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GREEN ROCKET PROPULSION RESEARCH AND DEVELOPMENT AT THE INSTITUTE OF AVIATION: PROBLEMS AND PERSPECTIVES

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Abstract

The paper presents the main activities of the Institute of Aviation (IoA) in the field of chemical rocket propulsion. The relatively "fresh" research and development team performed many useful works within the last 5 years, starting from the strategy and ideas. Nowadays, the Space Technology Department of IoA acts as a member of international consortia realizing space projects, as well as itself working on its own assignments financed by the European Space Agency (ESA) and IoA funds.

The important development aspect of rocket propulsion developed at IoA is the use of "green" propellants. These are chemicals, which are relatively safe for the environment and personnel, being a very promising alternative for storable toxic substances, e.g. hydrazine and derivatives, nitrogen tetroxide. R&D activities of STD are based on the use of Rocket Grade Hydrogen Peroxide (RGHP), also known as High Test Peroxide (HTP). This high-performance mono-propellant and oxidizer is regarded by European entities as one of the most promising candidates to replace hydrazine and its derivatives in the future. Due to numerous advantages, hydrogen peroxide is better suited for systems with human interaction that most of other propellant combinations.

The paper contains selected results of research on green rocket propulsion performed at IoA, in which 98% hydrogen peroxide was used as oxidizer and monopropellant. Three types of rocket engines: monopropellant, liquid bipropellant and hybrid have been investigated and are still being developed.

Keywords: *propulsion, rocket engine, experimental research, green propellant, hydrogen peroxide*

1. Introduction

Rocket propulsion technology was developed at the Institute of Aviation (IoA) in 1960's and 1970's. Polish engineers created the sounding rocket family called Meteor, in order to conduct research on atmosphere. The propulsion system was based on a solid propellant. The program was regarded as a great success, especially when Meteor 2K exceeded the altitude 100 km. Soon after that achievement, the program was stopped and never continued.

In 2007, the rocket propulsion research was re-activated at IoA. The team, originating from the Warsaw University of Technology, initiated activities in the area of liquid rocket propellants and engines. The research focused on green propulsion, which is consistent with the general trend and niche in Europe, alternative for existing storable systems. The main direction, taken by the Space Technology Department (STD), was 98% hydrogen peroxide based propulsion. This chemical has a great potential as rocket propellant. STD intended to develop all three kinds of engines utilizing hydrogen peroxide: monopropellant, liquid bipropellant and hybrid. Such an ambitious activity required to challenge many problems, such as: production of the highest grade peroxide (98%+ HTP), storability and material compatibility, study on its safety and handling aspects, catalysts for its decomposition and fuel trade-off.

2. Green space propulsion idea

Hydrazine and oxides of nitrogen have been the fundamental propellants for chemical space propulsion since 1960's [13]. These substances are still widely used by the space industry worldwide. Due to the opinion about their negative influence on the environment and personnel, hydrazine and oxides of nitrogen (especially nitrogen tetroxide) are regarded as undesired propellants. Indeed, these chemicals are toxic by inhalation, ingestion and skin absorption. Some cases of short-term human exposure on hydrazine are described by Kao *et al.* [11]. However, after proper treatment no permanent effects were noticed. One lethal case was described by Sotaniemi *et al.* [21]. A worker was exposed on inhalation once a week for 6 months. Hydrazine is also described as carcinogenic [10] and mutagenic [12]. The fact is that this research was performed on animals (mice, rats, rabbits, etc.). No cancer or mutagenic effect has been identified when hydrazine was exposed on human. Nevertheless, in 2011 the European Chemicals Agency (ECHA) included hydrazine into the list of substances of very high concern [7]. Furthermore, it may be placed into Annex XIV of Registration, Evaluation, Authorization and Restriction of Chemicals (REACH), which means that the use of hydrazine may be completely forbidden in Europe [1]. The space industry in Europe expressed concern about its future. Despite the fact that the space industry issued the statement about excluding this branch from the potential prohibition of using hydrazine and its derivatives, the alternative solution for replacing toxic propellants has been investigated.

The new term has been introduced to the space propulsion, called: “green” propellant. It has been defined as non-toxic and environmentally friendly chemical. From among all known propellants, able to be long term stored at ambient conditions, many hydrocarbon fuels are regarded as “green”. Considering monopropellants and oxidizers, the list of possible candidates is much shorter. The consortium of GRASP project (acronym of Green Advanced Space Propulsion), funded by the European Commission, identified the rocket grade hydrogen peroxide (RGHP) as the most promising candidate to be applied as the alternative for hydrazine in both: monopropellant and bipropellant modes [19]. The consortium consisted of industrial, R&D (including the Institute of Aviation) and academic entities. The European Space Agency (ESA) is also interested in green propulsion technology development [24].

Due to toxicity and potential carcinogenicity, all propulsion operations with hydrazine, requiring human interaction, need to be performed inside special infrastructure and using safety suits. Apart from environmental matters, the idea of “green” propellant is based on the avoidance of such expensive solutions. The propellant ought to be easy to handle. It means that low vapour pressure is also desired. To compare, hydrazine vapour pressure equals to 1.92 kPa at 25ºC [4]. In the case of hydrogen peroxide, it is 0.26 kPa at the same temperature [5]. These significant aspects of green propellants, especially hydrogen peroxide, create the considerable perspective for many small and medium entities to join into the space propulsion community and start their own research and development.

3. Hydrogen peroxide HTP-class as green propellant – main problems

Highly concentrated hydrogen peroxide is the second (after liquid oxygen) most efficient liquid oxidizer. Due to the capability of exothermic decomposition (2.887 MJ/kg of heat released during the reaction) it may also act as monopropellant. However, the highest-grade peroxide is still hardly available on the market due to very demanding production process. In the case of fractional distillation of lower concentration available on the market) vacuum conditions are required. The other method – fractional crystallization – is even more complicated and expensive.

Table 1 presents the specification of performance for various oxidizer/fuel configurations when applied for space propulsion (chamber pressure p_1 = 10 bar, vacuum conditions). Hydrazine gives 20% higher specific impulse than 98% HTP in monopropellant application. However, in bipropellant mode, performance of peroxide based propulsion and conventional storable oxidizer/fuel configurations are comparable. Furthermore, density specific impulse of all propellant configurations using 98% HIP is, in general, higher than these based on hydrazine. That attribute influences the total weight of the hardware.

Tab. 1. Performance of propellant combinations [9]

No.	Oxidizer	Fuel	Nozzle exp. ratio	O/F	Vacuum impulse, s	Density specific impulse, s
1	Hydrazine – monopropellant		60	N/A	230	235
2	98% HTP – monopropellant		60	N/A	192	275
2	IRFNA	UDMH	330	2.65	320	386
3	MON1	MMH	330	1.71	339	380
5	98% HTP	Jet-A1	330	6.09	328	432
6	98% HTP	TMPDA	330	5.05	330	417

The meanings of abbreviations, included in Tab. 1 are as follows:

- IRFNA – inhibited red fuming nitric acid,
- UDMH – unsymmetrical di-methyl hydrazine,
- MON1 – mixed oxides of nitrogen containing 1% of nitrogen oxide (NO),
- MMH – mono-methyl hydrazine,
- TMPDA – *N*,*N*,*N′*,*N′*-Tetramethyl-1.3-propanediamine,
- Jet-A1 – kerosene for commercial aircrafts.

When used as oxidizer, hydrogen peroxide may be decomposed prior to contact and formation of mixture with liquid or solid fuel. In the case of special fuel (hypergolic) application, direct liquid-liquid contact with peroxide causes spontaneous ignition. However, catalytic decomposition is still the only method of utilization of HTP in all operational propulsion systems up to date. Wernimont [25] claims that all trials of introducing liquid-liquid injection into the combustion chamber finally resulted in taking the decision to apply a catalyst bed. Austin and Heister [2] experienced several explosions when they tested their 650 N thruster based on hypergolic fuel and HTP combination. Moreover, hypergolic (with hydrogen peroxide) fuels are still at the low TRL.

The critical technology to utilize HTP for propulsion is its decomposition. The products of HTP decomposition are then used as the oxidizer. The chemical reaction of decomposition of hydrogen peroxide, which may be expressed by (1).

$$H_2O_2 \xrightarrow{k} H_2O + \frac{1}{2}O_2, \tag{1}$$

where k – reaction rate constant, expressed by (2).

$$k = A_p e^{\left(\frac{-E_A}{RT}\right)}, \tag{2}$$

where:

Ap – pre-exponential factor,

E_A – activation energy,

R – universal gas constant,

T – absolute temperature.

Thermal decomposition of hydrogen peroxide has never found the application in propulsion systems due to the difficulty in exceeding the activation barrier of decomposition reaction. The propellant requires pre-heating up to (at least) 425°C [8, 11]. According to McLane [14], hydrogen peroxide decomposes thermally in the temperature 470ºC-540ºC. The only practical solution is to apply a heterogeneous catalyst, preferably in the form of a bed (Fig. 1).

Catalyst lowers the activation energy, making possible to initiate its decomposition at ambient temperature. According to Wernimont *et al.* [26] 82% peroxide may be catalytically decomposed at -18°C, which is close to its freezing point.

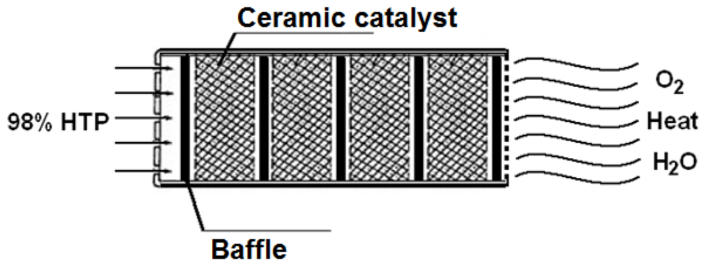

Fig. 1. Catalyst bed for decomposition of hydrogen peroxide [23]

The major problem for decomposition of 98% hydrogen peroxide is a catalyst able to withstand the temperature of decomposition products (920ºC – 960ºC depending on initial temperature) and thermal shocks. The most popular method to decompose HTP is a catalyst bed consisting of a pile of silver wire mesh screens. High catalytic activity of silver was experimentally confirmed by [16-18]. Since the mesh is made of pure silver, it withstands numerous rapid heating and cooling cycles. According to [15], the melting temperature of this metal is 961.8˚C. In order to keep mechanical properties of the catalyst support, the maximum hydrogen peroxide concentration for silver is 93% [3]. Potential candidates for the highest-grade peroxide are metal (e.g. silver) alloys and ceramics.

Another issue, connected to the practical application of hydrogen peroxide, is its long-term storability. According to Davies *et al.* [6], there are four classes of material compatibility with hydrogen peroxide. Only class-1 materials (including e.g. pure aluminium and PTFE), after additional surface treatment, may be used for long-term storage of hydrogen peroxide (e.g. satellite propulsion). It is not recommended to use class-1 liners covering class-2 (or higher) structures. In the case of a failure of the liner, the whole system fails. All these aspects make long-term storability of hydrogen peroxide challenging, still possible, however.

4. Research on green rocket propulsion at IoA – results and discussion

In 2014 STD performed complex research on catalytic decomposition of 98% hydrogen peroxide inside catalyst beds (working under real operational condition), using cost-effective alumina supported manganese oxide catalysts (Mn_xO_y/Al_2O_3), prepared *in situ*. The aim of the investigation was to identify the best (by means of performance and lifetime) catalysts for decomposition of 98% peroxide, with practical application for rocket propulsion. Fig. 2 presents the example of results – maximum peak temperature obtained during 5-second HTP flows through the catalyst bed. During the investigation 41 samples of catalyst supported on 7 various carriers (α- and γ-Al_2O_3 type) were tested [22].

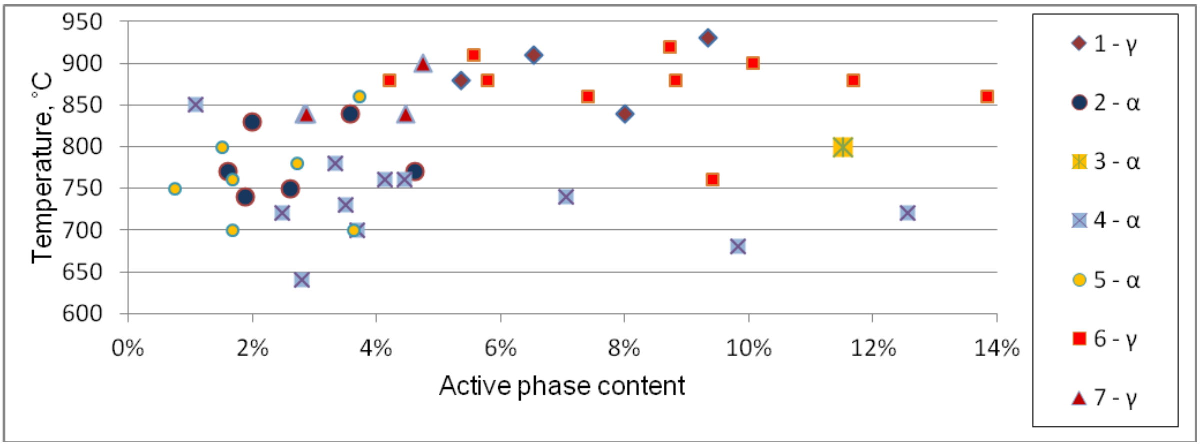

Fig. 2. Maximum decomposition temperature of 98% hydrogen peroxide obtained in 5-second flow time

The method applied to investigate catalysts was based on the measurement of three parameters: pressure, temperature (inside the catalyst bed at defined points) and thrust generated by the catalyst bed in a thruster configuration. The temperature was measured in the centreline of the catalyst bed, in its aft end cross section, using 1 mm K-type thermocouples. The measurement error for these thermocouples was ±4°C. The catalyst inspection, including mass loss evaluation and damage notification was performed after each test.

The temperature of adiabatic decomposition of 98% peroxide (at 18°C) is 940°C [9]. Results, collected during the research, confirmed that the catalyst bed performance strongly depends on the type of catalyst applied as well as the active phase content. Nevertheless, high performance was obtained in both transient (fast response during start) and steady (C* efficiency up to 96%) conditions.

One of the most crucial problems concerning ceramic-based catalysts, identified during the investigation, was thermal shock. It occurred when the propellant decomposed on the surface of cold catalyst. As a result, the catalyst experienced the rapid temperature rise. The rate of temperature build-up is in the range of 200 – 300 K/s. Most of catalyst carriers deteriorate after several thermal cycles. The test results confirmed that γ-Al_2O_3 is susceptible to thermal shocks. The other phase – α-Al_2O_3 withstood many thermal cycles with 98% hydrogen peroxide. However, due to low specific area (up to 2 orders of magnitude lower that γ-Al_2O_3), it gave relatively poor performance.

Results of the investigation of catalytic decomposition of 98% hydrogen peroxide identified the most promising catalysts to be applied in monopropellant (Fig. 3) and liquid bipropellant (Fig. 4-5) rocket propulsion. Due to the fact that performance of 98% peroxide in bipropellant mode is comparable with existing storable configurations, this type of engine may find practical application in a future launch vehicle and spacecraft. It was later decided to develop this type of rocket engine in IoA. The new concept was based on a serial connection of a catalyst bed (also developed by STD) and liquid fuel injection. This gas-liquid injection system is regarded as even lighter and better than liquid-liquid solutions [25]. The technology demonstrator of such an engine was designed and tested. The test results (by means of pressure, temperature and thrust profile) confirmed relevance of the idea. The proposal was presented to the European Space Agency (ESA) in order to develop this technology at TRL3. The purpose of this concept was to create an engine for GEO satellite orbit transfer (apogee boost engine). The project is ongoing and planned to finish until June 2017.

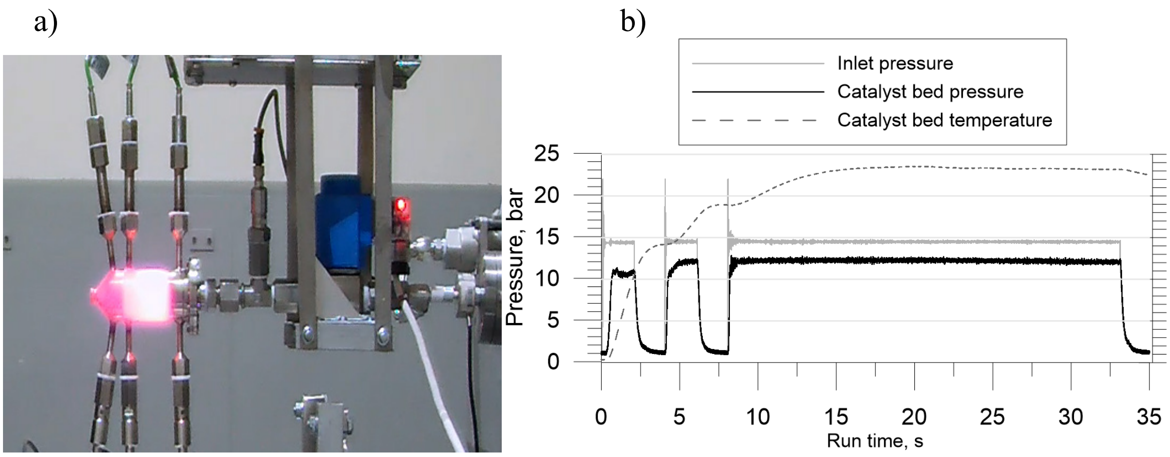

Fig. 3. The example of a monopropellant rocket engine hot test: a) video frame, b) catalyst bed parameters

Another example of catalyst bed usage for rocket propulsion is a hybrid rocket engine (Fig. 6), also developed at IoA [23]. The idea was to create a self-ignitable and restartable hybrid engine, which is much simpler than liquid bipropellant (only one liquid chemical to manage). Test results have confirmed that a high-performance catalyst bed is the critical technology to obtain rapid self-ignition of the fuel in the hybrid (as well as liquid) propulsion. Furthermore, a well-designed catalyst bed is a crucial component, responsible for high performance and flexibility of the engine. Potential application for a hybrid engine might be the future launch vehicle and spacecraft propulsion.

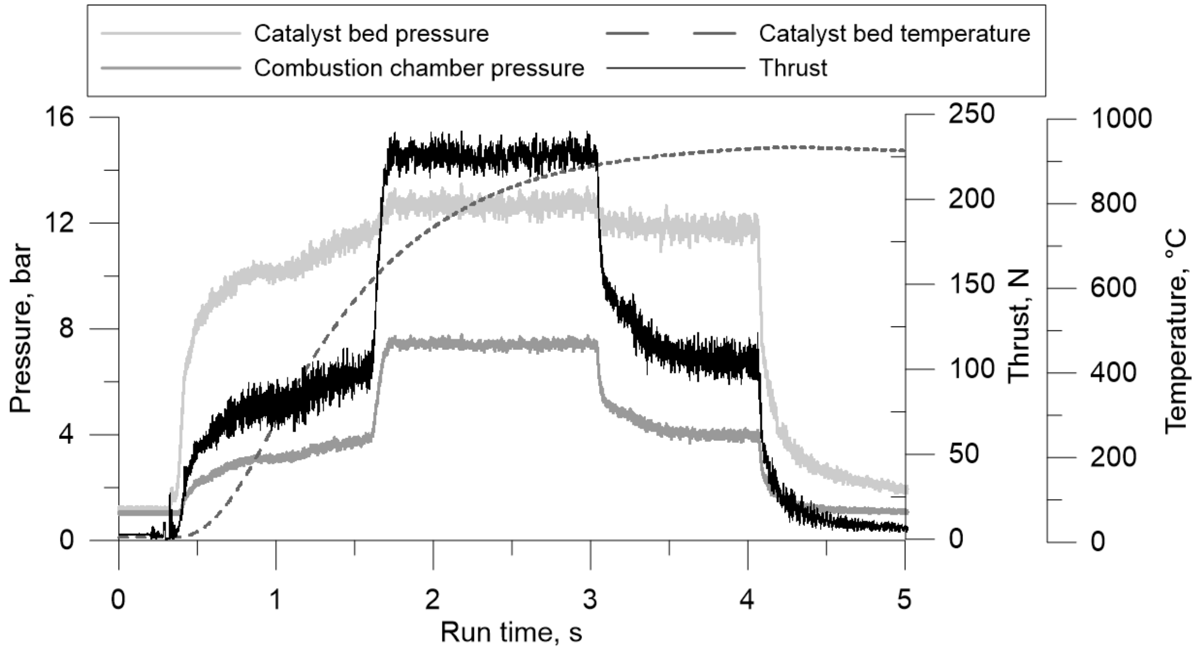

Fig. 4. The example of a liquid bipropellant rocket engine fire test results

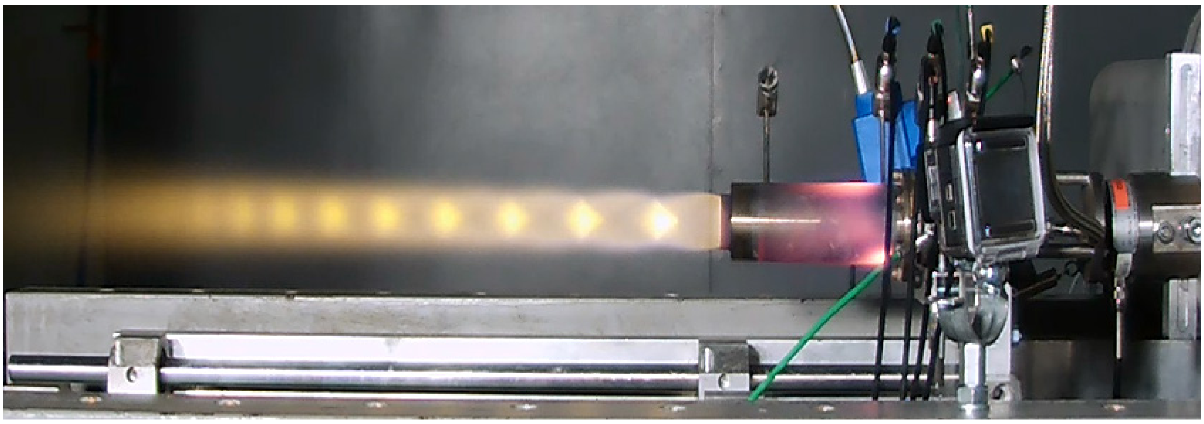

Fig. 5. Liquid bi-propellant rocket engine test run

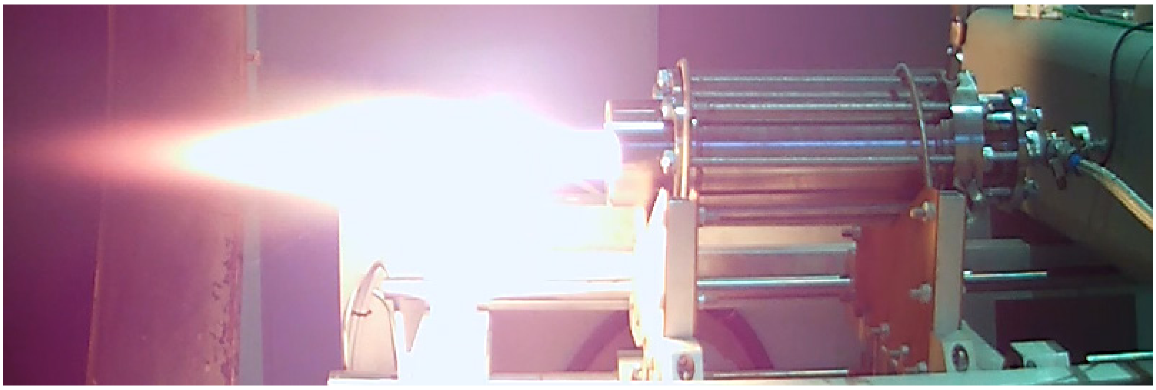

Fig. 6. 98% HTP/solid fuel hybrid rocket engine (technology demonstrator) rest run

During the test, campaign a great improvement in both: ignition delay and catalyst bed size and weight was noted. Starting from 200 mm long bed and 3.5 s of ignition delay (with respect to the oxidizer main valve opening), the final result achieved was below 0.5 s with 50 mm catalyst bed length. On the basis of test results, calculated performance of the engine, by means of specific impulse, was at the level of 86% of theoretical value (considering test conditions).

Conclusions

The recent trend in space propulsion systems is directed into green technologies. Research, completed by many space related entities, indicated rocket grade hydrogen peroxide as one of the most promising propellants for the future. Comprehensive experimental activities, performed by the Institute of Aviation, found many problems connected to the highest-grade hydrogen peroxide, including: production, material compatibility, handling and usage of this chemical in rocket propulsion.

The concern about production of 98%+ HTP is related to the safety issue. Compatibility matter makes a very limited list of structural materials possible to use with peroxide. Handling requires special care mainly associated to clean environment (impurities strongly influence on HTP self-decomposition ratio). The main issue for peroxide application as monopropellant for spacecraft reaction control systems is that it gives 20% lower performance than commonly used hydrazine. This significant drawback is a barrier in the process of replacing hydrazine by this green propellant.

The catalytic decomposition of HTP was identified as the common topic connecting all types of chemical rocket propulsion using this chemical: monopropellant, liquid bipropellant and hybrid. However, decomposition of 98% HTP is very challenging due to the thermal conditions inside a catalyst bed. Shuttering, as a result of a multi-cycle engine operation, strongly influences on the catalyst lifetime.

On the contrary, numerous advantages of green propulsion create significant perspectives for new researchers aiming to join the space community. Even if monopropellant mode cannot compete with hydrazine in the field of performance, bipropellant configuration (HTP/hydrocarbon fuel) is comparable to conventional storable fuel/oxidizer combinations. It may find application in future green propulsion systems for spacecrafts as well as for launch vehicles. High level of maturity of catalyst related technologies might guarantee the further success in green propulsion development and usage for launch services and satellites. Test results, obtained up to date, confirm the potential of Space Technology Department to develop these technologies.

References

[1] ASD Eurospace, *Exemption of propellant related use of hydrazine from REACH authorization requirement*, 2012.

[2] Austin, B. L., Heister, S. D., *Characterization of pintle engine performance for nontoxic hypergolic bipropellants*, 38th AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit, Indianapolis, 2002.

[3] Baumgartner, H. J., Hood, G. C., Monger, J. M., Sanborn, C. E., *Decomposition of concentrated hydrogen peroxide on silver II. High temperature decomposition*, Journal of Catalysis, Vol. 2, pp. 415-420, 1963.

[4] Boublik, T., Fried, V., and Hala, E., *The Vapour Pressures of Pure Substances. Second Revised Edition,* Elsevier, Amsterdam 1984.

[5] Daubert, T. E., Danner, R. P., *Physical and Thermodynamic Properties of Pure Chemicals Data Compilation*, Washington, D.C., Taylor and Francis, 1989.

[6] Davis, D. D., Dee, L. A., Greene, B., Hornung, S. D., McClure, M. B., Rathgeber, K. A., *Fire, explosion, compatibility and safety hazards of hydrogen peroxide*, NASA/TM-2004-213151, 2005.

[7] European Chemicals Agency, Agreement of the Member State Committee on the identification of hydrazine as a substance of very high concern, 2011.
[8] Giguere, P. A., *The Thermal Decomposition of Hydrogen Peroxide Vapour*, Canadian Journal of Research, Vol. 25(2), pp. 135-150, 1947.
[9] Gordon, S., McBride, B. J., *Computer Program for Calculation of Complex Chemical Equilibrium Compositions and Applications – II. User's Manual and Program Description*, NASA Ref Publ., No. 1311, 1996.
[10] International Agency for Research on Cancer, *Some aromatic amines, hydrazine and related substances, n-nitroso compounds and miscellaneous alkylating agents, evaluation of cancerogenic risk of chemicals to man*, Lyon: WHO, 1974.
[11] Kao, Y. H., Chong, C. H., Ng, W. T., Lim, D., *Hydrazine inhalation hepatotoxicity*, Occup Med 57, pp. 535–537, 2007.
[12] Kimball, R. F., *The mutagenicity of hydrazine and some of its derivatives*. Mutation Research/Reviews in Genetic Toxicology 2, Vol. 39, pp. 111-126, 1977.
[13] Marshall, W. M., Deans, M. C., *Recommended figures of merit for green monopropellants*, 41st AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit, San Jose, 2013.
[14] McLane C. K., *Hydrogen peroxide in the thermal hydrogen oxygen reaction I. Thermal decomposition of hydrogen peroxide*, Journal of Chemical Phisics, Vol. 17(4), pp. 379-385, 1949.
[15] Pappas, S., *Facts about silver*, http://www.livescience.com/37040 silver.html, 2014.
[16] Pirault-Roy, L., Kappenstein, C., Guerin, M., Eloirdi, R., Pillet, N., *Hydrogen peroxide decomposition on various supported catalysts effect of stabilizers*, Journal of Propulsion and Power, 18 (6), pp. 1235-1241, 2002.
[17] Romeo, L., Torre, L., Pasini, A., Cervone, A., d'Agostino, L., *Performance of different catalysts supported on alumina spheres for hydrogen peroxide decomposition*, 43rd AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit Cincinnati, OH, 2007.
[18] Rusek, J. J., *New decomposition catalysts and characterization techniques for rocket-grade hydrogen peroxide*, Journal of Propulsion and Power, Vol.12 (3), pp. 574-579, 1996.
[19] Scharlemann, C., *General assessment of green propellants*, GRASP Report, 2009.
[20] Shumb, W. C., Satterfield, C. N. i Wentworth, R. L., *Hydrogen peroxide*. Massachusetts Institute of Technology, 1954.
[21] Sotaniemi, E., Hirvonen, J., Isomaki, H., Takkunen, J., Kaila, J., *Hydrazine toxicity in the human. Report of the fatal case*, Ann. Clin. Res. 3, pp. 30-33, 1971.
[22] Surmacz, P., *Influence of various types of Al_2O_3/Mn_xO_y catalysts on performance of a 100 mm chamber for decomposition of 98%+ hydrogen peroxide*, Transactions of the Institute of Aviation, Vol. 240, pp. 58-68, 2015.
[23] Surmacz, P., Rarata, G., *Investigation of spontaneous ignition in a 100 N HTP/HTPB hybrid rocket engine*, Transactions of the Institute of Aviation, Vol. 240, pp. 69-79, 2015.
[24] Valencia-Bel, F., *Green Propulsion. State-of-art, prospectives and roadmap*, 2015.
[25] Wernimont, E. J., *Hydrogen Peroxide catalyst beds: lighter and better than liquid injectors*, 41st AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit, Tuscon, AZ, 2005.
[26] Wernimont, E. J., Ventura, M., Grubelich, M. C., Vaughn, M. R., Escapule, W. R., *Low temperature start & operation capability of 82% hydrogen peroxide gas generators*, 5th International Space Propulsion Conference, Heraklion, 2008.