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Hypergolic ignition behaviors of green propellants with hydrogen peroxide: The TMEDA/DMEA system

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ABSTRACT

For nearly-six decades, hydrazine and its derivatives have been the standard fuels for rockets and spacecrafts. However, their attractive features are offset by their toxicity and associated high handling and storage costs. This work presents a novel green fuel system based on N,N,N'N'-Tetramethylethylenediamine (TMEDA), dimethylaminoethanol (DMEA) and methanol or ethanol with high test peroxide (HTP). Drop tests were performed with 27 samples using both high speed photography and transient infrared imaging. Results have shown that neither pure TMEDA nor pure DMEA is hypergolic with high test peroxide (HTP) even with copper chloride (anhydrous or hydrated) as the catalyst. Interestingly, their combination provided a synergistic effect achieving hypergolic behavior with a consistently low ignition delay time (IDT) using only half a percent of catalyst, and the near-optimal hypergolic ignition behavior was achieved with a volume ratio of TMEDA to DMEA of 50:50. In addition, in order to adjust some properties of this blend, TMEDA/DMEA (50:50) was further mixed with methanol or ethanol with different ratios and they showed even better hypergolic ignition performance with IDT as low as 10 ms. Besides their good hypergolic ignition performance characteristics, these new fuel systems based on two propagators (TMEDA/DMEA) and a solvent (methanol or ethanol) also present low viscosity and comparable theoretical specific impulses compared to the conventional hydrazine-based systems. It is believed that this catalytically promoted hypergolic systems with HTP open up a new avenue to the replacement of conventional highly toxic hypergolic propellants.

1. Introduction

Hydrazine and its derivatives have been used as propellants in rockets and spacecrafts since the 1960s [1]. For monopropellant systems hydrazine is catalytically or thermally decomposed and for bipropellant systems monomethylhydrazine (MMH) or unsymmetrical dimethylhydrazine (UDMH) form hypergolic systems with nitrogen tetroxide (NTO). In other words, the propulsion system does not require an igniter to start the engine, increasing reliability, which is of paramount importance for space missions. However, hydrazine based propellants are highly toxic and carcinogenic, making testing, handling and launch preparation complex and expensive. In recent years NASA and ESA are considering the restriction or even prohibition in the use of hydrazine in the mid-term, thus a demand for propulsion units operating with eco-friendly propellants has emerged [2]. From then on, extensive studies on green propellants technology have spread all over the world.

1.1. Hypergolic hydrogen peroxide with promoted liquid fuels

Among the propellants under research, the use of highly concentrated hydrogen peroxide with a promoted fuel is a potential hypergolic alternative. Hydrogen peroxide is available in different concentrations with water, but concentrations higher than 70 % are required for use as a propellant [3]. HTP was first used by the German army during World War II both as monopropellant and as a hypergolic combination with a promoted toxic fuel called C-Stoff (mixture of methanol, hydrazine, water and a catalyst) [1]. As monopropellant, HTP is still in use today by the Russian manned spacecraft Soyuz [4], for example. Compared to nitrogen tetroxide (NTO) or nitric acid (HNO_3), H_2O_2 produces less O_2/mol of oxidizer (1 mol of H_2O_2 yields only 0.5 mol of O_2), resulting in a significant increase in the oxidizer to fuel ratio (O/F) as we can see in the following reactions [5,6]

Developed by	Oxidizer	Fuel		
		Ionic Liquid	**Solvent**	**Promoter**
USA (AFRL) [19]	H_2O_2	[THTDP] $[Al(BH_4)_4]$	-	-
China (XJTU/NWPU/ CAEP/HIT) [20-25]	H_2O_2	[EMIM][BH_3CN] [EMIM][BH_3CN] [EMIM][BH_3CN] [BMIM][DCA] [IM based][cyano (1H-1,2,3-triazole-1-yl) dihydroborate]	- - - - -	[Ferrocenyl-based][$B_{12}I_{12}$] (8wt%) [EMIM][Cu_xI_y] (10 wt%) [Ferrocenyl-based][Cu_xI_y] (10 wt%) [Ferrocenyl-based][Cu_xI_y] (10 wt%) Iodine (15 wt%)
Germany (DLR) [26-30]	H_2O_2	[BMIM] [Ac] [BMIM][SCN] [EMIM][SCN]	EtOH (10-20 wt%) - -	MAT (8-9 wt%) CuSCN (5 wt%) CuSCN (5 wt%)
South Korea (KAIST) [31,32]	H_2O_2	[EMIM][BH_4] [EMIM][BH_3CN] [EMIM][BH_3CN] [EMIM][BH_3CN] [EMIM][BH_3CN]	- Furfuryl alcohol ($\sim$ 45 wt%) - - -	MIMB (0-50 wt%) NaI (5-11 wt%) $CuCl_2$ (5 wt%) $NaBH_4$ (5 wt%) [diMIM]$_n$[Cu_2I_3]$_n$ (2-15 wt%)

Fig. 1. List of major countries (USA [19], China [20-25], Germany [26-30], South Korea [31,32]) developing green propellants based on H_2O_2 and ionic liquid. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
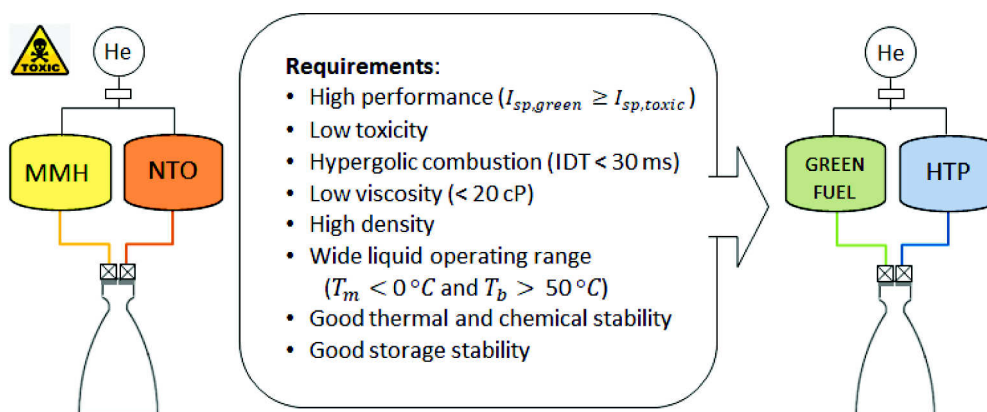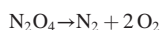

Fig. 2. Main requirements for quafilication as a promising green propellant. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1

Chemical structures and physicochemical properties of TMEDA and DMEA: melting point (T_m), boiling point (T_b) density at 25 °C (ρ), viscosity at 25 °C (μ) and enthalpy of formation (Δh_f).

		T_m [°C]	T_b [°C]	Δh_f [kJ/mol]	ρ [kg/m^3]	μ [cP]
TMEDA		−58.6 °C	121.1 °C	−19.7	776	0.9 (Ref. [36])
DMEA		−59.0 °C	134.1 °C	−253.7	890	3.24

$$HNO_3 \rightarrow 0.5\,H_2O + 0.5\,N_2 + 1.25\,O_2$$

$$N_2O_4 \rightarrow N_2 + 2\,O_2$$

$$H_2O_2 \rightarrow H_2O + 0.5\,O_2$$

As these oxidizers have substantially higher densities than their fuels combination, higher density specific impulse (ρI_{sp}) is achieved for a given fuel.

In the mid 1990s, the U.S. Air Force and U.S. Navy began to study hydrogen peroxide based hypergolic green propellants. A new class of non-toxic fuels, the Non-Toxic Homogenous Miscible Fuel (NHMF), was identified [7]. The NHMF contains 3 species, a polar organic compound (alcohol or ketone) miscible with hydrogen peroxide, a propagator (amine or amide) and an inorganic metal salt which react to form a
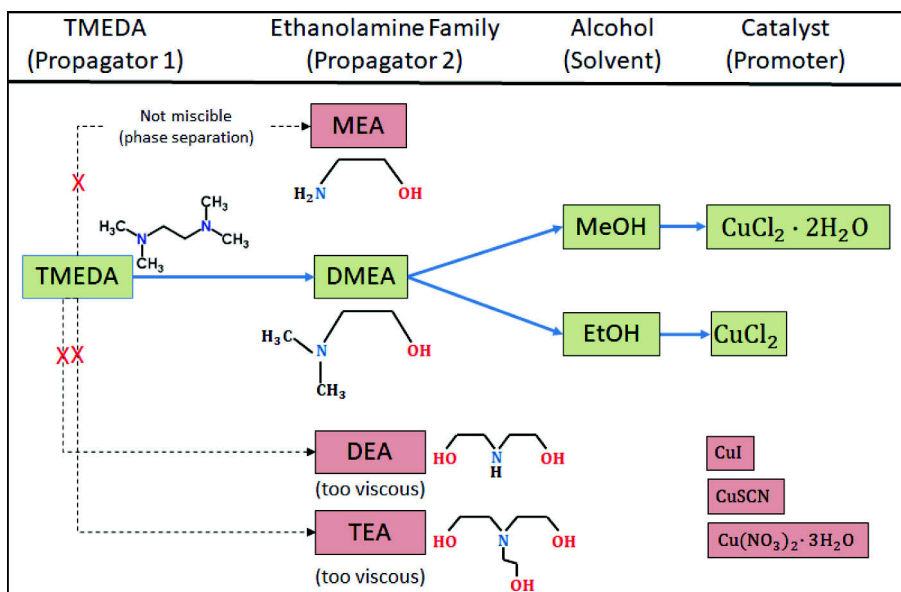
Fig. 3. Scheme of the screening procedure to select the potential fuels. The chosen compounds are in green and in red are the discarded ones. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2
Identification of fuel samples with a near-optimum amount of catalyst. The parameters used to calculate I_{sp} were the same used in Section 3.3.

| Fuel name	Volume Ratio	Additive	Hypergolicity	I_{sp} [s]
TMEDA	–	0.5 wt% CuCl$_2$·2H$_2$O	No ignition	354.5
DMEA	–	0.5 wt% CuCl$_2$·2H$_2$O	No ignition	348.6
MeOH	–	(0.5–5) wt% CuCl$_2$·2H$_2$O	No ignition	337.8
EtOH	–	(0.5–5) wt% CuCl$_2$·2H$_2$O	No ignition	343.4
System 1: TMEDA: DMEA				
FS1.1	(90:10)	0.5 wt% CuCl$_2$·2H$_2$O	No ignition	353.3
FS1.2	(80:20)	0.5 wt% CuCl$_2$·2H$_2$O	No ignition	353.0
FS1.3	(67:33)	0.5 wt% CuCl$_2$·2H$_2$O	Yes	352.3
FS1.4	(60:40)	0.5 wt% CuCl$_2$·2H$_2$O	Yes	352.0
FS1.5	(50:50)	0.5 wt% CuCl$_2$·2H$_2$O	Yes	351.4
FS1.6	(33:67)	0.5 wt% CuCl$_2$·2H$_2$O	Yes	350.5
FS1.7	(25:75)	0.5 wt% CuCl$_2$·2H$_2$O	Yes	350.1
FS1.8	(20:80)	0.5 wt% CuCl$_2$·2H$_2$O	Yes	349.6
FS1.9	(10:90)	0.5 wt% CuCl$_2$·2H$_2$O	No ignition	349.0
System 2: TMEDA: DMEA (FS1.5) + MeOH				
FS2.1	(45:45:10)	1 wt% CuCl$_2$·2H$_2$O	Yes	350.7
FS2.2	(40:40:20)	1 wt% CuCl$_2$·2H$_2$O	Yes	349.7
FS2.3	(1:1:1)	1 wt% CuCl$_2$·2H$_2$O	Yes	348.2
FS2.4	(25:25:50)	1 wt% CuCl$_2$·2H$_2$O	Yes	346.3
System 3: TMEDA: DMEA (FS1.5) + EtOH				
FS3.1	(45:45:10)	1 wt% CuCl$_2$	Yes	350.8
FS3.2	(40:40:20)	1 wt% CuCl$_2$	Yes	350.2
FS3.3	(1:1:1)	1 wt% CuCl$_2$	Yes	349.0
FS3.4	(25:25:50)	1 wt% CuCl$_2$	Yes	347.8
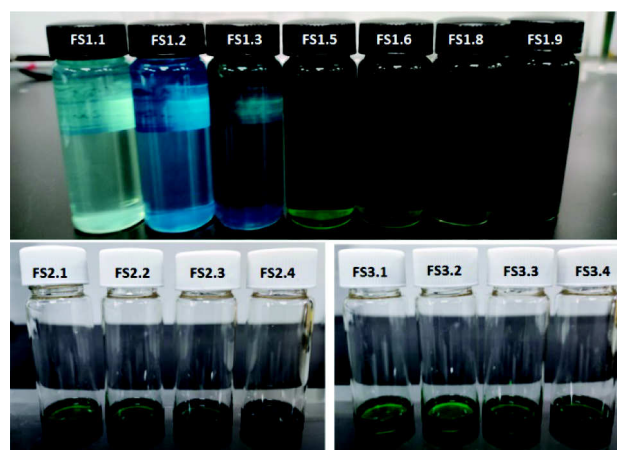
Fig. 4. Samples stored in vials filled with nitrogen.
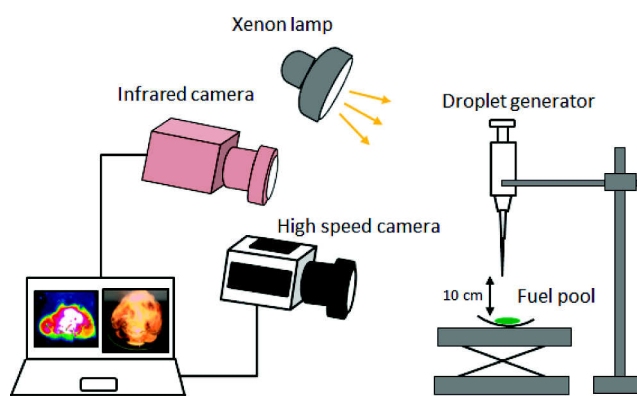

Fig. 5. Scheme of the drop test setup.

catalyst in solution or a colloid. In another U.S. patent [8], Amos Diede reported a new class of reduced toxicity hypergolic fuels by introducing reactive promoted fuels by using a strong reducing agent instead of the
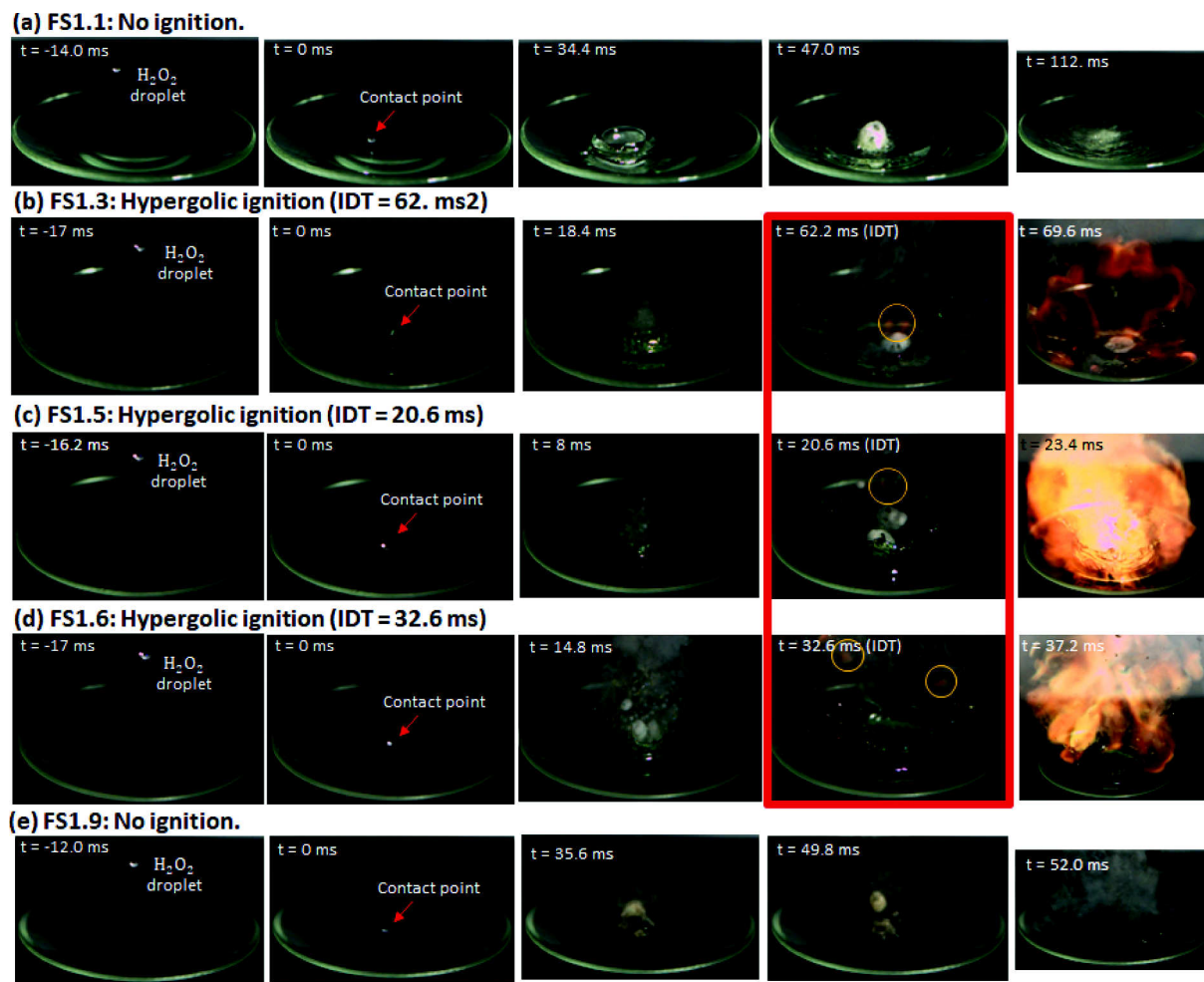
(a) FS1.1: No ignition.

(b) FS1.3: Hypergolic ignition (IDT = 62. ms2)

(c) FS1.5: Hypergolic ignition (IDT = 20.6 ms)

(d) FS1.6: Hypergolic ignition (IDT = 32.6 ms)

(e) FS1.9: No ignition.

Fig. 6. Drop test process for TMEDA/DMEA (System 1) with 98% hydrogen peroxide in drop tests.

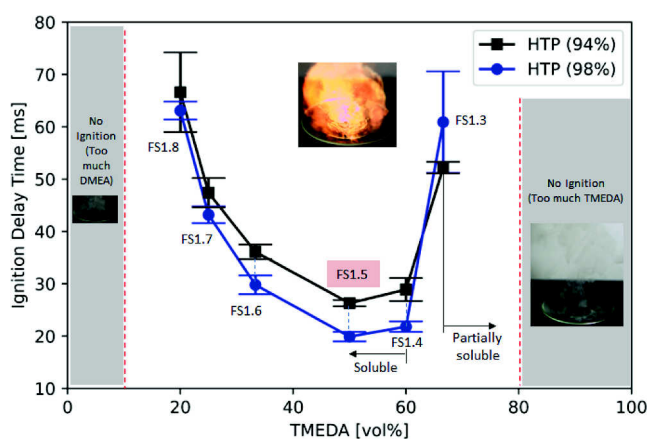**Fig. 7.** Ignition delay time for different proportions of the system TMEDA/DMEA using 0.5 wt% $CuCl_2 \cdot 2H_2O$ (FS1) with 94% and 98% hydrogen peroxide.

traditional catalytic fuels. The reactive promoted fuels are prepared by mixing a strong reducing agent with a base fuel. Sodium borohydride ($NaBH_4$) is the most preferred reducing agent but thiosulfate, thiocyanate and cyanides are also promising alternatives. Typical solvents (fuels) include triglyme, diglyme, dimethylaminoethylazide (DMAZ) and diethylenetriamine (DETA). Such fuels exhibit substantially different pre-ignition mechanisms than catalytically promoted ones.

Since then, hypergolic HTP with blends of reactive fuels are extensively studied at many universities and research institutes around the world [9–14].

Using sodium borohydride as a reactive promoter, Kwon and co-wokers from KAIST (Korea Advanced Institute of Science and Technology) developed enhanced reactive fuels by using more energetic solvents and applying them into a 500 N scale hypergolic bipropellant thruster with 90 % hydrogen peroxide. The reactive fuels are called Stock 0 (tetraglyme/$NaBH_4$), Stock 1 (tetraglyme/tetrahydrofuran/$NaBH_4$), Stock 2 (tetraglyme/tetrahydrofuran/toluene/$NaBH_4$) and Stock 3 (DETA/tetrahydrofuran/$NaBH_4$) [11–14].

Cong and co-workers from Dalian Institute of Chemical Physics selected promising candidates (catalysts and organic additives) to make kerosene hypergolic with high-concentration hydrogen peroxide. Hot tests in both steady-state and pulse-mode operations showed low ignition time and good performance [15]. Kerosene and liquid hydrogen (LH2) are the standard fuels for launch vehicles because they have good performance when burned with cryogenic liquid oxygen (LOX). However, kerosene has lower performance compared to many amines and other organic fuels when hydrogen peroxide is the oxidizer.

Investigators from Brazilian National Institute for Space Research (INPE) [16,17] studied hydrogen peroxide with a fuel mixture containing ethanol and ethanolamine with different transition metal catalysts. Through this study, it was concluded that the lowest ignition delay values were obtained using a fuel containing about 61.0 % ethanolamine, 30.1 % ethanol and 8.9 % by weight of hydrated copper nitrate ($Cu(NO_3)_2 \cdot 3H_2O$). In support of the drop test, tests were performed with
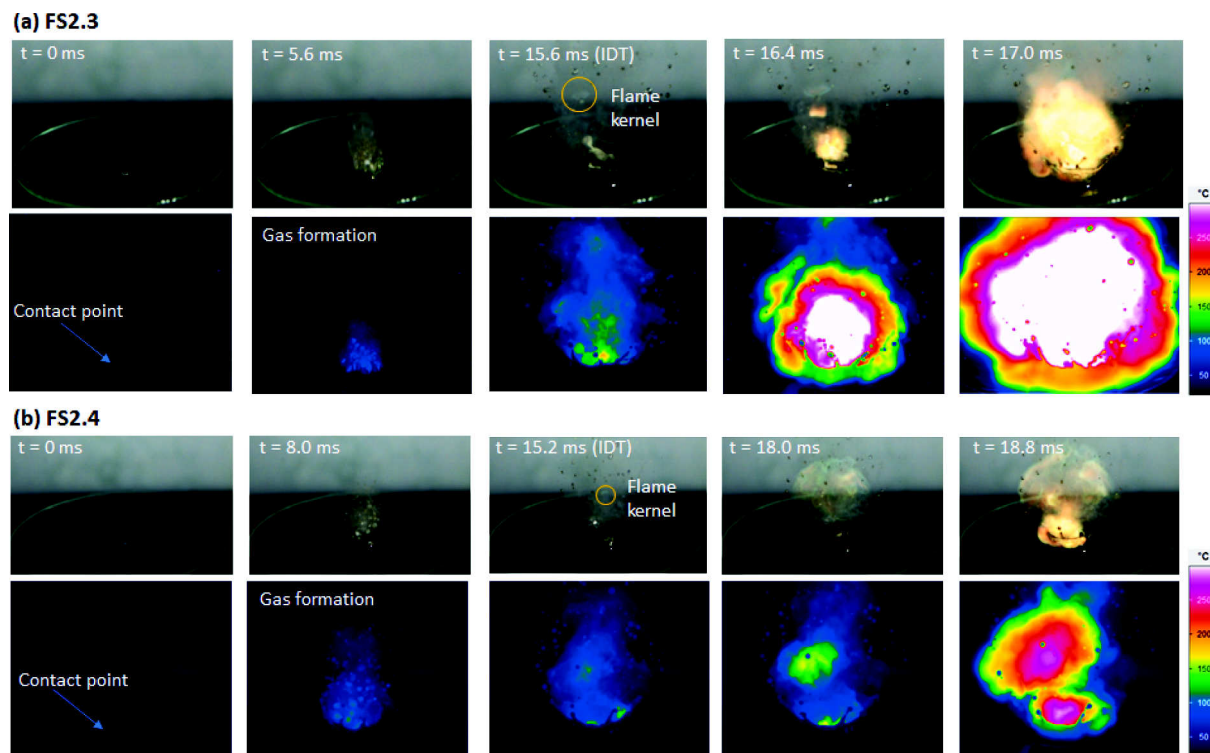
Fig. 8. Images of hypergolic ignition process for different proportions of MeOH in TMEDA/DMEA (samples FS2.3 and FS2.4) using 1 wt% CuCl$_2$·2H$_2$O with 98% hydrogen peroxide captured by High Speed Camera (Phantom v2012) and Infrared Camera (ImageIR). Note that the images are note precisely matched due to differences in frame speeds of both cameras.
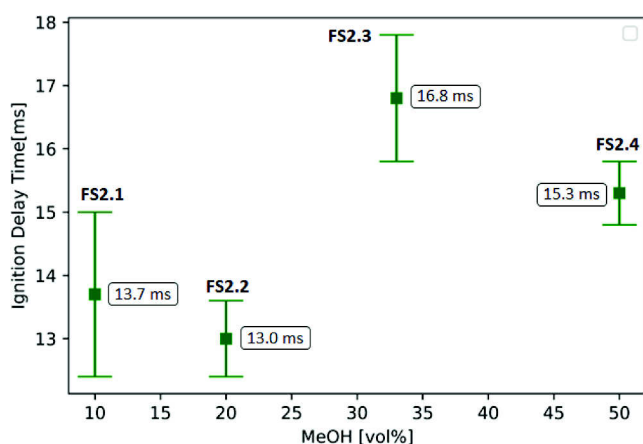

Fig. 9. Ignition delay time for different proportions of MeOH in TMEDA/DMEA (sample FS1.5) using 1 wt% CuCl$_2$·2H$_2$O with 98% hydrogen peroxide.

Fig. 10. Influence of anhydrous copper chloride concentration on IDT of TMEDA/DMEA/MeOH (1:1:1) with 95% HTP.

injectors of the impinging jet type which revealed ignition delays in the order of 12.5 ms. A green plume was demonstrated with a hot test in a 50 N thruster. Although ethanolamine shows good reactivity with HTP, it presents a relatively low specific impulse.

1.2. Hypergolic HTP with ionic liquids

A prospective new group of green fuels are room temperature ionic liquids (ILs). The most accepted definition of ILs are salts with a melting point below 100 °C that can be liquid at room temperature [18]. As potential fuel candidate, the meting point should be no more than 0 °C. In general, ILs have a very low vapor pressure (1 Pa) at ambient conditions due to their ionic composition. Another great advantage is the designability of these compounds and the variation of their physical
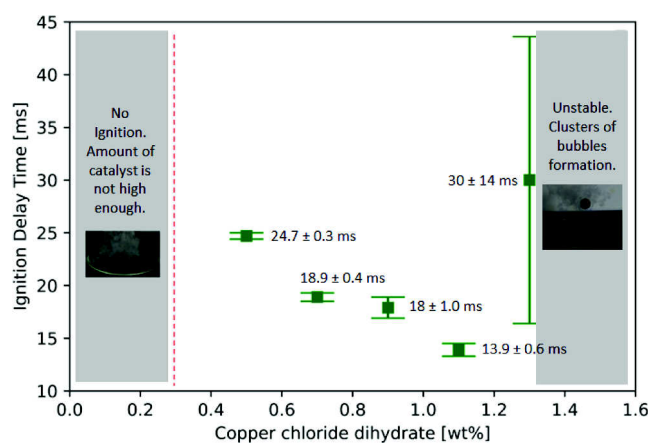
properties according to the specific requirement of their application. However, they suffer from some drawbacks such as low specific impulse, high viscosity, high cost and incomplete combustion, which limits their practical application. Nevertheless, interesting works have being currently carried out in the U.S. AFRL, German Aerospace Center (DLR), KAIST in South Korea and by many universities (e.g., Xi'an Jiaotong University) and research institutes (Chinese Academy of Sciences and China Academy of Engineering Physics) in China (see Fig. 1). It can be noted that only in DLR and KAIST organic solvents were used in order to improve solubility and decrease viscosity. In most of Chinese Universities and research institutes the focus seems to be on the development of a novel promoter which could potentially reduce the ignition delay time [20–25]. Instead of HTP, nitric acid has also been widely used with ionic liquids [33,34].
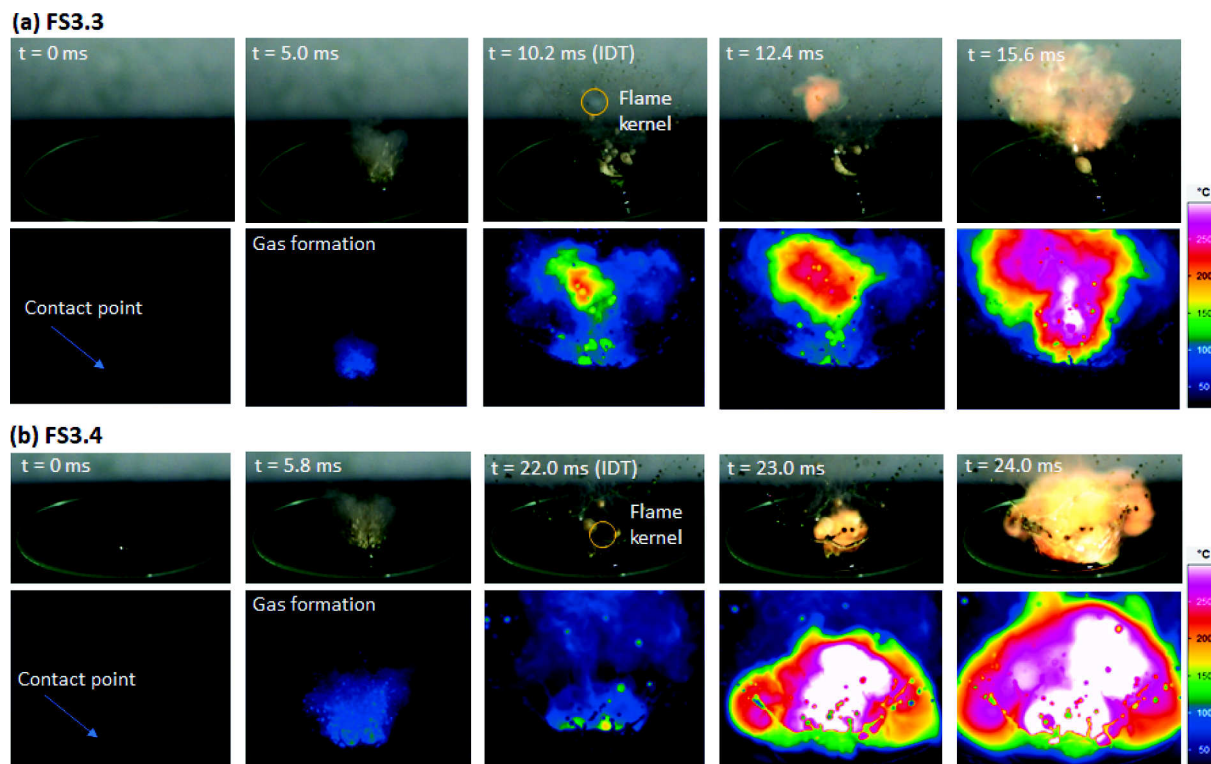
Fig. 11. Images of hypergolic ignition process for different proportions of EtOH in TMEDA/DMEA (samples FS3.3 and FS3.4) using 1 wt% CuCl$_2$ with 98% hydrogen peroxide captured by High Speed Camera (Phantom v2012) and Infrared Camera (ImageIR). Note that the images are note precisely matched due to differences in frame speeds of both cameras.
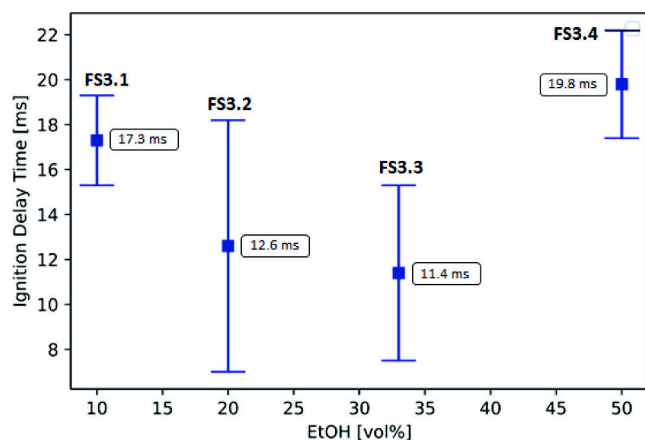

Fig. 12. Ignition delay time for different proportions of EtOH in TMEDA/DMEA(sample FS1.5) using 1 wt% CuCl$_2$ with 98% hydrogen peroxide.

Fig. 13. Viscosity and density for different proportions of the system TMEDA/DMEA using 0.5 wt% CuCl$_2$·2H$_2$O.

1.3. Objective

The purpose of this research is the development of hypergolic green propellants using concentrated hydrogen peroxide (70–98 wt%) as oxidizer and promoted green fuels for near-future rocket and spacecraft applications. For a potential practical application, the propellants should fulfil several requirements such as low ignition delay time (IDT <30 ms), low viscosity (<20 cP), wide liquid range and performance comparable to the conventional hypergolic toxic state-of-the-art MMH/NTO as shown in Fig. 2.

2. Experimental methodology

A screening procedure was performed to select the most promising fuels and additives candidates.

2.1. Fuels and additives candidates

2.1.1. Propagator: TMEDA/DMEA

Among various amines, N,N,N'N'-Tetramethylethylenediamine (TMEDA) is considered a promising candidate [34–37]. However, TMEDA has been used with white fuming nitric acid (WFNA) or red fuming nitric acid (RFNA) and is not hypergolic with hydrogen peroxide because of the poor solubility with the additives. How to solve this? Ethanolamine (MEA) is known to be hypergolic with HTP, however, its low performance is an impediment to further development. In addition,

Fig. 14. Comparison of specific impulse (I_{sp}) and density specific impulse (ρI_{sp}) of TMEDA/DMEA systems with HTP and conventional toxic combinations MMH/NTO and UDMH/NTO.

MEA is not miscible with TMEDA. Like MEA, diethanolamine (DEA) and triethanolamine (TEA) are also products from the same industrial reaction between ethylene oxide with aq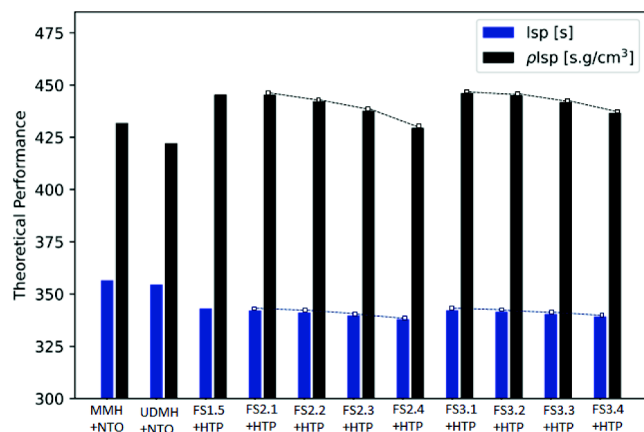ueous ammonia. However, both of them present extremely high viscosities of 380 cp (at 30 °C) and 921 cp (at 20 °C), respectively. In the search for alkyl-substituted ethanolamines, we identified dimethylaminoethanol (DMEA) as a promising candidate in a patent [8]. In this patent, Diede (2004) claimed that adding organic cobalt salts (8 wt%) to dimethylaminoethanol (DMEA) makes it hypergolic with HTP. However, to the authors' knowledge, after almost two decades later there is no publication of DMEA (pure or in a blend) promoted with cobalt salts as potential fuel. In this work, DMEA showed no hypergolicity with any of the selected additives. Nevertheless, the idea was to find a suitable match for TMEDA. Table 1 shows the chemical structures and physicochemical properties of TMEDA and DMEA.

2.1.2. Solvent: Methanol and ethanol

Alcohols are far less reactive than TMEDA and DMEA with HTP and give slightly lower specific impulses compared to both amines, but they were included in order to adjust some properties of the fuel blend, namely solubility and stability to name a few. Ethanol and methanol are

good options due to their low toxicity, low cost and relatively high performance. In addition, methanol has been used as a solvent to dissolve metal salts from the World War II (e.g., hypergolic toxic fuel C-Stoff) to today (e.g., hypergolic green fuel US Navy Block 0) [1,7,9]. Further, methanol is also the solvent of choice for ADN and HAN based monopropellant fuels which are already a flight-proven technology demonstrated in space [2]. Thus, the selected fuels were: N,N,N'N'-Tetramethylethylenediamine (TMEDA), dimethylaminoethanol (DMEA), ethanol (EtOH), and methanol (MeOH) (Fig. 3).

2.1.3. Catalyst: Copper salts

Catalytic and reactive additives are the two groups of promoters commonly added to a fuel to introduce hypergolic behavior with hydrogen peroxide. The second group is a strong reducing agent that directly reacts in contact with HTP via a redox reaction. Although there are other alternatives, virtually all research groups use sodium borohydride ($NaBH_4$) as a reactive additive. Since Diede's patent [8], this additive has been widely investigated by the propulsion community [10–14]. Handling of such strong reducing agent is challenging due to its high sensitivity to air and water which neutralizes its reactivity. Further, sodium borohydrate hydrolyzes in alcohols. As methanol and ethanol are important fuel candidates in the present work, sodium borohydrate was not considered for further investigations. Catalytic additives are transition metal salts of Co, Cu, Fe and Mn. These cations promote an exothermic decomposition reaction of the hydrogen peroxide, which releases oxygen and heats up the entire mixture environment. Ignition takes place when the autoignition temperature (AIT) of the fuel is reached. Hence, the concentration of H_2O_2 should not be <70 % (with the balance water) because otherwise heat from decomposition is absorbed by water and the adiabatic temperature may not reach the autoignition temperature of the fuel. Due to its versatility, low cost, and low toxicity copper is considered the most prominent and promising transition metal catalyst [38]. DMEA as well as its base organic compound MEA forms stable complexes with copper salts as in the following systems $[Cu(MEA)_2]^{2+}$ and $[Cu(DMEA)_2]^{2+}$ [39]. TMEDA is widely employed as a ligand for copper ions. It also forms stable complexes TMEDA-CuCl$_2$ that are soluble in many organic compounds [38]. However, unlike both alkanolamines, TMEDA presents substantially lower solubility in copper salts. Nevertheless, we are interested in their potential synergistic behavior. Thus, based on physicochemical compatibility and reactivity, anhydrous copper chloride ($CuCl_2$) and

Table 3
Properties of the fuel systems and comparison with a few relevant hypergolic green fuels. C-Soff is a toxic fuel but it was included because of its historical importance. The chamber pressure was set to 10 bar and the nozzle expansion ratio (ε) was set to 330.

Fuel name or type	Propagator (Fuel)	Solvent (Fuel)	Additive (Ignition source)		Oxidizer	Isp [s]	μ [cP]	IDT [ms]	Developed by
FS1.5	TMEDA/DMEA	-	CuCl$_2$·2H$_2$O	0.5 wt %	98 % HTP	351.4	1.5	20.0	XJTU, China (2022) [current work]
FS2.1	TMEDA/DMEA	MeOH	CuCl$_2$·2H$_2$O	1 wt%	98 % HTP	350.7	1.6	13.7	
FS2.2									
FS2.3	TMEDA/DMEA	MeOH	CuCl$_2$·2H$_2$O	1 wt%	98 % HTP	349.7	1.6	13.0	
FS2.4	TMEDA/DMEA	MeOH	CuCl$_2$·2H$_2$O	1 wt%	98 % HTP	348.2	1.5	16.8	
FS3.1	TMEDA/DMEA	MeOH	CuCl$_2$·2H$_2$O	1 wt%	98 % HTP	346.3	1.21.8	15.3	
FS3.2	TMEDA/DMEA	EtOH	CuCl$_2$	1 wt%	98 % HTP	350.8	1.7	17.3	
FS3.2	TMEDA/DMEA	EtOH	CuCl$_2$	1 wt%	98 % HTP	350.2	1.5	12.6	
FS3.4	TMEDA/DMEA	EtOH	CuCl$_2$	1 wt%	98 % HTP	349.0	1.4	11.4	
	TMEDA/DMEA	EtOH	CuCl$_2$	1 wt%	98 % HTP	347.8		19.8	
C-Stoff	Hydrazine	MeOH/ water	K$_3$[Cu(CN)$_4$]	–	98 % HTP (T-Stoff)	340.3 (319.6)	~1	–	HWK, Germany (1940 s, WWII) [1]
Block 0	MeOH	–	MAT	25 wt%	98 % HTP	322	~2	greater than10	US Navy (1990 s) [7]
Stock 2	Tetraglyme	THF/ Toluene	NaBH$_4$	5–8 wt %	98 % HTP	*347.0	2.3	5	KAIST, South Korea (2014-today) [11–14]
Stock 3	DETA	THF	NaBH$_4$	5–8 wt %	98 % HTP	*350.7	10.9	8	
Ionic Liquid	[AMIM][SCN]	–	CuSCN	5 wt%	98 % HTP	340.5	29.6	13.9	DLR, Germany (2015-today) [27–30]

*Estimated for pure tetraglyme and pure DETA. The proportions of the solvents are not available in the literature.

hydrated copper chloride ($CuCl_2 \cdot 2H_2O$) are selected (Fig. 3).

2.2. Preparation of fuels

The selected fuels have been mixed with the metal salts. It was noted that DMEA has better solubility than TMEDA with catalytic agents. However, neither TMEDA nor DMEA are hypergolic with the selected metal salts. To verifty any possible synergistic effect, both amines were mixed in different proportions with 0.5 wt% of catalyst (Table 2). It was noted during the preparation that 0.5 wt% is roughly the solubility limit for a 50:50 fuel mixture. Increasing the proportion of TMEDA leads to decreased solubility. As a result, the fuel mixture appears as pale blue as shown in Fig. 4. Since TMEDA is sensitive to air, its rapid oxidation causes precipitate formation. Preparation under inert atmosphere can improve stability. In order to improve both solubility and chemical stability, ethanol and methanol were added in different proportions to TMEDA/DMEA(50:50) as depicted in Table 2 and Fig. 3. In the present work, we injected nitrogen inside the headspace of the samples through the septum of the vials with a simple apparatus containing a syringe attached to a ballon filled with nitrogen. Ideally all the preparation procedure should be performed under inert atmosphere and the dissolved oxygen inside the liquids should also be removed. Further investigation of the shelf life of the fuel under inert atmosphere and at high pressures, which are the operational conditions in propellant tanks of rockets and spacecrafts, are out of the scope of this work.

2.3. Drop test

The drop test is a simple and fast approach to determine the reactivity of bipropellants. During the experiment a high speed camera (Phantom V2012), which was set to acquire 5000 frames per second (fps), records the collision, mixing and reaction of a single droplet of H_2O_2 on a small amount of fuel (fuel pool). A xenon lamp was used as the light source to attain clear images. This process and determination of the ignition delay time can be analyzed by means of the recordings. The ignition delay time is defined by the time period between the first contact between the components until the first flame is visible. Besides, an infrared camera (ImageIR) was used to record the temperature history. During the drop tests its resolution was set to 320×256 pixels at a frame rate of 500 fps. The The HTP droplet was dropped from height of 10 cm and defined as the distance between micropipette tip and the fuel pool. The average volume of HTP droplet was 15 μL. The amount of fuel in the watch glass was fixed in 1000 μL. A low IDT is desired as it prevents a hard start that could potentially damage or even destroy the engine. A schematic of the drop test setup is shown in Fig. 5.

Each test has been repeated at least three times under the same experimental condition. The standard uncertainty of the IDT was estimated by quantifying statistical and systematic (device resolution) uncertainties. To quantify the statistical uncertainty coming from the spread in results in a set of tests (at least three times), the standard deviation s is calculated with

$$s = \sqrt{\frac{1}{(n-1)} \sum_{i=1}^{n} (x_i - \overline{x})^2}$$

where x_i are the measured values (in this case IDTs), $\overline{x}$ is the average of the measured values and n the total number of tests. Since the images were captured at 5000 fps (or 5 frames per ms), the time resolution of the high-speed camera is 0.20 ms, which can be referred to as the device uncertainty. The overall standard uncertainty is the square-root of the sum of squared systematic and statistical uncertainties, and it was expressed as error bars of the respective IDT.

2.4. Characterization of physicochemical properties: Density and viscosity

Densities were measured simply by weighing a known volume of liquid fuel. We used a micropipette to collect the fixed amount of liquid (1000 μL) and an analytical balance by Mettler-Toledo at ambient conditions. Viscosity measurements were carried out on a Ostwald viscometer at 25 °C. The measurements of viscosities and densities were performed three times.

3. Results and discussion

3.1. Hypergolic ignition of fuel system 1 (FS1) with HTP

The hypergolic performance of fuels candidates with HTP have been measured in terms of the ignition delay time. The average IDT values from at least three tests were considered to compare the hypergolic performance of each fuel. Initially, the hypergolicity of pure TMEDA with each of the two additives was not confirmed with 98 wt% H_2O_2. Promoted DMEA, unlike its base fuel (ethanolamine), showed also very weak reactivity with HTP. It was found that both amines have limited solubility with the metal salts, especially TMEDA. Based on this preliminary tests, we were surprised that mixing both amines could induce hypergolic ignition. Interestingly, a near-optimal value (minimum IDT) occurred by mixing both amines in equal proportions (FS1.5). Except at the upper and lower proportion limits where the amount of one the fuels are too high (samples FS1.1, FS1.2 and FS1.9), all proportions of TMEDA/DMEA showed hypergolic behavior as depicted in Fig. 6. Fig. 7 shows the ignition delay time for different proportions of the system TMEDA/DMEA using 0.5 wt% $CuCl_2 \cdot 2H_2O$ (FS1.3, FS1.4, FS1.5, FS1.6, FS1.7 and FS1.8) with 94 % and 98 % hydrogen peroxide. It is interesting to see how increasing the concentration of hydrogen peroxide from 94 to 98 % causes a substantial increase in reactivity of the propellants system. As aforementioned, TMEDA is very sensitive to air and its rapid oxidation causes sedimentation within a few days after preparation. Although the use of inert atmosphere during preparation and storage can improve stability, this issue limits its application as a fuel. Thus, to prevent the fuel system from rapid autooxidation and also improve solubility, ethanol or methanol was added in different proportions to TMEDA/DMEA (sample FS1.5) as we explore in the following section.

3.2. Hypergolic ignition behaviour of fuel systems 2 and 3 (FS2 and FS3): TMEDA/DMEA (FS1.5) with MeOH or EtOH

Both alcohols have slightly lower theoretical performance than the two amines TMEDA and DMEA. However, by adding ethanol or methanol has the potential of increasing the solubility between the organic fuels and the catalyst which could improve the IDT. Moreover, a proper amount of alcohol could improve other relevant physicochemical parameters, for instance, lowering the viscosity. Initially, the near-optimal proportion of TMEDA/DMEA (sample FS1.5) was fixed. The hydrated form of copper chloride was used with methanol. Drop tests with samples using just 1 wt% catalyst confirmed the substantial improvement in IDT performance as shown in Figs. 8 and 9 using high speed and infrared cameras. Remarkably, the addition of 10–50 % methanol causes the IDT to be in the range of 10 ms to 20 ms. Note that this effect occurs because the amount of catalyst was increased from 0.5 to 1 wt%. For the same amount of catalyst used in FS1.5, the values of IDT tend to be over 20 ms by adding methanol or ethanol as shown in Fig. 10.

Based on the first results, it is intuitive to think that ultrafast IDT (below 10 ms) would be easily achievable by using a slightly higher amount of catalyst. However, further drop tests showed the 1 wt% catalyst is already a near-optimal value and higher amounts of catalyst makes the ignition unstable and unpredictable as presented in Fig. 10. With higher amounts of catalyst, the formation of clusters of bubbles (spherical foams) dominates the physical process and the drop test is not representative anymore. These foams can bounce on the surface of the fuel and eventually release a delayed flame kernel or the ignition may not even occur. Although the drop test is a suitable tool to examine

hypergolicity the combustion process inside a real combustion chamber is quite different. As propellants are atomized in the combustion chamber the phenomenon of foam formation does not take place consequently the ignition may be successful even inside the region of instability in a real rocket engine. However, it's advisable to avoid this area because the IDT performance of the fuel with low catalyst content is already promising and the specific impulse is also higher with less catalyst.

Instead of hydrated copper chloride, the anhydrous form of copper chloride (1 wt%) was added in the ethanol and mixed with FS1.5. Figs. 11 and 12 present the ignition delay time for different proportions of ethanol with 98 % HTP. As with methanol, all fuel mixtures also presented IDT in the range of 10 ms to 20 ms for hydrogen peroxide and using just 1 wt% catalyst. Further, as the length of error bars are relatively high, the differences in IDT values are not statistically significant. Although we cannot say which sample is better in terms of IDT performance, samples with higher alcohol content present disadvantages in terms of specific impulse but lower viscosity and they are less prone to precipitate formation. It should be highlighted that even though both alcohols present comparable IDT performance, the blends with methanol showed better chemical stability compared to ethanol formulations. Only samples with higher concentration of methanol showed no precipitate formation after 4 months. Precipitate formation is expected because TMEDA is senitve to oxygen. Thus, the stability of all fuel systems should be improved under inert preparation during the whole process (not only filling the headspace of the vials with nitrogen) and by removing the dissolved oxygen inside the blends. The study of the shelf life of the fuels under different pressures is beyond the scope of this paper. The effect of high pressures on the aging is also very important because in aerospace system the propellants are stored at high pressures and inert conditions inside the tanks. The better performance of methanol over ethanol in terms of chemical stability was expected due to its widely use as a solvent in industrial applications and as a solvent to dissolve salts in promoted fuel blends for aerospace propulsion since the World War II as we discussed previously.

3.3. Physicochemical properties and theoretical specific impulse

3.3.1. Physical properties

Density and viscosity are two crucial parameters for evaluating a potential propellant. High fuel density is desirable to reduce the size of the tanks and therefore reduce the structural weight. For a rocket, there will also be a gain in terms of aerodynamic losses. High viscosity propellant brings challenges in the atomization process which affects the combustion efficiency and stability. Both TMEDA and DMEA have low viscosity. Consequently, all their mixtures maintain this desirable feature (Fig. 13). Since the viscosity of our reference sample (FS1.5) is 1.48 cP, the addition of methanol or ethanol would further reduce this value. Because the amount of catalyst was doubled (0.5 to 1.0 wt%) in the samples FS2.1–2.4 and FS3.1–3.4, the viscosity may be slightly higher depending on the amount of the alcohol. For example, for samples FS2.1 and FS2.2 the viscosity is slightly higher (1.64 cP and 1.62 cP, respectively) whereas FS2.3 and FS2.4 present lower values (1.45 cP and 1.25 cP, respectively).

3.3.2. Theoretical performance

One key parameter to estimate the performance of a rocket engine is the specific impulse (I_{sp}), which is defined as the total impulse per unit weight of burned propellant. A better way to visualize this important parameter is to relate it to the effective exhaust velocity (v_e) of the combustion gases leaving the rocket nozzle according to the following equation:

$$I_{sp} = \frac{v_e}{g_0} \tag{1}$$

where g_0 is the standard gravitational acceleration. Hence, if the mass flow rate of the propellants ($\dot{m}_{prop}$) is given, both specific impulse and effective exhaust velocity can be used to estimate the thrust (F) of the engine

$$F = \dot{m}_{prop} v_e = \dot{m}_{prop} I_{sp} g_0 \tag{2}$$

Another key parameter is the density specific impulse (ρI_{sp}). The average density of propellants can be given as

$$\rho = \frac{\rho_{ox}\rho_{fu}(OF + 1)}{\rho_{ox} + \rho_{fu}(OF)} \tag{3}$$

where OF ($=\dot{m}_{ox}/\dot{m}_{fu}$) is the mixture ratio. The theoretical performance of the propellants (I_{sp}) were determined with the CEA NASA which is a recognized standard program for chemical equilibrium and rocket parameters calculations [40,41]. The tool calculates complex chemical equilibrium product concentrations from any set of reactants and determines thermodynamics and transport properties for the product mixture. The calculations assume equilibrium flow. The chamber pressure was set to 10 bar and the nozzle expansion ratio (ε), which is defined as the ratio between the exit area (A_e) and the area at the throat (A_t) of the nozzle, was set to 330. Fig. 14 shows the calculations for the hydrazine based fuels (MMH and UDMH) with NTO and TMEDA/DMEA systems with HTP.

It is interesting to note that although the specific impulse is slightly higher for conventional toxic propellants, their density specific impulse is lower compared to TMEDA/DMEA fuel systems. As already stated in section 1.1, H_2O_2 produces less O_2 compared to NTO, resulting in a significant increase in the oxidizer to fuel ratio (OF). As a result, the average density (Eq. (3)) is much higher for a given fuel. Increasing the amount of MeOH (from FS2.1 to FS2.4) or EtOH (from FS3.1 to FS3.4) the optimum OF is reduced and consequently also the density specific impulse. Table 3 summarizes the main results found in this work and also shows other relevant hypergolic green fuels under investigation around the world. Different from the new formulations in the literature our fuel system uses two propagators to start the ignition and the additive content is also substantially lower.

4. Conclusion

This study experimentally investigated the hypergolic ignition of a novel green fuel system with hydrogen peroxide. Neither TMEDA nor DMEA with the selected additives are hypergolic with HTP. Interestingly, a mixture of them provides a synergistic effect achieving hypergolic behavior with a consistently low IDT as low as 20 ms using a very low amount of catalyst (0.5 wt%). Methanol and ethanol were added to play dual roles as both an agent in enhancement the solubility and an agent in improving the chemical stability. It was demonstrated that by adding ethanol or methanol ultrafast IDT around 10 ms is possible with only 1 wt% of catalyst. Moreover, this fuel systems have low viscosity, comparable specific impulse and slightly higher density specific impulse than the standard toxic combinations of MMH/NTO and UDMH/NTO. Although the drop test is a suitable tool to examine hypergolicity, the IDT values are not representative for combustion chambers. Therefore, ignition tests under flowing conditions using injectors and a combustion chamber are necessary to validate the results under operating conditions. Nevertheless, these catalytically promoted hypergolic systems based on two propagators (TMEDA/DMEA) and a solvent (methanol or ethanol) with HTP have demonstrated their great potential as fast-igniting rocket fuels to replace conventional highly toxic hypergolic bipropellant formulations.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

the work reported in this paper.

Data availability

No data was used for the research described in the article.

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