + CCH 1%	6.3	1.1	8.1	1.1	31.4	3.5	85.9 *	28.7 *	9.59	0.11
70:30 + CCH 1%	6.8	1.3	10.5	1.6	37.6	6.2	74.0 *	14.0 *	13.49	0.05

* The reported data cannot reliably define the IDT as ignitions were not consistent. Ignition with 98% HTP was tested 12 times, with 87.5% HTP 18 times.

An example of the ignition sequence can be seen in Figure 9; the selections of each snap-shot followed the same logic used in Figure 7.
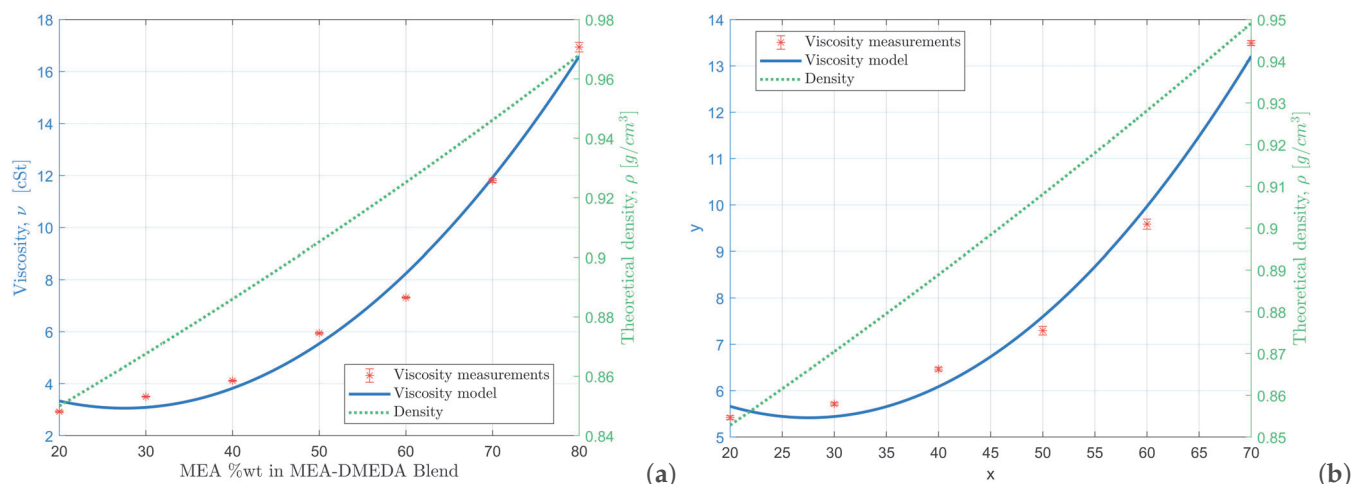
Figure 8. Theoretical density and measured kinematic viscosity of MEA-DMEDA blends: (**a**) MEA-DMEDA + CCH 0.5 wt% (i) theoretical density (green) and (ii) viscosity fitted model $R^2 = 0.9900$ (blue); (**b**) MEA-DMEDA + CCH 1 wt% (i) theoretical density (green) and (ii) viscosity fitted model $R^2 = 0.9874$ (blue).

Interesting results have been obtained in terms of IDT with different HTP grades. Considering the ignition results with 98% HTP, fixing the additive content, it is possible to notice that the trend for both TVG and IDT appears to be monotonic, strictly influenced by the increase in the viscosity and expected AIT increment related to MEA content in the blend. In particular, most MEA-lean formulations ignite remarkably fast, with samples containing less than 30% of MEA in the blend doing so within 30 ms. Additionally, it can be observed that, besides some exceptions, the standard deviations of the measurements increase with MEA content in the blend. On the contrary, tests with 87.5% HTP show far less satisfactory results with only most MEA-lean formulations igniting reliably. Indeed, differently from tests with 98% HTP, where all samples always ignite, it is possible to define a non-null failure rate for tests with 87.5% HTP. In particular, out of the entire batch, only those with 1 wt% of additive ignite reliably within the 100 ms hypergolicity threshold. The recorded ignition success rates are detailed in Figure 10. It can be noticed that the increment of MEA causes a monotonic decrease in the ignition success rate, with ignition deemed unreliable if failed more than once for reasons that could not be correlated with certainty to human errors committed during the testing procedure (i.e., droplet–fuel pool misalignment and air presence in the oxidizer feeding system influencing the droplet size). Results with 87.5% HTP allow us to conclude that the catalyst amount was too little for these fuels to be successfully employed with lower-grade HTP.

As previously mentioned, the addition of DMEDA strongly influences the additive solubility and, consequently, the storage stability of fuels. The upper limit of 1 wt% in the additive content is a consequence of the impossibility of achieving a homogeneous liquid solution/colloid with higher additive content. The low solubility issue is observed especially with MEA-lean formulations, which are the best performing. The instability appeared for samples with less than 40 wt% MEA in the blend about two weeks after production, precisely between testing with 98% HTP and 87.5% HTP. An ultrasound bath allowed us to re-homogenize the fuels, without appreciable difference with respect to the initial physical properties of the produced samples. Hence, later IDT tests are assumed to not be influenced by the storage time, even though a dedicated stability analysis shall be foreseen. As discussed in Section 3.1, DMEDA was observed to have a low tendency to stably bind considerable amounts of the additive. However, the destabilization of the final samples was not forecast given that the amount of additive was in no sample higher than its expected solubility threshold in MEA (the reader should consider that it was possible to solve 10% wt of CC in MEA, and CCH was observed to be easier to dissolve during fuel manufacture). Thus, the recorded instability allows us to infer that the bonding of

the two amines competes with the formation of coordination complexes between MEA and the salt. Further investigations are required to confirm this assumption. Despite this drawback, DMEDA was observed to greatly improve the impulse and viscosity of fuels, while obtaining satisfactory IDT with 98% HTP requiring a small additive mass fraction. The effects of DMEDA addition are summarized in Table 14.
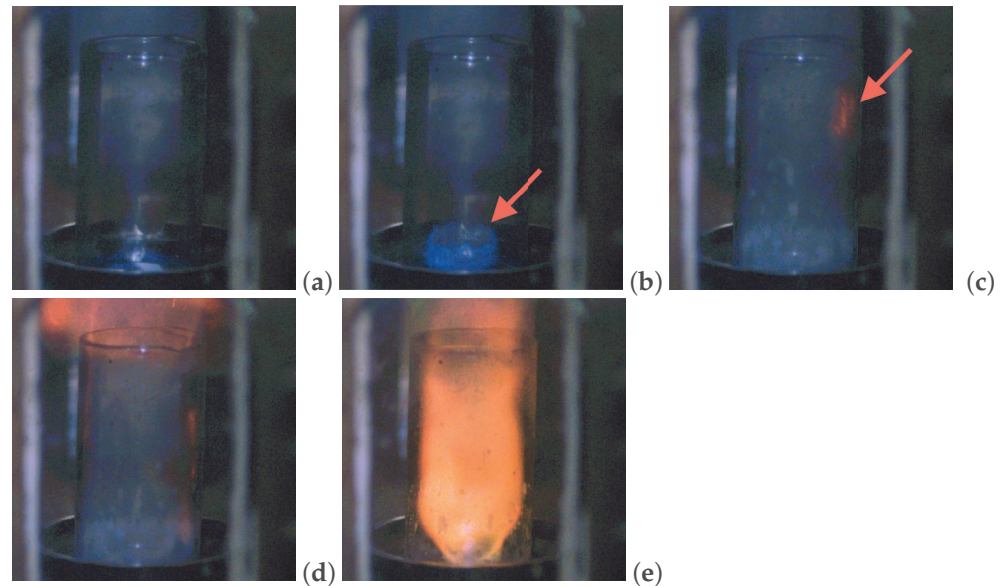

Figure 9. Example ignition sequence of MEA-DMEDA 20:80 + CCH 1% with 98% HTP: (**a**) $t = 0$ ms, contact; (**b**) $t = 3.5$ ms, first vapor generation; (**c**) $t = 17$ ms, ignition; (**d**) $t = 20$ ms, flame kernel enlargement; (**e**) $t = 45.5$ ms, reaction. Red arrows in (**b**) and (**c**) point, respectively, at the vapor cloud and ignition kernel to help locating them in the pictures.
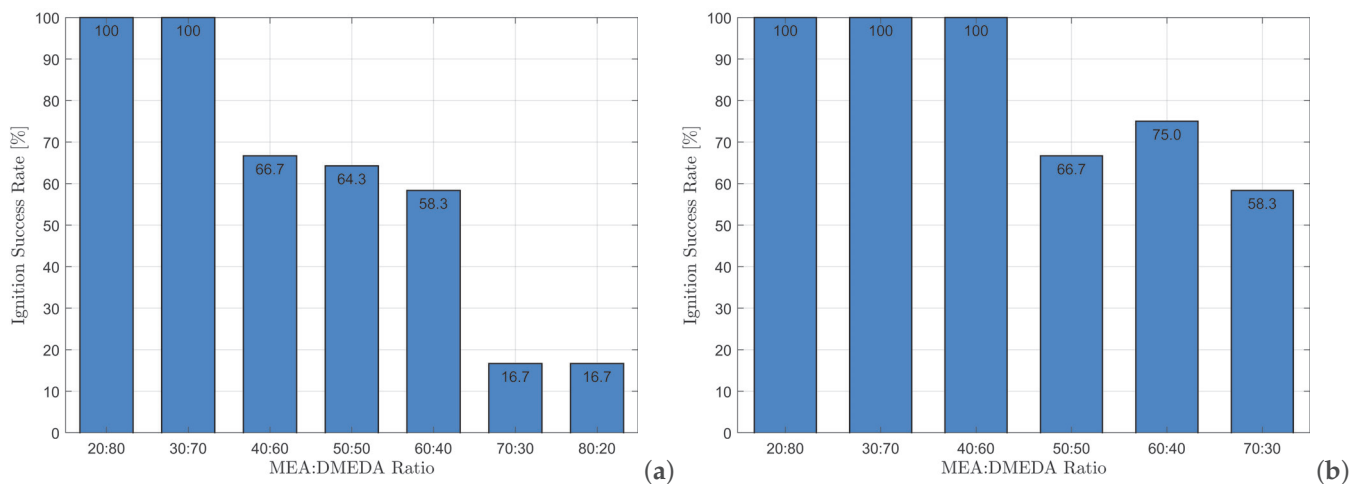

Figure 10. Ignition success rate of MEA-DMEDA blends with 87.5% HTP: (**a**) MEA-DMEDA + CCH 0.5%; (**b**) MEA-DMEDA + CCH 1%. Each formulation was tested 18 times.

Table 14. Effects of increasing DMEDA mass fraction.

Influenced Parameter	Effect
CCH solubility	Reduction
Storage Stability	Reduction
Viscosity	Reduction
Density	Reduction
TVG	Reduction
IDT	Reduction

5.3. Exploratory Tests with Ethanol

The decision to perform exploratory tests investigating the effects of the addition of ethanol was made to address the low solubility issues and further improve the fuel IDT. The results of a preliminary experimental campaign, aiming at evaluating the quality of a fuel formulation stemming from MEA-DMEDA blends, are reported here. Table 15 reports the results of the theoretical rocket performance evaluation. The results show that the addition of ETH results in a negligible variation in the theoretical impulses of the fuels with respect to similar formulations of the second batch (shown for the sake of clarity in parentheses in the same table).

Table 15. Fuels including ETH maximum gravimetric vacuum specific impulse, corresponding O/F, and volumetric specific impulse.

Formulation (MEA:DMEDA)	98% HTP			87.5% HTP		
	$I_{s,vac}$ [s]	O/F	I_v [s·g/cm^3]	$I_{s,vac}$ [s]	O/F	I_v [s·g/cm^3]
30:70 + ETH 10% + CCH 1%	322.6 (322.7)	4.3 (4.4)	412.2 (414.3)	310.3 (310.3)	5.1 (5.2)	389.6 (391.1)
50:50 + ETH 10% + CCH 1%	318.6 (318.3)	4.2 (4.2)	410.6 (411.8)	306.3 (305.9)	4.8 (4.9)	386.4 (387.8)
70:30 + ETH 10% + CCH 1%	314.1 (313.3)	3.9 (3.9)	406.8 (407.9)	301.7 (300.7)	4.6 (4.6)	383.1 (383.7)
80:20 + ETH 10% + CCH 1%	311.6 (310.4)	3.8 (3.8)	405.0 (405.6)	299.1 (297.8)	4.4 (4.4)	380.7 (381.0)

The values from the analogous formulation without ETH are reported in parentheses.

The results of the drop tests are summarized in Table 16, which shows that the effects of ETH addition depend on the formulation considered. In particular, the IDTs worsen for MEA-lean formulations while improving for MEA-rich formulations. This is not unexpected, as the addition of ETH has three consequences on the blend: (i) reduction in reactivity (i.e., the amount of amino functional group decreases in proportion), (ii) reduction in the autoignition temperature, and (iii) reduction in the viscosity. Concerning the third point, no measurements were performed, but it is a reasonable assumption given the properties of the considered substances (as seen in Table 4). These three changes have different effects on the IDT. It can be inferred that only MEA-rich formulations benefit from ETH addition, as a reduction in the AIT of the mixture, outweighing the reactivity reduction, is possible only for MEA-DMEDA ratios higher than 1 (the reader is reminded that $AIT_{DMEDA} < AIT_{ETH} < AIT_{MEA}$). Finally, it is reasonable to assume that the positive effect on IDT of viscosity reduction increases with MEA content. Further tests shall target a parametric analysis of ETH amount to optimize the fuel formulation.

Table 16. Fuels including ETH ignition test results.

Formulation (MEA:DMEDA)	IDT 98% HTP [ms]	
	Avg	Std
30:70 + ETH 10% + CCH 1%	29.1 (21.3)	4.2 (0.7)
50:50 + ETH 10% + CCH 1%	30.3 (30.3)	4.4 (4.7)
70:30 + ETH 10% + CCH 1%	34.2 (37.6)	1.3 (6.2)
80:20 + ETH 10% + CCH 1%	35.5 [*] (n/a)	2.0 [*] (n/a)

The values from the analogous formulation without ETH are reported in parentheses. [*] Unreliable data as fuel sample showed signs of ongoing reaction during testing. No corresponding MEA-DMEDA 80:20 sample was produced without ethanol. Each sample was tested at least three times.

Finally, Figure 11 shows an example of the ignition sequence. As seen already in Figures 7 and 9, the ignition takes place in the vapor phase, which is a common behavior of catalytically promoted fuels [16].
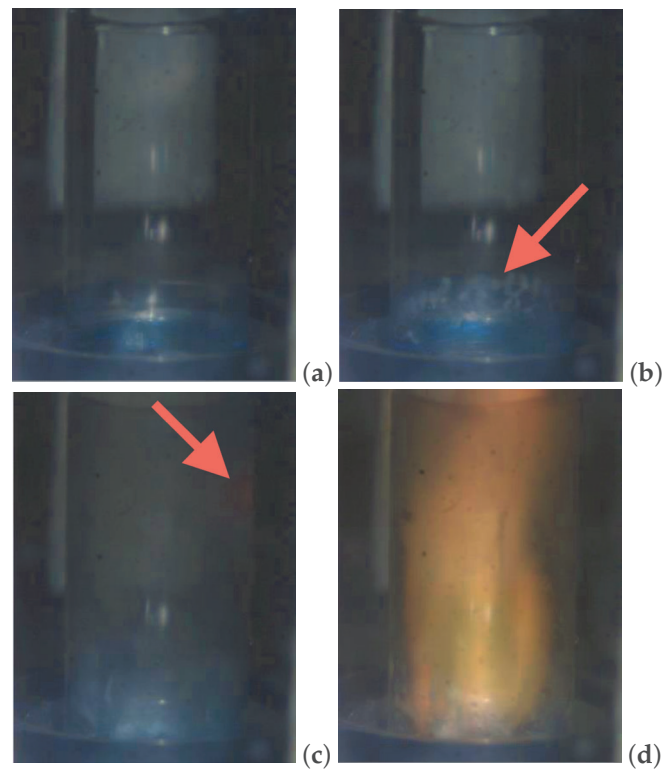
Figure 11. Example ignition sequence of MEA-DMEDA 50:50 + ETH 10% + CCH 1% with 98% HTP: (**a**) $t = 0$ ms, contact; (**b**) $t = 5.5$ ms, first vapor generation; (**c**) $t = 32$ ms, ignition; (**d**) $t = 35.5$ ms, reaction. Red arrows in (**b**) and (**c**) point, respectively, at the vapor cloud and ignition kernel to help locating them in the pictures.

5.4. Summary of Results

Four samples have been selected for a comparison of their theoretical impulses with respect to the conventionally used hypergols considered in Table 2. Each sample was selected within its group according to the smallest IDT. Their properties are summarized in Table 17, while the results are reported in Tables 18 and 19. It can be concluded that, out of the considered samples, only those where MEA is blended are capable of offering similar performances to the conventional hypergols. On the other hand, the volumetric specific impulse performs better than conventional ones, with gains ranging from 2% to 11% with blended formulations leading to higher gains due to higher O/F and specific impulse.

Table 17. Property comparison of the selected samples.

Property	MEA + CN 10 wt%	MEA + CC 5 wt%	M:D 20:80 + CCH 1 wt%	M:D 30:70 + ETH 10 wt% + CCH 1 wt%
TVG (98% HTP) [ms]	3.2	3.7	3.6	n/a
IDT (98% HTP) [ms]	16.3	18.5	18.4	29.1
Density [g/cm^3]	1.07	1.04	0.85	0.86
Viscosity [cSt]	56.74	48.25	5.42	n/a

Density values are theoretical ones. No TVG nor viscosity measurements were carried out for samples with ethanol.

Table 18. Percent difference between the gravimetric vacuum specific impulse of selected fuel samples with 98% HTP and traditional bipropellant couples.

Sample	MEA + CN 10%	MEA + CC 5 wt%	M:D 20:80 + CCH 1 wt%	M:D 30:70 + ETH 10 wt% + CCH 1 wt%
MMH/NTO	−10.5%	−10.3%	−3.6%	−4.2%
UDMH/NTO	−9.7%	−9.4%	−2.7%	−3.3%
UDMH/WFNA	−3.6%	−3.4%	+3.8%	+3.1%

Table 19. Percent difference between the volumetric specific impulse of selected fuel samples with 98% HTP and traditional bipropellant couples.

Sample	MEA + CN 10 wt%	MEA + CC 5 wt%	M:D 20:80 + CCH 1 wt%	M:D 30:70 + ETH 10 wt% + CCH 1 wt%
MMH/NTO	+2.0%	+2.0%	+6.1%	+5.2%
UDMH/NTO	+5.2%	+5.2%	+9.3%	+8.5%
UDMH/WFNA	+6.8%	+6.8%	+11.0%	+10.1%

6. Conclusions

The objective of the present work was to investigate the theoretical performances and the ignition delay time of some novel hypergolic green liquid storable propellant couples. Several monoethanolamine-based fuels have been presented and a parametric study was conducted to evaluate the influence of the type of additives, the additive content, the HTP grade, and the use of ethanol as co-solvent.

The couple monoethanolamine/high test peroxide 98 wt% is characterized by relatively low gravimetric vacuum specific impulse with respect to conventional hypergolic couples (i.e., monomethylhydrazine/dinitrogen tetroxide, unsymmetrical dimethylhydrazine/dinitrogen tetroxide, and unsymmetrical dimethylhydrazine/white fuming nitric acid) while providing a volumetric specific impulse $\approx 2\%$ larger than the one of the best conventional couple. The addition of catalytic additives to achieve hypergolic ignition leads to a further decrease in the gravimetric vacuum specific impulse and an increase in the volumetric specific impulse with respect to the baseline. The fuels (i) monoethanolamine +10 wt% of copper (II) nitrate trihydrate and (ii) monoethanolamine +5 wt% of copper (II) chloride anhydrous ignited, respectively, in 22.4 and 27.3 ms with 87.5% HTP, and in 16.3 and 18.5 ms with 98% HTP. However, the aforementioned fuels are characterized by large kinematic viscosities (39.87 and 48.25 cSt, respectively), thus demanding the study of novel solutions. Therefore, it was decided to investigate the blend of two amines (monoethanolamine and N,N-dimethylethylenediamine) with copper (II) chloride dihydrate. The characterization of these fuels showed a significant increase in the gravimetric vacuum specific impulse with respect to the fuels containing only monoethanolamine and a reduction in the kinematic viscosity (almost always lower than 15 cSt, reaching the minimum value of 2.93 cSt). However, the poor solubility of the catalytic additive in the blend limited the maximum permissible amount of additive to 1 wt%. Hence, some exploratory tests were conducted to investigate the possibility of employing ethanol as a solvent, which is known to not react spontaneously with hydrogen peroxide. The resulting theoretical rocket performances were not affected negatively by its addition. Finally, the drop tests still demonstrated ignition in less than 40 ms, with variations in the ignition delay time found to depend on the MEA-DMEDA ratio.

The discussed mixtures of amines and amines/ethanol in combination with hydrogen peroxide are promising propellant couples characterized by reduced toxicity of both original chemicals and combustion products. However, thorough investigations into the long-term storage stability and methodologies to improve the additive solubility must be performed. Additionally, a parametric analysis of the ethanol content shall be performed to optimize the fuel composition according to the figure of merits and properties considered throughout this paper.

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Abbreviations

The following abbreviations are used in this manuscript:

AIT	Auto-Ignition Temperature
CC	Copper(ii) Chloride Anhydrous
CCH	Copper(ii) Chloride Dihydrate
CEA2	Chemical Equilibrium with Application software
CN	Copper(ii) Nitrate Trihydrate
DEAE	N,N.diethylethanolamine
DMEA	N,N-dimethylethanolamine
DMEDA	N,N-dimethylethylenediamine
ETH	Ethanol
HTP	High Test Peroxide
IDT	Ignition Delay Time
MEA	Monoethanolamine
O/F	Oxidizer-to-Fuel Ratio
TEA	Triethanolamine
TMEDA	N,N,N',N'-tetramethylethylenediamine
TVG	Time-to-Vapor-Generation

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