



Article

Evaluating New Liquid Storable Bipropellants: Safety and Performance Assessments

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Abstract: Conventional storable bipropellants make use of hydrazine and its derivatives as fuels and nitrogen tetroxide as an oxidizer. In recent years, the toxicity character of these chemicals pushed the propulsion community towards “green” alternatives. Several candidates have been proposed among existing and newly developed chemicals, highlighting the need for a common and robust selection methodology. This paper aims at reviewing the most important selection criteria in the field of toxicity and discusses how to objectively define a green propellant, considering both the health and environmental hazards caused by the chemicals. Additionally, consistent figures of merit in the field of safety and handling operations and performance are proposed. In particular, operating temperatures, flammability and stability issues are discussed in the framework of physical hazards and storage requirements, while vacuum impulses, adiabatic flame temperature and sooting occurrence of the investigated couples are compared to the UDMH/NTO benchmark case. Hydrogen peroxide and nitrous oxide, and light hydrocarbons, alcohols and kerosene are selected from the open literature as promising green oxidizers and fuels, respectively. The identified methodology highlights merits and limitations of each chemical, as well as the fact that the identification of a universally best suited green couple is quite impractical. On the contrary, the characteristics of each propellant lead to a scenario of several “sub-optimal” couples, each of them opportunely fitting into a specific mission class.

Keywords: green propellants; toxicity; performance; storable rocket propulsion



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1. Introduction

Conventional storable propulsion solutions mostly rely on toxic and dangerous to handle hypergolic propellants. In particular, many pairs consist of corrosive oxidizers (such as white fuming nitric acid—WFNA, red fuming nitric acid—RFNA and liquid nitrogen tetroxide—NTO), and toxic fuels (i.e., hydrazine or its derivatives—unsymmetrical dimethyl hydrazine, UDMH, or monomethyl hydrazine, MMH). Despite the long heritage, the good performance and long-term stability, there has been a strong push to replace hydrazines in light of their universally cited toxicity. Substitutes to the highly corrosive and toxic oxidizers are similarly sought, thus challenging the maturity of the so-called “green propellants”.

The term “green propellants” has no precise definition. Typically, it identifies chemicals demanded to reduce personnel health and environmental hazards with respect to hydrazines. It may be considered to derive from the “Green Chemistry” concept introduced as “the design of chemical products and processes that are more environmentally benign and reduce negative impacts to human health and the environment” by Anastas and Warner [1]. However, the concept is broad, including waste reduction, production options, containment and monitoring for operators and environment as founding elements of its twelve principles. Moreover, as suggested by several authors, “green propellants” studies shall include considerations on the cost reductions strictly related to the demanded relaxed

safety operational and propellant management procedures [2–4]. Additionally, technical readiness and relevant capabilities in terms of performances and long-term storage need to complement safety and economic benefits [4–7], thus adding additional requirements to the “green propellants” assessment.

In the green storable bipropellants framework, interesting results have been achieved by propellant couples mainly based on two oxidizers: high-test peroxide (HTP) and nitrous oxide.

In the last two decades, extensive experimental and modeling activities have been carried out worldwide in the framework of hydrogen peroxide liquid bipropellants. The FP7-GRASP (Green Advanced Space Propulsion) project theoretically investigated a large number of storable green propellant candidates [8], leading to lab-scale testing of a 1.7–1.9 N thruster based on hydrogen peroxide in a concentration of 87.5% in combination with ethanol, kerosene, dipentene and turpentine [9,10]. Kerosene fuels/HTP have been extensively investigated at University of Purdue [11], at Surrey Space Centre [12], by the Korean KAIST [13,14], and at the Institute of Aviation in Poland [15,16]. Similarly, intense efforts have been put into the development of ethanol/HTP engines, along with the premixed monopropellant counterpart [17]. In Ukraine, a 400 N-class bipropellant rocket engine (AOMP-400) is under development by the Laboratory of Advanced Jet Propulsion (LAJP), using ethanol as fuel [18]. Preliminary fire tests using a 200-N class engine have also been recently documented at TNO by Mayer and Wieling [19], while thorough investigations with impinging jets in a lab-scale burner in a non-hypergolic configuration were conducted by Indiana et al. [20]. Other relevant results include combustion studies at Prime Institute of Poitiers on hydrogen peroxide in combination with ethanol, iso-octane and n-decane [21], as well as the 40-N thruster based on the 98%-HTP/propyne couple proposed in the framework of the FP7-PULCHER (Pulsed Chemical Rocket with Green High Performance Propellants) project [22].

Similar sets of information can be found on nitrous oxide. In the U.S., a DARPA project investigated the potentialities of catalytic decomposition of N_2O for a 200 N-bipropellant engine in combination with propane [23,24]. More recently, Herdy et al. [25] theoretically discussed the application of liquid mixtures of N_2O_4 and N_2O (i.e., forming the so-called Marshall Enriched Storable Oxidizer—MESO) and methane as fuel for cislunar propulsive applications. Other studies focused on modeling, development and testing of nitrous oxide and ethanol (NOEL) engines [26–31]. In particular, Tokudome et al. [27,28] demonstrated NOEL for use in bipropellant applications using a breadboard of 2 kN vacuum thrust, while Kakami et al. [32] tested a 1-N class thruster using arc assisted combustion. For low-thrust application, Asakura et al. [33] proposed a novel couple, testing a 0.4-N class N_2O /DME bipropellant thruster, whose combustion phenomena have been studied by Yamamoto and Tachibana [34]. Additionally, as part of the efforts to develop mixed monopropellant compositions, a wide range of studies are available in the open literature for combustion performance characterization of hydrocarbons/nitrous oxide mixture, employing ethylene and ethane [35–37].

The large number of ongoing studies on green propellants highlights both the scientific interest on the topic and the necessity shared by industries, research centers and space agencies to move towards cost-saving and safer solutions, answering to a booming space market and a continuously increasing number of launches per year. The present work aims at reviewing and discussing the recommended figures of merit behind the selection of notable green fuels and oxidizers. Health, environmental and physical hazards will be analyzed, relevant performance indexes will be presented, and potential storage and handling issues discussed. In particular, it must be noted that there is currently no universal agreement on quantitative means through which propellant greenness shall be assessed; hence, different screening measures will be analyzed. Section 2.1 provides an analysis of hydrazine/NTO toxicity and safety hazards, drawing the upper limits of the screening analysis, while Section 3 presents the most important figures of merit for evaluating new liquid storable bipropellants for space application. The analyzed fuels and oxidizers, as

well as the screening methodology suggested, are introduced in Section 4, and the results discussed in Section 5.

2. Where Do We Stand?

2.1. Fuels: Hydrazine and Its Derivatives

Modern occupational safety standards impose 0.01 ppm of hydrazine as the tolerable threshold limit value for airborne concentration of vapors to which workers can be exposed for 8 h/day [38]. Other relevant “Occupational Exposure Limits” (OELs) are listed in Table 1. In particular, the “Ceiling Recommended Exposure Limit” (REL), the “Time-Weighted Average Threshold Limit Value” (TLV-TWA), the “Permissible Exposure Limit” (PEL), and the “Immediately Dangerous to Life and Health” (IDLH) values—published by the National Institute of Occupational Safety and Health (NIOSH), the American Conference of Government Industrial Hygienists (ACGIH), and the Occupational Safety and Health Administration (OSHA), respectively—and the “Long Term Exposure Limits” (LTEL) as proposed by the European Union are reported for comparison purposes [24,39–43].

Table 1. Occupational exposure limits of typical storable propellants (ppm) [24,38,39,42,43].

	NTO	N ₂ H ₄	MMH	UDMH	Nitric Acid
NIOSH REL—Ceiling	1 ^a	0.03	0.04	0.06	4 ^a
ACGIH TLV—TWA	3	0.01	0.01	0.01	2
OSHA PEL—TWA	5 ^b	1	0.2 ^b	0.5	2
IDLH	13	50	20	15	25
EU-LTEL	N/A	0.01 ^c	N/A	N/A	N/A

^a ST. ^b Ceiling. ^c Binding Occupational Exposure Limit Value (BOELV).

The main reason for such strict OELs lies in the severely acute toxicity of hydrazine. Although limited statistics of acute toxic exposure in humans are available in the open literature and existing data are largely based on animal studies, a systematic review proposed by Nguyen et al. [44] provides evidence that hydrazine and its derivatives can cause severe neurologic, pulmonary, hepatic, hematologic, and soft tissue injuries. Additionally, hydrazine is classified as a carcinogen in accordance with the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) regulations and is included in the list of Substances of Very High Concern (SVHC) since 2011 [45].

Throughout the years, hydrazine toxicity concerns were sometimes considered overrated and relative handling procedures disproportionate with respect to other chemicals [4,46]. In support of the previous consideration, a study conducted by Wald et al. [47] on workers at a hydrazine-production facility between 1945 and 1971, and two follow-up evaluations in 1995 and 2015 [48,49], inferred the absence of statistically significant risk excess for any type of cancer. On the contrary, a positive exposure–response relationship of lung cancer among workers was shown by other two overlapping cohort studies by Ritz et al. and Boice et al. [50–52]. These contradictory conclusions should be viewed in light of the difficulties to identify specific hazards to hydrazine exposure, as the workers are also commonly exposed to other chemicals [53,54]. In this framework, in 2016, the IARC Monographs Working Group [55] reviewed several toxicological studies to finally assess the carcinogenesis in humans due to the exposure to hydrazine. Their conclusion of limited evidence in humans was complemented by sufficiently high evidence in experiments with animals, confirming the worldwide assessment that hydrazine is probably carcinogenic to humans [55].

From the physical and chemical properties viewpoint, hydrazine and its derivatives are quite hazardous chemicals, as shown in Table 2. They are able to sustain decomposition without any oxidant [56] and are characterized by low flash point value and large explosive range. However, a positive aspect is the very low vapor pressure of hydrazine that limits the accumulation of dangerous vapor in properly ventilated work areas.

Table 2. Properties of hydrazines, NTO and nitric acid. Data retrieved from Refs. [38,43,57,58].

	NTO	N ₂ H ₄	MMH	UDMH	Nitric Acid
Chemical Formula	N ₂ O ₄	N ₂ H ₄	CH ₆ N ₂	C ₂ H ₈ N ₂	HNO ₃
Molecular Weight	92.0	32.1	46.1	60.1	63.0
Freezing Temperature [°C]	−11.2	1.5	−52.4	−57.0	−41.6
Normal Boiling Point [°C]	21.2	113.5	87.5	63.3	121
Density @20 °C [g/cm ³]	1.448	1.008	0.878	0.791	1.513
Flammable Limits in Air [%]	Not flammable	4.7–100	2.5–98	2–95	Not Flammable
Saturated Vapour Pressure @20 °C [bar]	0.960	0.014	0.050	0.163	0.064
Flash Point [°C] *	-	40	-8	-15	-

* closed cup.

Hence, production, handling, transport and loading procedures have to be carefully managed. Hydrazine is required to be handled exclusively in qualified closed containers and in facilities carefully designed to ensure reasonably well-ventilated areas [4,46,56]. Minimization of residual drips or leakage is required, and safe procedures to quickly dilute and wash away any accidental spillage is mandatory [4]. Since mid-to-late 1990s, “Self-Contained Atmospheric Protective Ensemble” (SCAPE) suits (i.e., full body protection with air supply) are required for hydrazine loading operations. To give an idea on the strict procedures required, according to Schmidt et al. [46], at least two people must be suited up and present at all times, and a relief crew must be on standby in the next room for emergency.

Hydrazine is classified as very toxic to aquatic life on a short term basis, with long lasting effects [40]. Additionally, a United Nations Development Programme (UNDP) report notes that a spill of UDMH, apart from the inherent toxicity, is believed to rapidly degrade into even more toxic transformation products (such as the ones found in Kazakhstan generated by the Proton launch leftovers), that may last up to 34 years in dry soil [59,60].

2.2. Oxidizers: NTO and Nitric Acid

NTO. SCAPE suits were originally introduced during the flight test development phase for the Titan II intercontinental ballistic missile in 1961 for nitrogen tetroxide loading [4]. NTO is a strong oxidizing agent; it is non-flammable, even though when added to a fire it will act increasing the intensity of combustion, and it is non-explosive, although it may produce a violent explosion upon contact with some materials, such as hydrazines, amines and alcohols [43]. Additionally, it is highly corrosive and extremely toxic. In fact, according to Nufer [56], when liquid N₂O₄ or its vapors (i.e., NO) come into contact with the skin, eyes, or respiratory system, the reaction with water produces nitric acid (HNO₃) and nitrous acid (HONO) that typically destroy tissue, and may lead to permanent restrictive lung disease and, in extreme cases, death. Moreover, according to Ciezki et al. [61], a severe soil and water contamination occurs in cases of leakage.

Nitric Acid. Several types of nitric acid mixtures have been used as oxidizers. The most common one, red fuming nitric acid (RFNA), consists of concentrated HNO₃ containing between 5% and 27% dissolved nitrogen dioxide (NO₂). Nowadays, it is still one of the most studied oxidizers in combination with potential hypergolic “green” fuels [61]. However, it is extremely toxic and corrosive. According to the CLP classification [40,62], it is fatal if inhaled. Vapors from RFNA are poisonous, with an OSHA-PEL average limit value of 2 ppm (see Table 1). Few materials (such as certain types of stainless steel and gold) are satisfactory as storage containers and/or tubing, since nitric acid typically reacts with many wall materials, forming dissolved and, sometimes, insoluble nitrates. This condition may cause the blocking of valve and injector orifices [58].

3. Green Propellants Figures of Merit

The present section aims at outlining a set of recommended figures of merit for evaluating relative advantages and limitations of candidate fuels and oxidizers, based on the requirements set by the space agencies and in light of the hazards of hydrazine

underlined in Section 2.1. The discussion is focused on the following aspects, widely recognized as of relevance for the green propellants assessment [2–4,6–8,61]: (i) health and environmental hazards; (ii) handling and safety; (iii) performance; and (iv) costs. It is worth mentioning that there is a strong interconnection between the highlighted areas of interest, and the overall assessment cannot dismiss the interdisciplinary character of the analysis. Relevant figures of merits discussed in the open-literature are summarized in Table 3.

Table 3. Summary of open-literature selection criteria.

Figures of Merit	Evaluation Criteria
Toxicity	Acute and chronic toxicity based on LD50 and LC50 values; CMR substances; risk of exposure to toxic vapors that may accumulate in the work area due to regular evaporation and/or spillage; OELs value; HAZMAT requirements, spills and leakages handling; protective equipment definition.
Environmental Issues	Climate Change; Ozone Depletion; Ecosystem toxicity (acute and chronic aquatic and soil toxicity); HAZMAT requirements, spills and leakages handling.
Plume and decomposition products	Absolute toxicity quantification; asphyxiant potential; ecotoxicity; impact on humans, environment, spacecraft.
Flammability	Propensity for sustaining reactions at ambient conditions when exposed to ignition sources; lower and upper flammability limits; autoignition properties.
Reactivity-Instability	Propensity for undergoing violent chemical change, explosion, detonation, autodecomposition, thermal runaway reaction; requirements stemming from safety test criteria (card gap, fast cookoff, slow cookoff, explosive limits, fire hazards, impact sensitivity, critical diameter).
Vapor Pressure	Vapor pressure at room and mission-typical storage temperatures; handling safety (potential explosion, asphyxiant hazard); feed system complexity; tank weight; self-pressurization potentiality.
Material Compatibility	Long- and short-term compatibility verified by experimental tests on system hardware (i.e., pipes, filters, valves, miscellaneous components, seals, gaskets, instrumentation, etc.); corrosion of materials; chemical poisoning with chemical and physical properties alteration; unwanted material deposition; susceptibility to autodecomposition and explosion.
Operational Storage	Ground and mission temperature range; requirements for thermal conditioning for safe storage below decomposition onset; aging; sedimentation/separation of additives/ non-homogeneity of mixtures; freezing temperature limit.
Performance	Specific impulse and density specific impulse for mass- and volume-limited applications, respectively; combustion chamber and staged combustion temperatures; hypergolicity (i.e., natural and/or addition of reactive/catalytic additives); staged combustion; susceptibility to sooting (i.e., C/O and C/H ratio) and thermal sootback; duty cycle; reliability and performance repeatability.
Costs	Total life cycle cost; propellants; storage and handling feed system and tank material; storage conditions; personnel equipment; personnel medical health check; monitoring instrumentation; containment procedures; HAZMAT operations; transport, handling, pre-launch, launch, post-launch, disposal management.
Total Mass and Volume	Propellant mass; gross mass; tank mass; global system complexity affected by operating pressure, components, pressurization cycle, thermal conditioning, cooling system, propellant density, etc.

3.1. Toxicity

3.1.1. Health Hazards

A health hazard can be identified as the ability of a chemical to cause life threatening effects upon entering an organism through different routes of exposure (i.e., inhalation, skin absorption or ingestion). Its quantification is principally related to the exposure hazard to liquid, vapor or suspensions that may accumulate in the working environment and is strongly dependent on the concentration thresholds and the exposure period.

Acute toxicity estimate values are typically used for substance classification. Acute toxicity refers to the ability of a chemical to cause a harmful effect after a single exposure

by any route for a short period of time. Ratings are based on oral and dermal (LD50) and inhalative (LC50) experimental median lethal dose values, which identify the lethal thresholds for 50% of the test population, within 24 h of exposure [40]. Other possible means of classification include the regulatory limit on the amount or concentration of a substance in the air. Issued by the American Conference of Governmental Industrial Hygienists (ACGIH) [42], the Threshold Limit Value-Time Weighted Average (TLV-TWA) is an indication of the maximum average exposure on the basis of an 8h/day work schedule, while the Threshold Limit Value-Short Term Exposure Limit (TLV-STEL) identifies the 15-min exposure that should not be exceeded at any time during a workday. Similarly, the Immediately Dangerous to Life or Health concentration value (IDLH) [39] is a workplace exposure limit, defining the limit that poses an immediate hazard to life. Other relevant regulatory limits are issued by several national and international agencies, identifying aspects including permissible and recommended exposure limits.

Regardless of the classification methodology, any meaningful discussion of non-toxic propellants cannot separate the absolute quantification of toxicity from the actual risks [63,64]. TLVs enable to quickly recognize the relative hazards of chemicals, but the actual danger is identified by the probability that said value can be exceeded. For example, the magnitude of the hazard for a liquid shall include the saturated vapor pressure (SVP), which represents a measure of the easiness by which a material goes airborne, potentially producing a concentrated atmosphere. Hence, in order for a propellant to pose a low health risk, it should be characterized by high median lethal dose values to restrict the toxic effect in case of exposure and a low vapor pressure to limit the risk of vapor accumulation on ground, and thus the probability of exposure.

Another important exposure concern is related to the so-called CMR (i.e., carcinogenic, mutagenic, and reprotoxic) substance category, i.e., chemicals having the potential to cause cancer, cell mutation or to affect reproduction and fertility. The International Agency for Research on Cancer (IARC) [55] identifies four hazard categories on the basis of the strength of evidence that a chemical has a CMR potential based on human and/or experimental animal data. In the current EU classification (CLP Regulation 1272/2008/EU [62], substances that are known to have CMR potential for humans (i.e., category 1A), based largely on human evidence or that probably have CMR potential for humans, assessed on the basis of experimental animal data (i.e., Category 1B), are subject for authorization under the REACH Regulation [45], such as in the case of hydrazine (see Section 2.1).

3.1.2. Environmental Hazards

Environmental hazards of propellants can be analyzed in light of the toxicity of both the original chemicals and of final decomposition/combustion products, spreading to incomplete combustion. Hence, the analysis should take into account the effect of unwanted spillage, leakage in water and/or in soil, uncontrolled decomposition, ozone depletion and climate change [65]. Out of these, only ecosystem toxicity seems mostly relevant for in-space propulsion units considering the hazard involved in the whole life cycle of these reactants.

Ecological studies focus on local impacts in proximity to the launch site. In case of an accident involving the crash of a launcher during the ascending phase, contamination can occur on soil, groundwater, and vegetation leading to water quality, ecosystem acidification, plant damage and stunted plant growth, as thoroughly discussed by Dallas et al. [65].

3.2. Handling and Storage

Handling and storage requirements are developed, in the first place, on the basis of the physical hazards associated with chemicals [4]. In fact, their intrinsic properties may make them classifiable as explosive and/or flammable. Explosion/fire hazard shall take into account the fire potential, chemical reactivity, and incompatibilities with other materials that may lead to strong and uncontrolled reactions [58].

As far as the fuels are concerned, the main risk comes from accidental spillage. In this case, fuel vapors mix with air and may ignite on a hot spot or because of a spark. In this respect, a tight explosive range and a high lower flammable limit (LFL) are preferable. Similarly, the higher the flash point and auto-ignition temperature of the chemical, the lower the risk during operations, even for hardware integrity during testing and in case of anomalies.

During storage and transport of a chemical, the surrounding ambient temperature should be monitored [66]. It should be lower than its flash point, which increases with pressure. On the contrary, the auto-ignition temperature decreases as the storage pressure increases, thus posing more stringent rules during transport and also guidelines in case of emergencies for compressed and liquefied gas.

A spilled chemical may accidentally come in contact with incompatible materials, resulting in fires or leading to undesired violent reaction, that may run away as an explosion [56,58,67]. In general, compatibility problems may occur at any time during the mission, from propellant manufacturing up to onboard storage. Clearly, runaway reactions are not the only final result of these kinds of interactions, which, however, always lead to performance losses and/or system failure. Chemical reactions, although possibly slow, between the propellants and their containers may result in either contamination of the propellant with impurities or/and degradation/corrosion of the containment material. Hence, handling and storage considerations shall also take into account how long a propellant must remain safe. In fact, some substances that may pose no immediate risk when stored or accidentally spilled, but they may gradually be affected by contaminants. Autodecomposition or selective evaporation of components in case of mixtures in their storage tanks shall be considered as well, suggesting that the likelihood of propellants instability (even detonation under certain conditions) is an important factor for handling and storage requirements. As an example, reaction activation energies shall be quantified, in order to avoid thermally induced ignition at reasonable storage and feed temperatures.

Propellant vapor pressure plays also a crucial role in storability. High vapor pressure tends to drive high tank mass and feed system complexity. Additionally, in case of strongly temperature-dependent vapor pressure, the latter aspect is complemented by issues on performance repeatability and reliability. Additionally, high vapor pressures storage presents a safety hazard, since a leakage may lead to an explosion or present an asphyxiation hazard in enclosed working environments [58,63]. It is worth mentioning the connection between the vapor pressure and the critical point, which can be considered as the limiting value of the saturated vapor pressure of a liquid. Close to the critical point, the properties are more sensitive, thus adding uncertainties to the design process. Hence, in some cases, it may be appropriate to cool down the propellants to lower the storage pressure, leading to less stringent handling operations and reducing tank volume due to the propellant increased density [68]. However, in this way, potential thermal storage stability problems and an increased complexity of the feeding, transfer and loading line is expected.

Storability requirements span from ground to space storage temperature range. Hence to relax thermal storage containment and also permit operation of rockets in cold environments, the desirable freezing temperature is $-20\text{ }^{\circ}\text{C}$ at minimum [19]. Small amounts of freezing depressants may be added to lower the freezing point, provided the stability of the mixture.

3.3. Performance

Performance is a paramount criterion for space applications. Gravimetric specific impulse and volumetric specific impulse of new oxidizers and fuels should be at least similar to those of the “more toxic” counterparts. For a very precise mission, the size and mass of the propellant tanks and the available ΔV are defined starting from the specific impulse and the volumetric specific impulse [58,69]. The latter, in particular, is a good reference of how compact a system could be, for a given total impulse. This is especially important in systems where volume is very limited for any reason. Trade-off studies aiming

at identifying the nominal I_s involve combustion chamber pressure, expansion ratio and oxidizer-to-fuel mass ratio. The chosen O/F represents a reference point for system design, since it strongly affects the overall system layout. On one hand, the mass budget and tank layout depend on it (for a fixed chamber pressure and propellant couple); on the other, high O/F ratios are usually penalizing either film or regenerative cooling subsystems, since the available fuel cooling capacity is less than in the case of low O/F ratio. Hence, it is clear that any meaningful discussion of green propellants cannot be separated from the technologies that enable their utilization. As an example, decomposition and combustion chamber temperature determines the materials required for thruster survivability.

Green propellants ignition at the state of art is targeting the increase of system reliability, by avoiding external devices that can constitute a single point failure, which therefore require redundant components. A hypergolic action of fuel and oxidizer is sought, requiring rapid and vigorous chemical reactions. Otherwise, in case of a delayed ignition an excessive amount of highly energetic substances will accumulate in the combustor, potentially leading to hard start phenomena or even to destruction of the rocket engine. Several hypergolicity studies focus on making non-hypergolic propellant combination hypergolic by proper tuning of reactive and/or catalytic additives to fuels, opening to possible deposition problems during storage and need of careful repeatability assessment [7,61,70].

A viable alternative is represented by the staged combustion, where hot decomposition products (generally of the oxidizer, i.e., either HTP or N_2O) are injected in the combustion chamber at a temperature higher than the auto-ignition one of the other chemical [13]. The controlled decomposition is generally accomplished in a chamber separate from the main one, through the use of catalysts. The catalysts need to be capable of withstanding the very high reaction temperatures and the aggressive oxidizing environments, while simultaneously granting high decomposition efficiency, long life span for multiple ignitions and constant reliable performance.

3.4. Costs

Economical aspects play a crucial role in rocket propellant selection. Fuel and oxidizer availability and price dictate the possibility to perform short- and long-term research and deployment activities. However, the real key aspects for propellants' economical evaluation is determining and reducing the costs associated with handling and accident avoidance.

Schmidt and Wucherer [46] broke down the total cost into different components: (i) cost of the propellant and raw materials; (ii) hardware for transfer, handling, loading and decontamination operations; (iii) ground service equipment and personal protection; and (iv) disposal of residuals. These cost elements are expected to differ for toxic and nontoxic propellants. Toxic materials typically require complex propellant flow systems, designed to be two-failure tolerant with several prevention devices [2], and requiring cleaning and decontamination after use. Hydrazine and NTO fueling operations require trained workers and suspension of activities on spacecraft, increasing the costs and timing schedule. In this respect, a useful indication is supplied by Schmidt et al. [46,71], who provided the limiting time a worker can spend in SCAPE suits, ranging from 1 h 50 min when carrying an air pack to 3 h 50 min if an air hose is employed.

Personal protection equipment is needed for decontamination after use and a regular maintenance is mandatory to ensure protection of the operator. Additionally, regular medical health control of operators is mandatory. Health and safety concerns require constant surveillance, requiring instruments able to detect very low chemical contents in liquids, water and air. For accidental toxic spills or leaks, there should be adequate equipment for dilution, neutralization and detoxification with suitable chemicals, and for safe disposal of the contaminants from a test stand or launch platform [4,46]. Hence, it is clear that for less hazardous propellants, a safety increase will ease the overall operations and reduce the global costs.

4. Screening Methodology

4.1. Investigated Oxidizers and Fuels

The study focuses on hydrogen peroxide and nitrous oxide as oxidizers and light hydrocarbons, kerosene and alcohols, that are characterized by a proved scientific heritage in the open literature, as fuels (see Section 1). Selected oxidizers and fuels are summarized in Tables 4 and 5, along with their relevant properties. Additionally, their vapor pressures and liquid densities are shown in Figures 1 and 2, respectively. Toxic fuels and oxidizers introduced in Section 2 as well as liquid ethene (which is a cryogenic liquid, characterized by a NBP lower than 90 °C, as shown in Table 4), are included in the following discussion for comparison.

Table 4. Properties of investigated fuels. Data retrieved from Refs. [38,58,72].

Fuels	Chemical Formula	Molecular Weight	Freezing Point [°C]	Normal Boiling Point [°C]	Density [g/cm ³]
Methanol	CH ₃ OH	32.0	−98	65	0.792 @20 °C
Ethanol	C ₂ H ₅ OH	46.1	−114	78	0.789 @20 °C
Isopropanol	(CH ₃) ₂ CHOH	60.1	−88	82	0.784 @20 °C
Ethane	C ₂ H ₆	30.1	−183	−89	0.499 NBP
Propane	C ₃ H ₈	44.1	−188	−42	0.581 @NBP
Ethene	C ₂ H ₄	28.1	−169	−104	0.567 @NBP
Propene	C ₃ H ₆	42.1	−185	−48	0.611 @NBP
Ethyne	C ₂ H ₂	26.0	−84 *	−84 *	0.621 @NBP
Propyne	C ₃ H ₄	40.1	−103	−23	0.692 @NBP
Kerosene	C _n H _{1.953n}	- **	−48 **	170–247 **	0.800–0.810 ** @20 °C

* Triple point. ** Dependent upon the chemical compositions.

Table 5. Properties of investigated oxidizers. Data retrieved from Refs. [38,43,58].

Oxidizers	Chemical Formula	Molecular Weight	Freezing Point [°C]	Normal Boiling Point [°C]	Density [g/cm ³]
HTP 98%	98%H ₂ O ₂ + 2%H ₂ O	33.7	−2	148	1.437 @20 °C
HTP 87.5%	87.5%H ₂ O ₂ + 12.5%H ₂ O	32.0	−14	139	1.378 @20 °C
Nitrous Oxide	N ₂ O	44.0	−91	−88	0.787 @20 °C

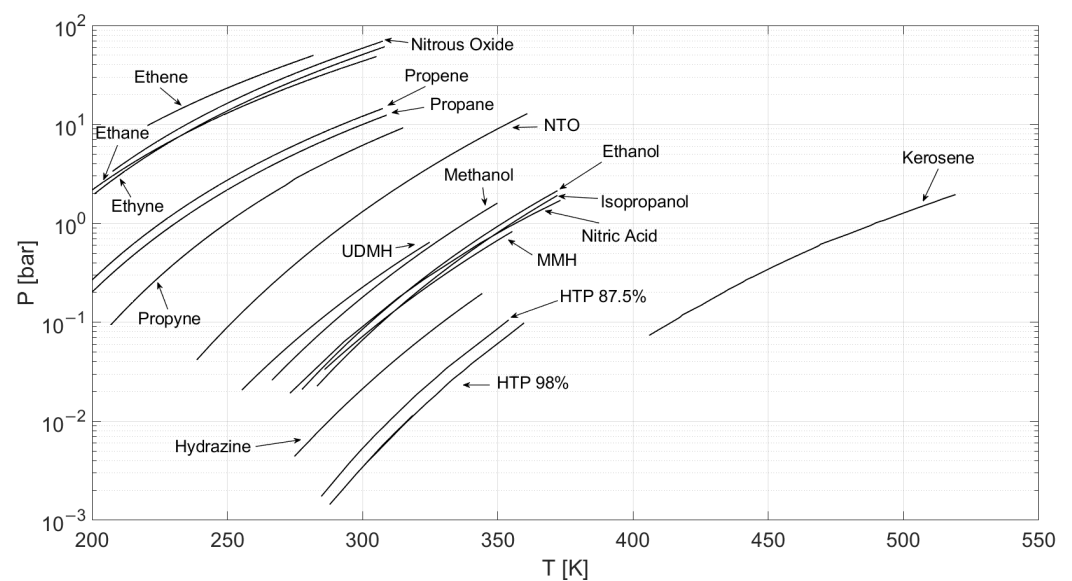


Figure 1. Oxidizers and fuels vapor pressure [38,58,72].

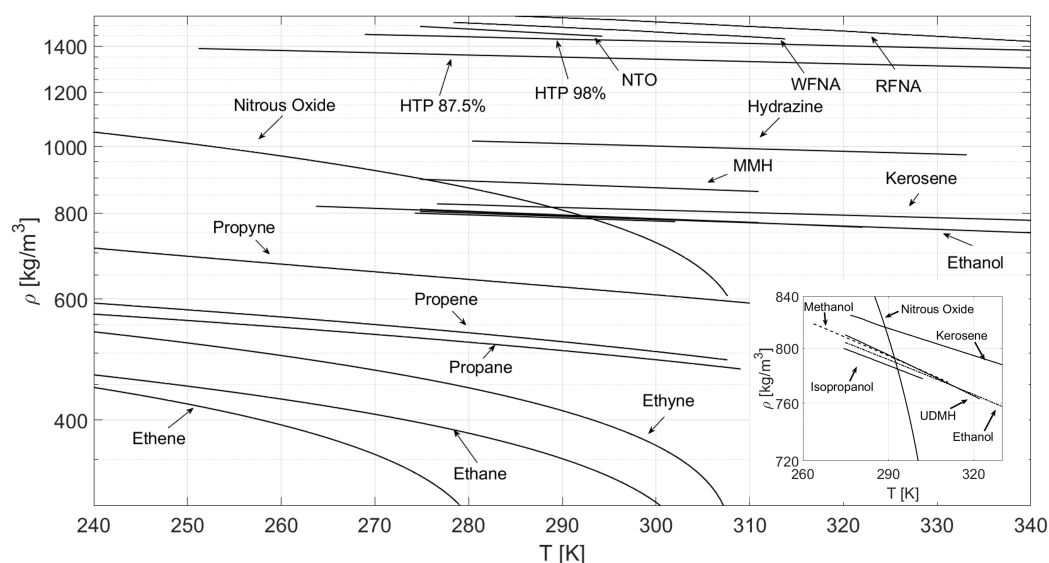


Figure 2. Oxidizers and fuels density [38,58,72].

4.2. Toxicity

In order to prioritize chemicals, three levels of toxicity are considered. Level 1 includes CMR chemicals, substances responsible for acute poisoning and requiring low concentrations to be fatal. In addition, very toxic chemicals for the environment belong to the same level, which therefore includes the least favorable substances for current employed storable propellant replacement. Those materials would require complex personal protection equipment and monitoring instruments, as well as regular maintenance and cleaning, thorough decontamination and toxic waste management. On the contrary, Level 3 chemicals pose no severe health consequences in case of accidental exposure, and minor protective health measures in propellant handling are required. Hence, from a toxicity assessment view point, the most promising “green” substances are collected in Level 3.

In first place, the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) Regulation (EC N. 1907/2006), under which a substance may be listed as “substance of very high concern” (SVHC) [45], is considered. If a chemical is listed as SVHC, its use within the European Union is subject to authorization or restriction. Hence, future “green” propellants not posing any REACH criticality are positively rated.

Secondly, hazards identification and classification are performed according to Regulation 1272/2008 [62] on classification, labeling and packaging of substances and mixtures within the European community (i.e., the CLP Regulation). It implements the United Nations Globally Harmonized System of Classification and Labelling of Chemicals (GHS) [73], and requires manufactures, importers, distributors and final users to self-determine the hazard classification according to the GHS system. Thus, impurities in the products may lead to different notifications of the same chemical hazards. However, it must be underlined that, in certain cases, the classification of a substance is harmonized at the EU level, through the harmonized classification and labeling (CLH). This is common practice for hazards of highest concern (i.e., CMR substances).

The present classification considers the information listed by the ECHA Infocards in the CLP framework. In particular, for each analyzed hazards class, the most severe category and hazard statement code included in at least 10% of chemical hazard reports sent to ECHA by suppliers is considered. The following classes are taken into account:

- Inhalative, dermal, and oral acute toxicity;
- Carcinogenicity, reproductive toxicity, and germ cell mutagenicity;
- Specific target organ toxicity in case of single, or repeated exposure.

In the GHS framework, very toxic and fatal chemicals belong to Categories 1 and 2 of the aforementioned hazards, therefore being listed among Level 1 substances of the

present analysis. The classification proceeds with decreasing toxicity levels, by listing GHS Category 3 toxic chemicals and GHS Category 4 harmful substances as belonging to Level 2 and 3, respectively. The ECHA Infocards are used to categorize substances' environmental hazards (see Table 6). In particular, (i) long-term and (ii) acute aquatic toxicity are taken into account according to the related GHS categories. Hence, Level 1 will contain very toxic to aquatic life substances, with both short- and long-term effects.

Table 6. cyanHealth hazards rating and prioritization.

Hazard Class		Level 1 Least Favorable ●	Level 2 Moderately Favorable ◐	Level 3 Most Favorable ○
REACH	-	SVHC substance	-	-
	Acute toxicity, oral	H300 Category 1, 2	H301 Category 3	H302 Category 4
	Acute toxicity, dermal	H310 Category 1, 2	H311 Category 3	H312 Category 4
	Acute toxicity, inhalation	H330 Category 1, 2	H331 Category 3	H332 Category 4
	Specific target organ toxicity single exposure	H370–H371 Category 1, 2	H335 - H336 Category 3	-
	Specific target organ toxicity repeated exposure	H372–H373 Category 1, 2	-	-
GHS	Germ cell mutagenicity	H340–H341 Category 1A, 1B, 2	-	-
	Carcinogenicity	H350(i)–H351 Category 1A, 1B, 2	-	-
	Reproductive toxicity	H360–H361 * Category 1A, 1B, 2	-	-
	Acute aquatic toxicity	H400 Category 1	-	-
	Chronic aquatic toxicity	H410–H411 Category 1, 2	H412 Category 3	H413 Category 4
NFPA	Health Hazard Levels	Category 4 Extreme	Category 3 Serious	Category 2, 1 Moderate–Slight
TI	-	$>TI_{\text{hydrazine}}$ High	<280 Medium	<50 Moderate
VPR	-	$>VPR_{\text{hydrazine}}$ High	$>5 \times 10^3$ Medium	$<5 \times 10^3$ Moderate

* F, D, f, d, and their combinations are also included.

The health prioritization according to the NFPA 704 of the U.S. National Fire Protection Association (NFPA) is included in the analysis to have a complete overview, and possibly seek a uniform classification involving different standards. It defines fire diamonds, introducing health, flammability and reactivity classifications. Health hazard levels account for acute and chronic toxicity as well as corrosive and irritant hazards that are evaluated separately by the GHS system. Level 1 includes NFPA Category 4 chemicals to which short exposure could cause death or major injuries, while substances causing minor harm or possible temporary incapacitation due to intense exposure belong to Level 3. Further details on the health hazards rating can be found in Table 6.

The quantification of the actual exposure danger is performed by combining threshold limit values and the volatility of the vapor cloud. In particular, the vapor hazard ratio (VPR) is introduced as proposed by Popendorf [64] and Pitt [63]. Considering chemicals in liquid state at 20 °C and standard atmospheric pressure, the VPR is a nondimensional quantity, defined as the saturated vapor pressure (SVP) divided by the time weighted average limit value, as in Equation (1). A similar idea led to the definition of the Toxicity Index (TI) based on the IDLH, proposed in 1998 by Quest Consultants [74].

$$VPR = \frac{SVP}{TWA} \quad (1)$$

For a chemical in a closed container, this is a quantitative measure of the danger in case of an accidental spillage or a commanded vapor relief and/or emergency depressurization. In particular, the VPR identifies the degree of dilution that should be required by the working environment ventilation system. The same rule applies for a compressed or liquefied gas. Any release in a workplace above the storage temperature or below the storage pressure could displace the air. Discarding any physical hazards considered in Section 4.3, the vapor pressure index is modified as suggested by Pependorf [64] by replacing the SVP with the atmosphere pressure:

$$\text{VPR}(*\text{gas}) = \frac{1}{\text{TWA}} \quad (2)$$

Chemicals with VPR and TI values higher than hydrazine are negatively ranked. Chemicals labeled as simple asphyxiant are considered of medium danger. If not available in the open literature, IDLH values are set as suggested by NIOSH as it practices with any nontoxic flammable gas, considering 10% of the lower explosive limit [24,43].

4.3. Handling and Storage

In the wake of the toxicity ranking, handling and safety considerations are carried out through quantitative means, as far as possible, and three levels are considered. Level 1 includes less advantageous chemicals, that may cause physical harm and may complicate handling procedures, as well as the overall system design. On the contrary, favorable physical and chemical properties in terms of flammability, compatibility, stability and storage requirements lead to ranking the analyzed propellants in Level 3. The classification methodology is detailed in the following paragraph and summarized in Table 7.

- LIQUID RANGE. The temperature window is evaluated according to the indications provided by Forbes and Van Splinter [75], as suggested by Kurilov et al. [7]. The desirable upper temperature limit is the same as required for tactical applications (70 °C). The upper temperature range for an environmentally controlled system (i.e., 30 °C) is also accepted. Low freezing point is required, at least as low as 0 °C. A lower limit is desirable for operations and testing in cold environment.
- VAPOR PRESSURE. Handling safety, as discussed in Section 4.3, is evaluated according to the vapor pressure. In particular, vapor pressure at ambient temperature lower than 1 bar is positively rated.
- VAPOR DENSITY. Vapor density data with respect to air are collected from Refs. [38,43,67], providing indications on the chemicals' tendency to sink and displace air.
- FLAMMABILITY. The NFPA 704 fire diamonds are considered for retrieving condensed information on flammability. In particular, it is evaluated considering the chemicals' flash point and boiling temperature. Chemicals that must be heated or that require a relatively high ambient temperature to ignite belong to Level 3. On the contrary, propellants that quickly vaporize at normal temperature and pressure or readily burn are classified among Level 1 ranks.
- REACTIVITY. Stability identifies the easiness of a chemical to undergo some type of reaction. Stability and reactivity classifications are evaluated through the NFPA 704 fire diamonds. In particular, the NFPA classifies as Category 4 (i.e., Level 1 in the present evaluation) a substance that readily undergoes explosive decomposition or detonates at normal temperature and pressure and a normally stable chemical, that may become unstable only at an elevated temperature and pressure, as Category 1.
- MATERIAL COMPATIBILITY. Material compatibility is evaluated from a qualitative point of view, considering hydrazine, as proposed in Ref [4], and NTO as the baseline. The "limited set of materials" category includes chemicals that impose severe restrictions due to their openly accepted compatibility issues with common space-employed materials (Titanium, Copper, Rubbers, Aluminum, TiAlV6, and others). Level 2 materials include chemicals that may cause peculiar requirements during handling/transfer/operations (i.e., high-temperature or corrosion resistant materials).

Table 7. Handling and storage rating and prioritization.

	Level 1 Least Favorable ●	Level 2 Moderately Favorable ◐	Level 3 Most Favorable ○
NFPA—Flammability	Category 4	Category 3	Category 2, 1
NFPA—Stability/Reactivity	Category 4	Category 3	Category 2, 1
Vapor Pressure * [bar]	>15	1–15	<1
Relative Vapor Density (air = 1)	>2	$1 < x < 2$	<1
Freezing Temperature ** [K]	>273	253–273	<253
Boiling Temperature ** [K]	<303	303–343	>343
Materials Compatibility	Limited Set of Materials	Substantial Subset of Materials	>90% Standard Materials

* at 20 °C. ** normal conditions.

4.4. Performance

The same three levels as presented before are considered for performance assessment. The closer a propellant couple can perform to current UDMH/NTO propulsion systems, the more positively it is ranked. The classification methodology is detailed in the following paragraph and summarized in Table 8.

Table 8. Performance rating.

	Level 1 Least Favorable ●	Level 2 Moderately Favorable ◐	Level 3 Most Favorable ○
Relative Specific Impulse	$\leq 90\% I_{s,ref}$	$90\% I_{s,ref} > I_s > 95\% I_{s,ref}$	$\geq 95\% I_{s,ref}$
Relative Volume Specific Impulse	$\leq 15\% I_{vol,ref}$	$15\% I_{vol,ref} > I_{vol} > I_{vol,ref}$	$\geq I_{vol,ref}$
Flame Temperature [K]	$> T_{ref}$	$90\% T_{ref} < T_f < T_{ref}$	$< 90\% T_{ref}$
Soot	>1	$0.45 \leq C/O \leq 1$	<0.45
Ignition	Ignition not proved	Proved ignition by catalysts addition to the fuel/ Proved staged combustion	Pure hypergolic substances

Theoretical rocket performance is estimated with the NASA Chemical Equilibrium with Applications (CEA) tool [76]. Computations are performed for a combustion pressure of 20 bar and flow frozen at the throat; the expansion ratio is set to 40. The vacuum specific impulse and specific impulse density values are compared with the reference performance figures obtained with UDMH/NTO combination considering propellants at 293 K. On the basis of openly published works and space agencies' indications, oxidizers and fuels that aim at replacing UDMH/NTO are positively rated if providing at least 95% of reference specific impulses. Ranking is performed at the optimum oxidizer-to-fuel ratio. Under the same operating point, the flame temperature is evaluated. It is worth underlining that the performance figures of merits are relative values, hence implicitly accounting for motor scaling effects that may affect a classification based on absolute numbers. As an example, the adiabatic temperature, which is the maximum temperature that can be attained by the combustion reaction under no heat loss to the surroundings, may be approached in large rocket motors. On the contrary, significant heat losses have to be considered when dealing with small devices, thus leading to the combustion chamber temperature being markedly lower than the ideal one.

Similarly, sooting occurrence is estimated. It is worth underlining that, in general, this figure of merit concerns not only soot deposition, but also black carbon rocket emissions, which play a role in the potential pollution caused by the spacecraft and its subsystems. Soot formation and destruction are complex kinetically driven processes, which start in the combustion chamber with the generation of polycyclic aromatic hydrocarbons (PAH). Further growth of the PAH by conglomeration of molecules, surface growth and coagulation and subsequent oxidation after mixing with oxidizing species such as O, O₂ and OH, lead to soot. According to thermodynamics, soot formation onset would occur for C/O-ratio larger than 1. However, the actual limit is experimentally set to about 0.45–0.50 [77], depending on the type of hydrocarbon and on the burning conditions. Hence, a C/O-ratio

lower than 0.45 is desirable. Species concentrations are recorded at the nozzle throat, as suggested by a previous paper on rocket exhaust pollution [78]. It must be noted that this prioritization cannot replace a systematic experimentation for reliable predictions, but provides useful insight.

Finally, since the performance benchmark is the hypergolic hydrazine/NTO combination, the ignition strategies for the proposed couples are briefly discussed. The classification considers (i) pure hypergolic substances; (ii) proved ignition by addition of catalysts to the fuel; proved fuels self-ignition; and (iii) no ignition proved in the open-literature.

5. Results and Discussion

The oxidizers and fuels prioritization and the variables/properties that enabled the analysis are listed in Tables 9–12 and shown in Figures 3–5, while a discussion of the merits and limitations of each candidate is provided next.

Table 9. Oxidizers toxicity metrics.

		NTO		Nitric Acid		Nitrous Oxide		HTP87.5		HTP98
REACH	○	--	○	--	○	--	○	--	○	--
GHS Acute toxicity, oral	○	--	○	--	○	--	○	--	○	--
GHS Acute toxicity, dermal	○	--	○	--	○	--	○	Warning	○	Warning
GHS Acute toxicity, inhalation	●	Very Toxic	●	Very Toxic	○	--	○	Warning	○	Warning
GHS Specific target organ toxicity—single exposure	◐	Warning	○	--	○	--	◐	Warning	◐	Warning
GHS Specific target organ toxicity—repeated exposure	○	--	○	--	○	--	○	--	○	--
GHS Germ cell mutagenicity	○	--	○	--	○	--	○	--	○	--
GHS Carcinogenicity	○	--	○	--	○	--	○	--	○	--
GHS Reproductive Toxicity	○	--	○	--	○	--	○	--	○	--
GHS Acute Aquatic Toxicity	○	--	○	--	○	--	○	--	○	--
Chronic aquatic Toxicity	○	--	○	--	○	--	◐	Warning	◐	Warning
NFPA—Health	◐	Serious	●	Extreme	◐	Serious	◐	Serious	◐	Serious
Toxicity Index	●	73,292	●	2560	◐	ASP	○	47	○	28
Vapor Hazard Ratio	◐	317,600	◐	32,000	◐	20,000 *	○	3500	○	2100

* VHR(gas).

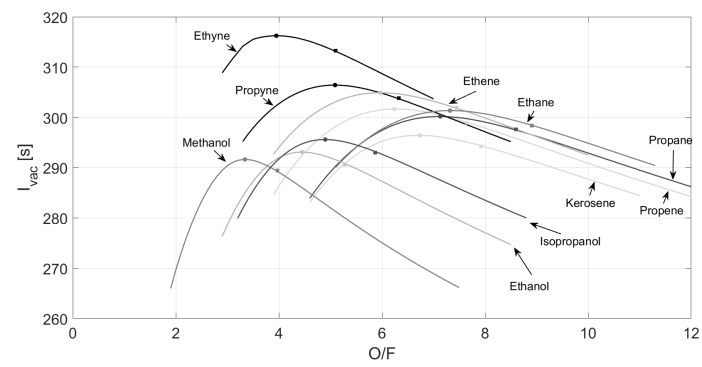
Table 10. Oxidizers handling and safety metrics.

		NTO		Nitric Acid		Nitrous Oxide		HTP87.5		HTP98
NFPA—Flammability	○	--	○	--	○	--	○	--	○	--
cyanNFPA—Stability/Reactivity	○	--	○	Minimal	○	--	◐	Serious	◐	Serious
Vapor Pressure @20 °C [bar]	○	0.9528	○	0.6400	●	50.356	○	0.0035	○	0.0021
Vapor Density	●	3.18	●	2.20	◐	1.53	○	1.11	◐	1.16
Freezing Temperature [K]	◐	262	○	231	○	182	◐	259	◐	271
Normal Boiling Temperature [K]	●	294	○	356	●	185	○	412	○	421
Materials Compatibility	◐	--	●	--	◐	--	●	--	●	--

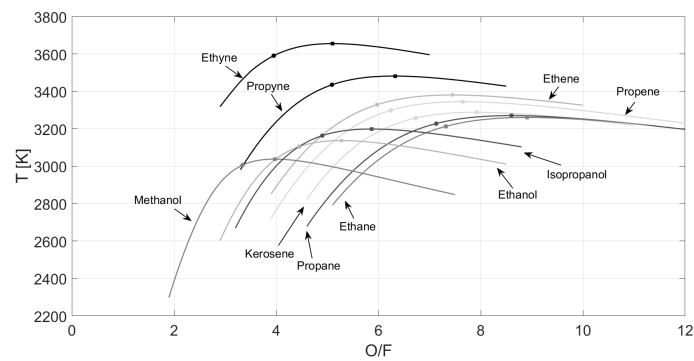
Table 11. Fuels toxicity metrics.

	N ₂ H ₄	MMH	UDMH	Methanol	Ethanol	Isopropanol	Propane
REACH	●	SVHC	●	SVHC*	○	--	○
GHS Acute toxicity, oral	●	Toxic	●	Fatal	●	Toxic	●
GHS Acute toxicity, dermal	●	Toxic	●	Fatal	●	Toxic	●
GHS Acute toxicity, inhalation	●	Fatal	●	Fatal	●	Toxic	●
GHS Specific target organ toxicity—single exposure	○	--	○	--	●	Warning	○
GHS Specific target organ toxicity—repeated exposure	○	--	○	--	○	--	○
GHS Germ cell mutagenicity	○	--	○	--	●	Warning	○
GHS Carcinogenicity	●	Danger	●	Danger	○	--	○
GHS Reproductive Toxicity	○	--	○	--	○	--	○
GHS Acute Aquatic Toxicity	●	Very Toxic	○	--	○	--	○
GHS Chronic aquatic Toxicity	●	Very Toxic	●	Very Toxic	○	--	○
NFPA—Health	●	Extreme	●	Extreme	○	Slight	○
Toxicity Index	●	280	●	2475	●	10,887	○
Vapor Hazard Ratio	●	1,400,000	●	4,950,000	●	16,330,000	●
	Propene	Propyne	Ethane	Ethene	Ethyne	Kerosene	
REACH	○	--	○	--	○	--	○
GHS Acute toxicity, oral	○	--	○	--	○	--	○
GHS Acute toxicity, dermal	○	--	○	--	○	--	○
GHS Acute toxicity, inhalation	○	--	○	--	○	--	○
GHS Specific target organ toxicity - single exposure	○	--	●	Warning	○	--	●
GHS Specific target organ toxicity - repeated exposure	○	--	○	--	○	--	○
GHS Germ cell mutagenicity	○	--	○	--	○	--	○
GHS Carcinogenicity	○	--	○	--	○	--	○
GHS Reproductive Toxicity	○	--	○	--	○	--	○
GHS Acute Aquatic Toxicity	○	--	○	--	○	--	○
GHS Chronic aquatic Toxicity	○	--	○	--	○	--	●
NFPA—Health	○	Slight	○	Slight	○	Minimal	○
Toxicity Index	●	500 *	●	588 *	●	345 *	●
Vapor Hazard Ratio	●	ASP	○	1000*	●	ASP	●

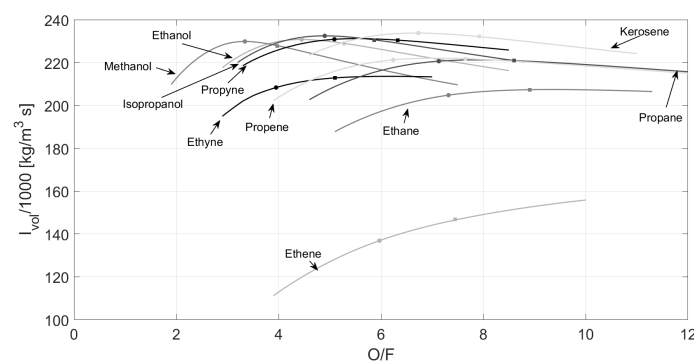
* VHR(gas).



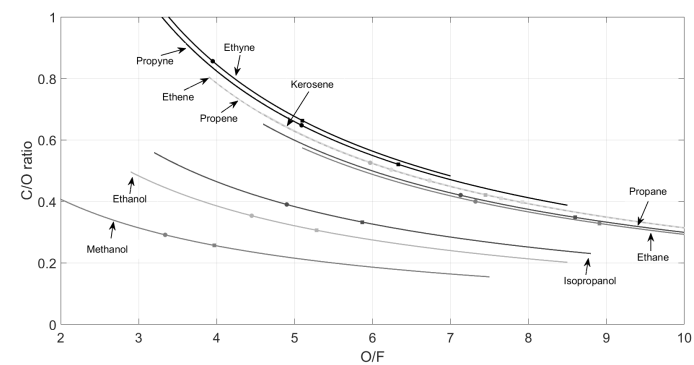
(a)



(b)

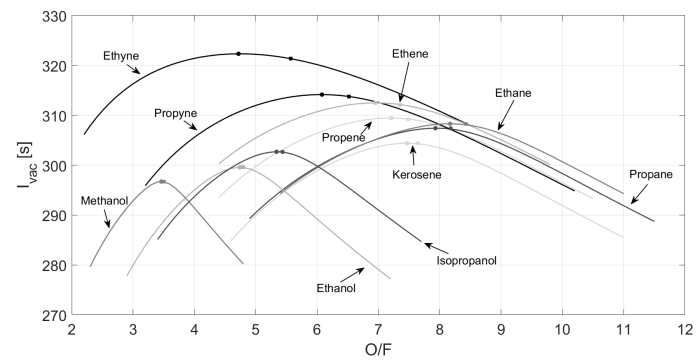


(c)

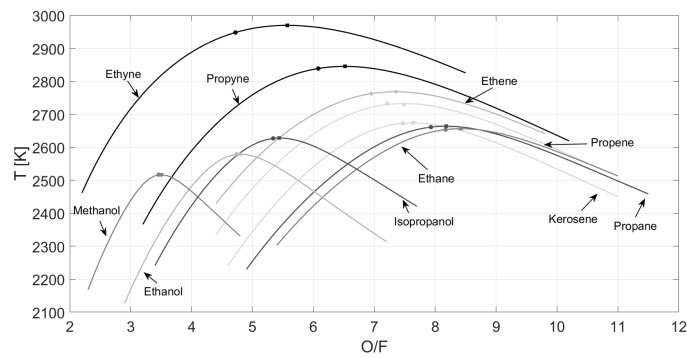


(d)

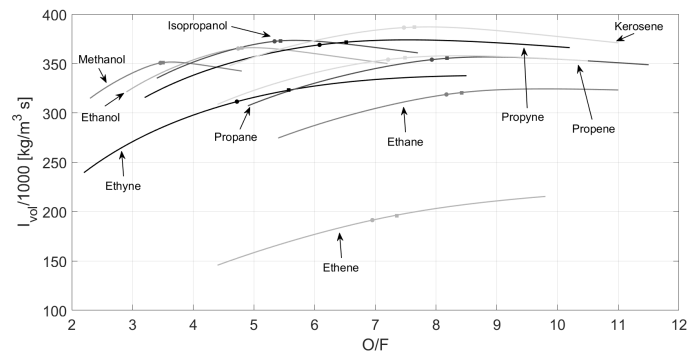
Figure 3. Nitrous Oxide-based propellants performances: (a) vacuum specific impulse; (b) chamber temperature; (c) density impulse; and (d) C/O ratio.



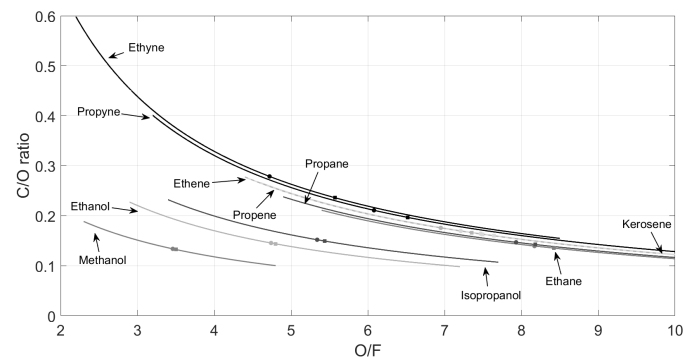
(a)



(b)

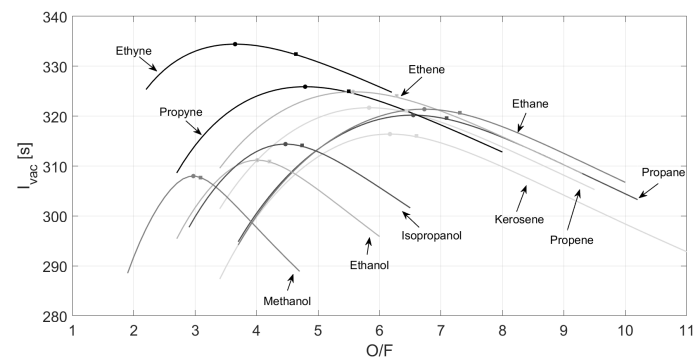


(c)

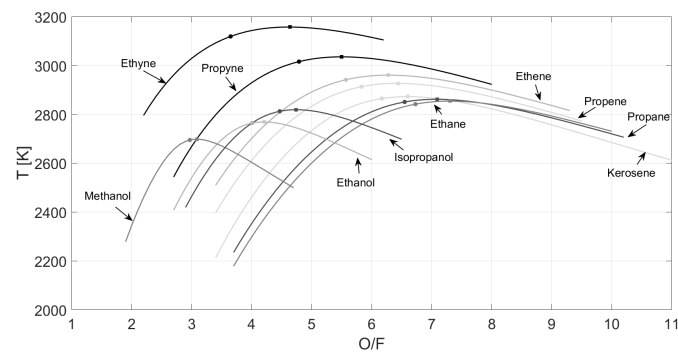


(d)

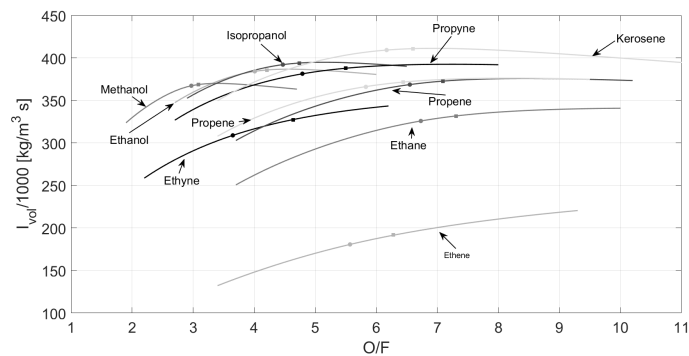
Figure 4. HTP 87.5%-based propellants performances: (a) vacuum specific impulse; (b) chamber temperature; (c) density impulse; and (d) C/O ratio.



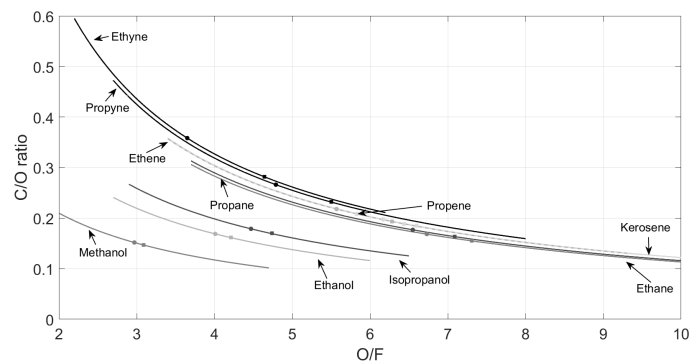
(a)



(b)



(c)



(d)

Figure 5. HTP 98%-based propellants performances: (a) vacuum specific impulse; (b) chamber temperature; (c) density impulse; and (d) C/O ratio.

5.1. Oxidizers

Both nitrous oxide and high-test peroxide are compliant with the imposed toxicity requirements for personnel and environment. However, their different chemical and physical properties, as well as their different stabilities, suggest that both candidates may be employed in future activities, even though with different targeted key performances.

Nitrous oxide is a non-toxic and non-flammable liquefied gas. However, as a greenhouse gas, attention must be paid to its global warming potential, which is 300 times larger than CO₂ [79]. According to the selected GHS classes, it is a completely green chemical, while the NFPA ranks it among the substances that may cause either a temporary or moderate residual injury within a short exposure period. This is mostly due to its asphyxiating potential, in view of its high and strongly temperature-dependent vapor pressure (~50 bar at 20 °C, see Figure 1). As it is shown in Table 13, the IDLH value is simply indicated as ASP, suggesting that the short term exposure limit is reached when the chemical approaches asphyxiating concentrations, (i.e., a value as high as to reduce available oxygen to below 19.5%), which is for a nitrous oxide concentration of approximately 5%. Additionally, its vapors are 1.5 times heavier than air, causing them to concentrate at low levels and displacing oxygen in confined space. From a system viewpoint, high vapor pressure results in high tank mass but, simultaneously, the self-pressurizing property may discard the need of a separate gas pressure feed system, relaxing the mass budget in the opposite way. However, a blow-down pressurization system is not recommended for constant thrust applications, due to the inherent pressure decay. Another important disadvantage is related to nitrous oxide density, as high as 1232 kg/m³ at NBP, and as low as 787 kg/m³ at 20 °C, thus penalizing its selection in volume-driven applications. The storage window at normal conditions is quite tight, with a low freezing point that enables in-space operations, while the upper boundary shall be opportunely tuned according to the vapor pressure dependency. Nitrous oxide can exothermically decompose into 36 wt% oxygen and 64 wt% nitrogen [76] if heated above 520 °C or in contact with several metal and metal oxide catalysts [80], reaching temperature as high as ~1600 °C. It is classified among Level 2 chemicals when considering materials compatibility, because of the thermal stresses imposed on both the decomposition chamber and on the catalysts, that may affect the bed lifetime and its performance repeatability, if a staged combustion configurations is considered. According to the NFPA classification, nitrous oxide is considered, by itself, normally stable, even under fire conditions, and not reactive with water. However, the reactivity of this chemical can be reconsidered in light of N₂O explosive events documented in the open literature. Merrill [81] provides a review of N₂O explosive hazards, underlining that early studies did not highlight a significant explosive nature of nitrous oxide because too small volumes were experimentally tested. On the contrary, the author identifies runaway monopropellant decomposition propagation through piping to storage tanks, impact or friction as primary concerns for N₂O systems. In particular, the need for developing means for stopping and measuring the increase in explosive sensitivity of fuel-contaminated N₂O was markedly suggested. In fact, the author highlights that the explosive events for nitrous oxide are markedly worsened by its gas and liquid solvent properties that can lead to fuel/N₂O undesired compositions.

High-test peroxide is a non-toxic and non-flammable chemical, that, however, is classified by GHS as harmful to aquatic life with long lasting effects. HTP vapors may cause respiratory (i.e., H335 in the GHS classification) and eye irritation, presenting an IDLH above 75 ppm and a TWA-TLV above 1.0 ppm. This limiting concentration is slightly lower than the corresponding values for NTO and nitric acid. However, HTP's extremely low vapor pressure leads to contained TI and VHR values, thus suggesting an actual exposure danger not comparable with the harms caused by both NTO, nitric acid and N₂O.

HTP chemical and physical properties vary with hydrogen peroxide concentrations and temperature, but the latter dependence is much less strict than in the case of nitrous oxide, thus less complicating the overall system design (see Figures 1 and 2). Additionally, the relatively high density (i.e., 1437 kg/m³ at 20 °C for 98% HTP) makes hydrogen peroxide a strong competitor for the "green oxidizer" leading role. As opposed to N₂O, hydrogen

peroxide is compliant with the normal boiling point requirement, while not fulfilling the freezing point limit of at least $-20\text{ }^{\circ}\text{C}$, thus complicating the eventual operations in cold environment. However, it must be noted that at a low concentration, HTP approaches the acceptable limit, even though performance penalties must be taken into account. Additionally, freezing depressants may be added to lower the freezing point, provided the stability of the mixture in the long-storage perspective. Preliminary accomplishments were obtained by adding ammonium dinitramide or ammonium nitrate in the substance by Weiser et al. [82].

Hydrogen peroxide exothermic decomposition into oxygen (i.e., 46% by mass [67,76]) and steam may be started catalytically or thermally. However, in general, HTP is characterized by an inherent tendency to slowly decompose. Its instability is one of the most important drawbacks of HTP, progressively lowering the concentration and thus making it unsuitable for long-term missions. Stabilizers are commonly added to the chemical to prevent or at least decrease the decomposition rate to a minimum, but at the same time they cause poisoning of the catalyst bed and performance degradation. In the open literature, several studies focused on the reactivity of the HTP in terms of propensity to detonation and/or explosion. According to Sackeim and Masse [4], HTP is negative at NOL card gap test, hence showing shock insensitivity. Detonation concerns are mostly related to hydrogen peroxide vapors. According to Ferlin [83], 85% H_2O_2 is capable of detonation at $45\text{ }^{\circ}\text{C}$ if significant initiation sources—such as a spark, hot wire or catalytically-active surface—are present. On the contrary, the author suggested that without a booster detonation as initiator, no detonation risk should be considered below $80\text{ }^{\circ}\text{C}$ and possibly even at higher pressure. At atmospheric pressure, hydrogen peroxide solutions are not usually explosive. However, its equilibrium vapor concentrations above 26 mole% become explosive in a temperature range even below the boiling point of the liquid. According to Ferlin, above four bars, this flammability limit remains constant at 33 wt%.

Stability concerns are also linked to HTP incompatibilities. In fact, a limited set of common materials can be used with HTP, such as pure aluminum 1060, fully austenitic stainless steel with passivation and conditioning, Teflon and polyethylene [67,84]. These limitations complicate the eventual quick-to-the-market solution based on COTS components that need to be carefully tested to ensure both short- and long-term compatibility. Additionally, conflicting results can be found in the open literature regarding the compatibility classification of some materials. As an example, according to Ref. [67], Inconel 718 shall be classified among Class 2 materials (i.e., materials satisfactory for repeated short-time contact with HTP) if the operating temperature is below $\sim 20\text{ }^{\circ}\text{C}$ with a high-quality surface finish (i.e., surface roughness lower than 10 rms). On the contrary, at the working temperature of about $\sim 70\text{ }^{\circ}\text{C}$, it is ranked among Class 4 materials, which are not recommended for use with HTP. However, recent efforts targeting the design and testing of HTP-based prototypes are dealing with Inconel 718, thus demanding further compatibility assessment [85].

5.2. Fuels

Human and environmental short- and long-term toxicity are peculiar characteristics of hydrazine and its derivatives, as discussed in Section 2.1 and summarized in Table 11. Hence, the selection of most suitable fuels shall focus on avoiding CMR classes and shall target acute toxicity ratings lower than hydrazine.

Broadly speaking, alcohols and light hydrocarbons are characterized by no or minimal toxicity in the GHS framework, except for methanol, which is ranked among Category 3 for acute toxicity. In particular, it features the same dermal and inhalation categories as hydrazine, while a different categorization is provided by the NFPA. However, according to Ref. [86], acute oral and inhalation exposures and, to a lesser extent, dermal absorption of high concentrations of methanol have led to central nervous system depression, blindness, coma and death, thus supporting the conclusion of high toxicity of methanol. In general, most of the hazard phrases concern specific target organ toxicity. In particular, (i) methanol is identified as possibly harming the optic nerve and the central nervous system (i.e., H370);

(ii) isopropanol may cause dizziness and drowsiness (i.e., H336); (iii) propyne may affect lung via inhalation route of exposure (i.e., H335); (iv) ethene may have a narcotic effect (i.e., H336); and (v) kerosene may harm the central nervous system via the inhalation route of exposure (i.e., H336). All selected fuels do not pose hazards to aquatic life, except kerosene. However, its chronic aquatic toxicity is classified as Category 2, i.e., one level lower than that of hydrazine, fulfilling the requirement of fuel toxicity lower than the former. In general, however, it must be taken into account that the physical properties of kerosene fuels fluctuate, depending on several factors such as the petroleum source, the refinement process, the accuracy of the manufacture, and the additives used to tune specific properties, such as the freezing point [58]. Hence, a more detailed analysis shall focus specifically on the jet fuels and their subtle distinctions.

Two behaviors can be observed due to the physical state at normal conditions and vapor pressure values. Light hydrocarbons with low carbon numbers are gaseous at standard conditions and can be stored as liquefied gases. As a consequence, storage at 20 °C requires high storage pressures depending on their vapor pressure. Ethane, ethene and ethyne, in particular, have steep temperature-dependent vapor pressure and density curves, leading to very low density values that may penalize volume-limited applications. Additionally, adiabatic expansion can produce sudden cooling and local freezing in valves. It must be noted that ethene is typically stored at its normal boiling point as a cryogenic liquid. Finally, despite the high TLVs listed in Table 13, large TI indexes characterize light hydrocarbons, comparable to that of hydrazine. Hence, any release of these compressed or liquefied gases in an atmosphere at a pressure lower than the storage one could potentially lead to concentrated hydrocarbons atmosphere, displacing air and raising flammability concerns. Hydrocarbons featuring high vapor pressure at 20 °C may be advantageous in case of implementation of self-pressurization system, in particular if in combination with nitrous oxide, with similar level of tank burst pressure. On the contrary, due to the typical vapor pressure of the other fuels, an external gas shall be preferably used for pressurization. Alcohols and kerosene are liquids at normal conditions and are characterized by low vapor pressure and small variations of density. Additionally, their actual exposure danger is very limited, hence making them promising for safe and green applications.

Table 13. Threshold limit values for the analyzed chemicals. Data from Ref. [38].

	TWA	IDLH
Methanol	200	6000
Ethanol	1000	3300
Isopropanol	200	2000
Ethane	ASP	2900
Propane	ASP	2100
Ethene	ASP	2750
Propene	ASP	2000
Ethyne	N/A	2500
Propyne	1000	1700
Kerosene	15	700
Nitrous Oxide	50	ASP
HTP	1	75

Important properties to be taken into account are the flammability and relative vapor density. In fact, if a container can release a dense gas, its vapor could sink and, if flammable, collect until it is at a concentration (i.e., lower flammability limits, see Table 14) sufficient for ignition. Even if not flammable, it could collect in the lower floor or, alternatively, it may present an asphyxiation hazard or lead to an uncontrolled explosion. All the analyzed fuels are classified by the NFPA as highly flammable and are characterized by vapor density relative to air larger than 1, except for ethene and ethyne. In particular, chemicals that will ignite under most ambient temperatures and have a flash point below 23 °C and a boiling point of only 38 °C are ranked among NFPA—Category 3 of serious flammability. On the contrary, chemicals that readily burn and have a flash point below normal room

temperatures belong to the most dangerous level. Among this last category, the analyzed alkanes, alkenes and alkynes can be recognized. Alkynes present reactivity issues, as indicated by the NFPA stability categorization. In fact, ethyne tends to detonate for adiabatic compressions and explode even with negligible triggers, often being substituted by ethylene, which is more stable and has a tighter explosive range [57] (see Table 14). On the other hand, propyne may incur an explosive decomposition when subjected to an initiating source or heated under confinement, causing explosion issues because of the very low explosive limit (i.e., LEL = 1.7 %) [57]. This is mostly due to the triple carbon–carbon bond, which increases alkynes sensitivity to shock and vibration.

Table 14. Flammable limits in air. Data from Ref. [38].

	LFL %	UFL %
Methanol	6	36.5
Ethanol	3.3	19
Isopropanol	2.3	17
Ethane	2.9	13
Propane	2.1	9.5
Ethene	2.75	28.6
Propene	2	11
Ethyne	2.5	100
Propyne	1.7	11.7
Kerosene	0.7	5

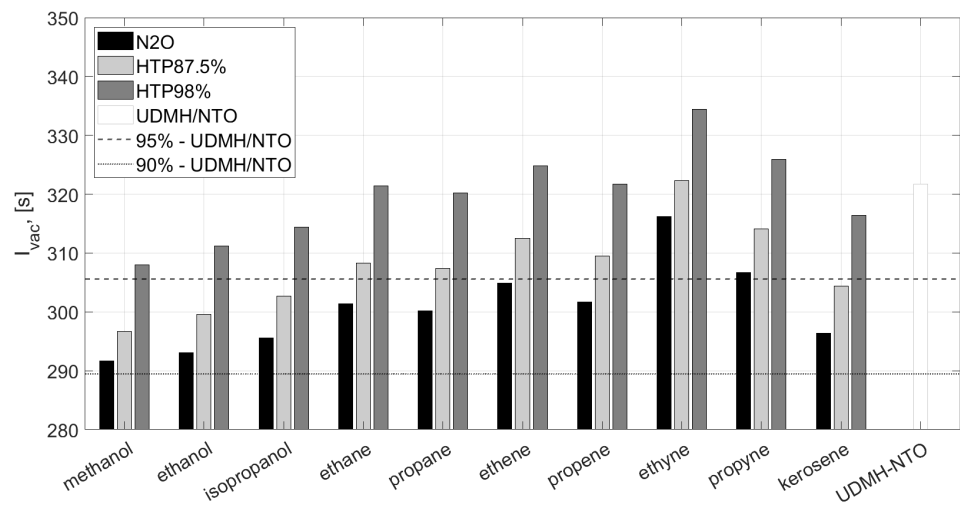
The melting point requirement is satisfied by all of the proposed fuels, while the low boiling points of light hydrocarbons, even though favorable from a performance view point in terms of atomization in the combustion chamber, is not favorable for on ground and in orbit operations. Ethanol, isopropanol and kerosene are the only fuels satisfying the global temperature window requirement.

5.3. Performance

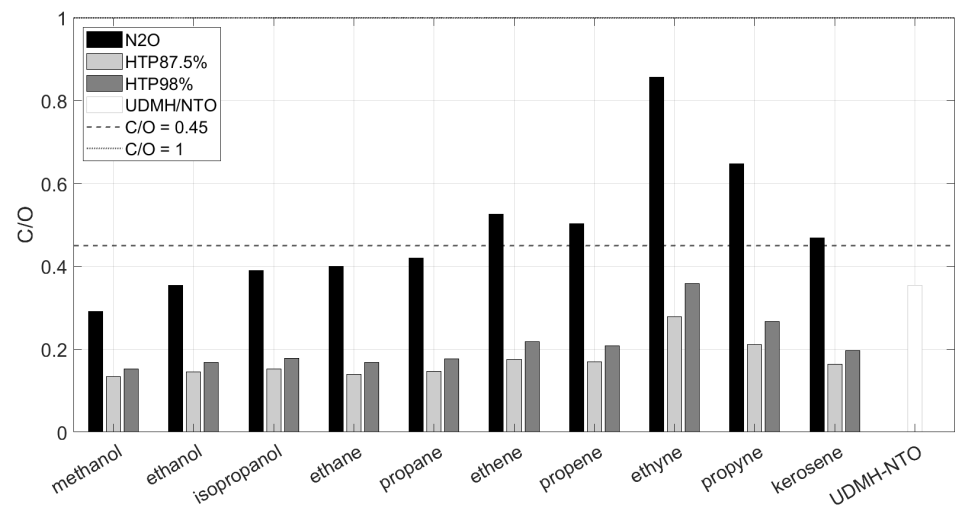
Vacuum and density specific impulses, combustion chamber temperature and sooting occurrence of nitrous oxide- and HTP-based bipropellants are compared in Figure 6, while Figures 3–5 highlight the performance against the oxidizer-to-fuel ratio.

HTP-based propellants feature vacuum impulse larger than nitrous oxide, and increasing with HTP concentration, due to the progressively larger content of reacting oxygen. At the same time, the density impulse is also favorable to hydrogen peroxide due to its high density at ambient conditions, almost doubling the one of liquefied nitrous oxide. However, it is worth remembering that for comparison purposes the density of the chemicals are computed at 20 °C, thus penalizing light hydrocarbons and nitrous oxide—for which a storage conditions close to the NBP is preferable-, as well as ethene, that as already said is stored as cryogenic liquid. In fact, as an example, nitrous oxide and propane at NBP would lead to a maximum density impulse of $\sim 325 \times 10^3 \text{ kg/m}^3 \text{ s}$, which is larger than the value showed in Figure 3c, but still lower than the hydrogen peroxide-based counterparts.

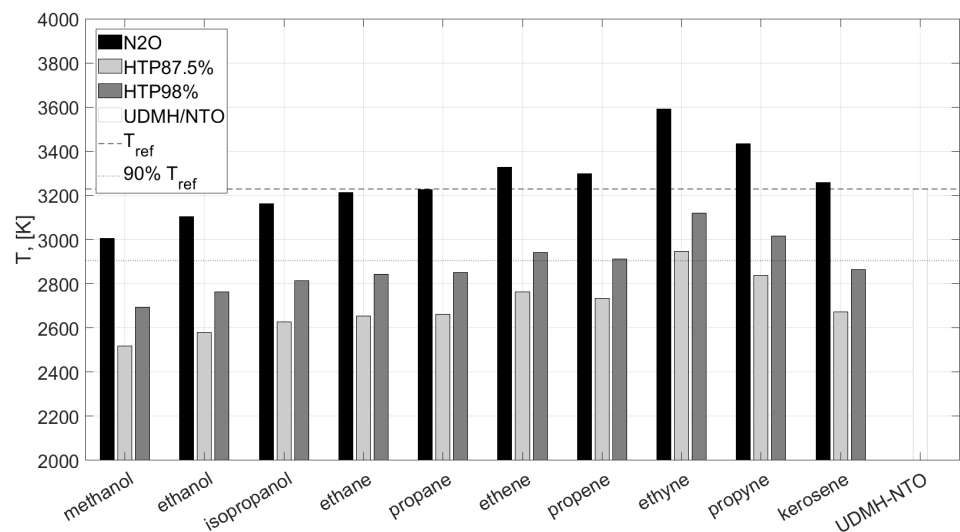
Alcohols are characterized by an energy density lower than hydrocarbon fuels, and it is clear that unsaturated hydrocarbons are better than saturated ones, with decreasing performance as the chain length increases. Maximum vacuum impulse is obtained for O/F between 3 to 5 for alcohols and 4 to 9 for light hydrocarbons, reducing the amount of fuel for cooling purposes in the latter case. However, as shown in Figures 3–5, the I_{vac} curve is flatter than in the case of the alcohols, enabling the possibility of choosing nominal design point different than the optimal O/F without important performance loss. Hence, a trade-off analysis shall be considered between performance, temperature and subsystem requirements in order to select the proper O/F design point. However, such a detailed analysis is beyond the scope of the present assessment.



(a)



(b)



(c)

Figure 6. Performance comparison between selected green propellant couples: (a) vacuum specific impulse; (b) sooting behavior; and (c) chamber temperature.

In general, all the propellant combinations based on the highest HTP concentration limit to a maximum of 5% the vacuum specific impulse decrease with respect to UDMH/NTO. This limit is never approached by nitrous oxide couples, that achieve performance reductions up to almost 10% with methanol as fuel. Large temperature results from the combustion of nitrous oxide with the selected fuels. The computed variables are comparable with the chamber temperature achieved by UDMH/NTO, but 200 °C to 500 °C higher than HTP bipropellants. Hence, this latter solution would ease the cooling process and the thermal stresses in the thrust chamber [77].

H₂O₂ is less prone to soot production. When N₂O is considered, almost all the propellant combinations approaches the kinetically-driven limit of C/O < 0.45, even surpassing it in case of alkenes, alkynes and kerosene. The amount of soot produced depends on the O/F value. Figure 3d show that nitrous oxide and light hydrocarbons are prone to sooting occurrence across a wide range of O/F, while in case of HTP soot production seems to be limited to low O/F, reasonably far from the one corresponding to the maximum performance. However, the reader should be aware that light hydrocarbons (except for methane, not included in the present analysis) and kerosene are widely known for soot production above 900–1000 °C. Moreover, as the chain length increases, achieving a complete combustion during short firings will be difficult, thus increasing the risk of soot formation. Hence, these aspects should be taken into account for the heat transfer analysis of the thrust chamber and the fuel injectors design.

Ignition strategies of the analyzed fuel target both hypergolic ignition by means of catalysts addition and the staged combustion approach. The reader should be aware that a detailed discussion of the topic is out of the scope of the present assessment, hence the authors suggest referring to dedicated reviews [70,87]. Pure hypergolicity, as in the case of the UDMH/NTO benchmark, is not documented for any of the proposed couples. However, it is known that it is possible to make ethanol and methanol spontaneously ignite with hydrogen peroxide by adding a catalyst to the fuel [70,88], while staged combustion ignition has been experimentally proved for kerosene/hydrogen peroxide [13,15], ethanol/hydrogen peroxide [10] and propene-/propylene and nitrous oxide [24]. Additionally, some tests in the PULCHER framework investigated propyne/hydrogen peroxide staged combustion, highlighting promising results, despite a long warm-up phase being needed to properly achieve a safe ignition [22,89]. As far as the other proposed couples are concerned, the authors are not aware of dedicated ignition studies. However, the staged combustion approach should be feasible for all the selected couples since the theoretical decomposition temperatures of nitrous oxide and hydrogen peroxide are markedly larger than the fuel self-ignition ones.

Finally, the required propellant percent mass and volume relative to the reference UDMH/NTO couple are proposed in Figure 7. In particular, a generic upper stage mission featuring $\Delta V = 3000$ m/s is considered. Nitrous oxide is excluded from Figure 7b, as the results are out of scale due to its low mixtures density. Globally, hydrocarbons can reduce the mass slightly compared to less costly alcohols, which on the contrary enable volume saving along with kerosene fuel. Therefore, if volume reduction is an import selection criteria, use of jet fuels and alcohols along with hydrogen peroxide (98%) is recommended.

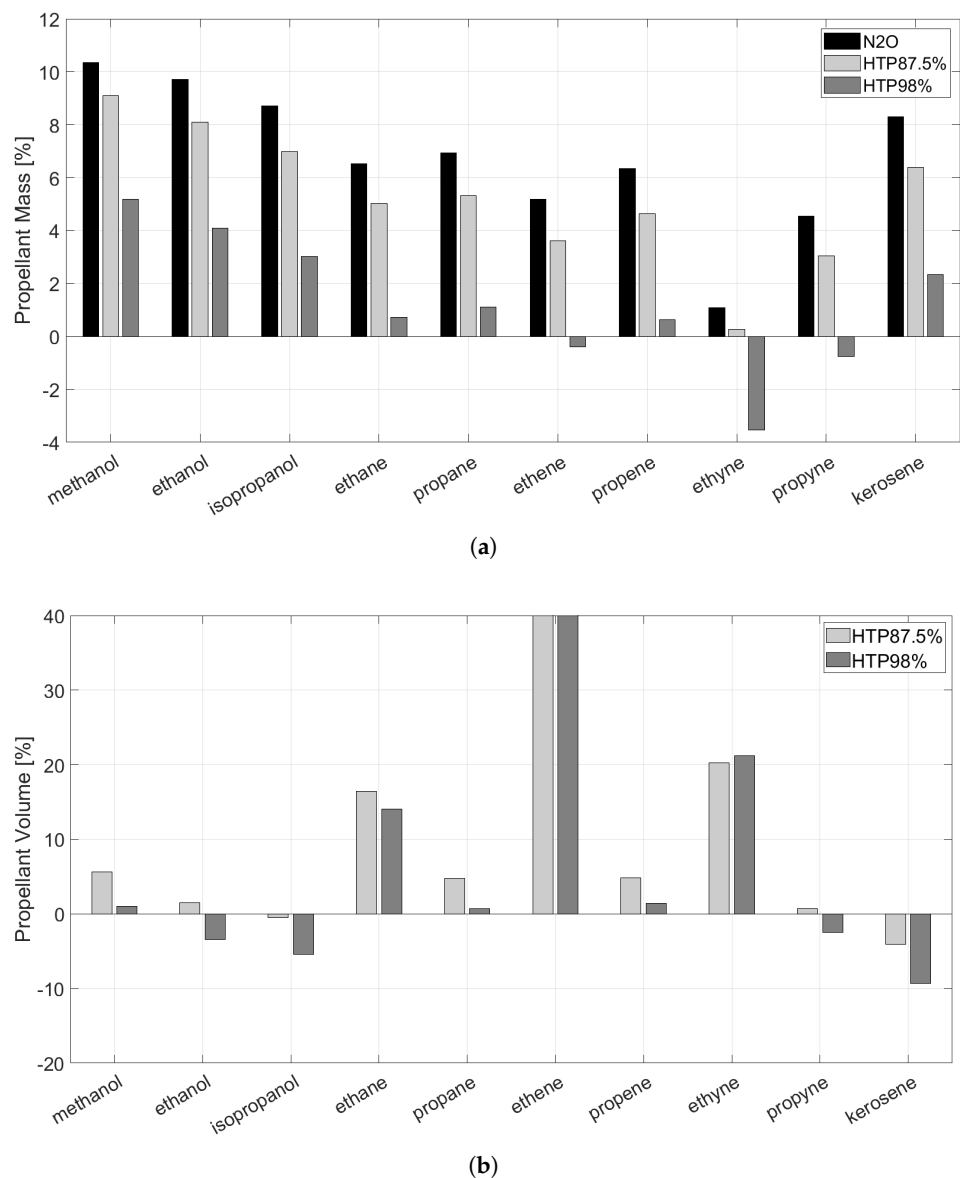


Figure 7. Relative mass and volume with respect to UDMH/NTO system for a generic upper stage mission (i.e., $\Delta V=3000$ m/s).

6. Conclusions

The ranking of suitable figures of merit has been proposed for novel propellant candidates that aim at substituting hydrazines/NTO-based systems. In particular, the main goal of the present paper was the derivation of a consistent and quantitative set of criteria that could lead to a systematic and simple selection methodology.

Toxicity has been evaluated considering both the health hazards and the soil/water potential contamination caused by the chemicals during the propellant lifecycle. In particular, the GHS framework and the NFPA ranking have been used for the classification. Additionally, the actual exposure danger has been considered by relating substances threshold limit values for personnel exposure and the likelihood of exposure imposed by the volatility of the substances. Handling and safety requirements constitute the second macro-category of the analysis. In particular, physical hazards and storage requirements enabled the identification of ranges of temperature, flammability and stability problems. Finally, performances in terms of vacuum and density specific impulse, among the others, have been included in the discussion.

The intrinsic characteristics of the analyzed propellants have made clear the absence of an optimal propellant couple and the need of a careful identification of mission and operational requirements to guide the selection. Different propellants may result from a screening process if considering (i) mass or volume-limited applications, (ii) short- or long-term mission, (iii) selection of COTS materials, (iv) requirements on pressurization schemes, (v) minimization of thermal conditioning, etc. By clearly understanding the drivers for each mission, an educated selection of fuels and oxidizers may be accomplished, possibly reducing the development of an excessive number of solutions.

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Abbreviations

The following abbreviations are used in this manuscript:

ACGIH	American Conference of Government Industrial Hygienists
ASP	Asphyxiant
CLP	Classification, Labeling and Packaging
CMR	Carcinogenic, Mutagenic, Reprotoxic
COTS	Commercial Off-the-Shelf
ECHA	European Chemicals Agency
GHS	Globally Harmonized System of Classification and Labeling of Chemicals
HAZMAT	Hazardous Materials
HTP	High-Test Peroxide
IDLH	Immediately Dangerous to Life and Health
LC50	Lethal Concentration, %50
LD50	Lethal Dose, %50
LFL	Lower Flammable Limits
LTEL	Long Term Exposure Limits
N/A	Not Available
NBP	Normal Boiling Point
NFPA	National Fire Protection Association
NIOSH	National Institute of Occupational Safety and Health
NP	Not Pertinent
NTO	Nitrogen Tetroxide
OEL	Occupational Exposure Limit
OSHA	Occupational Safety and Health Administration
PEL	Permissible Exposure Limit
REACH	Registration, Evaluation, Authorisation and restriction of Chemicals
REL	Recommended Exposure Limit
RFNA	Red Fuming Nitric Acid
SVHC	Substances of Very High Concern
ST	Short Term
SVP	Saturated Vapor Pressure
TI	Toxicity Index
TLV	Threshold Limit Value
TWA	Time-Weighted Average
VHR	Vapor Hazard Ratio

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