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Review

Hypergolic Ignition with High-Test Peroxide: Progress in Catalytic, Reactive, and Ionic Liquid Fuels

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Abstract

Traditional hypergolic propellants, such as hydrazine derivatives combined with nitrogen tetroxide, present severe toxicity, operational, and environmental hazards. High-test peroxide has emerged as a leading green oxidiser replacement due to its low volatility, high density, and benign decomposition products. This review comprehensively analyses recent advancements in HTP-based hypergolic fuel formulations, categorising them into three major emerging families: catalytically-promoted, reactive, and ionic liquid-based systems. By evaluating key parameters such as ignition delay times, specific impulse and toxicity, this work identifies a clear technological shift from fundamental chemical screening to increasingly more mature solutions. While historical targets defined hypergolicity below 100 ms, recent advanced formulations routinely achieve it under 10 ms requiring minimal additive concentrations (<5 wt%), directly competing with legacy systems. Furthermore, this review highlights critical open challenges that limit commercial adoption, including the long-term storage stability of catalytic blends, high toxicity of reactive systems, and the lifecycle toxicity and high cost of frequently employed ionic liquids. Ultimately, it is concluded that rather than a single universal replacement, the future of green hypergolic propulsion lies in a plurality of solution, where each family is tailored to specific niches defined by mission requirements and cost structures.

Keywords: catalytic fuels; green propulsion; HTP, hypergolic propellants; ionic liquids; reactive fuels

1. Introduction

Hypergolic propellants are fuel and oxidizer pairs capable of spontaneous ignition upon contact. They have long been the preferred choice for many applications within the framework space propulsion. Such applications include, but are not limited to, reaction control systems, upper stage propulsion, and kick-motors. The lack of need of an external energy source for ignition makes the engine architecture simpler, lighter, and more reliable, making these engines a preferred choice for long-term missions. Additionally, given the typically low time-of-response of these solutions, they can meet the readiness requirements of time-critical operations such as orbit stabilization, orbital disturbance rejection, and collision avoidance.

Currently, the technological landscape is dominated by highly toxic or corrosive propellants. Amongst the most commonly used ones, hereafter referred to as legacy propellants, are fuels such as hydrazine and its derivatives (e.g., MMH and UDMH), and oxidisers

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such as NTO and nitric acid. As their use comes with potentially serious health hazards, their handling requires the use of personal protective equipment such as Self-Contained Atmospheric Protective Ensemble (SCAPE) suits and can only be performed by specifically trained personnel. Most notably, hydrazine has been listed as substance of very high concern (SVHC) by the European chemicals agency (ECHA) since 2011, and its use faces scrutiny [1]. Therefore, for reasons related to health and environmental risks, and costs associated with their use, recent years have seen a rising interest in propellant pairs characterised by similar performances with significantly reduced risks and costs. Moreover, their adoption would also allow new players to enter in the market of space propulsion. These propellants are commonly referred to as green or non-toxic propellants [2,3]. However, there is no universally accepted, rigorous definition of what constitutes a green propellant; rather, the criteria are often shaped by the engineering priorities of the researcher. In fact, these attributes often only acquire meaning when a novel propellant is assessed in comparison with a legacy one.

This review surveys recent advances in green hypergolic propulsion employing HTP as an oxidiser and provides a snapshot of the current state of the art. Crucially, while a vast number of chemical formulations have been proposed in recent years, the literature remains highly fragmented, lacking a unified synthesis that systematically organises these disparate data points according to a taxonomic approach. Therefore, proposed formulations are grouped according to the formulation strategy and design philosophy adopted, with the objective of offering a coherent, clear, and comprehensive overview of the field, while simultaneously providing a unifying synthesis based on performance and toxicity parameters (where minimum tolerable hazards still represent a grey area) highlighting the main trade-offs of each fuel class. By establishing this rigorous and comprehensive framework, the ultimate objective of this work is to provide propulsion engineers with a unified view of the current green hypergolic formulation panorama, allowing a quicker and more data-driven fuel development.

1.1. HTP as a Green Oxidiser

High-concentration solutions of hydrogen peroxide, also known as high-test peroxide (HTP), are increasingly being considered as promising propellant either as oxidiser in a propellant couple or as monopropellant [2,4–6]. Such interest can easily be justified looking at how hydrogen peroxide compares to other commonly used oxidisers. A selection of properties for 98% HTP is presented in Table 1, together with those of most considered alternatives. The selection of this grade is made on the grounds of it being the highest rapidly commercially available, and the fact that high-grade solutions decay more slowly over time [7]. The interested reader will find a more complete list of HTP properties in Refs. [7–10].

Table 1. Property comparison of HTP with alternative oxidisers [2,7,11–14].

Property	NTO	Nitric Acid	98% HTP	Nitrous Oxide
Formula	N_2O_4	HNO_3	H_2O_2–H_2O	N_2O
Molar mass [g/mol]	92.0	63.0	33.8	44.0
Liquid range † [°C]	−11:21.2	−41.6:121	−2.5:149	−90.8:−88.5
Density † [g/cm^3]	1.45	1.51	1.44	0.002 (gas)
Viscosity † [cP]	0.4	0.75	1.25	-
Vapour Pressure † [kPa]	96	6.4	0.16	5140
Theoretical oxygen yield [mol/mol]	2	1.25	0.5	0.5

† Values evaluated at standard conditions, i.e., 20 °C and 1.01 bar.

Compared to both NTO and nitric acid, HTP exhibits a lower oxygen yield, which translates into higher oxidiser-to-fuel (O/F) ratios which bring, given its high density, the volumetric specific impulse to values higher than most legacy couples, which is a clear advantage for volume-constrained applications. Additionally, its extremely low vapour pressure makes its exposure hazard not comparable with that of NTO or nitric acid. Finally, compared to nitrous oxide (which is also considered a green oxidiser), handling is simpler since it is naturally stored as a liquid, and its vapour has a significantly lower global warming potential.

Being HTP a strong oxidiser, special attention shall be put on material compatibility. In facts, it is extremely reactive in presence of transition metals which trigger its highly exothermic decomposition. As a consequence, some materials such as austenitic steel require passivation and conditioning before being usable. Generally safe materials in contact with HTP include: PTFE, PE, and aluminium. However, as it is naturally unstable, hydrogen peroxide concentration falls over time with a decay affected by the storage conditions [7,15,16]. In particular, Ventura et al. [15] reported that, thanks to recent advancements in HTP manufacture, the daily estimated active oxygen loss significantly reduced (up to a factor of 1000 compared to early 1940s formulations). Additionally, storage in highly compatible and properly passivated materials made it possible to store HTP for years with negligible concentration loss. An exemplary case is represented by a storage test, lasted 17 years, in which the concentration of HTP was observed to decay from 90% to 84% (less than 0.4%/year) for a tank stored outdoor in Texas. A parallel experiment in which the temperature was fixed to 5 °C showed instead no significant concentration decay, clearly highlighting the temperature effect on the stability. The feasibility of HTP-based propulsion for years-long missions (less than 5 years) was demonstrated already in the 1960s with several satellites including Syncom II and III, and Early Bird. Hence, it is clear that long-term storage of HTP requires suitable materials, passivation procedures, and thermal management strategies. However, systematic data addressing the effect of prolonged thermal cycling representative of orbital environments remain scarce and require dedicated investigation.

1.2. Hypergolic Fuels with HTP

For a fuel to energetically react with hydrogen peroxide, potentially leading to the ignition of the mixture, two fundamental conditions must hold: the fuel shall (i) be a reducing agent (i.e., it must facilitate the oxygen reduction from the peroxide -1 state to -2), and (ii) have a basic character to promote the destabilisation of the peroxide molecule (i.e., promote the dissociation of H_2O_2 into HO_2^- and H^+, which are extremely reactive chemical precursors [17]). A list of several organic and inorganic compounds reactivity with hydrogen peroxide is available in Refs. [7,10].

However, achieving true hypergolic ignition with a single combustible substance is generally difficult; as a consequence, the use of more energetic additives has become the norm to impart higher reactivity. Overall, two main strategies have emerged: (i) catalytic promotion, and (ii) reactive fuel formulation. In both cases, ignition occurs, according to the Semenov's theory, once the amount of heat released by the reaction exceeds that absorbed by the environment [18]. Nevertheless, the two strategies differ in the mechanism leveraged to achieve the necessary heat release. In catalytic fuel, a catalytic additive is incorporated to the fuel to decompose the peroxide hence triggering combustion once the auto-ignition temperature (AIT) of the fuel is reached. Such catalysts typically are transition metal salts, either organic or inorganic, based most commonly on copper, iron, and cobalt [19]. In contrast, reactive fuels, rely on special additives capable of directly reacting with the oxidiser. These additives are typically alkaline metal hydrides, such as

lithium or sodium borohydrides, which are extremely strong reducing agents. As a result, the two mechanisms lead to different ignition phenomena: in the first case ignition occurs in vapour phase, whereas in the second case it occurs in liquid phase [20]. In recent years, a third strategy, focused on the fuel itself rather than on the use of additives, has emerged: the use of ionic liquids. These salts, liquid at room temperature, are capable of reacting energetically with the oxidiser. One of their main advantages is the large degree of freedom given by the fact that their chemical structure can be tailored directly to meet specific requirements, making the use of additives optional. In the following sections of the present review, each strategy is discussed highlighting recent and promising developments.

1.3. Requirements

The ignition delay time (IDT) of a propellant pair is a widely accepted parameter to assess the suitability of a propulsive solution. Conventionally, it is measured as the time elapsed between propellants contact and first light emission. Propellant combinations with shorter IDT are generally regarded as better. Besides guaranteeing a low system response time, a small IDT limits the risk associated with a hard start [21], i.e., the potentially catastrophic pressure rise within the combustion chamber occurring with the simultaneous ignition of the gas filling it. Conventionally, the IDT consists of two distinct contributions: (i) a physical delay, and (ii) a chemical delay [22]. Consequently, achieving a short IDT imposes requirements on both the chemical reactivity and the physical properties of the propellants, such as viscosity and chemical miscibility. A conventional maximum threshold value of 100 ms is typically identified, below which a propellant couple can be considered hypergolic [23]. However, to better reflect recent technological advancements, this review considers an ignition occurring within a stricter 25 ms threshold as satisfactory. It is worth noting that this 25 ms limit refers to data gathered via drop tests. Although absolute IDT values are inherently dependent on the experimental configuration, drop test results remain highly valuable for assessing the intrinsic ignition characteristics of a propellant combination. Moreover, when used during the propellant screening phase, they can be regarded as a conservative design reference, since a rocket engine would typically be tailored to the selected propellant through appropriate injector design and operating conditions. Such optimisation generally promotes mixing and atomisation, reducing the physical contribution to the ignition delay and potentially resulting in shorter ignition times than those observed in drop tests.

A second important figure of merit is the propellant pair vacuum gravimetric specific impulse, $I_{s,vac}$. Being an indicator of the specific propellant consumption of a given solution, its importance is evident. As reference, the legacy couple MMH/NTO maximum value is here considered. All reported computations were carried out with NASA CEA code [24] according to the following assumptions: (i) Bray nozzle approximation, (ii) combustion chamber pressure of 20 bar, (iii) nozzle expansion ratio of 100, (iv) infinite combustion area ratio, and (v) pure anhydrous substances, and include the presence of additives.

To provide a unifying toxicity assessment the indication provided by the European Chemicals Agency on its public repository [25] have been taken as reference. Accordingly, the following list of unacceptable hazard statements from the Globally Harmonized System (GHS) in Table 2, implemented by ECHA, is derived:

Table 2. Non acceptable health GHS statements for true green formulations.

Risk	Statement
Oral toxicity	H300: Fatal if swallowed
Dermal toxicity	H310: Fatal in contact with skin
Inhalation risk	H330: Fatal if inhaled
Mutagenic	H34*: Risks of genetic defects
Carcinogenic	H35*: Risks of cancer
Reprotoxic	H36*: Risks of damage to fertility or unborn child
Organ-targeting	H37*: Risks of specific organ damages

* Indicates all GHS hazard statements with the corresponding prefix (e.g., H34* includes H340 and H341)

It follows that, despite what stated by the discoverers of each formulation, for the purpose of this discussion a fuel cannot be considered truly as a green fuel if the aforementioned requirements were not met for any of the ingredient of the fuel. In case of violation of these requirements, a proper comment is given. In particular, owing to the severity of the associated health hazards, substances classified or even suspected of being carcinogenic, mutagenic, toxic for reproduction, or organ-targeting (i.e., those associated with H34, H35, H36*, and H37* hazard statements) were not considered eligible for a green classification.

The complete list of the propellant couple requirement, drawn from the engineering sensitivity of the authors, is reported in Table 3. To be intended as strong recommendations, they will be used throughout this review to assess the suitability of the discussed solutions. Clearly, the ultimate selection of a propellant couple is ultimately subjected to inevitable trade-off with other mission requirements [3].

Table 3. Green propellant couple required properties.

Property	Target Value	Note
Max. sp. impulse, $I_{sp,vac}^{max}$	317.0 † [s]	Higher is better
IDT	25 [ms]	Lower is better
Density, ρ	0.85 [g/cm^3]	Higher is better
Dynamic viscosity, μ	10 [cP]	Lower is better (only for liquids)
Liq. Range	(−20; 60) [°C]	Wider is better
Toxicity	See Table 2	According to GHS as implemented by ECHA

† Values corresponding to the maximum achievable $I_{sp,vac}$ by the legacy couple MMH/NTO, reduced by 5%.

The remainder of this review is organised as follows. The three fuel families considered in this work, namely catalytically promoted fuels, reactive fuels, and ionic liquids, are discussed in Section 2, Section 3 and Section 4, respectively. A discussion summarising and comparing the three families is then presented in Section 5. Finally, conclusions are drawn in Section 6.

2. Catalytically Promoted Fuels

2.1. Introduction

The catalytic promotion of the fuel represents a conceptually simple approach to impart hypergolicity to a fuel. In principle, any fuel can be used, provided that it is chemically compatible with the catalyst. This strategy is facilitated by the fact that hydrogen peroxide decomposition can easily be catalysed by a wide range of transition metal salts. Throughout the years, several studies have investigated such systems with varying degrees of success, employing salts based on copper, iron, manganese, cobalt, silver, and other metals [17,19,26]. In these salts, the metal cation acts as the catalyst, either alone or as part of a complex with

ligands, while the anion defines the salt miscibility and final fuel properties, including viscosity and combustion enthalpy.

The development of non-toxic catalitically promoted fuels started in the US in the 1990s with research into the so-called non-toxic hypergolic miscible fuel (NHMF) [27–29]. Since then, as research progressed, additional challenges emerged, along with corresponding mitigation strategies. The following subsections review the subsequent evolution of catalytically promoted fuels, grouping the various approaches into distinct families based on the underlying design strategy.

2.2. Amino-Based Formulations

One of the most remarkable successes of the research into NHMF was the fuel called Block 0. It consisted of 22 wt.% of manganese(ii) acetate tetrahydrate (MAT) dissolved in methanol. In a further improvement by Frolik et al. [27], performances could be improved with the addition of up to 4 wt.% of potassium ethylenediaminetetraacetate as solubility enhancer. Reportedly, this low-toxicity fuel could ignite in less than 20 ms with 90% HTP in a drop test condition. However, in spite of such remarkable results in terms of IDT, Block 0 is characterised by significant storability issues such as additive deposition. This aspect, which precluded its use in long-duration missions, is a direct consequence of the high additive content. Regrettably, this is often the case when a poorly reactive fuel such as alcohols are utilised as fuel [23]. Besides storage stability, large additive fractions, included to compensate for the fuel limited intrinsic reactivity with HTP, are commonly associated with other drawbacks, including: (i) reduced specific impulse due to heavier combustion products, (ii) increased nozzle throat erosion, and (iii) higher fuel viscosity. Consequently, minimizing the additive content is a key design objective, which in turn requires fuels with an inherently higher reactivity toward hydrogen peroxide.

Chemical compounds belonging to the amine family have been repeatedly identified as promising constituents of hypergolic fuel formulations with high-test peroxide. This is primarily due to the intrinsic chemical reactivity of amines toward hydrogen peroxide [7,10,17], which contrasts with the limited reactivity of alcohols and aromatic oxygenated fuels. Amines are known to undergo rapid oxidative reactions with hydrogen peroxide, leading to the formation of reactive oxygen species and strongly exothermic pathways that promote ignition, or more generally, facilitate peroxide decomposition through electron-transfer processes. Their presence as ligands, in transition metal complex can further increase the catalytic activity of the latter [19], leading to a shorter IDT, a property that has earned them the designation as propagators in the literature. As a result, amine-based fuels require significantly lower additive content compared to oxygenated fuels, which makes them attractive candidates for hypergolic systems. Such differences are clearly visible in the already mentioned work of Florczuk et al. [23]. In fact, a fuel sample containing *N,N,N′,N′*-Tetramethyl-1,3-diaminopropane (TMPDA) ignited in less than 10 ms with only 5 wt.% loading of cobalt(ii) 2-ethylhexanoate with 98% HTP as oxidizer. Regrettably, this additive is toxic to human reproduction according to ECHA. Interestingly, in a pattern also observed by Refs. [30,31], a large increase in the additive fraction does not constitute a significant improvement in the fuel final IDT.

The same catalytic agent, cobalt(ii) 2-ethylhexanoate, was loaded in two tertiary monoamines,*N,N*-dimethylbutylamine and *N,N*-dimethylhexylamine by Blevins et al. [32]. In their study, the catalyst content was limited to 5 vol.% and 98% HTP was used as oxidiser. (The additive was employed as part of a mixture containing 35 wt.% of mineral oil (which detracts from the fuel reactivity), and its average density is close to $1 g/cm^3$, bringing the true salt content to be about 3÷4 wt.%). The results were extremely promising as ignitions were recorded in, approximately, 10 ms and 13 ms for the two amines, respectively. The

two amines differ only by the length of the aliphatic chain which translate into different vapour pressures, 6 kPa and 0.5 kPa, respectively and an expected larger viscosity of *N*,*N*-dimethylhexylamine. It is these authors opinion that the higher vapour pressure of *N*,*N*-dimethylbutylamine gives it a shorter IDT since a more reactive atmosphere forms on top of the liquid fuel pool. In the same study, Blevins et al. noted no significant differences in the result varying the oxidiser droplet size and fall height. Comparing these results with the work of Florczuk et al. [23], it is interesting to notice that, despite being on paper more reactive, due to the presence of an additional amine on C3 instead of a methyl, TMPDA performs worse than *N*,*N*-dimethylbuthylamine. This seems to suggest that either the higher vapour pressure, or the formation of a different coordination complex could offset the theoretical benefits of having multiple functional groups in a promoter.

Monoethanolamine (MEA) is one of the most studied amines. Its wide availability, driven by large scale applications in many fields such as chemical production and CO_2 scrubbing [33], makes it a low-cost compound. It is relatively non-toxic, with no properties of concern according to ECHA. However, its high viscosity and low $I_{s,vac}$ make it unsuitable as propellant. Nonetheless, its low cost and high reactivity with HTP, make it a convenient reference compound and a benchmark for the development of novel formulations. In their screening of hypergolic substances, Melof et al. [26] found MEA to be one of the best fuels, giving it a score of 3/3 for ignition potential when paired with copper(ii) chloride (CC). A confirmation of this combination high potential is available in Refs. [4,20]. Formulation optimisation of MEA and CC, have been conducted at SPLab of Politecnico di Milano [34,35]. Both studies measured the IDT via drop tests. The first study employed CC in its dihydrate form achieving an optimal IDT of approximately 25 ms with 96% HTP for a salt content of about 6 wt.%. The second study confirmed the optimal concentration being close to 6 wt.% and achieved ignition in approximately 30 ms and 20 ms with 87.5% and 98% HTP, respectively. In the same paper the authors studied the use of copper(ii) nitrate trihydrate (CN) achieving an optimal IDT of about 16 ms and 22 ms for 98% and 87.5% HTP, respectively. The two salts were observed to lead to different trends, with a more clear minimum in case of CC, possibly due to the steeper viscosity increment caused by CC than CN at higher concentrations. The combination MEA with CC 10 wt.% was also tested by Ak et al. [36]. The authors investigated both drop tests and engine firings using 85% HTP. From the drop tests, they determined that a fuel temperature above 25 °C was required for ignition within 50 ms. Most interestingly, they observed that the initial temperature of the fuel matters more than that of the oxidiser. This could be explained by the fact that a pre-heated peroxide require less energy to initiate the decomposition process. Regrettably, engine tests were not able to replicate the IDT of drop tests. In particular, the ignition delay (intended as time elapsed between injection and pressure rising to 90% of its stationary value) was measured at 130 ms with pre-heated fuel to 40 °C. The authors did not provide information about the ignition conditions which may have lead to such performance worsening.

Beside MEA, others amines have been screened for their potential use as hypergolic fuels at SPLab, Politecnico di Milano. Based on the results of Melof et al. [17], which reported 1,2-diaminopropane (DIMP) to ignite with the peroxide, this amine was tested with some organic salts to assess its usability as propellant. Rapisarda et al. [31] tested it with several organic copper(ii) salts, finding good solubility with copper(ii) methacrylate (CM). A test campaign with 96% HTP revealed IDT as low as 26 ms with 9 wt.% of CM. It was observed that larger additive fractions do not improve significantly the reactivity of the amine. It was supposed that the viscosity increment related to salt addition is not enough to compensate the increment in reactivity achieved with higher salt content. As part of the same research, two more diamines were preliminary tested by Caffiero et al. [30],

N,*N*-dimethylethylenediamine (DMEDA) and *N*-methyl-1,3-diaminopropane (MDP), the latter being investigated for the first time as hypergolic propellant. They were tested with three organic cupric salts (given the lack of solubility with cupric chloride or nitrate): copper(ii) ethylacetoacetate (CE), copper dibutyrate (CD), and CM. The drop tests were conducted with 96% HTP. The two amines showed different trends and solubility. DMEDA was found not compatible with CM but largely compatible with CE and CD. With these two additives, the IDT decreased monotonically reaching IDT as low as 8 ms for 8 wt.% salt content. Interestingly, comparing the samples on a per-copper basis revealed that CE, despite a significantly smaller copper content (20 wt.% vs. 27 w.t%, circa) led to consistently faster ignitions, suggesting the higher reactivity of the ethylacetoacetate ion than butyrate. The second screened amine, MDP, showed good solubility with all three salts and a clear optimal formulations for a salt content between 2÷3 wt.% with ignitions consistently close to 10 ms for all three. Per-copper comparison allowed to infer that CM (copper content of about 27 wt.%) performs better than CE and CD. Despite extremely good IDT and low toxicity (neither amine has proven properties of concern according to ECHA), no data are available concerning long-term stability.

Hallit et al. [37] reported in a patent the finding of a family of highly hypergolic fuels with >85% HTP based on the use of azide compounds. In particular, they claimed a hypergolic fuel constituted by: (i) an azide compound having at least one tertiary nitrogen and at least one azide functional group, and (ii) a transition metal compound. In addition, the authors of the patent acknowledge the optional presence hydrocarbons in the fuel to tune its properties and cost within the limitation that the cumulative mass fraction of the promoter and hydrocarbon is less than 90%. Concerning the amine, the patent specified that the linking group between the two nitrogen functional groups must be a C_{2-8} alkylene and the two substituent groups on the tertiary nitrogen shall be C_{1-4} alkyl. According to these specifications, 2-*N*,*N*-dimethylaminoethylazide (DMAZ) can be used. Concerning the catalyst, they claimed the selection within the group of cobalt and manganese-based carboxylate and naphthenate.

A collection of the promising formulations reported in this section is available in Table 4. It can be noted that of the reported formulations, only those containing MEA are not able to satisfy the constraint on the specific impulse, nor the viscosity stated earlier.

Table 4. Amino-based catalytic fuels.

Fuel	Additive	HTP Grade	IDT [ms]	Ref.	$I_{s,vac}^{max}$ [s] (O/F)	Notes
TMPDA	5 wt.% cobalt(ii) 2-ethylhexanoate	98%	<10	[23]	329.6 (5.11) †	Additive: H360D
N,*N*-dimethyl-buthyl-amine	3+wt.% cobalt(ii) 2-ethylhexanoate	98%	10	[32]	329.5 (5.60) †	=
N,*N*-dimethyl-hexylamine	3+wt.% cobalt(ii) 2-ethylhexanoate	98%	13	[32]	329.1 (5.73) †	=
MEA	6.1 wt.% CC dihydrate	96%	25	[34]	299.4 (3.45)	Viscosity ≈ 50 cP
MEA	10 wt.% CN trihydrate	98%	16	[35]	301.4 (3.20)	Viscosity ≈ 60 cP
MEA	10 wt.% CN trihydrate	85%	30	[36]	287.5 (3.66)	=

Table 4. *Cont.*

Fuel	Additive	HTP Grade	IDT [ms]	Ref.	$I_{s,vac}^{max}$ [s] (O/F)	Notes
DIMP	9 wt.% CM	96%	26	[31]	328.5 (5.49)	Small IDT benefits with salt >5 wt.%
DMEDA	8 wt.% CE	96%	8	[30]	325.2 (4.68)	-
MDP	2 wt.% CM	96%	9	[30]	328.2 (4.80)	-
DMAZ	15 wt.% cobalt Hex-Cem	90%	16	[37]	-	Additive: H360D

† Additive content neglected.

2.3. Alcohol-Based Formulations

Despite a low intrinsic reactivity with hydrogen peroxide, as seen in Section 2.2, alcohols have been extensively used as part of hypergolic fuel formulations. The main motivations include: (i) reducing the final fuel cost employing widely available substances; (ii) limiting the final fuel toxicity; and (iii) acting as co-solvent, thereby increasing fuel shelf stability and additive solubility. Blending is often the sole viable strategy to limit the catalyst loading in presence of alcohols. In fact, as shown by Florczuk et al. [23], the ignition of pure ethanol with 98% HTP required up to 15 wt.% of cobalt(ii) 2-ethylhexanoate to reach an IDT of 63 ms in a drop test setup.

In his review of the effort carried out by the Naval Air Warfare Center Weapons Division, China Lake, California, Rusek et al. [29], emphasised affordability as a key parameter in the development of any novel fuel formulation. Although the exact formulations of the discussed fuels were not disclosed, the reported optimum O/F ratio below 3 may suggest that inexpensive alcohols were used instead of hydrocarbon fuels such as aviation kerosene. Indeed, alcohols generally exhibit lower stoichiometric O/F ratios than hydrocarbons; for example, typical alcohols have optimum O/F ratios close to 4, whereas hydrocarbon fuels such as kerosene typically require values above 6.

In a subsequent patent, Rusek et al. [38], defined a NHMF whose composition include: (i) 50–75 wt.% of polar organic species miscible with HTP selected from the group of C_1 to C_6 alcohols and C_1 to C_4 ketones; (ii) 0.1–15 wt.% of propagators to be selected among substituted or unsubstituted monoamines, amides, and diamines; and (iii) between 0.1–30 wt.% of inorganic metal salts selected among salts of manganese, copper, cobalt and iron. Alternatively, a fuel composed by: (i) 50–75 wt.% of polar organic species including a lower alcohol; and (ii) 0.1–30 wt.% of MAT, is claimed. For a preferred formulation, a solution of 95.4 wt.% of dipotassiumethylenediaminetetraacetate and 4.6 wt.% of MAT, IDT as low as 6 ms were reported although no information on the HTP grade was provided.

Subsequently, Lormand et al. [39] reported that the formulations proposed by Rusek at al. suffered from stability issues, especially when subjected to heat and humidity. To address such limitations, a new five-component NHMF was proposed. They claimed a fuel consisting of: (i) 60–90 wt.% of a polar organic species comprising a lower alcohol; (ii) 5–23 wt.% of MAT or other inorganic metal salts based on manganese, copper, cobalt, or iron; (iii) 1–15 wt.% of polar amide species; (iv) 1–10 wt.% of acetic acid; and (v) 1–10 wt.% of an alkali acetate. The addition of acetic acid was reported to improve the stability and solubility of the fuel, while the inclusion of alkali acetate served as buffer to control the final fuel pH, reducing its acidity. Although the IDT of these fuel formulations were not disclosed, samples were claimed to have retained their hypergolicity without precipitation after both cold and hot storage periods, with no additional information about the storage time.

More recently, Mayer et al. [40] patented similar fuel formulations. The claimed formulations include: (i) 60–90 wt.% of an organic fuel selected amongst C_1–C_6 alcohols; (ii) 9–30 wt.% of catalytic agent, whose anion is preferably nitrate, acetate or acetylacetonate, and whose cation is preferably iron, palladium, cobalt, or manganese; (iii) less than 0.9 wt.% of acetic acid and alkali acetate; and (iv) 1–10 wt.% of *N*,*N*-dimethylformamide (DMF). Regrettably, this amide is classified by ECHA as a substance of concern due to its toxicity for human reproduction.

The use of an alcohol appears to be especially beneficial when highly reactive but viscous and high-temperature freezing amines, such as MEA are employed. In particular, Melof et al. [26], tested a blend with 47.5 wt.% of MEA, 47.5 wt.% furfuryl alcohol and 5 wt.% CC reporting it as the fastest to ignite among the screened fuels, faster than a similar sample with no alcohol. This behaviour can be explained by the reduction in the fuel viscosity and the higher vapour pressure achieved through an alcohol addition. Regrettably, furfuryl alcohol is classified as a suspected human carcinogenic by ECHA.

In recent years, however, several studies have specifically aimed to make MEA a viable candidate for catalytic hypergolic propulsion by combining it with alternative alcohols, seeking to retain favourable ignition characteristics. Maschio et al. [41] conducted a design of experiment to determine the optimal formulation minimising the IDT for a fuel based on MEA, ethanol, and copper(ii) nitrate trihydrate as catalytic additive. The resulting formulation consisted of: 61 wt.% MEA, 30.1 wt.% ethanol, and 8.9 wt.% of copper(ii) nitrate and achieved an IDT of about 16 ms with 90% HTP. This fuel was later tested by Maschio et al. [42] in a 50 N engine, demonstrating its applicability beyond the conventional drop test level. A combustion efficiency of 84% was reported.

In a follow-up study Mendoza et al. [43], performed an analogous optimisation study employing n-butanol in place of ethanol. Once again, the optimal formulation comprised of: 60 wt.% MEA, 31.5 wt.% butanol, and 8.5 wt.% of additive. However, the IDT increased almost by a third to 21.5 ms with 90% HTP. The degraded performance observed with butanol can be attributed to a smaller vapour pressure, and higher viscosity (approximately twice that of ethanol). Nevertheless, given its high density, the use of the formulation including butanol may be better suited for volume constrained applications, where a longer IDT can represent an acceptable trade off. A summary of the formulations described in this section is available in Table 5.

Table 5. Alcohol-based catalytic fuels.

Fuel	Additive	HTP grade	IDT [ms]	Ref.	$I_{s,vac}^{max}$ [s] (O/F)	Notes
Methanol	22 wt.% MAT	90%	20	[27]	307.7 (3.29)	Methanol: H370
Benzaldehyde	20 wt.% IC hexahydrate	98%	50	[23]	315.2 (3.51)	-
Ethanol	15 wt.% cobalt(ii) 2-ethylhexanoate	98%	63	[23]	-	Additive: H360D
Methanol	30 wt.% MAT + 0.05 wt.% K_2EDTA	94%	14	[38]	308.5 (2.97) †	Methanol: H370
Methanol	18 wt.% MAT + 7 wt.% acetamide + 5 wt.% acetic acid + 1 wt.% potassium acetate	98%	-	[39]	314.9 (3.10)	=

Table 5. *Cont.*

Fuel	Additive	HTP grade	IDT [ms]	Ref.	$I_{s,vac}^{max}$ [s] (O/F)	Notes
Ethanol	+ 10 wt.% DMF + 10 wt.% manganese(ii) acetate	98%	-	[40]	313.7 (3.45)	DMF: H360D
Ethanol:furfuryl alcohol (1:1 mass)	5 wt.% CC	98%	-	[26]	317.5 (3.47)	Furfuryl alcohol: H351 and H373
MEA + 30.1 wt.% ethanol	8.9 wt.% CN	90%	16	[41]	299.9 (3.71)	-
MEA + 31.5 wt.% butanol	8.5 wt.% CN	90%	22	[43]	302.4 (4.08)	-
Ethanol	33 wt.% (TMEDA:CD 1:1 mol)	96%	20	[44]	316.4 (3.98)	Covered by [45]

† K_2EDTA content neglected.

2.4. Double Promoter Strategy

Despite clear advantages in terms of reduced fuel cost and increased salt solubility, the presence of an alcohol in formulation introduces some drawbacks, including a lower specific impulse and reduced overall fuel reactivity. The double promoter strategy represents an alternative approach in which two different promoters, typically two amines, are simultaneously present in the fuel. This approach exploits each one individual properties enabling finer tuning of the final fuel characteristics [46].

In their work, Caffiero et al. [35] proved the efficacy of this strategy by blending MEA with *N*,*N*-dimethylethylenediamine (DMEDA). With respect to MEA, DMEDA exhibits a significantly smaller compatibility with the selected additive, CC dihydrate, but exhibits smaller viscosity, higher vapour pressure, lower freezing point, and significantly higher specific impulse. Consequently, only a small additive loading was required to achieve reliable ignition with 98% HTP, and formulations containing 0.5 wt.% and 1 wt.% additive were therefore prepared and tested. In particular, increasing DMEDA content in the blend, provided shorter IDT, higher specific impulse, and smaller viscosity. In this formulation, the alkanolamine (MEA) primarily acted as co-solvent for the salt, while the diamine (DMEDA) provided high reactivity and favourable physical properties. Noticeably, DMEDA has no properties of concern according to ECHA. In a subsequent preliminary investigation, Caffiero et al. [30], blended DMEDA with MDP leveraging the higher compatibility of DMEDA with the selected additive, CE, and the higher ageing stability of MDP. In this case, with a 2 wt.% salt content, ignitions reliably within 15 ms were observed with 96% HTP, with shorter ignition achieved with larger MDP fractions. Regrettably, samples with large fraction of MDP showed signs of additive deposition after some months.

The double promoter strategy is also at the basis of a family of green fuels, named PAHyp, developed by Mota et al. in a series of works [47–51]. In their first work [47], culminated with the identification of the so-called PAHyp 0, the authors investigated the positive synergic effect arising from the contemporary presence of dimethylaminoethanol (DMEA), an alkanolamine, and TMEDA, a polyamine. Ignitions were investigated utilizing a drop test setup. The selection of these amines was motivated by the high intrinsic reactivity of TMEDA, and the superior additive compatibility of DMEA. From a performance standpoint, the two amines exhibits nearly identical results. However, DMEA

is more than three times more viscous and slightly denser than TMEDA. Interestingly, when tested individually, neither of them was able to achieve hypergolic ignition with CC as catalyst. Conversely, when blended together, consistent ignitions within 20 ms were observed with only 0.5 wt.% of CC with 98% HTP. To further enhance the salt solubility, mitigate the risk of additive deposition over time, and further lower the fuel viscosity, a co-solvent in the form of either methanol or ethanol was added. When methanol was employed, CC in its dihydrate form was used. Under these conditions, the IDT was found to be as low as 13 ms for a 1:1:1 TMEDA:DMEA:methanol volume ratio, with 1 wt.% of additive. Noticeably, for this volume ratio, an increase in the additive mass fraction past 1 wt.% led to a significant worsening of the ignition performances with IDT rising to 30 ± 14 ms. On the other hand, when ethanol is used, anhydrous CC was used yielding even better results. In facts, ignition within 12 ms were recorded for the formulation consisting of 25 vol.% TMEDA, 25 vol.% DMEA, and 50 vol.% Ethanol with 1 wt.% of CC.

A further study into PAHyp 0, was later published by Mota et al. [51]. Three salts were considered for addition to the TMEDA/DMEA system: (i) CC dihydrate, (ii) copper(ii) acetate (CA) monohydrate, and (iii) cobalt(ii) acetate tetrahydrate. Of these three, only CC required the presence of methanol to be solved, as the other two were compatible with the binary amine system. After initial screening, only CC and CA were tested in a jet-impingement setup. Ignition envelopes for samples containing CC and CA were established. In the former case, the required amount of salt was found to be in the range 0.5–1 wt.%, and the amount of methanol (for a 1:1 volume ratio of TMEDA:DMEA) to be between 30–60 vol.%. In the latter case, the optimal amount of CA was found to be 0.5–1.5 wt.% and that of DMEA to be 40–80 vol.%. Interestingly, FTIR analysis performed after 5 months and 1 year of storage revealed no appreciable change in the spectra, proving these fuels resilient to ageing. When subjected to impinging tests, ignitions as low as 10 ms were recorded. An unlike doublet with a unity jets momentum ratio was used. The results clearly confirmed the drastic effect of impinging velocity on the ignition; an optimal velocity range exists, beyond which ignition could not be achieved as the contact time was too short.

Fuels belonging to the PAHyp 0 family were once again studied by Dias et al. [52] with the use of gelled 98% HTP. In this study, the oxidiser was gelled with 6 wt.% of hydrophilic fumed silica and reverse drop tests (i.e., with the fuel being dropped onto the oxidiser), were conducted. As expected, the IDT were lower than those observed in Ref [47]. Overall, for a blend composed by TMEDA, DMEA, and methanol (1:1:1 vol. ratio) with CC as catalytic additive returned IDT equal to 50 and 17 ms with catalyst loading of 0.5 and 1 wt.%, respectively. Additionally, when droplet impact velocity was increased from 0.3 to 1.23 m/s the IDT reduced from 42 to 15 ms with 1 wt.% of additive. The temperatures reached during the ignition events, however, were found not to depend on the catalyst loading (coherently with Jindal et al. [53] findings) and impact velocity but were related to the boiling point of methanol and AIT of TMEDA.

In a subsequent work [48], a novel formulation, called PAHyp 1, was proposed. To enhance additive solubility without the need of a co-solvent, such as methanol, DMEA was replaced by *N*-methyldiethanolamine (MDEA), which possesses one additional hydroxyl group. Regrettably, it has a hundred time larger viscosity than TMEDA and about thirty times larger viscosity than DMEA. Ignition tests were conducted employing a drop test setup. Interestingly, MDEA showed a certain degree of hypergolicity when paired with CC even without TMEDA. Impulse-wise no appreciable difference exists with the three amines so far considered. Blends containing this new alkanolamine were tested again with CC dihydrate. Given the large difference in the physical properties of the two amines, for a

fixed salt content, monotonic trends in viscosity and IDT were observed, with better results achieved for a smaller MDEA volume fraction. Conversely, from a storability point of view, a smaller TMEDA fraction is desired; in particular, TMEDA fractions below 40 vol.% were found necessary to achieve storage stability for more than 15 months. Overall, PAHyp 1 represents an improvement over its predecessor, with reliable ignitions within 10 ms achieved with 96% HTP for selected formulations.

The use of MDEA was further investigated in a follow-up study by Mota et al. [49]. In this new iteration, called PAHyp 2, MDEA was blended with *N*-methylimidazole (MIm). Drop tests were conducted to characterize the ignition behaviour. Once again, CC dihydrate was selected as the catalytic agent, after preliminary screening with CN and CA monohydrate proved unsuccessful. Compared to TMEDA, MIm provides a slightly lower specific impulse, and is more viscous. However, it shows significantly higher compatibility with the additive. Three additive mass fractions: 1, 2, and 3 wt.% were investigated with 95% HTP as oxidiser. Ignitions in about 9 ms were recorded for a sample composed of 50 vol.% MIm, 50 vol.% MDEA, and 3 wt.% CC dihydrate. Across the entire test matrix, ignition always occurred within 30 ms. Similarly to what done for PAHyp 1, a long-term storage stable region was identified, corresponding to an additive content of 1–2 wt.% and MIm fraction of 40–60 vol.%. However, in comparison with PAHyp 1, viscosity of PAHyp 2 formulations is considerably higher.

Due to high viscosity of MIm, TMEDA was reintroduced as part of a forth green fuel formulation called PAHyp 3 [50]. In this iteration, TMEDA was blended with another alkanolamine, *N*-methylethanolamine (MMEA), making the first reported use of this compound as propellant. MMEA exhibits a specific impulse comparable to that of N-methylimidazole, but with approximately three times higher viscosity. As a result, the TMEDA/MMEA blend was found to be less viscous than PAHyp 1 and PAHyp 2 formulations. For this blend, CN trihydrate was identified as the best additive. With an additive content of 2 wt.% CN, and 94% HTP, ignitions in less than 15 ms were recorded for MMEA vol. fractions of 40% and 50% in drop tests. In the same study, these fuels were tested in a jet-impinging setup yielding an IDT comparable to those obtained in drop tests.

Interestingly, the double promoter strategy is so powerful that, in the open literature, examples can be found in which the achieved synergic effect of two promoters makes the presence of an additive completely optional. For instance, in the patent of Stevenson et al. [54], a fuel formulation based on the combination of solely two different amines is disclosed. In addition, the optional use of an additional gelling agent such as fumed silica in a quantity 0.5-10 wt.% is acknowledged. In particular, they claimed that mixtures of an aminidine compound and a tertiary-tetra amine compound are hypergolic with HTP, NTO and nitric acid. One example formulation consists of a blend between *N*,*N*,*N*′,*N*′-tetramethylenediamine (TMEDA) and DMAZ. The IDT can be minimised for a DMAZ to TMEDA ratio in the range 20–40%, reaching values below than 10 ms. A summary of selected formulation is given in Table 6. It can be noted that all formulations respect the requirements on the specific impulse and toxicity stated in Table 3.

Table 6. Double promoter-based catalytic fuels.

Blend	Additive	HTP Grade	IDT [ms]	Ref.	$I_{s,vac}^{max}$ [s] (O/F)	Notes
MEA:DMEDA (30:70 mass)	1 wt.% CC	98%	21	[35]	322.7 (4.37)	IDT doubles with 87.5% HTP
MDP:DMEDA (30:70 mass)	2 wt% CE	96%	15	[30]	326.2 (4.80)	-
TMEDA:DMEA: ethanol (1:1:1 vol)	1 wt.% CC	98%	12	[47]	324.8 (4.27)	-
TMEDA:MDEA (30:70 vol)	2 wt.% CC	98%	26	[48]	328.0 (3.96)	-
MIm:MDEA (1:1 vol)	3 wt.% CC	95%	10	[49]	320.4 (3.98)	High viscosity blend
TMEDA:MMEA (1:1 vol)	2 wt.% CN	94%	14	[50]	321.2 (4.60)	-

2.5. Kerosene-Based Formulations

For a hypergolic fuel to achieve widespread adoption, certain criteria, such as cost, constituents availability, and ease of manufacturability, must be satisfied. Within this framework, the inclusion of an hydrocarbon in the fuel formulation is highly desirable. Amongst the possible candidates, kerosene has received the most attention. Indeed, it stands out as an attractive candidate due to a combination of several favourable factors including: (i) widespread availability, which translates into significantly lower cost compared to any compound so far discussed (with the exception of ethanol); (ii) relatively low toxicity; (iii) high volumetric energy density; and (iv) well established supply chains. Moreover, kerosene benefits from a long heritage in both aviation and space propulsion, well-defined handling procedures, and excellent storability. When combined with hydrogen peroxide, its optimal performance at high oxidiser-to-fuel ratios further enhances the volumetric specific impulse, owing to the high density of the oxidiser.

However, imparting hypergolicity to kerosene is challenging. Its intrinsic chemical stability prevents spontaneous reaction with HTP, as kerosene lacks the reactive sites required to trigger hypergolic ignition, contrasting sharply with amine-based fuels. Owing to this non-reactivity, the ignition becomes largely dependent on the thermal decomposition of the molecules into light radicals, a process hindered by the length of the carbon chains, which requires a larger amount of energy and time. Finally, the non-polar nature of kerosene further hinders the ignition process as mixing with HTP, which is polar in nature, is energetically unfavourable, therefore limiting the available reaction interfaces. The low polarity of kerosene also severely limits the solubility of the metal salts commonly employed to catalyse peroxide decomposition, with most inorganic salts being practically insoluble. As a consequence, kerosene-based hypergolic formulations often require the use of co-solvents capable of forming soluble metal complexes.

In their review, Hurlbert et al. [55], detailed the results of a screening study conducted to assess the solubility of some catalytic additives, and related catalyst-promoter complexes, in aviation kerosene. The screening involved organic metallic salts such as hydrocarbon sulfonates, and carboxylates of several transition metals such as copper, iron, manganese, cobalt, and chromium. As promoters a selection of phenols, aldehyde amines, and even hydrazines was considered. The first investigation on naphthyl sulfonates returned no satisfactory results, as no salt or salt-promoter complex both dissolved in kerosene and ignited the fuel. A second investigation into dodecyl benzene sulfonate of cobalt, chromium, iron and copper yielded some satisfactory results with certain combination such as fer-

rous dodecyl benzene sulfonate and tert-butyl p-phenol, said to ignite immediately the kerosene blend.

Another example of successful hypergolic ignition of kerosene-based fuel was reported by Cong et al. [56]. In their study, although the exact fuel formulation was not disclosed, the high reactivity of manganese(iii) and cobalt(ii) cations is attested with 90–96% HTP. As part of the test campaign, these fuels were ignited in a demonstrator engine achieving combustion efficiency up to 97%. Moreover, they declare that all considered fuels showed no sign of degradation after three-months storage.

Dobbins et al. [45,57] reported in details the invention of what they defined as catalyst systems. These systems were designed to impart hypergolicity to a wide variety of organic fuels (including both hydrocarbons and alcohols) while overcoming typical issues such as fuel auto-oxidation and additive precipitation. The catalyst system consists of three components: (i) a promoter, (ii) a transition metal salt; and (iii) an antioxidant (optional). The promoter, once again belonging to the class of the amines, must be selected among alkyl-substituted diamine or triamines. The catalyst is required to be a metal salt of an aliphatic carboxylic acid with manganese, copper, silver, or cobalt as the cation and acetate, propionate, and butyrate as the anion. Finally, the antioxidant is a terminal or internal acetylenic compound containing between 1 to 20 carbon atoms. Its role is to render the salt-promoter complex impervious to auto-oxidation through a mechanism referred to as molecular cage effect by the authors. According to their indication, this catalyst system should be prepared anaerobically to enhance its efficacy, prior to its addition to the selected fuel, as excess promoter may need to be removed. According to the patent, the final fuel composition typically consists of: 50–97 wt.% of fuel, 1.8 wt.% of metal salt, 1–20 wt.% of amine, and optional trace amount of antioxidant.

The formulation framework identified by Dobbins et al. in their patent proved sufficiently general and robust that several subsequent studies have confirmed the high reactivity of fuel blends falling within its defined boundaries. Recently, at SPLab [44] a fuel sample produced according to one of the example formulation proposed by Dobbins et al. was synthesised and tested with 96% HTP. The fuel, composed of 66.7 wt.% ethanol and 33.3 wt.% of catalyst system based on TMEDA and CD in a 1:1 molar ratio, ignited reliably in 20 ms and showed no signs of degradation after 1-year storage under ambient conditions. Further confirmation of the potential of the formulations provided by Dobbins et al. was provided by Florczuk et al. [23], who tested a blend of Jet A-1 and TMPDA in an 80/20 ratio. In that study, hypergolic ignition was achieved within 22 ms using 20 wt.% cobalt(II) neodecanoate with 98% HTP.

In another study, Caffiero et al. [58] investigated the IDT of blends based on Jet A-1, DMEDA, and CE. Three catalyst contents, (2.5, 5, and 7.5 wt.%) and four kerosene levels (0, 25, 50, and 75 wt.%) were tested with 96% HTP. Clearly the shortest IDT, lower than 10 ms were obtained with the kerosene-free formulation with the highest catalyst content. It was reported that the reduction in the IDT slows significantly down from an average 38% to 12% when the catalyst loading rises from 2.5 to 5 and further to 10 wt.%. In addition, samples with the highest kerosene content benefitted the most from the salt increase; when the catalyst content is increased from 2.5 to 7.5 wt.% the IDT of samples with 75 wt.% of kerosene reduced by 74%, that of samples with no kerosene reduced by 28%. Despite promising IDT and good miscibility, over time, samples containing more than 50 wt.% of kerosene showed signs of ageing and additive deposition.

In a subsequent preliminary study by Caffiero et al. [30], the blend based on Jet A-1 and DMEDA was compared with the one based on Jet A-1 and MDP. CE was employed as the catalyst and 96% HTP as the oxidiser. In the first case, the catalyst-to-amine ratio was set to 4, 6, and 8 wt.%, while in the second case it was set to 2, 3, and 4 wt.%. This

choice was motivated by the need to centre the experimental domain around the presumed optimal catalyst-to-amine ratio. Each produced sample was then diluted with Jet A-1 to obtain samples with 0, 25 and 50 wt.% of kerosene. Testing the samples containing DMEDA confirmed the results of the previous study, as the optimum was found at the corner of the test domain corresponding to no kerosene and 8 wt.% catalyst. In contrast, testing samples containing MDP revealed the existence of a predicted IDT minimum (of 10 ms circa) located at a non-null kerosene mass fraction (12 wt.%). This behaviour was attributed to differences in the physical properties of kerosene and the promoters. Specifically, the lower AIT and higher vapour pressure of kerosene than MDP were sufficient to compensate the negative effect of its low reactivity when present in a sufficiently small amount. This interpretation also explained what occurred in presence of DMEDA whose considered properties are similar, if not better than, those of kerosene. Finally, in the same study, the dilution of DMEDA/MDP blends mentioned in Section 2.4 with kerosene was performed, demonstrating the feasibility of a four-component mixture with IDT below 25 ms when the hydrocarbon mass fraction is 25 wt.%. However, the same unstable behaviour was observed when a larger mass fraction of MDP was present than DMEDA.

Yuan et al. [59] developed and tested the ignition of a kerosene-containing hypergolic fuel called W2. This fuel contains 21 wt.% of kerosene, 8 wt.% of MAT, a polar organic solvent (presumably methanol), and a dispersion medium to homogenise the fuel. Drop tests with a non disclosed HTP grade led to IDT almost twice that of Block 0 (20.5 vs. 11 ms). However, the maximum specific impulse, thanks to the presence of kerosene is circa 10% higher. To accelerate the ignition process, a novel cyclonic injector was designed. The new injector consists of a single element swirl injector in which both propellants are injected in the same vortex chamber, allowing propellant mixing inside the injector element itself. IDTs as low as 38 ms were achieved under atmospheric conditions.

More recently, Jindal et al. [53] performed an extensive analysis on a kerosene-based semi-hypergolic fuel. Most noticeably, the investigated formulations consisted only of kerosene and manganese(ii) acetylacetonate (MAA), without any promoter. The lack of the latter is shown in the IDT, never shorter than 60 ms in any of the tested conditions and formulations. The study covered variations in HTP concentration (6 grades from 85 to 98%), catalyst loading (12 concentrations, from 0.5 to 10 wt.%), O/F ratios (4 levels, from 7.5 to 4.5) and initial fuel temperature (20 and 50 °C). From the IDT standpoint, they observed an improvement (both in terms of delay and ignition consistency) for higher catalyst loading, higher HTP grade, higher O/F ratios, and higher fuel temperature. A similar positive influence of temperature was experimentally found by Ak et al. [36]. Interestingly, increasing the catalyst content past 5 wt.% yielded diminishing returns. When the fuel temperature was raised from 20 to 50 °C, the average IDT reduction for all four considered O/F ratios was about 33%, highlighting the significant effect temperature has on the ignition mechanism. When comparing ignitions at different catalyst loading, it was observed that the temperature increment leads to more sizeable improvement for the smaller catalyst loading. A further analysis into the IDT, lead to the identification of three parts: (i) HTP decomposition delay, measured from propellant contact to first vapour emission; (ii) physical delay, measured from the previous to the formation of an expanding vapour cloud; and (iii) chemical delay, measured from the previous to first light emission. They observed that higher HTP grade, O/F, and catalyst loading all cause a reduction in the HTP decomposition and chemical delay, given the larger presence of reactive species, while it did not affected the physical delay. Additionally, the following trends for each phase characteristic temperatures were observed: (i) the temperature of HTP decomposition decreases with HTP grade, O/F, and catalyst loading, as more reactive species allows the decomposition at lower thermal energy inputs; (ii) the temperature associated with

physical delay remains stable varying all parameters, suggesting that physical mixing and vaporisation are dependent on reaching a specific thermal threshold; and (iii) the temperature of the chemical delay reduces with the same dependences showed by that of HTP decomposition due to the increase of the pre-exponential factor of the Arrhenius law, signifying higher frequency of effective molecular collisions, which allows chemical reactions to occur at lower temperature. In a similar pattern to what occurred with the IDT, increasing the catalyst loading past 5 wt.% leads to diminishing returns in terms of pre-exponential factor increase. Calculation of the activation energy starting from the IDT and temperature, revealed that, differently from the pre-exponential factor, its value stays the functionally the same for all considered conditions. Finally, measurement of the flame temperature led to the conclusion that, despite not being particularly efficient from an IDT standpoint, an increment in the catalyst loading leads to higher combustion temperatures, with evident benefits in the final specific impulse of the propellants, although its improvement is partially compensated by a larger average molar mass of the combustion products. A collection of formulations discussed in this section is reported in Table 7.

Table 7. Kerosene-based catalytic fuels.

Blend	Additive	HTP Grade	IDT [ms]	Ref.	$I_{s,vac}^{max}$ [s] (O/F)	Notes
Jet A-1:TMEDA (80:20)	20 wt. cobalt(ii) neodecanoate	98%	21	[23]	-	Additive: H372
Jet A-1:DMEDA 50:45 wt.%	5 wt.% CE	96%	24	[58]	327.1 (5.41)	-
Jet A-1:MDP 50:48.5 wt.%	1.5 wt.% CE	96%	18	[30]	327.6 (5.48)	-
Jet A-1 + 50 wt.% MDP:CE (16.6:1 mass)	3.01 wt.% CE	(96%)	18	[30]	327.6 (5.48)	-
Kerosene	4 wt.% MAA	(98%)	80 †	[53]	330.9 (5.94) ‡	MAA: H351

† Results relative to O/F equal to 7.5. ‡ Additive content neglected.

2.6. Double-Salt Strategy

The strategies that have been discussed so far addressed several common fuel issues (e.g., final cost, toxicity, salt solubility...) by focusing on the liquid phase of the formulation, with the additive being selected as is from a broad pool of available compounds based primarily on compatibility considerations. However, a less explored approach, here referred to as double-salt strategy, also exists. This strategy focuses on enhancing the catalyst effectiveness, therefore reducing the amount required in the fuel, by exploiting the existence of synergistic effects between salts containing different cations.

In their review, Hurlbert et al. [55] reported that ignition of kerosene could be made instantaneous if a mix of salts is used instead of only one. Specifically, they reported the instantaneous ignition of a fuel composed of mixed salts of iron and copper, p-tert-butylcatechol and kerosene, but other high reactivity blends were achieved mixing salts of copper and cobalt, copper and chromium, and copper, cobalt, and chromium employing TMEDA as promoter. Melof et al. [17], in their additive and promoter screening acknowledged the possibility of improving the results by mixing together iron and copper based salts. Cong et al. [56], reported that the results, already discussed in Section 2.5, can be further improved if salts of manganese(iii) and cobalt(ii) are both present in the formulation. Finally, although, not performance-improving, the use of a couple of catalyst is reported also in Ref. [40].

2.7. Gelled Fuel Strategy

Finally, a strategy employed to address solubility issues is gelation. This approach consists in the inclusion of a gelling agent in the formulation to homogenise the blend. However, this homogeneity comes at a cost: if not carefully formulated, gelled fuels can easily exhibit longer ignition delay times than their non-gelled counterparts, as the increased viscosity hinders mixing between fuel and oxidiser. From a system-level perspective, a more viscous fuel show a worse atomization performance, which need to be compensated by ad hoc-schemes or increasing the injector pressure drop. Nevertheless, when these drawbacks are acceptable, gelation represents a viable solution for achieving long-term stability of hypergolicity-imparting additives within a given fuel.

Wook et al. [60] developed and patented a gelled hypergolic formulation with HTP. The claimed fuel formulation consists of: (i) ethanol, as fuel; (ii) MEA, as promoter; (iii) at least one gelling agent (e.g., methylcellulose, agarose, silicon dioxide) to be used in varying proportions and always below 20 wt.%; (iv) a catalyst, selected among MAA (1–10 wt.%), copper(i) chloride (5–30 wt.%), or manganese(ii) chloride (1–10 wt.%). Additionally, in an abandoned claim, the presence of metal particles (e.g., aluminium and boron) is suggested to further enhance reactivity; For their effect on the fuel refer to Ref. [61].

Subsequently, Wook et al. [62] applied for a new patent on gelled hypergolic formulation. According to the new claims, the gelled fuel consists of: (i) a $C_1 - C7$ alcohol, (ii) at least one amino-based or glycol-based compound (including ethylene glycol) as promoter; (iii) hydroxypropyl cellulose as gelling agent in amounts ranging from 0.6 to 4 wt.%; (iv) energetic additives including aluminium, boron, magnesium, or carbon particles in amounts ranging from 0.4 to 4 wt.%; and (v) at least one transition metal catalyst based on manganese, copper, and chromium. Additionally, in some embodiment of this invention, the oxidiser itself can be gelled separately, with the use of cellulose-based gelling agent. Although, it was not ultimately granted, this patent clearly demonstrates how gelation provides solution stability, enabling the inclusion of additional energetic materials, such as aluminium and boron powder, whose inclusion was otherwise not possible, albeit at the expense of increased viscosity and associated system-level penalties.

Jyoti et al. [61] reported the results of their study on gelled MEA. The IDT was measured via drop test, employing 90% HTP. As gelling agent, a combination of polyvinylpyrrolidone and fumed silica (in a 1:1 mass ratio) was employed. The gelation of the fuel allowed the stable suspension of energetic nanopowders, specifically, aluminium, boron, and carbon. As catalytic additives, CC dihydrate and MAA were used at concentrations below than 1 wt.%. As baselines, non-gelled samples and gelled samples without nanopowders were produced. Noticeably, samples without gelling agents and energetic nanopowders did not ignite at 1 wt.% of either additive. Gelled samples with no nanopowders were able to ignite in, 2 and 20 ms, with CC and manganese salt, respectively, suggesting the positive effect of gelling agents on fuel reactivity. Concerning samples with the energetic nanopowders, the following order of reactivity was observed: boron > carbon > aluminium. In particular, boron loaded samples exhibited the shortest IDT, equal to 3 and 4 ms, for copper and manganese-based catalysts, respectively. However, it must be stated that the drop test procedure, employed by Jyoti et al. differs from the standard, in that a constant flow of oxidiser droplet is released until fuel ignition, and that may have led to an artificial reduction of the IDT by providing a less controllable, and larger, amount of oxidiser. Finally, a direct comparison of the two additives showed that CC always leads to faster ignitions than MAA. However, no clear trend in the critical catalyst concentration (i.e., the minimum amount of salt required for hypergolicity) emerged, as depending on the formulation, lower amount of CC than MAA could be required.

Kurilov et al. [63], reported the successful use of a gelling agent to combine two insoluble compounds: TMEDA and CC. As gelling agent, 6 wt.% of Aerosil 200 (SiO_2) was used. Testing the ignition of the resulting fuel in a drop test setup returned an average IDT of 14 ms with 96% HTP, and just 1 wt.% of additive.

TMEDA was also employed as the basis of a catalytic gelled fuel in the study by Ricker et al. [64]. As catalytic agents, the use of silver nanoparticles (obtained through citrate, glucose and polyol method), platinum nanoparticles, and manganese dioxide nanoparticle was tested. The IDT was measured through drop tests employing 96 % HTP. An initial series of tests revealed that, regardless of particle size and synthesis method, silver nanoparticles outperform platinum and manganese dioxide in terms of IDT. A subsequent series of tests, aimed at identifying the most effective silver nanoparticles, showed that particles obtained with the citrate method imparted the highest reactivity. This result was somewhat unexpected, given the intermediate particle size associated with the citrate synthesis method were not the smallest, and prompted further investigation into the role of the capping agents used during nanoparticle synthesis. Silver nanoparticles produced via the polyol method were therefore tested using either polyvinylpyrrolidone (PVP) or citrate as stabilising agents, revealing that citrate-stabilised particles leads to significantly shorter IDTs. From a stability standpoint, formulations employing PVP were found to be less stable than those containing citrate. This enhanced stability was attributed to a more negative ζ potential, indicative of increased electrostatic stabilisation of the colloidal dispersion according to DLVO theory. Finally, a comparison between dried and ethanol-dispersed silver nanoparticles was conducted. Regardless of the synthesis method and stabilising agent, the use of ethanol-dispersed particles consistently resulted in smaller IDT. The shortest IDT, equal to 9 ms, was achieved with a fuel containing 5 wt.% of silver nanoparticles dispersed in ethanol as catalyst, stabilised with 10 wt.% of sodium citrate.

Table 8 contains some of the formulations presented in the discussed papers.

Table 8. Gelled catalytic fuels.

Fuel	Additive	HTP Grade	IDT [ms]	Ref.	$I_{s,vac}^{max}$ [s] (O/F)
MEA	5.5 wt.% PVP + 5 wt.% SiO_2 + 2 wt.% Al + 0.5 wt.% CC	90%	4	[61]	-
TMEDA	5.5 wt.% SiO_2 + 1 wt.% CC	98%	14	[63]	325.2 (4.89)
TMEDA	Gelling agent + 5 wt.% Ag nano	96%	17	[64]	-

3. Reactive Fuels

3.1. Introduction

As discussed in Section 1, hypergolicity can also be achieved by incorporating a reactive additive that directly reacts with the oxidiser, rather than promoting its catalytic decomposition. Reactive additives, which typically belong to the metallic hydride family, exhibit exceptionally high reactivity towards hydrogen peroxide. The enthalpy released in the reaction is approximately eight times greater than that associated with catalytic decomposition processes [65]. As a result, reactive fuels generally achieve significantly shorter IDTs, thus mitigating the probability of hard start events [66]. An additional distinguishing feature of reactive systems is that pre-ignition chemistry is initiated predominantly in the liquid phase [20]. This characteristic may reduce the sensitivity of IDT to spray atomization quality and ambient pressure. Moreover, reactive additives tend to have a limited negative impact on the specific impulse, since their reaction products exhibit a lower average molar mass than those generated in catalytic systems [67]. Finally, the reduction of solid residues

or heavy decomposition products reduces the risk of nozzle throat erosion, which is a critical durability concern in space propulsion systems.

In contrast with the wide variety of catalytic additives investigated in the literature, research on reactive additives has so far largely converged on a single compound, specifically, sodium borohydride ($NaBH_4$), due to its relatively low toxicity and enhanced chemical stability compared to other compounds, such as lithium borohydride ($LiBH_4$), and lithium-aluminum hydride ($LiAlH_4$), despite lower energetic performance [68]. Additional advantages include its low cost, being the cheapest metallic hydride on the market and wide commercial availability [69]. Regrettably, $NaBH_4$, as well as other metallic hydrates, presents several drawbacks. Its reactivity is rapidly degraded upon exposure to water or oxygen, through the following reactions [67]:

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2, \quad (1)$$

$$NaBH_4 + 2O_2 \rightarrow NaBO_2 + 2H_2O. \quad (2)$$

These reactions may lead to the precipitation of sodium metaborate ($NaBO_2$), depending on the solvent system, and cause IDT worsening. Therefore, the additive and fuel must always be handled under controlled conditions [23]. This requirement increases the production cost of reactive fuels and requires to the use of high-purity solvents because trace water impurities can weaken the performance. Furthermore, $NaBH_4$, although being the least toxic metallic hydride under study, presents non negligible hazard to operators, as its reproductive toxicity has been classified with the level 1B by ECHA, meaning that the exposition to the substance may damage the fertility of the unborn child (H360). Despite these limitations, $NaBH_4$ remains the reference reactive additive in reactive hypergolic fuels, with research efforts primarily focused on solvent-based formulation strategies. The following subsections review these approaches, grouping the proposed formulations into distinct families based on their underlying design strategy.

3.2. Basic Reactive Fuel Architecture

Due to the high reactivity of metallic hydrides, most common reactive fuels generally feature a simple structure, in which a solvent is utilised to dissolve the additive. The primary requirement in solvent selection is the ability to effectively solubilise the reducing additive while exhibiting suitable flammability and physical properties for propulsion applications. Reactive additives are insoluble in apolar hydrocarbons, such as kerosene and dissolve only in aprotic polar solvents. Consequently, glymes, amines, and amides are the classes of compounds most commonly adopted in reactive fuel formulations. Nevertheless, the use of hydrocarbons in reactive fuels is possible by gelling the propellant with a suitable gelling agent, as described in Section 3.4.

The development of reactive hypergolic fuels can be traced back to the work of Diede et al. [70], who patented a formulation consisting of approximately 6–10 wt.% of a reducing agent dissolved in a fuel. The patent identifies several classes of potential reducing agents, including: (i) metallic hydrides, such as $NaBH_4$, $LiBH_4$, and potassium borohydride (KBH_4); (ii) sulfur- and nitrogen-based salts, such as thiosulfates, thiocyanates, and cyanides; and (iii) organometallic compounds, including organoaluminum species. Despite the wide range of options considered, $NaBH_4$ is explicitly identified as the preferred additive. Suitable solvents proposed in the patent include: (i) glymes, such as bis(2-methoxyethyl) ether (diglyme) and tri(ethylene glycol) dimethyl ether (triglyme); and (ii) amino-based compounds, including DMAZ and diethylenetriamine (DETA). These solvents were selected for their ability to dissolve the reducing agents while maintaining

partial miscibility with HTP. Both triglyme- and DETA-based formulations containing 6–8 wt.% $NaBH_4$ were successfully fired in a rocket engine, employing both 96 wt.% and 74 wt.% HTP. Ignition delay times on the order of 1–3 ms were reported in the former case, while tests performed with 74 wt.% HTP exhibited immediate and smooth ignition, although no quantitative ignition delay data were reported for this condition. Furthermore, an additional firing test conducted at a reduced ambient pressure of approximately 1 kPa with triglyme and 96% HTP still yielded IDTs between 1 and 3 ms. According to the authors, after drying to remove residual water, the fuels exhibit good long-term stability, with no observable changes detected over time. Despite the promising ignition performance of these formulations, safety considerations represent a significant drawback. From a regulatory perspective, both triglyme and DETA exceed established toxicity thresholds. Triglyme, like other glyme compounds, is classified as a SVHC by the ECHA due to its reproductive toxicity, although the authors noted that this hazard could be mitigated by triglyme very low vapour pressure. These safety concerns limit the practical applicability of such formulations, despite their favourable hypergolic performance.

Subsequently, Makhali et al. [66] extended the previous work by investigating three additional solvent candidates: (i) tetraglyme, (ii) DMF, and (iii) dimethyl sulfoxide (DMSO), while further exploring the already established triglyme, using 8–12 wt.% $NaBH_4$ as an additive. These solvents exhibit high density (around 1 g/cm^3), low viscosity, moderate specific impulse, and a wide liquid range, except for DMSO, which permits to obtain only relatively low specific impulse with respect the other candidates, and a high freezing point (T_{fr} = 19 °C). Drop-test results showed IDTs below 15 ms at 88.5% HTP. Further impingement-jet tests yielded slightly reduced IDTs, below 10 ms, except for tetraglyme, which exhibited an IDT of approximately 12 ms. Similar to triglyme, tetraglyme and DMF exceed established toxicity thresholds, being included in the SVHC list of the European Chemicals Agency, whereas DMSO presents a significantly lower hazard profile.

Based on these results, Anderson et al. [71] patented formulations employing these four solvents as reduced-toxicity propellants, despite the mentioned regulatory concerns of glymes and DMF, on the basis that they can be handled using standard propulsion-system equipment. Long term storage of the reactive fuels was evaluated at ambient and sub-zero (−29 °C) temperatures. All formulations showed good long-term stability at high temperature; however, under low temperature, $NaBH_4$ precipitated or recrystallised in DMF and DMSO-based fuels. Notably, despite the lower toxicity of DMSO compared to the other compounds, no further studies appear to have been reported on this formulation. Moreover, subsequent investigations found that the saturated solution of $NaBH_4$ in DMF is thermally unstable above 90 °C and can cause violent exothermic reactions, resulting in the spontaneous ignition of the flammable gases produced [72].

With the aim of broadening the solvent selection and identifying low-toxicity alternatives, Florczuk et al. [73] investigated $NaBH_4$ using a wide set of solvents, including alcohols, amines, and selected hydrocarbons. Through preliminary screening drop tests, ethanol and selected amine-based blends, including methanol–amine and amine–amine mixtures, were observed to exhibit high reactivity. Formulations based on MEA, as well as MEA blended with morpholine, piperidine, or dimethylamine (DMA), exhibit IDT below 15 ms when formulated with approximately 8 wt.% $NaBH_4$ and tested with 98% HTP. Despite their good reactivity and relatively low toxicity, these propellants contain MEA, which is characterised by a low specific impulse and unfavourable physical properties, such as a high freezing point and a high viscosity. For these reasons, no further studies have been reported on these formulations.

The same authors [23] investigated also pyridine (PYR) as a promising amine in combination with $NaBH_4$. They found that PYR with 8 wt.% of $NaBH_4$ ignites in 3 ms with

98 % HTP, quicker than DETA with 10 wt.% of the same additive. PYR shows good physical properties, high enthalpy of formation and low toxicity with respect to other promising solvents. In a subsequent research by Kang et al. [74], two novel solvents: propylamine (PRO) and butylamine (BUT) were investigated in a screening campaign together with already tested fuels, including triglyme, tetraglyme, DETA and PYR. Drop tests were conducted with 90% HTP employing a fixed 5 wt.% concentration of $NaBH_4$. In particular PRO and BUT exhibit IDTs of respectively 8 and 16 ms. In the same work, Kang et al. studied the influence on IDT of liquid and gas phase reactions using optical and acoustic sensors, identifying the rate-determining step for each formulation. The results indicated that liquid-phase reactions dominate in the glyme combustion, while gas-phase reactions significantly influence the hypergolic ignition of most amino-based reactive fuels, except for PRO. Accordingly, glymes and PRO are the preferable solvents for simplifying injector design and minimizing combustion instabilities.

Concerning the factors affecting the IDT, Kapusta et al. [75] investigated the combined influence of pressure and temperature using a matrix comprising ambient pressure conditions of 0.1, 0.5, 1, and 2 MPa and temperatures of 22, 40, and 60 °C. By testing triglyme with 10 wt.% $NaBH_4$ and 93.5% HTP, the authors demonstrated that both parameters exert a significant effect on ignition behaviour. Specifically, trends similar to those reported by Pourpoint et al. [65] for catalytic fuels were observed, with ignition delay times increasing at lower pressures and lower temperatures. Comparing the two trends, it can be noted that the rate of deterioration with temperature is comparable at high pressure, while under ambient pressure the sensitivity of reactive formulations to temperature is smaller. In contrast, Diede et al. [70] reported that the transition from ambient pressure to 1 kPa does not cause a visible increase in the ignition delay time.

The main results discussed so far are summarised in Table 9.

As shown in Table 9, despite the high $NaBH_4$ loading, the specific impulses calculated for HTP concentrations from 96 wt.% meet the 317 s requirement in all cases, except for MEA-based formulation. When considering the O/F ratios, triglyme-based formulations may be preferable to amine-based ones, as the former exhibit lower O/F ratios, resulting in smaller differences between fuel and oxidiser tank volumes. Conversely, higher O/F ratios lead to increased volumetric specific impulse due to the high density of hydrogen peroxide.

More recent studies on $NaBH_4$ solvent formulations focused on stability analyses and on formulation optimisation. Lee et al. [67] investigated the ageing of triglyme blended with 4 wt.% $NaBH_4$. The analysis consisted of an accelerated ageing conducted over four weeks at 25 and 50 °C. The effects of moisture and oxygen were examined independently by monitoring changes in chemical composition, density, viscosity, optical properties, and IDT. Samples stored under air, dry air, nitrogen, and vacuum showed progressively lower levels of degradation, in the same order as listed. In addition, the detrimental effect of humidity was analysed separately. Throughout the study, only minor variations in physical properties were observed; however, as it can be seen in Table 10, the IDT exhibited a steady increase over time even under vacuum conditions, attributed by the authors to the presence of residual water originating from triglyme impurities. Soudarin et al. [76,77] identified the minimum $NaBH_4$ concentration required to achieve ignition with triglyme, namely 2.4 wt%, reporting an optimal ignition delay time of around 5 ms in the range between 4 and 6 wt.% of additive with 90 wt.% HTP. The results are slightly improved with respect with the 9 ms declared by Kang et al. with the same formulation [74]. Viscosity measurements further indicated that concentrations above 6 wt.% resulted in viscosities exceeding 10 cP, with peaks above 20 cP above 9 wt%. Impingement jet tests through a 2v1 unlike triplet using the optimized formulation with 6 wt.% of $NaBH_4$ shows comparable results with the previous drop tests.

Table 9. Reactive fuels table. The toxicity info in the note column refers to the solvent.

Fuel	$NaBH_4$	HTP Grade	IDT [ms]	Ref.	$I_{s,vac}^{max}$ [s] (O/F)	Notes
Triglyme	7 wt.%	96.0%	1–3 †	[70]	319.2 (3.65)	Triglyme: SVHC and H360Df
DETA	7 wt.%	96.0%	2–3 †	[70]	324.9 (4.25)	-
Triglyme	8 wt.%	88.5%	10.6	[66]	311.2 (4.10)	See first row
Tetraglyme	10 wt.%	88.5%	12	[66]	311.0 (4.10)	Tetraglyme: SVHC and H360FD
DMF	12 wt.%	88.5%	9.1	[66]	309.5 (4.10)	Fuel H360D
DMSO	8 wt.%	88.5%	10.6	[66]	301.0 (3.75)	High freezing point T_{fr} = 19 °C
Triglyme	8 wt.%	88.5%	9.0 ‡	[66]	311.2 (4.10)	See first row
Tetraglyme	10 wt.%	88.5%	12.0 ‡	[66]	311.0 (4.10)	See fourth row
DMF	12 wt.%	88.5%	7.0 ‡	[66]	309.5 (4.10)	See fifth row
DMSO	8 wt.%	88.5%	7.0 ‡	[66]	301.0 (3.75)	-
DETA	5 wt.%	90.0%	29.3	[74]	318.1 (4.73)	-
Triglyme	5 wt.%	90.0%	9.2	[74]	313.0 (4.02)	See first row
Tetraglyme	5 wt.%	90.0%	8.7	[74]	312.8 (4.00)	See fourth row
PRO	5 wt.%	90.0%	8.0	[74]	319.1 (5.90)	PRO: H361f
BUT	5 wt.%	90.0%	14.0	[74]	318.9 (6.10)	-
PYR	5 wt.%	90.0%	18.7	[74]	314.5 (5.10)	-
DETA	10 wt.%	98.0%	6.5	[23]	326.8 (4.10)	-
PYR	8 wt.%	98.0%	3.0	[23]	322.1 (4.40)	-
Triglyme	7 wt.%	98.0%	5.1	[23]	321.0 (3.50)	See first row
MEA	7 wt.%	98.0%	14.0	[73]	303.2 (3.65)	High freezing point and viscosity

† Result obtained through impinging-jet-test. The injector type is not specified. ‡ Result obtained through impinging-jet-test. 60° 4v1 pentad injector.

Table 10. Drop test results in terms of IDT of a 4-week ageing campaign conducted at 50 °C on a reactive fuel formulation of Triglyme with 4 wt.% of $NaBH_4$ and 90% HTP [67].

Storage	IDT [ms]	STD [ms]
Fresh fuel	8.6	0.7
Room air	11.8	0.8
Dry air	9.8	0.4
N_2	9.3	0.3
Vacuum	8.9	0.5

3.3. Multiple-Solvent Strategy

Some of the most performing solvents employed in reactive fuel systems, such as tetraglyme and DETA, exhibit suboptimal physical or chemical properties, despite their excellent additive-dissolving capability. Both compounds are characterised by a low vapour pressure and mid net energy content. Consequently, several studies have introduced additional co-solvents into the final fuel formulations to improve specific properties while preserving long-term storage stability.

Kang et al. [69], starting from an already tested tetraglyme/$NaBH_4$ formulation (referred to as Stock 0), developed two new blends: Stock 1, obtained by adding tetrahydrofuran (THF), and Stock 2, in which toluene was further introduced. The resulting fuels exhibit increased vapour pressure, lower viscosity and higher net energy content than the baseline. However, the added co-solvents exhibit toxicity concerns. In fact, THF is suspected to be carcinogenic, while toluene shows broad agreement for being reprotoxic [25]. Drop tests revealed slightly reduced IDTs, ranging from 4 to 17 ms at 90, 95, and 98% HTP

concentrations for both Stock 1 and Stock 2 formulations, with the latter exhibiting superior performance. Consequently, Stock 2 was selected for further investigation through engine firing tests to assess the feasibility of the multiple-solvent formulation for commercial application. A firing test was conducted using a 500 N thruster equipped with a pentad, unlike impinging-jet injector, operating with the Stock 2–90% HTP propellant combination. A high ignition rise time ($\tau = 158$ ms) was recorded, together with a reduced c* efficiency of 88.3%, and pressure oscillations reaching 7.69% of the average pressure, both worse than reference values of commercial thrusters.

A subsequent study [21] focused on hard-start mitigation by varying the O/F ratio and HTP concentration. Drop tests with the Stock 2 formulation showed that, under oxidiser-rich conditions, the IDT increases drastically across the investigated HTP concentrations. The authors demonstrated that hard-start events could be avoided by adjusting the initial O/F ratio toward fuel-rich conditions or by using higher HTP concentration. Under one of these conditions, ignition rise times below 100 ms and combustion efficiencies above 90% were achieved; however, combustion instabilities slightly exceeding 5% were still observed at 95% and 98% HTP concentrations. The multiple solvent strategy was later applied to DETA by the same authors, [78] which is more viscous than tetraglyme, but exhibits superior dissolving capability. DETA was mixed with THF for the previous reasons. The formulation was stored under ambient atmosphere for four months without any observable sedimentation; however, a degradation in IDT performance was reported. Nonetheless, a successful static fire test was also achieved with registered combustion instabilities below 2%, and a c* efficiency of approximately 89%.

Finally, the multiple-solvent strategy can be found also in the aforementioned patent by Anderson et al. [71], where the claim of a formulation comprising kerosene, a sufficient amount of triglyme, and at least 1 wt.% of the additive was stated. One representative formulation consisted of 33.3 wt.% kerosene, 58.7 wt.% triglyme, and 8 wt.% $NaBH_4$, forming a translucent yellow solution with no visible precipitates. Despite the limited solubility of $NaBH_4$ in kerosene, the authors reported no recrystallisation over a one-month period at ambient temperature and over six months at −29 °C. An IDT of approximately 21 ms was measured with 85.6% HTP. By comparison, a formulation without kerosene exhibited an IDT of 10.6 ms at 88.5% HTP, indicating that the low reactivity of kerosene and its immiscibility with HTP lead to an increase in ignition delay time. The results of the multiple-solvent strategy are summarised in Table 11.

Table 11. Multiple-solvent strategy in reactive fuels. The toxicity info in the note column relates on the solvent. Already discussed substances toxicity are omitted.

Fuel	$NaBH_4$	HTP Grade	IDT [ms]	Ref.	$I_{s,vac}^{max}$ [s] (O/F)	Notes
Tetraglyme	NA	90.0%	15.0	[69]	313(4.05)	Tetraglyme: SVHC and H360FD
Tetraglyme /THF †	NA	90.0%	15.0	[69]	-	THF H351
Tetraglyme /THF /Toluene †	NA	90.0%	12.9	[69]	-	Toluene: H361d and H373
DETA/THF †	12–15 wt.%	90.0%	25.0	[78]	-	THF: H351
DETA/THF †	12–15 wt.%	95.0%	12.0	[78]	-	=
DETA/THF †	12–15 wt.%	98.0%	7.0	[78]	-	=
Triglyme:Kerosene 58.7:33.3 wt.%	8 wt.%	85.6%	21	[71]	309 (5.59)	Triglyme: SVHC and H360Df

† Percentage composition is not specified.

3.4. Gelled Fuel Strategy

As described in Section 2.7, fuel gelation represents a viable strategy to enhance system stability while simultaneously reducing handling hazards. In the case of reactive fuels, gelation enables the homogeneous dispersion of additive particles in organic fuels, such as kerosene and its derivatives, which are normally incompatible with metallic hydrides. Therefore, gelation can be used as a method to use low cost and widely available hydrocarbons in reactive fuels avoiding stability issues over time. Additionally, this strategy significantly lowers the vapour pressure of the propellant and mitigates the risk of catastrophic failure in the event of piping or tank leakages, as the leakage rate is substantially reduced.

Natan et al. [79] investigated the hypergolicity of a gelled reactive fuel composed of kerosene, 4 wt.% fumed nano-silica as a gelling agent, and 7 wt.% of suspended $NaBH_4$ particles. Drop tests performed with 92% HTP resulted in IDTs $\leq$8 ms. Subsequently, Connell et al. [80] measured the first light emission and ignition onset in an impinging-jet configuration using three gelled fuel formulations based on n-heptane, n-dodecane and kerosene, containing 1–7 wt.% $NaBH_4$ and 3.1 wt.% fumed silica. The two measurements were necessaries, as the first light emission did not necessarily lead to ignition. The early light emission is attributed to localized exothermic reactions between $NaBH_4$ and H_2O_2 that generate transient hot spots and reactive species, which are insufficient to raise the mixture to the gas-phase autoignition temperature and therefore do not necessarily lead to sustained ignition. A minimum IDT of 20 ms was observed at around 4 wt.% $NaBH_4$ using heptane. n-dodecane was found constantly slower than n-heptane, probably because of the decreased volatility and higher heat of vaporization with respect to n-heptane. Moreover, samples with kerosene exhibited the worst IDTs, approximately 68% longer than those of n-dodecane. The authors [80] suggest that, since kerosene contains a range of hydrocarbons (typically C6–C16), and given the finite amount of chemical energy available within the ignition kernel volume, the presence of high-molecular-weight hydrocarbons may hinder successful ignition kernel formation because of their larger volumetric heat capacities and vaporization enthalpies, increasing the sensible enthalpy required.

Due to the rheological and mass-transfer limitations inherent to gelled reactive fuels, IDTs are significantly higher than those measured for liquid systems, and large experimental deviations are observed in the impinging-jet tests. The most relevant results about gelled reactive fuels are shown in Table 12. From a performance standpoint, the specific impulse penalty associated with the presence of the gelling agent is negligible, while the volumetric specific impulse is enhanced because of the increased propellant density. However, the use of gel fuels needs to take into account high pressure losses as a result of gel viscosity and low combustion efficiency caused by poor atomization.

Table 12. Gelling reactive fuels results.

Fuel	$NaBH_4$	Gelling Agent	HTP Grade	IDT [ms]	Ref.	$I_{s,vac}^{max}$ [s] (O/F)
Kerosene	7 wt.%	4.0 wt.%	92%	<8	[79]	319.9 (6.70)
n-heptane	6 wt.%	3.1 wt.%	86%	20.0	[80]	313.6 (7.80)
n-dodecane	6 wt.%	3.1 wt.%	86%	27.8	[80]	313.2 (7.80)
Kerosene	6 wt.%	3.1 wt.%	86%	46.3	[80]	312.2 (7.40)

3.5. Hybrid Additive Strategy

A further development within the hypergolic fuel design space is represented by the so-called hybrid additive strategy, which exploits the synergistic combination of catalytic and reactive additives within the same formulation. The objective of this approach is to

further reduce the IDT, pushing the performance of green hypergolic fuels closer to that of conventional toxic propellant pairs, which typically exhibit IDTs in the 1–3 ms range [81]. Regrettably, the implementation of such a strategy is not straightforward. In fact, metallic hydrides, commonly employed as highly reactive additives, are generally incompatible with conventional peroxide catalysts based on transition-metal salts, as their coexistence often leads to undesired side reactions and catalyst deactivation. As a result, alternative catalytic systems for hydrogen peroxide decomposition were investigated.

Kim et al. [72] demonstrated the effectiveness of this strategy by combining $NaBH_4$ with two iodide salts, namely sodium iodide (NaI) and ammonium iodide (NH_4I). Five solvents were considered: ethylenediamine (EDA), DIMP, DETA, DMF, and dimethylacetamide (DMA). Unfortunately, with the exception of DIMP and DETA, the tested solvents do not meet the requirement of Table 2, while NaI is reportedly reprotoxic. As reported in Table 13, the fastest ignition was observed in a specific reactive-to-catalytic additive ratio, regardless of the solvent used. In particular, minimum IDTs were obtained for the mass ratios $NaBH_4$:NaI = 6.5:3.5 and $NaBH_4$:NH_4I = 6.5:3.5, achieving IDTs below 3 ms. The authors postulated that this synergistic effect arises from the rapid catalytic decomposition of HTP, which generates highly reactive intermediate species that react rapidly with the metal hydride, thus accelerating the overall ignition process. Nevertheless, the authors themselves noted that the reason why a specific additive ratio yields the fastest ignition remains unclear. Moreover, little attention has been dedicated to the interactions between catalytic and reactive additives, and the possibility of competitive or side reactions occurring within the formulation has not been systematically investigated. Concerning the theoretical maximum specific impulse, despite the high amount of additive and the moderate HTP concentration, all the formulations except for DMA respect the stated requirement in Table 3.

Table 13. Hybrid-additive fuels results with 94.7 % HTP [72].

Fuel	$NaBH_4$	Catalyst	IDT [ms]	$I_{s,vac}^{max}$ [s] (O/F)	Note
EDA	6.5 wt.%	3.5 wt.% (NaI)	2.8	322.0 (4.10)	EDA: SVHC, NaI: reprotoxic H361 and H373
DIMP	6.5 wt.%	3.5 wt.% (NaI)	3.1	321.8 (4.50)	NaI: H361 and H373
DMA	6.5 wt.%	3.5 wt.% (NaI)	3.6	315.4 (4.10)	DMA: H360D, =
EDA	6.5 wt.%	3.5 wt.% (NH_4I)	2.7	322.2 (4.10)	EDA: SVHC, =
DIMP	6.5 wt.%	3.5 wt.% (NH_4I)	2.9	322.1 (4.50)	-
DMA	6.5 wt.%	3.5 wt.% (NH_4I)	3.1	315.7 (4.10)	DMA: H360D
DETA	6.5 wt.%	3.5 wt.% (NH_4I)	4.8	322.4 (4.20)	-

4. Ionic Liquids

4.1. Introduction

Over the last decades, a new approach to the development of green hypergolic fuels based on ionic liquids (ILs) has emerged. Ionic liquids are salts that remain in the liquid state at temperatures below 100 °C. Interest in these compounds arises from their exceptional tunability: by tailoring the chemical structure of either the cation or the anion, it is possible to synthesise liquids with properties specifically suited to propulsion applications. In particular, selected ILs can exhibit high reactivity toward commonly used oxidisers and, in some cases, even intrinsic hypergolicity. Such structural tailoring can also be exploited to adjust their physical properties to meet specific mission requirements. From a chemical standpoint, ILs are commonly classified according to the nature of the anion, as it primarily governs the reactivity and hypergolic behaviour with a given oxidiser. In contrast, the

cation is typically selected to tailor the physical properties of the fuel, although it can also influence the IDT.

Generally speaking, ILs are characterised by negligible vapour pressure at ambient conditions and high density, resulting in more favourable properties compared to conventional toxic fuels [82]. The former property reduces inhalation risks, enhancing operational safety, while the latter enables smaller fuel tanks, thereby contributing to an overall reduction in system mass. Moreover, ILs exhibit high thermal stability, a desirable feature for in-space propulsion applications, where propellants are required to withstand repeated thermal cycles.

Nevertheless, ILs also present several drawbacks that are common to most of their subclasses. As shown in Table 14, they exhibit higher viscosities and melting temperature than conventional liquid propellants and a moderate theoretical maximum gravimetric specific impulse, which, in some cases, falls below the minimum desired value reported in Table 3. Furthermore, although many ILs are highly reactive with more toxic oxidisers, such as HNO_3 and NTO, only a limited number of families are known to be hypergolic with HTP [83]. This limitation often implies the use of ignition-promoting additives, partially offsetting one of the key advantages of ionic-liquid-based fuels.

From an industrial perspective, ionic liquids are in most cases more expensive and complex to produce, as they typically require multi-step synthesis routes, whereas conventional catalytic and reactive propellant components are readily commercially available substances. Finally, although limited information is currently available regarding the toxicity of ionic liquids themselves, it is well established that many of the synthetic pathways employed for their production or for the preparation of their additives involve the use of highly toxic compounds, such as toluene, THF, methanol, and cyanide or nitrile containing reagents (e.g., methyl cyanide (MeCN) and $NaBH_3CN$) [84]. Although such hazards appear fundamentally incompatible with the definition of a green propellant, the scientific community currently lacks standardized criteria for this classification [2]. Consequently, research organizations often adopt proprietary frameworks that focus exclusively on the safety of the final product during operational handling. Nevertheless, under the toxicity thresholds established in Section 1.3, some of these propellants cannot be considered fully compliant with the requirements of this study when considering their full life-cycle.

Following the identification by Schneider et al. [85] in 2008 of the first ionic liquid family (namely dicyanamide-based ionic liquids, $[N(CN)_2]$) hypergolic with WFNA, subsequent studies have shown that, with HTP, hypergolicity is essentially limited to borohydride- and thiocyanate-based anions. While part of the ongoing research effort is focused on understanding the relationship between chemical structure and reactivity to develop self-igniting ionic liquids with HTP, an alternative and widely explored strategy consists in inducing hypergolicity in otherwise non-hypergolic ionic liquids through the addition of properly synthesised additives [84]. Consequently, the following subsections review these approaches, named self-igniting ionic liquid strategy and additive-dependent ionic liquid strategy. Given the intrinsically high viscosity and low vapor pressure of ionic liquids, a strategy common to both approaches involves the addition of a suitable solvent, typically characterized by lower viscosity and higher vapor pressure, in order to improve mass transfer, mixing with the oxidiser and, ultimately, ignition behaviour [84].

4.2. Self-Igniting Ionic Liquids Strategy

Due to the strong reducing character of the B–H bond toward hydrogen peroxide, ionic liquids containing hydride-based anions were among the first candidates explored for self-igniting behaviour with HTP.

Schneider et al. [86] first demonstrated the hypergolicity of borohydride-based ionic liquids by pairing the anions $[BH_4]$ and $[Al(BH_4)_4]$ with trihexyltetradecylphosphonium (THTDP), achieving IDTs of 3 s and 30 ms, respectively. Despite these promising results, the resulting fuels suffered from high viscosity and poor moisture stability, limiting their practical applicability [87]. Subsequently, Bhosale et al. [88] produced three ionic liquids based on $[BH_4]$ and cyanoborohydride $[BH_3CN]$ anions, while using 1-ethyl-3-methyl imidazolium [EMIM] and 1-methyl-1H-imidazol-3-ium [AEMIM] as cations. Only $[EMIM][BH_4]$ ignited within 1 s, with an average IDT of 18.5 ms; however, the fuel is solid at ambient temperature. More recently, Wang et al. [89] reported the synthesis of novel hypergolic borohydride-based ILs starting from $[EMIM][BH_4]$ and butyl-3-methylimidazolium borohydride ($[BMIM][BH_4]$) through an in situ synthetic approach employing low-viscosity inorganic superbases. In particular, the use of 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) significantly reduced the fuel viscosity, from an initial value of 486.6 cP down to approximately 58 cP [84]. The lowest reported IDT within this class was 28.3 ms with 90% HTP.

To date, only three borohydride-based anions, (i) $[BH_4]$, (ii) $[BH_3CN]$, and (iii) $[Al(BH_4)_4]$, have been reported to exhibit hypergolicity with HTP [84]. Despite their excellent ignition performance, the practical application of these ILs is constrained by synthesis-related issues, notably the required use of sodium borohydride, which presents high level of hazard, as discussed in Section 3.

Regarding thiocyanate-based ionic liquids, Lauck et al. [82] discovered their potential and hypergolic character with HTP employing two commercially available compounds, namely, 1-ethyl-3-methyl imidazolium thiocyanate ([EMIM][SCN]) and 1-butyl-3-methylimidazolium thiocyanate ([BMIM][SCN]). The obtained IDTs of the two substances with HTP (96.1%) was, on average, 31.7 ms for [EMIM][SCN], and 45 ms for [BMIM][SCN]. The authors noted that the difference between the two fuels performances confirmed the approximate 10 ms difference between [EMIM] and [BMIM] cations already found by previous researches [90,91]. The two ionic liquids, beyond their hypergolic character with HTP, combine several favourable properties including low melting points (below 0 °C), moderate viscosities (below 40 mPas), and, in the case of [EMIM][SCN], a positive enthalpy of formation. Although their theoretical specific impulse is slightly lower than that of the conventional MMH/NTO propellant couple, both fuels exhibit a volumetric specific impulse approximately 10% higher, owing to their relatively high densities (1.11 and 1.07 g cm^{-3} for [EMIM][SCN] and [BMIM][SCN], respectively). Thermogravimetric analysis further revealed good thermal stability, with decomposition temperatures exceeding 210 °C. In addition, these ionic liquids are associated with comparatively low health hazards. Nevertheless, their relatively high IDTs, moderate viscosities, elevated market cost, and the presence of sulfur-oxide species among the combustion products remain notable drawbacks. After the promising findings of the previous investigations, Ricker et al. [92] studied the influence of the cationic structure on [SCN] ILs. Six thiocyanate-based ionic liquids featuring pyridinium and pyrrolidinium cations were synthesised as potential fuel candidates for use with 97.4 wt.% HTP. The drop test results showed that ionic liquids containing pyridinium cations consistently exhibited shorter IDTs than their pyrrolidinium counterparts. Among the tested compounds, 1-Ethylpyridinium thiocyanate ([EPy][SCN]) displayed the shortest IDT (26.8 ms), along with the lowest viscosity (27.5 mPas), a relatively high density (1.13 g cm^3), and excellent thermal stability, with a decomposition temperature of 247 °C. A year later, Ricker et al. [93] presented seven novel protic ionic liquids with imidazolium-based cationic structures and thiocyanate anions. All the substances were hypergolic with HTP and presented higher volumetric specific impulse with respect to the reference toxic couple. An impressive IDT of 7.3 ms was achieved with 97%

HTP by 1-H-imidazolium thiocyanate [Him][SCN], which however, was solid at ambient temperature. Blending 35 wt.% of [Him][SCN] with 65 wt.% of [EMIM][SCN] resulted in a promising formulation with IDT of 16.7 ms, high density (1.154 g/cm^3) and moderate viscosity (40.4 cP). A summary of the most relevant results reported for self-igniting ionic liquids with HTP is provided in Table 14. With the exception of $[HIM_{0.35}][EMIM_{0.65}]$ [SCN], self igniting ILs present a slightly lower specific impulse than the reference value of Table 3. Nevertheless, the moderate O/F ratio below 5 is favourable for the same reasons explained in Section 3.2.

Table 14. Self-igniting ionic liquids results.

Fuel	T_m [a] [°C]	η [b] [cP]	HTP Grade	IDT [ms]	Ref.	$I_{s,vac}^{max}$ [s] (O/F)
$[EMIM][BH_4]$ (DBN)	50	-	95.0%	18.5	[88]	330.8 (4.74)
$[EMIM][BH_4]$	-	58	90.0%	28.3	[89]	325.0 (5.24)
[EMIM][SCN]	−6	23	96.1%	31.7	[82]	314.2 (3.97)
[BMIM][SCN]	−29	36	96.1%	45	[82]	316.4 (4.33)
[EPy][SCN]	-	28	97.4%	26.8	[92]	311.6 (4.34)
$[HIM_{0.35}][EMIM_{0.65}]$ [SCN]	-	40	97.0%	16.7	[93]	319.9 (3.73)

[a] Melting temperature. [b] Dynamic viscosity at 25 °C.

4.3. Additive-Dependent Ionic Liquids Strategy

Despite the favourable properties of ionic liquids, the intrinsic reactivity of individual compounds is generally insufficient to achieve IDTs below 10 ms while preserving all the physical properties required for a practical propellant. Consequently, extensive research efforts have focused on the use of additives capable of overcoming the main limitations of ionic-liquid-based fuels.

The first significant successes of this strategy were reported by Chinnam et al. [94], who in 2018 synthesised two iodine-based organometallic salts containing the $[B_{12}I_{12}]^-$ anion, incorporating either a ferrocene ($[FcCH_2NEtMe_2]^+$), or a copper complex cation ($[Cu(en)_2(CH_3CN)_2]^{2+}$). The addition of 8 wt.% of either additives to [EMIM][BH_3CN] resulted in a reduction of the IDT from approximately 30 s with 70 wt.% HTP to 45 ms, and further down to 17 ms when using 95 wt.% HTP [84]. The strong reduction in IDT was attributed to the synergistic effect between the metal-based catalyst and iodine. The role of iodine was later independently confirmed by Wang et al. [84], who demonstrated that the addition of 15 wt.% iodine rendered previously non-hypergolic ionic liquids hypergolic.

In 2020, Bhosale et al. [83] conducted further investigations on five different additives, including Co(ii), Cu(ii), and Mn(ii) metal salts, $NaBH_4$, and a novel additive synthesised by the authors, namely 1,3-dimethylimidazolium copper iodide ($[diMIM]_n[Cu_2I_3]_n$). When evaluated at a concentration of 5 wt.%, the transition metal salts exhibited limited solubility in the ionic liquid matrix, while $NaBH_4$, although soluble, proved to be unstable during long-term storage. In contrast, $[diMIM]_n[Cu_2I_3]_n$ demonstrated complete solubility and remained stable for up to 30 days. The use of this additive reduced the IDT from values exceeding 1 s to 116 ms and 173 ms for [EMIM][BH_3CN] and [AEIM][BH_3CN], respectively. Increasing the additive concentration to 15 wt.% further decreased the IDT to 29 ms; however, this improvement was accompanied by a significant increase in viscosity, which approximately doubled from 19 cP to 44 cP, making it less appealing for a commercial use. Finally, these fuels showed comparable specific impulse to that of other ionic liquids. Despite the positive effect of iodine-based promoters on IDT reduction, additives offering higher reactivity at lower concentrations were later preferred and tested in rocket engine hot-fire campaigns. As an example, in a subsequent work, Bhosale et al. [95] synthesised two novel copper–cyanoborohydride-based additives, namely

[Cu^{II}(1H-imidazole)$_4$(BH_3CN)][BH_3CN] and [Cu^{II}(1-methylimidazole)$_4$(BH_3CN)$_2$], hereafter referred to as Cu-P1 and Cu-P2, respectively. Both compounds were found to be intrinsically hypergolic with 95 wt.% HTP, exhibiting IDTs of 3.75 ms for Cu-P1 and 8.5 ms for Cu-P2. When employed as additives at a concentration of 13 wt.% in different fuel formulations, Cu-P1 imparted a significant enhancement of hypergolic performance. In particular, [EMIM][BH_3CN] doped with 13 wt.% Cu-P1 showed an IDT of 9.5 ms with 95 wt.% HTP, while a comparable formulation based on tetraglyme (one of the solvents typically used in reactive fuels, see Section 3) achieved an IDT of 9.0 ms under the same conditions. A 1:1 mass ratio blend of [EMIM][BH_3CN] and tetraglyme containing 13 wt.% Cu-P1 further reduced the IDT to 7.8 ms with 95 wt.% HTP, although a longer delay of 16.5 ms was observed when using 70 wt.% HTP. The [EMIM][BH_3CN]/tetraglyme (1:1) formulation with 13 wt.% Cu-P1 exhibited a density close to 1 g/mL^{-1} and a moderate viscosity of approximately 12 cP, indicating favourable handling properties. These results marked a first turning point, demonstrating that properly designed copper–cyanoborohydride additives can simultaneously achieve sub-10 ms IDTs and acceptable physical properties, overcoming one of the main limitations of earlier additive strategies.

Building on this high-performing copper-based additive, Bhosale et al. [87] explored new promising formulations comprising Cu-P1 (3–13 wt.%), [EMIM][BH_3CN], and varying amounts of ethanol. Using an initial 50:50 wt. ratio of [EMIM][BH_3CN] and ethanol, IDTs below 10 ms were achieved with at least 7 wt.% Cu-P1, reaching a remarkable minimum IDT of 4.1 ms at 13 wt.% Cu-P1 with 95% HTP. From these analyses, an optimal Cu-P1 concentration of 9 wt.% was selected. Subsequent investigations on ethanol content showed that it could be varied between 40 and 80 wt.% and retain IDTs below 8 ms. Taking into account optimal rocket-fuel parameters such as viscosity, density, and IDT for hot-fire tests, the formulation containing 9 wt.% Cu-P1 in [EMIM][BH_3CN]/ethanol (50/50 wt.%), denoted ILethCu01, was selected for further study. This formulation was successfully tested 21 times on a 50 N thruster, with only a single hard start, likely caused by irregular propellant injection through the feeding line, but with no engine failure. Notably, the combustion efficiency and combustion instability were 96% and 3.56%, respectively, with instability remaining below 5%, indicating suitability for rocket applications and low impact on fuel performance. The chemical stability of ILethCu01 was confirmed by Raman spectroscopy, with no residue observed even after prolonged storage. Individual spectra of ethanol, [EMIM][BH_3CN], and Cu-P1 were also analysed to identify key peaks of each functional group for comparative purposes. The –CH_3 peak of [EMIM][BH_3CN] and ethanol overlapped in ILethCu01, consistent with the expected spectral contributions of the mixture. Overall, this study demonstrated that additive-based ionic liquid formulations can transition from drop-test validation to repeated hot-fire operation, confirming the practical viability of the additive-dependent strategy.

Regarding thiocyanate-based ionic liquids, Lauck et al. [82] started from the most promising self-igniting thiocyanate-based ionic liquid [EMIM][SCN] and introduced copper thiocyanate (CuSCN) as an additive to further reduce the IDT, a combination that became known as HIP_11. With 5 wt.% of CuSCN, the IDT decreased from 31.7 ms to 4.5 ms, despite a concomitant increase in viscosity from approximately 20 to 30 cP. Based on these promising performances, Negri et al. [96] tested the bi-propellant combination [EMIM][SCN] + CuSCN (at 1 wt.% and 5 wt.%) with 97% HTP in a 25 N (sea-level theoretical thrust) engine. The authors were the first to demonstrate that an ionic liquid paired with HTP could be successfully ignited within a rocket engine and sustain a static firing test. Of 35 firings, several tests conducted with 1 wt.% CuSCN failed to ignite, indicating that this formulation was insufficiently reactive. In contrast, all tests performed with 5 wt.% additive resulted in successful ignitions, achieving combustion efficiencies higher than

92.8% and limited combustion instabilities between 1.1% and 1.7%. The pressure rise time, defined as the interval required for the chamber pressure to increase from 10% to 90% of its average value, was very short—below 13 ms in all but one test—highlighting the excellent dynamic response of the system. A similar formulation consisting of 2.5 wt.% of CuSCN in [EMIM][SCN] was recently tested by Manassis et al. [97], employing 98% HTP. The focus of the test campaign was to assess the ignition of a 50 N thruster under sub-atmospheric pressure. Two injectors, a pentad and a configuration composed of four unlike doublets, were tested at progressively lower ambient pressures, down to 10 mbar. Despite damage to the film cooling manifold during the campaign, which affected the global O/F ratio at very low pressures, the results revealed significant findings. In particular, the IDT was not found to depend strongly on the ambient pressure, possibly owing to progressive propellant heating during the tests compensating for the low-pressure effects. Differences were noted between the two designs: the injector with four doublets achieved IDTs near 10 ms, which were consistently lower than the values recorded for the pentad injector (15–25 ms). Similarly to the IDT, the combustion efficiency, roughness, and rise time showed little overall dependence on the ambient pressure. These findings confirm the robustness of HIP_11's hypergolic response, suggesting its suitability for reliable operation in vacuum conditions without the significant ignition delays typically expected at reduced pressures. Compared to cyanoborohydride-based systems, thiocyanate ionic liquids require simpler additives and lower concentrations, while still achieving comparable ignition performance, making them attractive for more practical implementations.

Bhosale et al. [87] analysed thiocyanate ionic liquids producing a formulation composed of [EMIM][SCN], ethanol, and a new synthesised copper additive called Cu-P3, whose composition is not specified. From a drop test analysis and a performance versus physical properties trade off, the chosen formulation was called ILethCu02 and contained 63.7 wt.% [EMIM][SCN], 27.3 wt.% ethanol and 9 wt.% Cu-P3. The viscosity and density of the fuel were 1.032 g/cm^3 and 5.72 mPas, respectively, at 25 °C. The wide liquid range of the fuel, from −80 to 290 °C, demonstrates its operability over a broad temperature range, and the average IDT of the fuel was 7.85 ms with 95 wt.% HTP. Theoretical performance on specific impulse is in line with known requirements, and the optimum propellant point is found for an O/F of 3.8, which translates into a limited difference in tank sizes between fuel and oxidiser. ILethCu02/95 wt.% HTP was further tested in a 50 N hypergolic rocket engine with a chamber pressure of 10 bar. Despite successful static fire tests that were conducted, tests revealed a maximum combustion efficiency of 85% and combustion instability in the range of 3–8% at different O/F and mass flow rate of propellant. The authors do not provide a possible explanation for these results. This degradation in combustion performance, despite fast ignition, suggests that ignition delay alone is not sufficient to guarantee stable combustion, and that additive-induced changes in reaction kinetics or vaporization behaviour may affect flame stability.

Finally, Merz et al. [98] deepened the thiocyanate based formulations, developing a metal-free, low-viscosity hypergolic ionic liquid based fuel designated as "GreenTEA", based on [EMIM][SCN], ammonium thiocyanate (NH_4SCN) and a molecular solvent. It was reported that although stand-alone NH_4SCN reacts vigorously with HTP within 5 ms, it fails to produce a flame on its own due to the absence of a sustainable hydrocarbon combustible fraction; however, when blended with the ionic liquid matrix, it yields a fully hypergolic fuel. To mitigate the inherent viscosity of the ionic liquid, molecular solvents, specifically water, ethanol, and methanol, were investigated. The optimization process targeted a specific impulse of no less than 95% of the baseline MMH/NTO bipropellant system, an ignition delay time below 25 ms, and a dynamic viscosity under 10 cP. Even though the ethanol and methanol based mixtures met these threshold criteria and remain under

development, their viscosity-reducing effect was inferior to that of water. Consequently, the water-based variant was selected for hot-fire testing, despite the more pronounced penalty on the specific impulse; the optimized composition (which was not disclosed in the work due to patentability concerns) yields a dynamic viscosity of 5.66 cP and an IDT of 18.5 ms. This configuration was successfully evaluated using a 50 N thruster under both atmospheric and vacuum conditions. The experimental campaign encompassed steady state hot fire operations lasting several seconds as well as millisecond scale pulses, consistently demonstrating rapid and reliable ignition characteristics. Table 15 summarizes the most promising results for additive-dependent ionic liquids, including a performance comparison of GreenTEA formulated with the different molecular solvents.

Table 15. Additive-dependent ionic liquids results.

Fuel	Additive	HTP Grade	IDT [ms]	Ref.	$I_{s,vac}^{max}$ [s] (O/F)
[EMIM] [BH_3CN]	8 wt.% $[FcCH_2NEtMe_2]^+$ $[B_{12}I_{12}]^-$	95.0%	17	[94]	-
[EMIM] [BH_3CN]	8 wt.% $[FcCH_2NEtMe_2]^+$ $[B_{12}I_{12}]^-$	70.0%	45	[94]	-
[EMIM] [BH_3CN]	15 wt.% $[diMIM]_n[Cu_2I_3]_n$	-	29	[83]	-
[EMIM] [BH_3CN]	13 wt.% Cu-P1	95.0%	9.5	[95]	332.4 (4.35)
Tetraglyme	13 wt.% Cu-P1	95.0%	9.0	[95]	320.0 (5.32)
[EMIM] [BH_3CN]/Tetraglyme (1:1 mass)	13 wt.% Cu-P1	95.0%	7.8	[95]	326.6 (3.95)
[EMIM] [BH_3CN]/Tetraglyme (1:1 mass)	13 wt.% Cu-P1	70.0%	16.5	[95]	290.6 (6.35)
[EMIM] [BH_3CN] ETH (1:1 mass)	13 wt.% Cu-P1	95.0%	4.1	[87]	326.2 (4.22)
[EMIM] [BH_3CN]/ETH (1:1 mass)	9 wt.% Cu-P1	95.0%	<8	[87]	326.3 (4.30)
[EMIM] [SCN]	5 wt.% CuSCN	96.1%	13.9	[82]	312.4 (3.86)
[EMIM] [SCN]	5 wt.% CuSCN	97%	13	[96]	313.1 (3.81)
[EMIM] [SCN]/ETH (63.7:27.3 mass)	9 wt.% Cu-P3	95%	7.9	[87]	-
[EMIM] [SCN]/Water	NH_4SCN	97%	17.5	[98]	306.0 (3.09)
[EMIM] [SCN]/Methanol	NH_4SCN	97%	19.2	[98]	313.5 (3.74)
[EMIM] [SCN]/ETH	NH_4SCN	97%	20.5	[98]	314.0 (3.59)

While the impressive performance achieved by ionic liquids combined with tailored additives and solvents highlights their potential as replacements for hydrazine derivatives, most of the additives explored so far introduce industrial and production complexities comparable to those of the ionic liquids themselves. Nevertheless, simpler formulations, such as those proposed by Negri et al. [96] and Merz et al. [98], which rely on ionic liquids and commercially available additives, provide an encouraging pathway toward the development of more practical and scalable hypergolic fuels. Tangible industrial validation of this approach has been recently demonstrated by the startup ISPTech [99], which advanced its HIP_11 propulsion technology, featuring [EMIM][SCN] plus CuSCN as fuel, to TRL 5. A vacuum test campaign comprising over 130 hot-fire tests on a 22 N demonstrator proved ignition reliability at ambient pressures below 5 mbar. The thruster demonstrated stable operation for up to 7 s, low combustion roughness, and efficiencies up to 97%, positioning ionic liquids as leading candidates for near-term commercialization.

5. Discussion

5.1. Catalytically Promoted Fuels

In Section 2, six distinct strategies were outlined to address the core challenges of catalytic fuel promotion, namely cost, chemical reactivity, and excessive additive loading. The first approach, which investigates amines as primary fuels, leverages their high intrinsic reactivity. The reported literature demonstrates varying degrees of success, characterized by reasonably short IDTs and high $I_{sp,vac}$ values, with the notable exception of MEA, which exhibits poor ignition performance and unfavourable physical properties when used alone. Regrettably, some of the most prominent formulations within this category rely on toxic additives, rendering their green classification debatable.

The second strategy, based on utilizing alcohols either alone or blended with other promoters, directly addresses propellant cost and availability by employing widespread substances such as ethanol. However, the low intrinsic reactivity of alcohols with HTP necessitates high solute concentrations, which potentially induces chemical stability and storage issues. To mitigate this high additive requirement, blends incorporating highly compatible amines (such as MEA) have been evaluated, yielding effective compromises between IDT, cost, and reduced toxicity. Also in this case, some of the most interesting formulation rely on substances exhibiting different levels of toxicity according to ECHA classifications, such as methanol or furfuryl alcohol.

The double-promoter strategy attempts to overcome the limitations of single-amine formulations by employing synergistic amine pairs. This approach has succeeded in improving additive compatibility, reactivity, and physical properties with varying degrees of success; the reported formulations exhibit specific impulse and IDTs meeting the requirement listed in Table 3, alongside remarkably low catalyst loadings and a genuine green character. The most notable success of this approach is the PAHyp fuel family developed by Mota et al. [47–51], showing high reactivity and long-term stability. Nevertheless, long-term storage stability of any new double-promoter fuel requires careful monitoring, as several high-performance blends are prone to destabilisation or stratification over time.

To further reduce formulation costs, significant research has focused on hydrocarbon-based options, specifically kerosene-based hypergolic propellants. As demonstrated by Jindal et al. [53], pure kerosene performs poorly in terms of IDT due to its lack of reactive molecular sites, large hydrocarbon chain size, and miscibility issues with the polar oxidiser. Consequently, kerosene has to be blended with carefully selected compatible amines or reactive catalytic complexes to achieve acceptable IDT without significantly reducing the specific impulse achievable with hydrocarbons. Due to the non-polar nature of kerosene, achieving a homogeneous and stable blend with highly polar reactive substances remains a major technical bottleneck, requiring substantial stabilization efforts.

To limit the overall additive content, which otherwise penalises the specific impulse and accelerates throat erosion, the use of multiple salts represents a highly compelling, though significantly less explored, alternative. Under this framework, the catalytic activity of a primary metallic species is enhanced by combining it with a secondary metal to trigger a synergistic catalytic effect. Currently, the main limitation of this strategy lies in the scarcity of comprehensive data clarifying the underlying cooperative kinetic mechanisms and formulation disclosure.

Finally, the critical issue of solution stability can be approached from a rheological perspective. Rather than limiting additive content, a gelling agent can be introduced to structurally stabilise the fuel matrix, allowing higher catalyst loading which lower significantly the IDT. Additionally, it enables the stable suspension of energetic metallic powders. This addition, which is otherwise impossible in liquid systems, significantly

enhances the volumetric energy release during combustion, yielding positive effects on both IDT and specific impulse.

Overall, the catalytic promotion of fuels represents a highly viable pathway toward high-performance, low-toxicity hypergolic propulsion without requiring excessively complex manufacture routes. Nevertheless, rigorous attention must be paid to long-term solution stability, residual toxicity, and physical properties, regardless of the specific formulation path chosen. Paradoxically, despite being historically the first family to be investigated, catalytically promoted fuels currently remain the furthest from commercial implementation. This delayed maturation is a direct consequence of the frequently encountered stability issues, and an ever-evolving formulation landscape that has yet to converge toward a standardized baseline propellant choice underpinning a marketable propulsive solution.

5.2. Reactive Fuels

In Section 3, the reactive fuel family was evaluated, characterized by the deployment of highly reducing additives that react directly upon contact with the oxidiser. Consequently, the ignition process is inherently faster and more energetic, as the intermediate catalytic decomposition step of the peroxide is bypassed. Fuels within this family exhibit a higher degree of formulation maturity since, regardless of the specific solvent, almost all investigations have converged on the use of a single primary additive: sodium borohydride.

Four distinct sub-strategies have been identified, primarily targeting performance enhancement rather than drastic paradigm shifts. The first, labelled baseline strategy, relies on a single fuel to dissolve the reducing additive. The reported results demonstrate ignition delay times that routinely compete with legacy bipropellant baselines such as MMH/NTO, dropping as low as 1 ms (Diede et al. [70]). Similar to the dual-promoter approach seen in catalytic fuels, subsequent research explored solvent blending, which yielded satisfactory IDTs even when paired with reduced HTP concentrations, while maintaining competitive theoretical specific impulse values. Within this framework, the stabilization of kerosene into a homogeneous, fast-igniting blend using a lower grade of HTP, as demonstrated by Anderson et al. [71], represents a notable advancement. Alternatively, hydrocarbons have been successfully incorporated into reactive formulations by exploiting gelation, enabling stable matrices that achieve reasonable IDTs with sub-90% HTP concentrations.

Finally, hybrid-additive systems combining both reactive and catalytic mechanisms were investigated by Kim et al. [72], delivering extremely short IDTs (<5 ms). Interestingly, iodine-containing compounds were employed instead of conventional transition metal catalysts. Regrettably, comprehensive kinetic data elucidating the mechanisms behind this synergistic acceleration remain scarce; nonetheless, this approach represents a highly viable path toward reducing the overall additive loading.

The reactive fuel family offers undeniable advantages in terms of ignition kinetics, even when utilizing lower-grade HTP. However, it suffers from critical, often unaddressed toxicity issues. A potential alternative could be represented by substituting the high-performing sodium borohydride with lithium borohydride. While the latter also offers a lower molecular mass, potentially benefitting the specific impulse, it remains to be seen whether its severe solubility limitations and high hygroscopicity would justify the performance trade-off. Overall, reactive fuels display a superior level of technological convergence compared to their catalytic counterparts, and a more advanced investigation into hot-tests. Future advancements should focus on optimizing fuel selection, specifically by displacing glymes and other substances of very high concern (SVHC), potentially investigating amines as done by Kang et al. [74], refining gelation strategies, and incorporating hybrid catalytic systems to enhance reactivity while systematically reducing the required mass fraction of the additive agent.

5.3. Ionic Liquids

The third fuel family, discussed in Section 4, represents a fundamental paradigm shift in fuel design, as the molecular structure of the propellant itself is engineered to deliver the target hypergolic responsiveness and propulsive performance. These ionic liquid-based fuels are salts melting below room temperature, whose intrinsic hypergolicity is primarily governed by the nucleophilic reactivity of the anion with hydrogen peroxide. Consequently, competitive ignition delay times are achievable even in the absence of external catalytic additives. In particular, thiocyanate- and borohydride-containing ionic liquids have been identified as the most reactive candidates, with IDTs reliably falling within the 50 ms threshold and potentially dropping below 25 ms (Table 14).

Further advancements in both ignition kinetics and specific impulse have been demonstrated through the incorporation of tailored additives. This trend is exemplified by the work of Bhosale et al. [95], where the introduction of specifically synthesised, highly soluble copper-based catalytic additives significantly accelerated the IDT while maintaining satisfactory specific impulse values. Generally, these additives require dedicated, multi-step synthesis routes designed to guarantee chemical compatibility and long-term stability within the ionic matrix. Although this increases procurement costs and processing complexity, it provides a powerful mechanism to fine-tune energy release and overall combustion behaviour.

Despite being the most recent family to enter the green propulsion arena, and the high viscosity that typically characterises ionic liquids, these fuels are currently the most promising candidates for rapid commercial translation. This is particularly evident within European research programs, notably in Germany, where mature formulations have recently undergone advanced characterisation in system-representative environments, pushing their technology readiness level forward [99].

However, several operational barriers still remain to be addressed. The majority of high-performance ILs are custom-synthesised compounds or special commercial chemicals (such as [EMIM][SCN]) characterized by limited production volumes and high costs. Furthermore, comprehensive lifecycle toxicity assessments are still largely missing; nonetheless, the negligible vapour pressure inherent to ionic liquids represents a major intrinsic safety advantage, eliminating operator inhalation hazards. Future research must aggressively target the unfavourable physical properties of ILs, focusing on mitigating their high viscosity and structural corrosiveness. To this end, the innovative approach demonstrated by Merz et al., which leverages the strategic blending of low-viscosity co-solvents such as water and ethanol, and a metal-free additive, represents a vital step toward practical application.

5.4. Fuel Families Comparison

To better visualise how the three fuel families compare, in terms of the most relevant quantitative parameters, the IDT and specific impulse, the data reported in the preceding summary tables have been compiled into a comprehensive scatter plot (Figure 1). To maintain clarity and avoid an overly dense graphical representation without compromising the validity of the comparison, only formulation results obtained using an HTP concentration of 94% or higher have been included.

The three families, distinguished by colour, occupy slightly distinct regions within the IDT–$I_{sp,vac}$ plane. Due to the high versatility of the catalytic promotion approach, which translates into diverse chemical strategies and a vast array of active compounds, the results for catalytic fuels appear scattered across a broad portion of the graph. Notably, their IDT values are highly promising, with the majority falling well within the defined 25 ms satisfaction threshold, while simultaneously delivering high theoretical specific

impulse that satisfy the requirement reported in Table 3, especially when amino-based, double-promoter or kerosene-based formulations are employed.

Conversely, reactive fuels perform best in terms of ignition kinetics, consistently exhibiting the shortest IDTs. While their maximum theoretical specific impulse is competitive, it remains slightly lower than that achievable with catalytically promoted propellants. Furthermore, owing to the minor variations in their core chemical formulations, the data points for reactive systems are relatively clustered. However, as previously highlighted, this family suffers from unresolved toxicity concerns, as sodium borohydride, which fundamentally underpins the reactivity of this fuel class, currently remains irreplaceable.

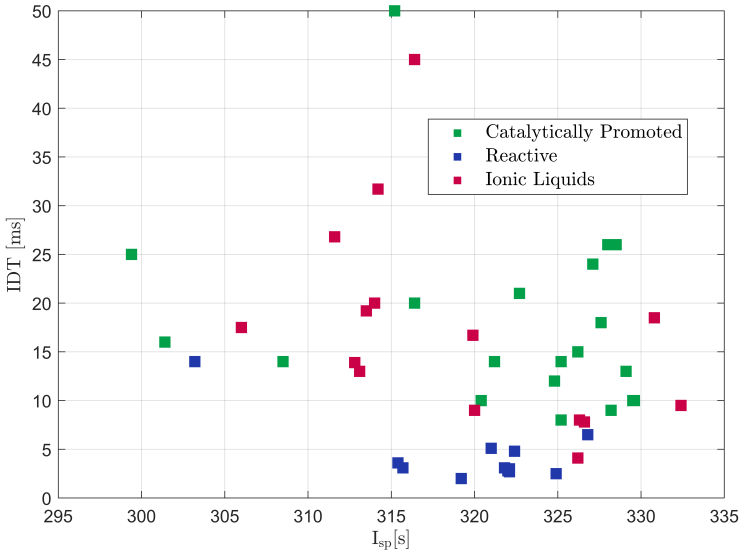

Figure 1. Green propellants performances on a IDT-$I_{sp,vac}$ plane.

Finally, data points for ionic liquid-based fuels appear highly dispersed across the plane, reflecting the exceptional freedom available in cation-anion selection and additive tailoring. Although these formulations generally cannot compete with reactive systems in terms of ultra-short IDTs, specific blends achieve highly competitive specific impulse values while successfully maintaining their ignition delays within the acceptable 25 ms threshold. However, a comprehensive comparison with the other two families is currently hindered by data scarcity, as literature often lacks precise information regarding the enthalpies of formation for many newly synthesised ionic compounds. Furthermore, despite their promising energetic potential, the majority of these formulations are still characterised by high viscosity (as reported in Table 14) and high production costs, both of which currently represent major obstacles to their widespread adoption.

Beyond the quantitative trade-offs mapped in the IDT–$I_{sp,vac}$ plane, a clear divergence emerges among the three fuel families regarding their green character. An analysis of the formulations compiled in the summary tables reveals that approximately one-third of the catalytic systems, all of the reactive formulations, and virtually none of the ionic liquids fail to satisfy the green requirement. This trend is closely linked to the specific chemical architecture of each class: the vast design space of catalytic promotion allows for a careful, toxicity-driven selection of substances; conversely, the reactive field is heavily monopolised by sodium borohydride, a suspected reprotoxic agent, while ionic liquids inherently benefit from negligible vapour pressures. Nevertheless, a comprehensive sustainability assessment for IL-based propellants cannot neglect the environmental footprint of the hazardous chemical precursors required for their multi-step, often laboratory-scale synthesis, and the lack of long-term studies.

In terms of manufacturing ease, catalytically promoted fuels are clearly superior. Since they rely predominantly on commercially available raw materials and encompass a wide variety of candidate molecules, selecting stable, and benign components is straightforward; their production is simple, requiring only the blending of the liquid and solid phases. For reactive systems, the high hygroscopicity of sodium borohydride demands strictly controlled, moisture-free processing environments to ensure initial fuel stability, a constraint that also penalises their long-term storage handling. Currently, ionic liquid-based fuels represent the most complex family to manufacture, a bottleneck that is expected to persist until sufficient commercial demand drives the industrial scaling of special liquids and tailored additives, reducing the need for custom, costly, small-scale synthesis.

Significant differences also emerge from an economic perspective. Low-cost catalytic formulations are easily attainable due to the abundance of inexpensive commercial alternatives. Similarly, despite their toxicity drawbacks, reactive formulations benefit from the high industrial production volumes of baseline solvents (such as glymes) and reducing agents (sodium borohydride), keeping raw material costs relatively low. In contrast, ionic liquids exhibit a stark cost penalty, as their limited commercial availability inflates procurement prices.

A comprehensive graphical synthesis of this multidimensional comparison is presented in Figure 2. The three fuel families are qualitatively evaluated across six key engineering vectors: specific impulse, IDT, manufacturing complexity, cost, technological maturity, and toxicity. Scores are assigned reflecting how the three families compare relatively, rather than denoting quantitative differences; a score of 3 indicates that a family represents the most favourable option for that category, whereas a score of 1 designates the least advantageous one. Consequently, on all axes, a larger area invariably correlates with a more optimized operational profile. To assess the best solution in terms of IDT and specific impulse, the median of the results selected in Figure 1 was considered.

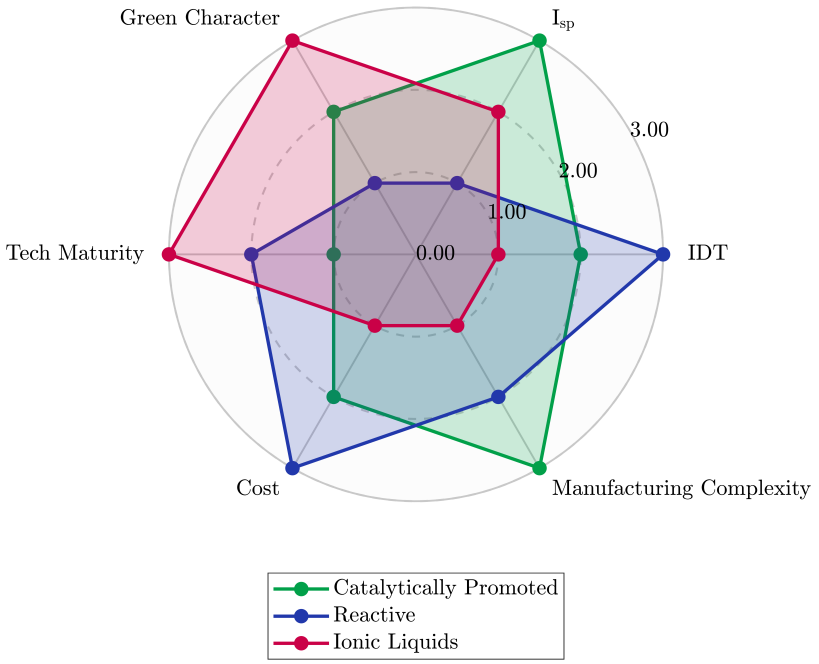

Figure 2. Radar plot of relative performance of each fuel family.

6. Conclusions

Research into green HTP-based hypergolic fuels continues to expand towards more mature solutions, exhibiting significantly lower toxicity compared to legacy hypergolic propellants but remaining capable of maintaining competitive performance. Today, the

technological panorama is defined by three fuel families: (i) catalytic, (ii) reactive, and (iii) ionic liquid-based, each presenting distinct trade-offs between chemical reactivity, physical properties, cost, and toxicity.

- Catalytic fuels have largely overcome their historical limitations of high catalyst loading and sluggish ignition. Recent formulations utilizing advanced solvents and dual-additive systems routinely achieve ignition delay times below 15 ms with reduced required additive concentrations. While exploratory work on kerosene-based and gelled catalytic formulations opens flexible design spaces, their practical feasibility remains unproven. The primary bottlenecks for this class are the lack of comprehensive long-term ageing data and the absence of extensive hot-fire test bench campaigns, which represent the next critical milestone for commercial transition.
- Reactive fuels, leveraging strong reducing agents like $NaBH_4$, consistently deliver the shortest ignition delay times, directly competing with the reference legacy MMH/NTO baseline. Research has shifted from exploratory chemistry to system-level validation, including thruster firing tests that have highlighted specific challenges in combustion efficiency and high-frequency instabilities. However, despite claims of greenness, toxicity remains largely an unaddressed issue. Many high-performance formulations still rely on hazardous solvents like glymes, which are flagged as SVHC by ECHA, while the reference additive is a recognised substance toxic to human reproduction. To achieve a genuine green transition, future research must shift away from these substances without compromising the remarkably fast kinetics of the reducing agent.
- Ionic liquids-based fuels offer exceptional chemical tunability and have achieved notable success. While neat ionic liquids generally struggle to meet all the requirements for commercial hypergolic fuels, the addition of suitable additives has demonstrated the feasibility of achieving near-threshold performance. Several formulations based on commercially available ionic liquids and additives have been successfully tested in static firing experiments, yielding promising results in terms of combustion efficiency and reduced instability, paving the way for commercial applications. Nevertheless, the main limitation of many ionic-liquid-based formulations lies in their complexity. These fuels often require in situ synthesis, leading to increased costs and limited accessibility. Additionally, some synthesis routes involve hazardous chemicals.

In conclusion, although each fuel family presents distinct advantages and drawbacks, all three are converging toward a set of mature candidate formulations. It is therefore foreseeable that, rather than a single winning solution, the future will see these families converge into their niche applications tailored to specific mission constraints, launch architectures, and cost structures.

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Abbreviations

The following abbreviations are used in this manuscript:

AEMIM	1-methyl-1H-imidazol-3-ium
AIT	Auto-ignition Temperature
BMIM	1-butyl-3-methylimidazolium
BUT	Butylamine
CA	Copper(ii) acetate
CC	Copper(ii) chloride
CD	Copper dibutyrate
CE	Copper(ii) ethylacetoacetate
CM	Copper(ii) metachrylate
Cu-P1	$Cu(ii)(1\text{-H-imidazole})_4(BH_3CN)][BH_3CN]$
Cu-P2	$[Cu(ii)(1\text{-methylimidazole})_4(BH_3CN)_2]$
DETA	Diethylentriamine
DIMP	1,2-Diaminopropane
DMA	Dimethylacetammide
DMAZ	2-*N*,*N*-dimethylaminoethylazide
DMEA	Dimethylaminoethanol
DMEDA	*N*,*N*-dimethylethylenediamine
DMF	Dimethylformammide
DMSO	Dimethylsulfoxide
dMim	1,3-dimethylimidazolium
ECHA	European Chemicals Agency
EDA	Ethylendiamine
EMIM	1-ethyl-3-methyl imidazolium
Epy	1-Ethylpyridinium
GHS	Global Harmonized System
Him	1-H-imidazolium
HTP	High-Test Peroxide
IC	Iron(iii) chloride
IDT	Ignition Delay Time
IL	Ionic Liquid
MAA	Manganese(ii) acetylacetonate
MEA	Monoethanolamine
MeCN	Methylcynide
MDEA	*N*-methyldiethanolamine
MDP	*N*-methyl-1,3-diaminopropane
MMEA	*N*-methylethanolamine
MMH	Monomethyl Hydrazine
NHMF	Non-toxic Hypergolic Miscible Fuels
NTO	Dinitrogen Tetroxide
O/F	Oxidiser to Fuel Ratio
PoC	Properties of Concern
PYR	Pyridine
PVP	Polyvinylpyrrolidone
PRO	Propylamine
RCS	Reaction Control System
SCAPE	Self-Contained Atmospheric Protective Ensemble
SCN	Thiocyanate
SVHC	Substances of Very High Concern
TMEDA	*N*,*N*,*N*′,*N*′,-tetramethylethylenediamine
THF	Tetrahydrofuran
THTDP	trihexyltetradecylphosphonium

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