Hypergolic ignition of amine-based fuels with hydrogen peroxide

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Abstract

The objective of this work is to study promising green combinations given by amine-based fuels and high-test peroxide as oxidizer. To promote the catalytic decomposition of HTP, three cupric salts in combination with ethanolamine were investigated, and the ignition delay time was measured by means of an automated drop test set-up implemented at the Space Propulsion Laboratory of Politecnico di Milano. A blend of two different amines was tested to verify possible performance and fuel thermophysical properties improvement. Interesting ignition delay times were achieved and the exploitation of ethanol to increase the catalytic additives solubility was preliminary evaluated.

1. Introduction

Conventional liquid bipropellant propulsion systems for in-space applications are powered by the hypergolic combination of hydrazine and its derivatives (i.e., monomethylhydrazine, MMH or unsymmetrical dimethyl hydrazine, UDMH) as fuels and dinitrogen tetroxide (NTO) as oxidizer. These couples are characterized by long heritage, high propulsive performance and long-term stability. However, these liquids are difficult to handle in light of their universally cited toxicity. Modern occupational safety standards impose 0.01 ppm of hydrazine as the tolerable threshold limit value for airborne concentration of vapors to which workers can be exposed for 8 h/day [1]. The reason for such a strict limit lies in the carcinogenic nature of hydrazine, which is included in the list of Substances of Very High Concern (SVHC) since 2011 [2]. In fact, although limited statistics of positive exposure-response correlation in humans are available in the open literature, the high evidence in experiments with animals led the IARC Monographs Working Group in 2016 to confirm that hydrazine is probably carcinogenic to humans [3]. Similarly, substitutes to the highly corrosive and toxic oxidizer are sought.

Nowadays, academies, companies and space agencies are extensively studying the so-called green propellants. Several fuels and oxidizers have been reviewed in the open literature to assess their health and environmental hazards, the handling and safety requirements and the resulting performance to properly evaluate their suitability for conventional storable liquid bipropellants replacement [4-8]. Among the oxidizer candidates, high concentration hydrogen peroxide has gained significant attention due to its low toxicity, high density, low vapor pressure, and environmentally safe decomposition products. However, pure substances which exhibit hypergolic behavior with H_2O_2 are scarce [9], leading in the last decades to the development and investigation of different nontoxic fuel blends.
In fact, from the rocket propulsion point of view, a fast, efficient, and spontaneous ignition of a fuel and an oxidizer upon contact is desirable for system robustness and repeatable performance. A hypergolic propellant couple allows multiple and reliable starts of the rocket engine without complex external ignition mechanisms, markedly simplifying system layout and operations [10]. Short ignition delay time may enable shorter (and, hence, lighter) combustion chamber and fast response times [11, 12]. Additionally, by avoiding the accumulation of unburnt fuel and oxidizer in the combustion chamber, hard start phenomena can be avoided [13,14].

The present paper focuses on the theoretical investigation and experimental characterization of ethanolamine-based fuel blends. Specifically, in Section 2 a background is presented. In Section 3 the experimental diagnostic tool and the

theoretical performance computations are discussed. Section 4 presents the experimental campaign aiming at the ignition delay time quantification. In particular, several tests performed on solutions of copper chloride and copper nitrate in amine-based mixtures are presented. Additionally, theoretical performance in terms of gravimetric and volumetric impulse of the selected fuels are discussed, along with an analysis about the combustion products and their environmental impact on selected fuel formulations. The paper closes with conclusions in Section 5.

2. Background

In recent years, hypergolic propellants based on hydrocarbons, amines or alcohols with catalytic or reactive additives have been intensively tested [9-10, 12-18]. The additive is dissolved into the liquid fuels, and it is responsible for initiating the combustion. If upon contact with HTP (high-test peroxide), the additives promote oxidizer decomposition, the fuel blend can be classified as a catalytic fuel. The catalyst upon contact/mixing with HTP promotes the release of a highly reactive form of oxygen and heat, resulting in an ignition once the autoignition temperature (AIT) of the fuel is reached. Hence, in catalytic hypergolic fuels, the ignition is mainly controlled by the HTP decomposition time scales. On the contrary, if the additive vigorously reduces hydrogen peroxide, the high exothermic reaction between the promoter and the oxidizer triggers the ignition. Hence, the fuel blend can be referred to as reactive fuel.

As discussed by Guseinov et al. [9], the most active catalysts for hydrogen peroxide decomposition are some metal oxides and salts that have been mostly reported to be used as solutions in polar solvents, mainly based on alcohols and ketones. Unfortunately, hypergolicity of this kind of catalytic fuels is generally reported to be attained with a large amount of catalyst (>10%), thus lowering the performance in terms of ideal specific impulse and demanding dedicated studies on the long-term stability on storage since the suspended catalyst may precipitate. Propagators, such as substituted or unsubstituted amines, amides, or diamines, have been reported to be added to the formulation to increase the solubility of the catalysts [15,18]. The propagator itself can react with HTP. In fact, according to a screening study performed by Melof and Grubelich [10], the fuels having amino functionalities (i.e., ethanolamine, diethylenetriamine, and ethylenediamine) show vigorous reactions with 90% HTP. As summarized in Table 1, primary amines have been known to vigorously decompose hydrogen peroxide [19]. On the contrary, a different number of organic substituents directly attached to the nitrogen result in a very different reaction with hydrogen peroxide, suggesting the need of additives to achieve hypergolicity.

Table 1: Reactions of Hydrogen Peroxide with Amines [19].

Primary Amines		
$RNH_2 + H_2O_2$	→	Vigorous decomposition of peroxide; reaction difficult to control; no products isolated.
Secondary Amines		
$(R)_2NH + H_2O_2$	→	$(R)_2NOH$ Hydroxylamine
Tertiary Amines		
$(R)_3NH + H_2O_2$	→	R_3NO Amineoxide

Pure ethanolamine (MEA) was proved to attain spontaneous ignition in the presence of 90% hydrogen peroxide without the need for a catalyst, while a fuel blend composed by MEA with a 1 wt% of copper (II) chloride (CuCl₂,) was reported to instantly ignite upon contact with peroxide [10]. Similarly, Ak et al. [20] demonstrated the hypergolic ignition of ethanolamine fuel with 5% to 10% CuCl₂, obtaining in the latter case an ignition delay of 30 ms. Additionally, they reported the sensitivity of ethanolamine mixtures to temperature. Florczuk and Rarata [11] tested a blend composed by 4% copper chloride dihydrate in ethanolamine with 98% HTP, obtaining an average ignition delay time of 37 ms. The major drawbacks of ethanolamine are the high freezing point and viscosity. On the contrary, solvents such as alcohols are cheap, stable on storage and have low freezing points and good combustion performance. Hence, the addition of an alcohol may act as freezing point depressant. Additionally, also the viscosity of the obtained fuel may

be lowered. A mixture of 47.5% furfuryl alcohol, 47.5% ethanolamine, and 5% copper (II) chloride was tested by Melof and Grubelich [5]. The authors reported that a hypergolic ignition was obtained with 70% HTP and that with 90% HTP it provided a much shorter ignition than a mixture comprised solely of ethanolamine and the catalyst. Maschio et al. [21] presented a DoE study aiming at minimizing the ignition delay of a mixture of MEA and ethanol (ETH), catalyzed by copper nitrate trihydrate. In particular, the optimized fuel composed by 61% monoethanolamine, 30% ethanol, and 9% hydrated copper nitrate (weight percent) yielded a minimum ignition delay of 15.7 ms in contact with 90% hydrogen peroxide and was subsequently tested in a 50 N bipropellant engine [22]. Several researchers have been active in the field of hypergolicity studies of amino-based fuels – in both gelled and liquid forms, particularly focusing on new methods to increase performance, stability of the mixture and additive solubility, thus highlighting the strong potentiality of this kind of chemicals [6, 10-11, 13, 16, 20-27].

3. Methodologies

3.1 Drop Test Set-up

The drop test set-up implemented at the Space Propulsion Laboratory (SPLab) of Politecnico di Milano is highlighted in Figure 1 and Figure 2. The ignition delay time is measured by dropping a known quantity of hydrogen peroxide onto a static pool of the fuel, while recording the reaction with a high-speed camera.
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 to load the fuel sample without the need to dismantle the heavy lid of the chamber. An inert atmosphere during the tests, along with the evacuation of the combustion gases after the experiments, can be guaranteed by introducing nitrogen inside the chamber.

The system for high-test peroxide (HTP) supply (2) consists of a linear actuator, connected to the plunger of a syringe. The linear actuator (EyPiNS, 10 cm stroke, maximum speed of 1 cm/s and force of 750 N) is remotely operated to push the plunger of the syringe (Hamilton Company, model 1002 LT SYR), and, hence, to drop a controlled amount of oxidizer into the combustion chamber. Inside the chamber, a glass vial contains the fuel under testing. The oxidizer drop tower is characterized by a manual safety valve, introduced to exclude the oxidizer from the system during the set-up of the experimental test.

The ignition delay is determined through a high-speed imaging technique. Additionally, HTP drops impact and ignition may be recorded also by means of 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 system set up for this purpose is managed through an Arduino Due controller, acting as the interface between the operator and the hardware. The implemented drop test setup is characterized by considerable sensors redundancy and valves ensuring safe operations. In case of electronic components malfunctions leading to continuous oxidizer supply or unwanted pressure raising, the operator can manually operate on the setup restoring nominal operating conditions.

The tests were conducted under ambient operating conditions, i.e., P = 1 atm and T ≈ 20 °C. The amount of fuel used for each run was fixed to 100±5 mg, while the oxidizer drop size was dictated by the selected syringe and hydrogen peroxide concentration (% wt) - see Table 2 for further details.
The high-speed recordings were carried out using a Phantom Camera v710 (ViSiON Research). The recording speed was set to 2000 fps. Several tests were conducted in order to properly evaluate the average IDT and the corresponding standard deviation.

Table 2: Oxidizer droplet size.

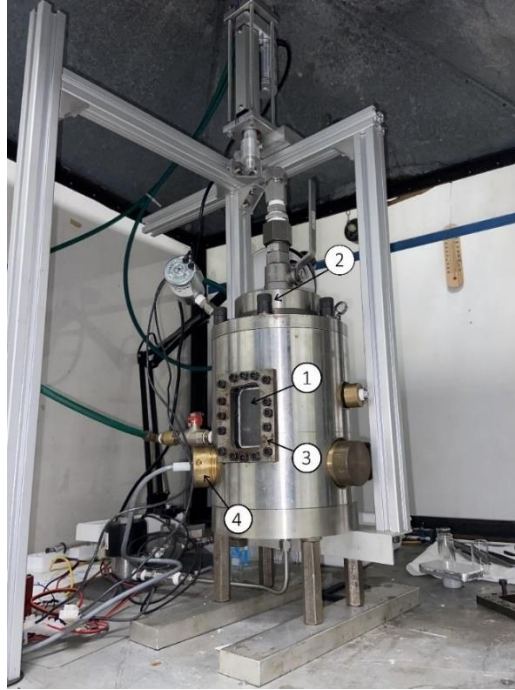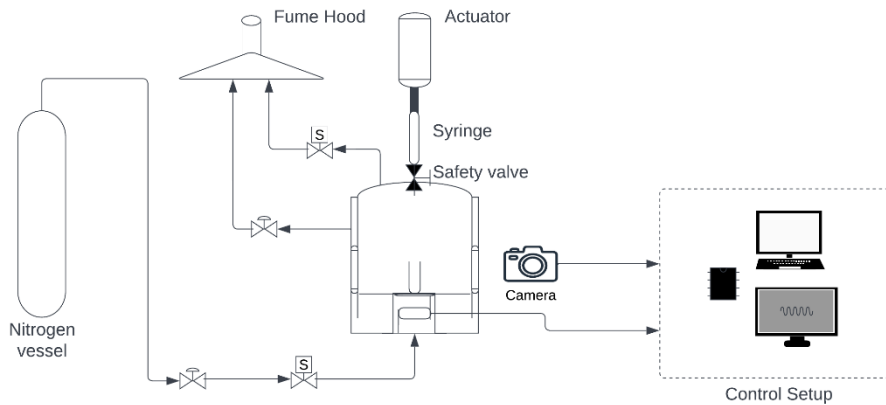| Oxidizer (% wt)	Mass (average) [mg]	Mass (standard deviation) [mg]
HTP 87.5%	63.6	3.4
HTP 98%	67.3	3.5

Figure 1: Drop Test Reaction Chamber.

Figure 2: Drop Test Apparatus Scheme.

3.2 Theoretical Performance

Theoretical rocket performances were estimated with the NASA Chemical Equilibrium with Applications (CEA) tool [28]. In particular, the computations of the vacuum specific impulse ($I_{s,vac}$) were performed for a combustion pressure of 20 bar and flow frozen at throat (simplified Bray model). The expansion ratio ε was set to 100. The figures of merit were evaluated for different oxidizer-to-fuel ratio (O/F), defined as the ratio between the oxidizer and the fuel mass flow rates. The density specific impulse (I_v) was computed considering the theoretical density of the propellant (ρ_{prop}) at the respective O/F:

$$\rho_{prop} = \frac{\rho_{oxidizer} \; x \; \rho_{fuel} \; x \; (O/_F + 1)}{\rho_{oxidizer} + \rho_{fuel} \; x \; (O/_F)} \tag{1}$$

4. Results and Discussion

4.1 Test 1: MEA – Based Fuels

4.1.1 Ingredients

Ethanolamine. Ethanolamine was selected as the baseline fuel for the present hypergolicity study. As discussed in Section 2, several researchers considered its use as hypergolic fuel with HTP. In fact, even though the couple MEA/HTP 98% is characterized by relatively low vacuum specific impulse - as shown in Table 3 -, the density impulse is almost 2% larger than the one provided by the couple MMH/NTO, leading to several advantages in case of volume-restricted applications.

Table 3: Performance values and relative O/F for the relevant propellant combinations.

Propellant	O/F	$I_{s,vac}$ [s]	I_v [s $\cdot$ g/cm^3]	T_c [K]
MMH/NTO	1.8	336.9	391.7	3224.3
UDMH/NTO	2.15	333.6	380	3252.5
UDMH/WFNA	2.8	312.8	374.3	2938.5
MEA/HTP98%	3.6	304.2	398.5	2553.8

Table 4: List of chemical substances used in the fuel manufacture during Test 1.

Name	Producer	CAS	Abbreviation
Monoethanolamine	Thermo Scientific	141-43-5	MEA
Copper II Nitrate trihydrate	Thermo Scientific	10031-43-3	CN
Copper II Chloride anhydrous	Thermo Scientific	7447-39-4	CC
Copper II Chloride dihydrate	Thermo Scientific	10125-13-0	CCH

Table 5: Ethanolamine relevant properties.

Abbreviation	Formula	Molar mass [g/mol]	Freezing Point [°C]	Density [g/cm^3]	Kinematic Viscosity [cSt]
MEA	C_2H_7NO	61.08 [a]	10 [a]	1.012 [a]	28.89 (avg) 0.18 (std) [b]

[a] From Thermo Fischer.

[b] Measured with Schott-KPG-Ubbelohde capillary viscometer

Table 6: Ethanolamine toxicity assessment.

	Hazard Statements	NFPA 704 Fire Diamond	OSHA PEL TWA [ppm]	ACGIH TLV TWA [ppm]	IDLH [ppm]
MEA	H302, H312, H332,[c] H314, H318, H335, H412	[b] 2 / 3 / 0	3 [a]	3 [d]	30 [b]
N_2H_4	H301, H311, H330,[c] H314, H318, H317, H350, H400, H410	[b] 4 / 4 / 3	1 [a]	0.01 [d]	50 [b]

[a] NIOSH, 2022   [d] ACGIH, 2023

[b] Cameo Chemicals

[c] Thermo Fisher

The list of the chemicals employed during the first phase of the activity, named "Test 1" is shown in Table 4, while Table 5 and Table 6 list the most important properties of ethanolamine. 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 by (i) the American Conference of Government Industrial Hygienists (ACGIH), (ii) the Occupational Safety and Health Administration (OSHA) and (iii) 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 Labelling of Chemicals (GHS)" and the health prioritization according to the NFPA 704 of the U.S. National Fire Protection Association (NFPA). MEA shows a significantly decreased acute toxicity with respect to hydrazine and a larger TLV-TWA, even though the difference of the threshold limit values is strongly dependent upon the institute taken as reference for the analysis of the exposure limitations. Additionally, even though MEA is shown to be harmful to aquatic life (H412), 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 reprotoxic) substances, i.e., chemicals having the potential to cause cancer, cell mutation or to affect reproduction and fertility. Hence, MEA can be considered as an appropriate substance for further green propellants studies.

Catalysts. Anhydrous copper chloride ($CuCl_2$), hydrated copper chloride ($CuCl_2 \cdot 2H_2O$) and copper nitrate ($Cu(NO_3)_2 \cdot 3H_2O$) are selected as catalytic additives. The associated hazard statements in the framework of the "Globally Harmonized System of Classification and Labelling of Chemicals (GHS)" are shown in Table 7. Note that the two forms of Copper (II) Chloride are equivalent from the safety assessment point of view. It is clear that relevant environmental hazards are associated to both the catalysts, highlighting the need of precise manufacturing procedures and residuals disposal.

Table 7: Catalysts toxicity assessment.

	Hazard Statements
CC	H302 + H312, H315, H400, H411
CN	H314, H318, H400, H411

4.1.2 Manufacturing Process

The catalytic additives were dissolved in MEA by means of a magnetic stirrer and an ultrasound washer. The stirrer was operated at 700 rpm and at room temperature, followed by 5 minutes of ultrasound washing. No precipitation of solid material for any of the additives and of the fuels concentrations was observed after the mixing process. All the additives are characterized by a high solubility in water, while the solubility in ethanolamine has not been openly discussed. According to Florczuk et al. [11] ethanolamine presents limitation in miscibility with CCH above 4% by weight, while other studies [21] were able to investigate higher concentrations of the additives dissolved in the fuel. Hence, the solubility of the two copper salts was directly determined during the manufacturing of the formulations, leading to a maximum weight concentration of 20% and 10% for CN and for CC, respectively. The fuels were produced between the months of November 2022 and January 2023 and stored at ambient conditions in controlled dry air. Tests were conducted within the months of January and February 2023.

4.1.3 Influence of additives

The ignition delay times of the substances were determined according to the method described in Section 3.1. Example of the ignition sequence is highlighted in Figure 3, while Table 8 lists the most important results in terms of viscosity, time-to-vapour generation (TVG) and IDT resulting from drop tests with 87.5% HTP (PROPULSE®875 by Evonik.). Note that the viscosity was measured with a Schott-KPG-Ubbelohde capillary viscosimeter.

Broadly speaking, CN almost always led to faster ignitions, even though the two additives can be considered providing similar performances. In general, two different trends can be deduced from the measurements. CN-based fuels showed a sharp IDT decrease by increasing the catalyst content from 1% wt to 5% wt, reaching its minimum around the 10% wt fraction. After this point, a slow IDT increase can be observed since the high additive fraction starts to decrease the efficiency of the mixing process due to the high viscosity of the resulting mixture. On the other hand, the CC trend shows a clear minimum for an additive content close to 5% wt. Similarly, to CN-based fuels, the steeper IDT increment observed with CC after the optimal formulation can be directly linked to the viscosity increment, which is larger if compared to CN-based fuel formulations with the same additive content. Among the produced samples, MEA+CN 10% wt and MEA+CC 5% wt were the ones showing the best IDT. However, the former is characterised by a kinematic viscosity 18% higher than the latter. This downside can be avoided by selecting a slightly lower amount of CN. In fact, the MEA+CN 5% wt fuel grants a viscosity 17% lower than MEA+CC 5% wt while still retaining very good IDT.

Considering the specific impulses of the samples of "Test 1", Figure 4 and Figure 5 show the almost identical performances achieved by the two additives. Thus, the choice of the most suitable composition shall be a trade-off between viscosity, IDT and $I_{s,vac}$ and, in more advanced design phases, shall include also rocket sub-system design.

Table 8: Test 1 Campaign results - influence of additives. Drop Tests with 87.5% HTP.

Formulation	TVG avg [ms]	TVG std [ms]	IDT avg [ms]	IDT std [ms]	Kinematic Viscosity [cSt]	
					Avg	Std
CN						
1%	9.8	1.8	91.3	8.2	30.07	0.17
2.5%	6.6	1.0	43.9	6.7	34.07	0.36
5%	5.1	0.6	29.1	2.7	39.87	0.55
10%	3.9	0.4	22.4	2.0	56.74	1.65
20%	4.9	0.6	28.5	4.8	119.14	5.68

CC						
1%	7.0	1.0	56.8	4.8	26.14	0.75
2.5%	5.6	0.9	48.3	7.1	35.09	0.41
5%	3.3	0.3	27.3	1.8	48.25	0.42
10%	4.2	0.5	47.1	6.2	100.71	2.16
CCH						
1%	N/A	N/A	67.3	6.5	N/A	N/A
5%	3.9	0.2	32.1	3.4	N/A	N/A

The minimum number of tests was 12 except for CCH 1% formulation that was tested 5 times.

Additional considerations can be derived from the comparison between the results of CC- and CCH-based fuels. The IDTs of MEA+CCH fuels are larger because the catalyst contains two moles of water per mole of copper which do not participate in the reaction, while, on the contrary, remove part of the heat released by HTP decomposition because of its evaporation. The difference in TVG and IDT of the two forms of Copper (II) Chloride was found to depend on additive concentration. In particular, as shown in Table 8, the smaller the additive amount, the larger the difference in the performances offered by the two forms of Copper (II) Chloride. As shown in Section 4.1.3, a dependence on the HTP grade should also be expected. Note that in general, the decrease of the additives content leads to larger error bars, progressively worsening the ignition performances, thus requiring particular attention when processing the results and paving the way to possible misfirings.
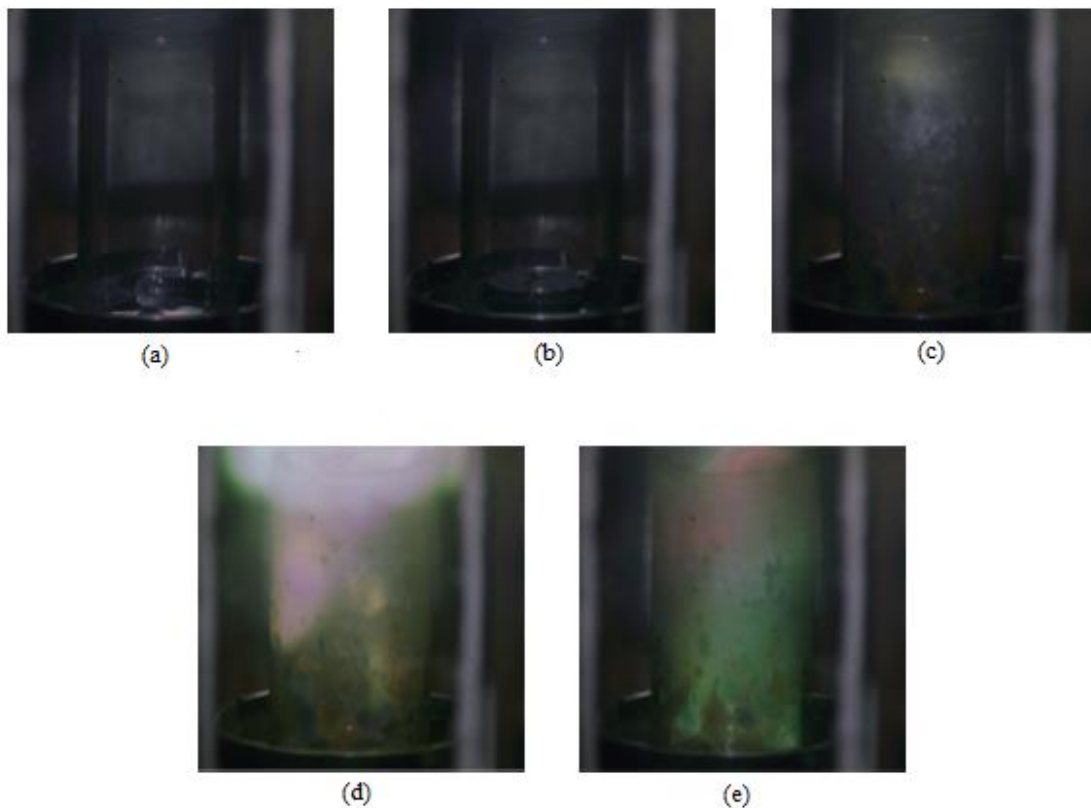

Figure 3: Example of ignition sequence. MEA+CN 10% wt with 87.5% HTP: (a) t = 0 ms contact; (b) t = 4 ms, first vapour generation; (c) t = 23 ms, ignition; (d) t = 24.5 ms, flame kernel enlargement; (e) t = 43.5 ms, reaction.
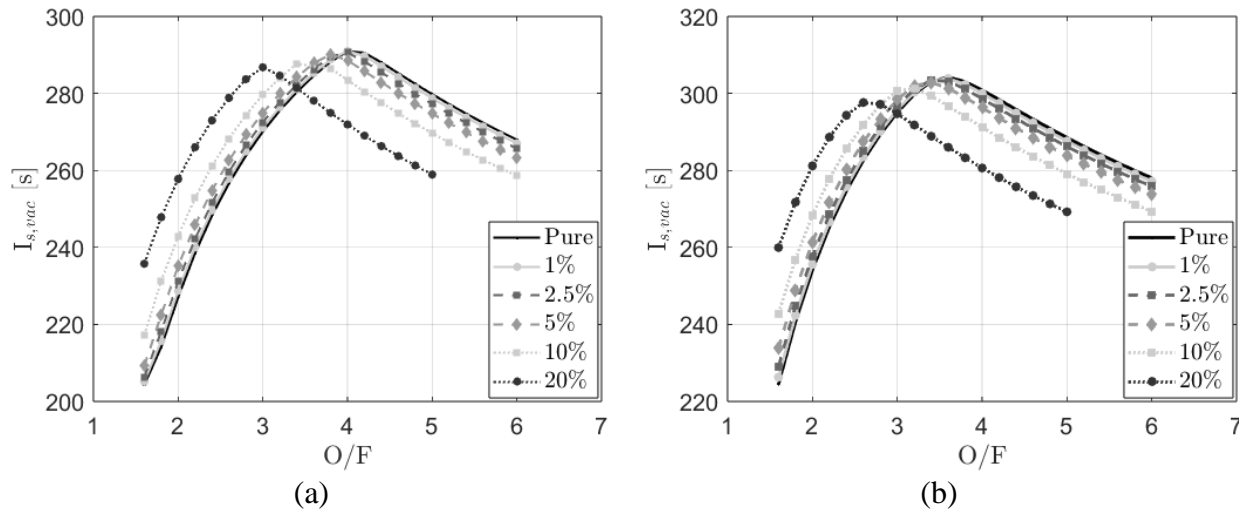
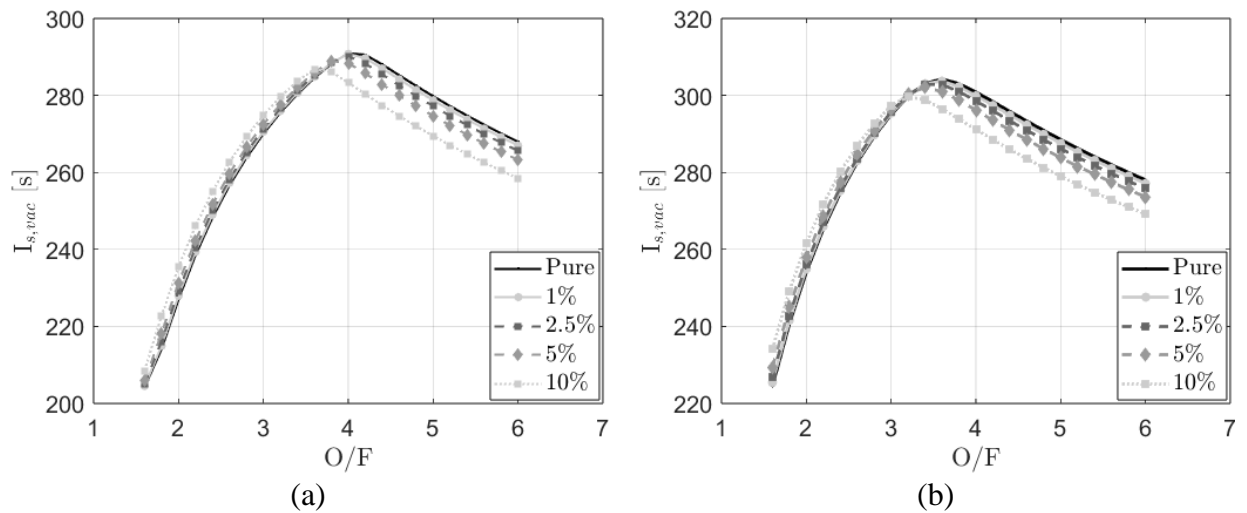Figure 4: Specific impulse of MEA+CN: (a) HTP 87.5% and (b) HTP 98%.

Figure 5: Specific impulse of MEA+CC: (a) HTP 87.5% and (b) HTP 98%.

4.1.3 Influence of HTP grade

The influence of the HTP grade is shown in Figure 6. In particular, 87.5% HTP and 98% HTP (JAKUSZ SpaceTech Sp. z o.o.) were employed as oxidizer. The IDT increases with the decrease of 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 may 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 of the fuel. Broadly speaking, as shown in Figure 6, the IDT-based optimal fuel formulation is almost constant. However, as shown in Figure 4 and Figure 5, the increase of hydrogen peroxide grade moves the optimal O/F (i.e., defined as the O/F providing the larger vacuum specific impulse) towards slightly lower values (i.e., towards an increase of oxidizer mass flow rate for a fixed fuel one). Thus, an increase of the density impulse can be foreseen due to the beneficial effects of larger vacuum specific impulse and propellant density.
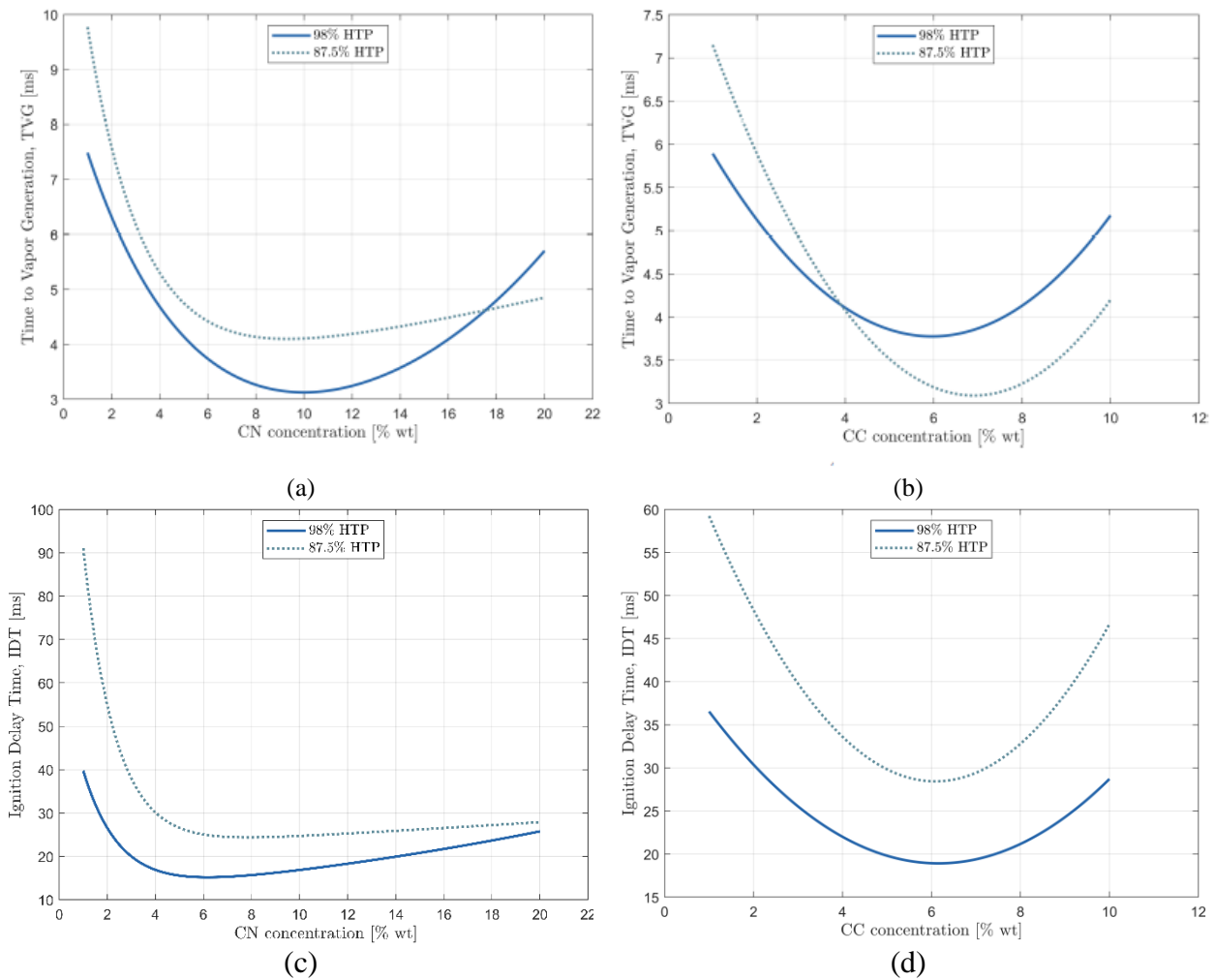
(a)

(b)

(c)

(d)

Figure 6: MEA-based fuel TVG and IDT variation with HTP grade: (a) TVG of CN-based fuels; (b) TVG of CC-based fuels; (c) IDT of CN-based fuels; (b) IDT of CC-based fuels. Note that regression curves resulting from the experimental measurements are shown in the pictures.

4.1.4 Combustion Products

Combustion products were evaluated at optimal oxidizer-to-fuel ratio with the NASA Chemical Equilibrium with Applications (CEA) tool [28]. In particular, the computations were performed for a combustion pressure of 20 bar while the expansion ratio ε was set to 100. The oxidizer taken into consideration is HTP 98% wt. Pure substances and anhydrous additives were assumed in the analysis. The mass fractions of the resulting combustion products at the exit section of the nozzle for additive-rich formulations are listed in Table 9, while Figure 7 shows the behaviour of solid products at different CN %wt. Note that equilibrium conditions were taken into account for this purely theoretical evaluation. In fact, the flow frozen-at-the-throat assumption is relevant for performance computation, while the shifting equilibrium condition may give insight into the theoretical equilibrium chemistry behaviour. Most of the product mass faction is composed by water, carbon dioxide and nitrogen. ($\approx$ 97%), while in general the solid mass fraction is extremely contained (always lower than 2 %). Similar results were obtained for health-concerning products (i.e., carbon monoxide and hydrochloric acid).

Table 9: 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 %	-
CO_2	30.97 %	30.16
H_2	0.05 %	-
H_2O	61.21 %	62.68 %
N_2	5.77 %	4.80 %
Cu (cr)	1.83 %	0.86 %
HCl	-	1.13 %
Other	-	0.37 %
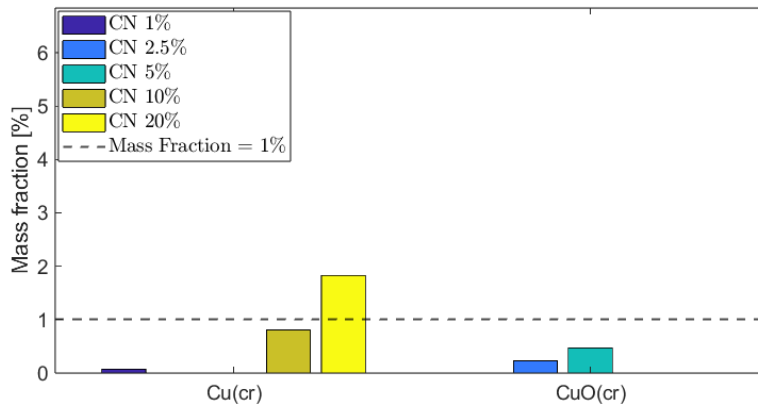
Figure 7: Solid combustion products for CN-based formulations.

4.2 Test 2: Amine 2 – MEA Fuels Blends

Despite the satisfactory results in terms of IDTs, MEA-based fuels are characterised by low specific impulse and high viscosity (see Table 8). A possible solution to the aforementioned drawbacks is the use of different amines and/or the blending of MEA with other substances. Hence, a candidate amine, named now on "Amine 2", was selected and a campaign named "Test 2" was undertaken to evaluate the quality of Amine 2– MEA fuels blends. Note that "Amine 2" is not hypergolic with hydrogen peroxide, and it is characterized by very poor solubility of the additives. In particular, the fuels were produced in the month of January 2023 following the procedure highlighted in Section 4.1.2 and stored at ambient conditions in controlled dry air. Two additive (CCH) contents, as well as different relative concentration between Amine 2 and MEA were investigated. Tests were conducted within the months of January and February 2023 with 98% HTP.

Results of the drop tests are shown in Table 10, Figure 1 and Figure 8. The Amine 2 – MEA Fuels Blends successfully targeted low IDTs and low viscosity values (refer to Table 11). All the produced samples were characterized by a remarkably low kinematic viscosity (< 20 cSt). Moreover, the MEA-lean formulations, i.e. samples in which the MEA fraction in the amine blend was equal to 30%, ignited with 98% HTP in less than 30 ms despite having only 1% wt of

additive. The standard deviations of the measurements, apart from some exceptions, appear to increase with MEA content of the blend.

As shown in Table 10 and Table 11 the additive content has an influence on both the IDT (both the average and the standard deviation values) and the viscosity. Having fixed the additive content (CCH = 1% wt) , the trends showed by TVG and IDT seem to be monotonic, strictly linked to the increase of the viscosity with MEA content, with less viscous formulation igniting faster.
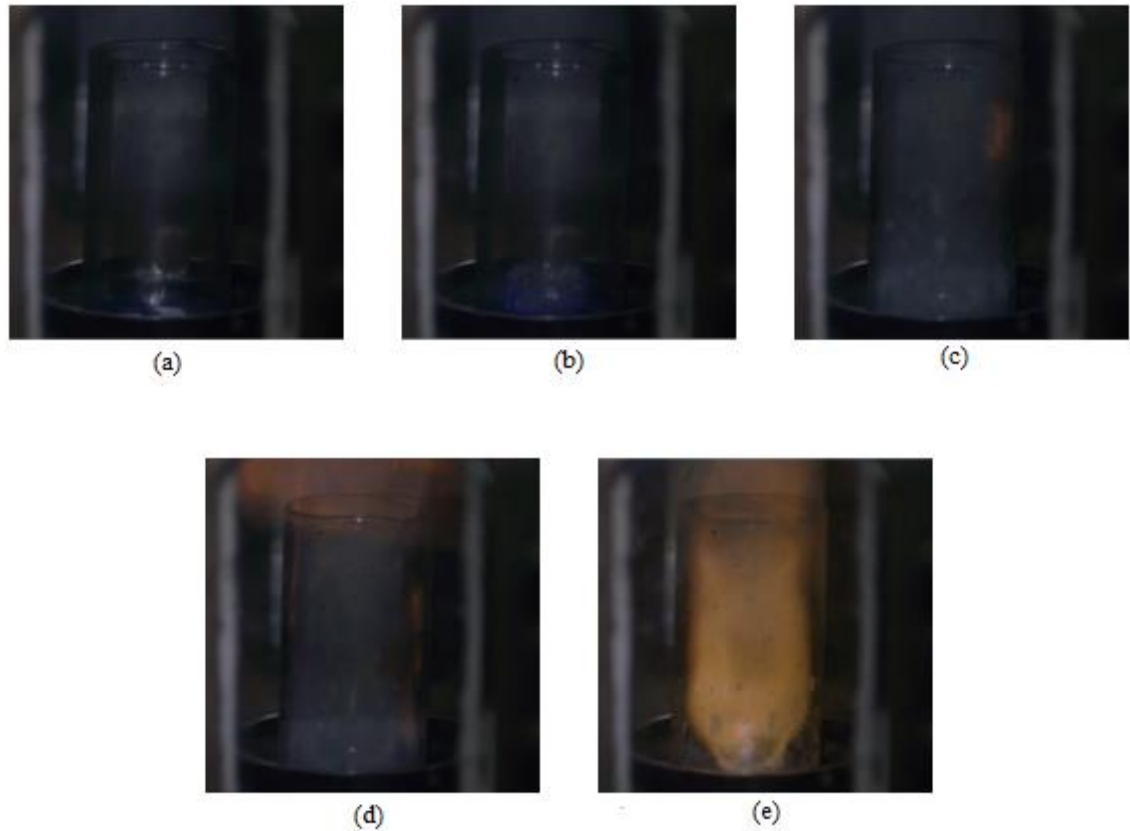
Figure 8: Example of ignition sequence. MEA/Amine 2 + CCH 1% wt with 98% HTP: (a) t = 0 ms contact; (b) t = 3.5 ms, first vapour generation; (c) t = 17 ms, ignition; (d) t = 20 ms, flame kernel enlargement; (e) t = 45.5 ms, reaction.

Table 10: MEA/Amine 2 blends - drop test results with 98% HTP.

MEA/Amine 2 [%wt]	TVG avg [ms]	TVG std [ms]	IDT avg [ms]	IDT std [ms]
1% wt CCH				
30:70	3.7	0.4	21.3	0.7
50:50	5.9	0.9	30.3	4.7
70:30	6.8	1.3	37.6	6.2
0.5% wt CCH				
50:50	6	0.8	37.3	6.3

One of the most critical points of the produced blend is the low solubility of CCH. The additive amount hits the upper limit of 1 %wt because of the impossibility to achieve a homogeneous liquid solution/colloid with higher CCH content. The low solubility issue occurs in particular with MEA-lean formulations, which are the most interesting from the performance viewpoint. The instability of such fuels is related to the fact that the bonding between the two amines competes with the formation of coordination complexes between MEA and Cu (II) ion. In fact, neglecting the amount of Amine 2, the ratio between CCH and MEA is always below 10% wt, which is well within the solubility limit experimentally proved during "Test 1". Hence, further investigations are required to clear this aspect. Despite this, a general improvement of viscosity, IDT and $I_{s,vac}$ (refer to Figure 9) was shown.

Table 11: MEA/Amine 2 blends – kinematic viscosity characterization.

MEA/Amine 2 [%wt]	Viscosity avg [cSt]	Viscosity std [cSt]
1% wt CCH		
30:70	5.71	0.04
50:50	7.29	0.09
70:30	13.49	0.05
0.5% wt CCH		
50:50	5.94	0.03

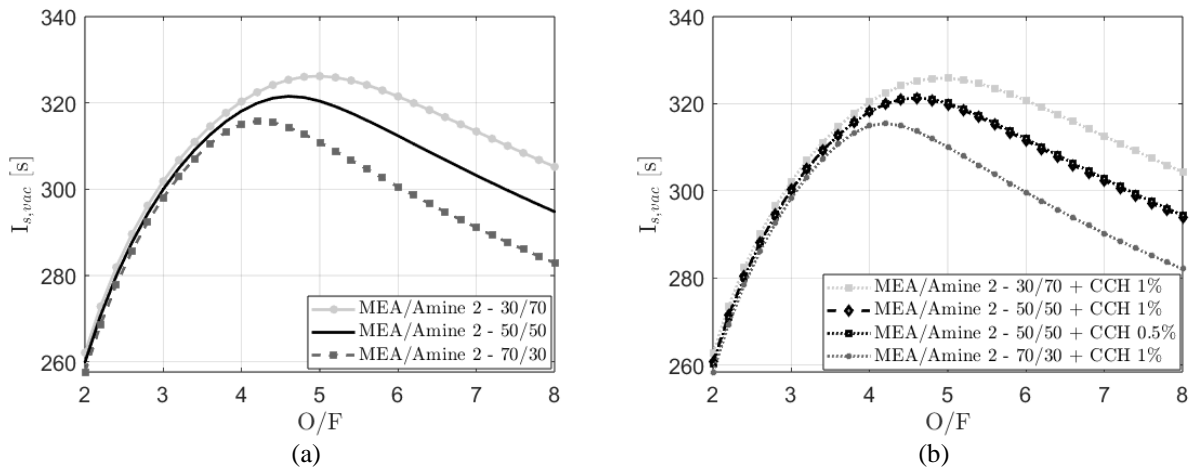Figure 9: Specific impulse of (a) MEA/Amine 2 with HTP 98% and (b) with CCH.

4.3 Test 3: Influence of Ethanol

According to the open literature pure alcohols do not react with hydrogen peroxide and require a large amount of catalyst to achieve fast ignition. However, for example, it has been shown that the addition of ethanol is beneficial from both the viscosity and the IDT point of view, if its content is opportunely tailored [21] – refer to Table 12 for ethanol properties. Additionally, ethanol has the potential of increasing the solubility between the organic fuels and the catalyst, leading to possible IDT improvements and less storage issues, while granting, as shown in Table 13, a green character [22].

The results of a preliminary experimental campaign, named "Test 3", aiming at evaluating the quality of a fuel formulation stemming from "Test 2" are shown in Figure 10 and Figure 11. In particular, the quantity of ethanol

(Alcohol Reagent ACS, 94 to 96%, MilliporeSigma™) and of the catalytic additive (CCH) in the fuel formulations were fixed to 10 %wt and 1 %wt respectively, while varying the proportions between MEA and Amine 2. Additionally, 98% HTP was used as oxidizer. The fuels were produced in the month of June 2023, stored at ambient conditions in controlled dry air and immediately tested.
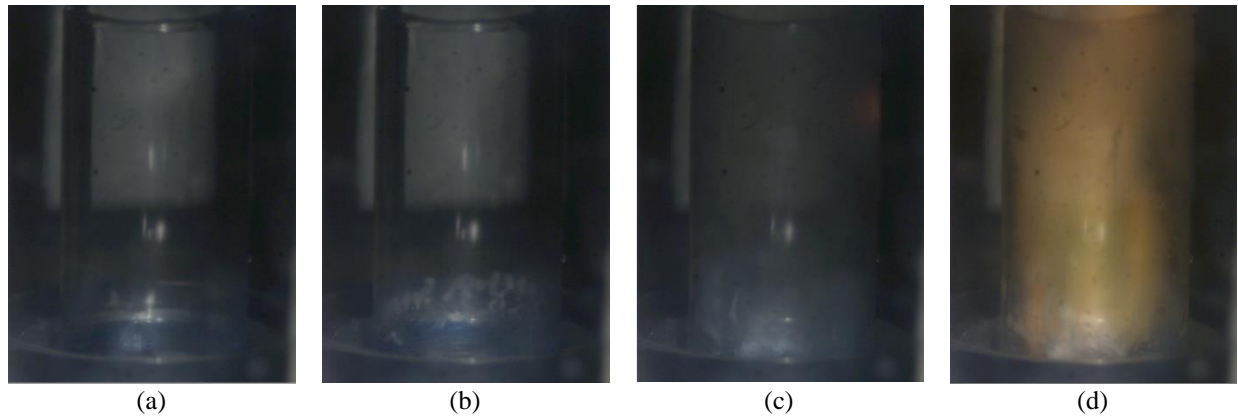

(a)   (b)   (c)   (d)

Figure 10: Example of ignition sequence. Ethanol (10% wt) + MEA/Amine 2 (50:50 % wt)+ CCH 1% wt with 98% HTP: (a) t = 0 ms contact; (b) t = 5.5 ms, first vapour generation; (c) t = 32 ms, ignition; (d) t = 35.5 ms, reaction.
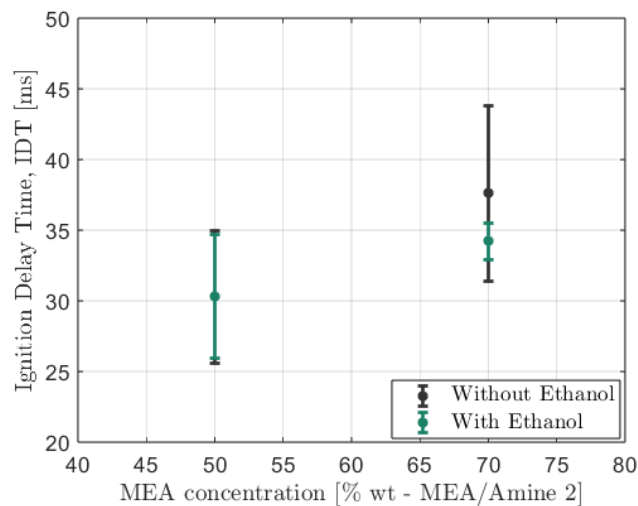

Figure 11: Ethanol (10% wt) influence on the ignition delay time. Drop tests results with 98% HTP and 1 %wt CCH.

Table 12: Ethanol relevant properties.

Abbreviation	Formula	Molar mass [g/mol]	Freezing Point [°C]	Density [g/cm³]	Viscosity [cP]
ETH	C_2H_5OH	46.08	-114.1	0.789	1.074

As shown in Figure 11, the addition of ethanol seems to decrease both the IDT average and standard deviation values for large values of MEA in the original formulation. This aspect is particularly interesting since it is achieved while slightly decreasing the amino functionality amount, hence limiting the reducing agent character of MEA. Further tests shall target a parametric analysis of the ethanol amount to identify its limiting quantity for successful ignition.

Additionally, a slightly larger optimal specific impulse with respect to the formulations without ethanol is highlighted in Figure 1, showing promising results also under the performance point of view.

Table 13: Ethanol toxicity assessment.

Hazard Statements	NFPA 704 Fire Diamond	OSHA PEL TWA [ppm]	ACGIH TLV TWA [ppm]	IDLH [ppm]
H319	(b) [diamond: 3/2/0]	1000 [a]	1000 [d]	3300 [a]

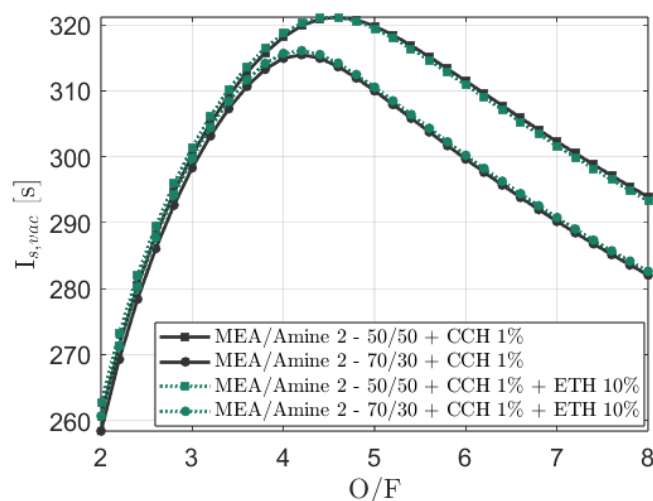[a] NIOSH, 2022   [c] ACGIH, 2023

[b] Cameo Chemicals

Figure 12: Ethanol (10% wt) influence on the vacuum specific impulse.

5. Conclusion

The objective of the present work was to investigate the theoretical performance and the ignition delay time of green liquid storable propellant couples. In particular, several ethanolamine-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 usage of ethanol as solvent.

The couple MEA/HTP 98% is characterized by relatively low vacuum specific impulse with respect to reference propellants, such as MMH/NTO, UDMH/NTO and UDMH/WFNA, while providing a density impulse 2% larger than the one provided by the couple MMH/NTO. The addition of catalytic additives to achieve hypergolic ignition leads to a further decrease of the vacuum specific impulse and an increase of the density impulse with respect to the ideal case. The ethanolamine + 10% wt copper II nitrate trihydrate and ethanolamine + 5% wt copper II chloride anhydrous couples led to ignition delay times with 87.5% wt hydrogen peroxide of 16.4 and 27.3 ms, respectively. These results can be furtherly decreased employing 98% HTP. However, the aforementioned fuels are characterized by large kinematic viscosities (39.87 cSt for the former and 48.25 cSt for the latter), thus demanding the study of novel solutions. Hence, a novel mixture of amines (ethanolamine and "Amine 2") along with 1% wt of copper II chloride dihydrate was proposed, leading to a significant increase of the vacuum specific impulse with respect to the MEA-case and a

dramatic decrease of the measured kinematic viscosity (down to 5.71 cSt), while providing acceptable ignition delay times (< 40 ms). However, the poor solubility of the catalytic additive in the blend limits the maximum permissible amount of CCH to 1% wt. Hence, some preliminary tests were conducted to investigate the possibility to employ ethanol as a solvent. In particular, the resulting theoretical performance were almost unaffected by the addition of the alcohol, which is known to not react spontaneously with hydrogen peroxide. Similarly, the drop test experimental tests still provided IDTs lower than 40 ms.

The discussed mixtures of amines and amines and ethanol in combination with hydrogen peroxide are promising propellant couples characterized by reduced toxicity - of both original chemicals and combustion products. However, the long-term storage shall be thoroughly investigated as well as methodologies to improve the additive solubility or at least ensure the stability of the solvent-solute bindings of formulations characterized by additive contents larger than the limiting ones. Chemical characterizations of the selected mixtures may aid in the development of such formulations, targeting the use of such fuels in real applications.

Acknowledgements

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