Hydrogen Peroxide as a High Energy Compound Optimal for Propulsive Applications

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Abstract: This paper presents the authors' experience in the field of the safe preparation and utilisation of HTP (98%+), a storable propellant that is finding use in various engineering applications. Brief characterisations of the material as well as examples of its potential use within relevant industries are provided. Additionally, some of the existing data and current research are included to demonstrate the full potential of this material which meets most of the needs of the propulsion industry. The laboratory technique for obtaining the substance that has been developed recently at the Institute of Aviation is briefly described. Utilisation of the method based on a special glass apparatus allows reproducible amounts of the substance to be obtained with relatively little risk.

1 Introduction

This paper presents a potentially "novel", in terms of renewed interest, and "green", in terms of its benign environmental nature, liquid high energy compound that is currently being used as both a rocket monopropellant and an oxidizer. The substance is known as HTP (98%+), High Test Peroxide, an aqueous solution of hydrogen peroxide of over 98% concentration and high purity. This compound is already under extensive experimental research by the European Space Agency (ESA) for its practical utilisation in space propulsion applications, as it may be successfully used in various rocket engines. Historical technical data, together with stability, storability and detonatability data, the current authors' experience,

and modern literature test data are provided within the paper to present its most important characteristics and safety issues. Moreover, HTP (98%+) is currently becoming a promising alternative to the currently used hazardous satellite propellants. This novel, in terms of its chemical quality (superior to the solutions utilised in the sixties) and renewed interest (after the period when HTP (98%+) was nearly forgotten in favour of hydrazine), high-energy liquid green propellant is a 98%+ aqueous solution of hydrogen peroxide of high purity (HTP class). It does not suffer from the disadvantages of the rocket propellants typically used for satellite applications, viz. toxicity, corrosivity and volatility.

HTP (98%+) has the potential to become one of the most versatile liquid rocket oxidizers and monopropellants. It is a dense, low vapour pressure, totally transparent and low viscosity liquid that has the appearance of water. In the US it is also known as RGHP, rocket grade hydrogen peroxide. Additionally, the material is characterised by relatively high performance and an unparalleled (especially among rocket propellants) benign nature: it is practically non-toxic, low irritatant (slightly stinging to skin) and has low corrosivity. When HTP (98%+) is subjected to the decomposition process (catalytic and/or thermal) it generates entirely environmentally benign hot gaseous decomposition products, as they consist of water and of about 46% oxygen by weight [1]. Thus, HTP (98%+), as a propulsive material, is attracting renewed interest as a promising replacement for the currently used storable rocket (satellite) propellants [2]. This is mostly due to its potential availability and truly environmentally benign nature, especially taking into account its non-toxic decomposition products, relatively high energy density (in the case of HTP (98%+) and its potential for hypergolic ignition with some catalytically or energetically promoted organic fuels [3, 4].

When used as an oxidizer in a liquid rocket engine, the performance of the top grade of HTP (98%+) is second only to that of liquid oxygen (LOX) [5]. An important advantage of this material is the fact that it remains a low volatile liquid at ambient pressure under a wide range of temperatures (Table 1). Additionally, the higher the density (concentration) of HTP (98%+) as a propellant, the greater is its propulsive efficiency (specific impulse) as the temperature of the decomposition products rises. However, the propellant cost increases with its concentration, and the higher temperature of the decomposition products together with the presence of atomic oxygen affects the material properties. Anhydrous hydrogen peroxide (100%) contains 47% of oxygen by weight, and about 2.8 MJ/kg of energy is released during the process of its decomposition into gaseous oxygen and water – the volume expansion exceeds 4500 under normal conditions [2].

It is also worth mentioning that DMAZ (2-dimethylaminoethylazide), the compound developed by the US army in the late 1990s, may be one of the most successful potential green fuels to be utilised with HTP (98%+) in bi-propellant systems [6, 7]. The theoretical performance for this couple is very close to hydrazine-NTO – the optimal I_{sp} is 331.5 m/s (calculated at IoA using the CEA code for 10 bar combustion chamber pressure, at a nozzle expansion ratio of 330 and frozen in the throat section).

The decomposition process of HTP can occur in both liquid and gas phases, with the possibility of controlled velocity, as soon as it comes into contact with a catalytically active substance (*e.g.* catalyst bed) or is subjected to a sufficiently high temperature:

$$H_2O_2(l) \rightarrow H_2O(l) + 1/2O_2(g) + q,$$
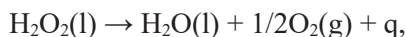
where q = −98.1 kJ/mol [8].

When HTP (98%+) is used as a mono-propellant for space applications, it gives about 20% less performance than hydrazine, one of the most utilised and dangerous satellite propulsive materials today [8]. However, when used in a bi-propellant system or in a hybrid rocket motor configuration, its performance is comparable to other liquid rocket oxidizers such as N_2O_4, HNO_3 or LOX. The volume specific impulse of HTP (98%+) is higher than that of most other propellants due to its high density (1.44 g/cm³) [9]. Additionally, due to its low vapour pressure (about 2 mm Hg at room temperature), it is relatively easy to handle [10]. Obviously, it is a non-flammable liquid, but easily acts as a powerful oxidizing agent that can cause spontaneous combustion when it comes into contact with reducing agents, organic (flammable) materials or fuels with catalytically active additives (*e.g.* impurities).

Highly concentrated hydrogen peroxide has quite a long and abundant history of various successful applications as a versatile propulsive material. It has been used in quite a number of rocket devices for over the 70 years since World War II.

Beginning in the late 1950s, the transition from HTP usage to hydrazine usage began to be noticeable. The main reason for that was the fact that, during the period of the Cold War, most research was focused mainly on the performance of propellants, with little attention to their toxicity, as environmental or personnel concerns were of lesser importance. Some of the historical ideas and arguments from that shift are still present in specialist literature, especially those authored by Sutton [11]. Many of these give rather an unfavourable depiction of HTP as a propellant in favour of hydrazine. This is one of the reasons why hydrogen peroxide for propulsive applications is still perceived as an exceptionally unstable

or dangerous substance even by aerospace specialists. The situation, especially during the last decade, has seriously changed as hydrazine and its derivatives have been classified as extremely dangerous substances and HTP is gaining more and more attention as a near-future rocket oxidiser and mono-propellant (*e.g.* GRASP Project funded by the European Union where HTP was identified as the most promising oxidiser for rocket bi-propellant systems) [12].

Consequently, nearly two generations back, highly concentrated and chemically pure solutions of hydrogen peroxide (known as HTP) were extensively used within the rocket propulsion industry, mostly in the USA, both by the military but also by NASA missions. Thus, the first specification for concentrated hydrogen peroxide solutions used as propellants was developed (known as MIL-P-16005E) in the US at that time [13]. This specification was the result of many years of experience with this propulsion material, gained during its preparation, usage, storage and transportation. Furthermore, this specification (with only minor adjustments) is still in use by the rocket propulsion community around the world.

Generally, it may be stated that a chemically pure (sometimes stabilised, usually by additives other than phosphates, in the case of its catalytically driven decomposition) and highly concentrated solution of HTP (98%+) is a powerful (rocket) oxidizing agent and an efficient, environmentally friendly monopropellant that is very suitable for small rocket engines, and also for other applications (*e.g.* pneumatic actuators, gas-generators, chemical laser systems, vacuum aspiration, hypergolic research, hybrid research or APU units) [14]. In particular, it may be used in the attitude control system on satellites, as it has already been successfully applied there (in lower concentrations, in the SynCom II communication satellite) in the past [9].

A comparative view of the most important features of HTP (at 98.0% solution) and the most currently used satellite propellant, hydrazine, is presented in the Table 1 (some data taken from General Kinetics Inc., note that hydrazine is flammable) [5].

Propellant (rocket) grade hydrogen peroxide (HTP (98%+) is still not readily available in Europe. The material is available in the US from FMC Company, however, its purchase and transportation to Europe is relatively time consuming and costly due to some of the formal requirements a client must fulfil. Thus, small research groups are emerging that tend to prepare their own HTP (even at 98%+ concentration), usually by vacuum fractional distillation or fractional crystallization techniques, from commercially available, special grades of hydrogen peroxide as the stock. Such an approach guarantees some practical benefits, besides the obvious cost savings. For instance, the product prepared

in situ may be easily adjusted (in terms of concentration, purity and stabilizer additive levels) for a particular research purpose.

Table 1.   Comparison of the most important features of HTP (98%+) and hydrazine [2, 5]

	HTP (98%+)	Hydrazine
Molecular formula	H_2O_2	N_2H_4
Appearance	colourless liquid	colourless liquid
Odour	none	ammonia
Active O_2 content [%]	46	-
Boiling point at 760 mm Hg [°C]	149	113
Freezing point [°C]	−3	1
Density at 25 °C [g/cm³]	1.431	1.01
Vapour pressure, 30 °C [mmHg]	3	19
Flash point [°C]	decomposition above 75 °C	~ 40
Autoignition temperature [°C]	rapid vapour decomposition above 122	270
Flammability limits [% in air]	none	4 ÷ 100

2   Material and Methods

For the present research activities, a laboratory installation for HTP (98%+) preparation in relatively small quantities (a few litres per week) has been established at the Institute of Aviation (IoA) facility. The currently exploited method is based on a vacuum fractional distillation technique and is performed in a specially designed glass apparatus (Figure 1). The process (concentration) is also combined with the evaporation step (purification) of each batch being processed. The conditions that are held during the process of HTP (98%+) preparation are briefly summarized in the Table 2.

The material prepared in the IoA laboratory is chemically pure HTP (98%+), fairly stable and storable under ambient conditions. The total output of the unit is nearly 300 kg of HTP (98%+) per year. The apparatus is made of chemically resistant borosilicate glass, and the only materials that have contact with the hydrogen peroxide or its vapours are glass and PTFE (both materials classified as compatibility class I).
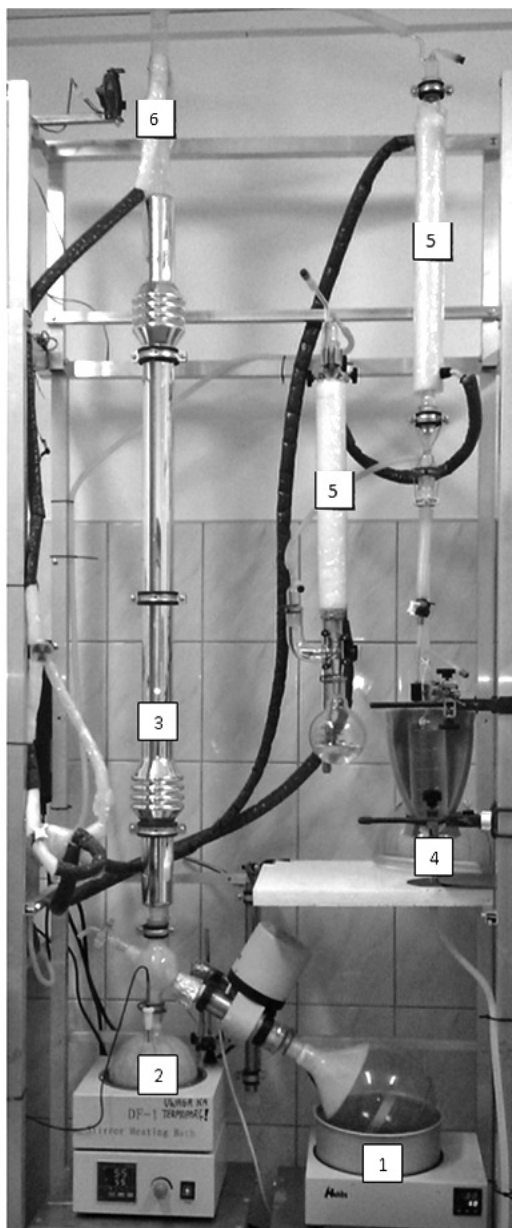
Figure 1. The laboratory installation for HTP (98%+) preparation: 1 – rotary evaporation vessel; 2 – stationary vessel; 3 – fractional distillation column (packed, vacuum coated, silvered); 4 – cylindrical funnel; 5 – Liebig condensers; 6 – reflux condenser.

Table 2. The conditions held inside the apparatus during HTP (98%+) preparation

Time [min]	Temperature of vessel		Reflux	Pressure [mbar]
	Rotary [°C]	Stationary [°C]		
0	60	50	OFF	3
5		50	ON	
15		55	ON	
30		55	OFF	
		55	OFF	
		55	OFF	
		58	ON	
		58	ON	

The amounts of HTP (98%+) grade that are sufficient for current research purposes that are prepared in house are in fact highly concentrated (at least 98.0 up to 99.0%), chemically pure (TDS below 0.2 ppm) and stable (stability parameter below 0.15%, pH below 2), initially unstabilized aqueous solutions of hydrogen peroxide. However, when kept for longer than one month, solutions are stabilised by the addition of sodium nitrate and sodium stannate, 15 mg of each per litre of HTP (98%+).

The raw material is 60% hydrogen peroxide of high purity (specially pure, reagent grade hydrogen peroxide with the lowest level of phosphate stabiliser) usually purchased in 30 L HDPE containers from Chempur.

3   Safety

Any grade of HTP can be used completely safely if proper, rigorous safety precautions and procedures are strictly followed. First of all the personnel handling HTP (of all grades) must be aware of its special features (*e.g.* potential high risk of fire or even explosion when misused). Personal protective equipment for working with it must be selected on the basis of a reasonable hazard assessment, just as with other hazardous materials. Apparently, thousands of metric tons of hydrogen peroxide, most of them concentrated up to 60%, are used annually in various industries around the world. The most prevalent hazard of HTP (98%+) is skin contact with droplets too small to notice. This temporarily causes benign but slightly painful bleached spots which should be rinsed with cold, fresh water – Figure 2.

Figure 2.   Skin after contact with a few droplets of HTP (98%+).

Hydrogen peroxide of any class is not considered as a flammable, explosive or toxic substance. However, one has to always keep in mind that uncontrolled spills of HTP (98%+) may create hazardous situations, especially when they occur near flammable materials or organic dirt (*e.g.* textiles, cotton, paper, leather, wood, organics, *etc*.). Thus, some factors, especially larger amount of impurities (contact with grease or dirt for example), may cause spontaneous decomposition of HTP (98%+), and, as a consequence, fire or even explosion may occur. For example, leather items usually contain catalytic dirt (especially shoes, from contact with the ground) and as such must be avoided when handling virtually any quantity of HTP. Furthermore, the decomposition rate of HTP may be significantly increased when the solution is exposed to contact with certain metals (*e.g.* manganese, cobalt, iron or copper).

Generally, HTP (98%+) is a very stable material under normal conditions, when properly stored. The authors' experiences show that the rate of active oxygen loss in 1 dm^3 containers made of HDPE is much less than 1% per year at normal ambient temperatures.

4   Results and Discussion

The results obtained from the preparation process for HTP (98%+) in the laboratory installation are presented in Table 3.

Table 3.   Summary of results

	Volume [mL]	Concentration [%]	Total Dissolved Solids [ppm]
Stationary vessel	550	97.8	0.07
Rotary vessel	450	99.0	0.35
HTP	$\Sigma 1000$	98.4	0.28
Distillate	1000	3.0	25

The results of an additional (extended) chemical analysis of an HTP (98%+) sample from IoA (performed by an external chemical laboratory) are presented in Table 4.

Table 4.   Results of chemical analysis of an HTP (98%+) sample from IoA

Element	Ag	Ca	Cd	Cr	K	Mg	Mn	Na	P (total)	Zn
Conc. [ppm]	<0.05	3.80	<0.05	<0.05	<0.50	<0.20	<0.05	4.40	<0.50	<0.05

Ready to use HTP (98%+) is stored under controlled conditions (+8 °C) in special HDPE vessels; stored for relatively long periods (up to one year with virtually no sign of decreasing concentration). Thus, the material is ready to use for research purposes even after a year or longer.
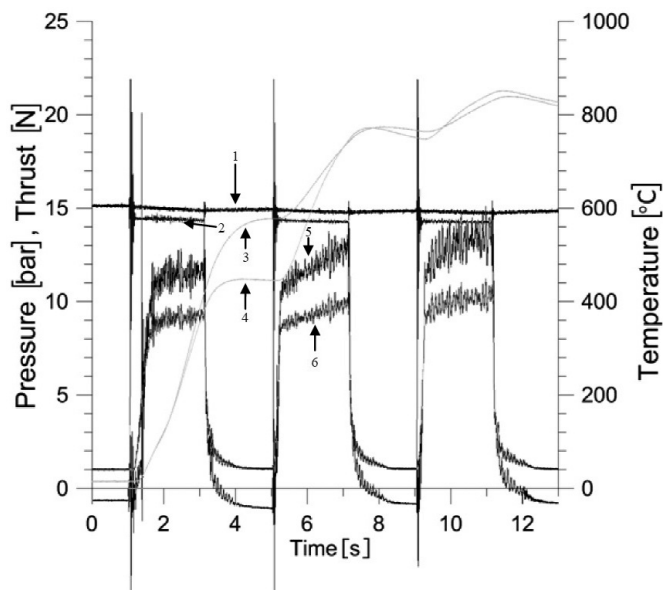
4.1 Decomposition process of HTP (98%+)

The catalytically driven decomposition of HTP (98%+) is a very exothermic process; Figure 3 illustrates an example. The catalyst bed used for the test has been assembled using ceramic-supported catalysts, prepared in-house, in the framework of the ESA project. The thermal emission from the hot catalyst bed surface is visible as the temperature of the catalyst bed section reaches 950 °C.

These experiments with the catalytically driven decomposition of HTP (98%+) were performed in order to evaluate the performance of a composite catalyst bed. The composite (structured) catalyst bed consisted of supported (on alpha aluminium oxide) manganese oxides and metal-ceramic grid catalysts (with platinum nano-crystals as an active phase). An illustrative example of the performance of such a catalytic system is shown in Figure 4. An analysis of the results has proved that this composition of the catalyst bed gives a high performance, by means of both dynamics (short pulses) as well as steady-state long-lasting flows (up to 30 s). What is more, during the long tests all of the parameters remained constant and no catalyst shattering was observed.
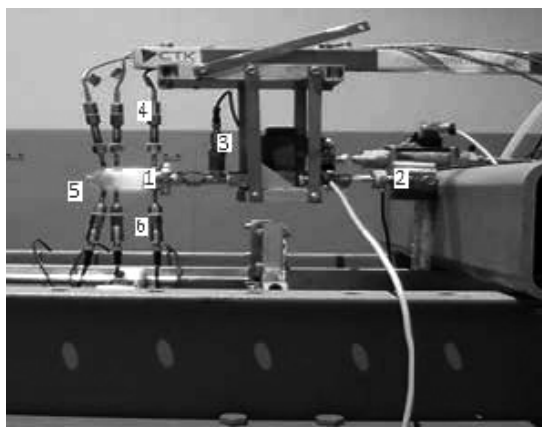
Figure 3. An example of the catalytically driven decomposition process of HTP (98%+): 1 − decomposition chamber; 2 − load cell; 3 − pressure transducer on the HTP (98%+) line; 4 − the set of thermocouples; 5 − the nozzle; 6 − the set of pressure transducers.


Figure 4. Results of the catalytically driven decomposition process of HTP (98%+) – three pulses, 2 s each: 1 − tank pressure [bar]; 2 − inlet pressure [bar]; 3 − inlet catalyst bed temperature [°C]; 4 − outlet catalyst bed temperature [°C]; 5 − thrust [N]; 6 − chamber I, II section pressure [bar].

The research activities at IoA also include the investigation of prototype liquid rocket engines based on so called "green" propellant combinations. Some promising novel propellants (*e.g.* dimethylaminoethylazide, DMAZ) have been synthesized *in situ* and subjected to the tests. DMAZ is being tested as a fuel for HTP (98%+) as it has the potential to replace the toxic, carcinogenic monomethylhydrazine [6, 7].

An example is shown in Figure 5. The hot test of the research rocket liquid engine of 250 N, used kerosene (Jet-A) as fuel and HTP (98%+) as the oxidizer. The latter was decomposed in a catalyst chamber filled with ceramic pellets and metal-ceramic grid catalysts-similar to the one shown in Figure 3. The system is characterised by simplicity and reliability, and the absence of any catalyst preheating device.
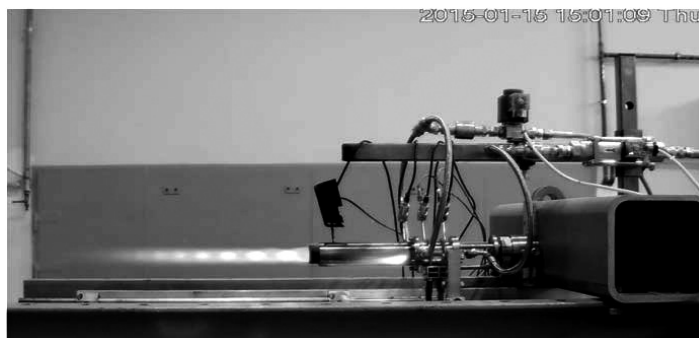
Figure 5.   The hot test of a research rocket liquid engine of 250 N, with kerosene as fuel and HTP (98%+) as the oxidizer. The research set-up is equipped with 3 thermocouples and 2 pressure transducers placed in the catalyst bed.
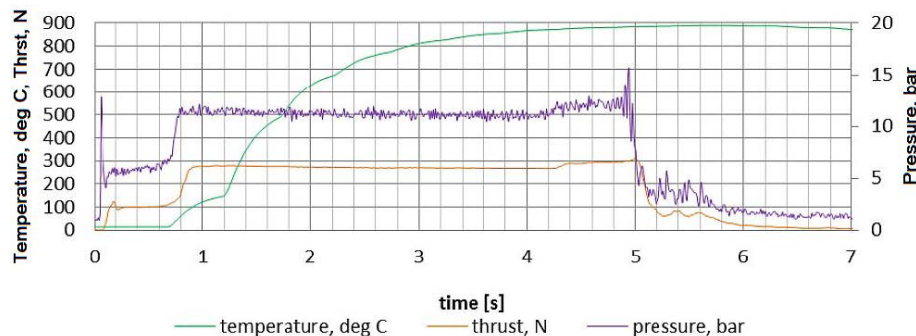
Figure 6.   The results of the hot test of a research rocket bi-propellant engine of 250 N [15].

The bipropellant mode occurred 0.7 s after oxidizer flow initiation. However, for safety reasons, fuel injection was initiated 0.5 s after the monopropellant mode flow started. No combustion instabilities, connected with reaching the full bipropellant mode, occurred – see Figure 6 [15].

Acknowledgements

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