PulCheR-PULSED CHEMICAL ROCKET WITH GREEN HIGH PERFORMANCE PROPELLANTS:
30TH MONTH PROJECT OVERVIEW

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ABSTRACT
PulCheR (Pulsed Chemical Rocket with Green High Performance Propellants) is a three-year research project co-funded by the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement n°313271. The project is mainly aimed at demonstrating the feasibility of a propulsion system that uses propellants injected in the combustion pressure at low pressure and exploits the unsteady dynamics of the pulse mode to let the pressure inside the chamber increase more than the feeding one and the chamber temperature exceed the adiabatic constant pressure combustion temperature as effect of the quasi-constant volume reaction. During the project particular attention has been focused on “green” propellants. The project is currently in its last year and it is yielding many discoveries, such as the non hypergolicity of 98% HTP and propyne. Other discoveries are expected for the last part of the third year project, when the PulCheR monopropellant thruster will work for the first time and the new bipropellant thruster with HTP and propyne will be tested together with the new combustion chamber made of high temperature resistance materials.

NOMENCLATURE

\( c^* \) = characteristic velocity
\( I_{sp} \) = specific impulse
\( O/F \) = oxidizer to fuel ratio
\( p_c \) = chamber pressure
\( T_{ON} \) = valve open time
\( v \) = velocity
\( \eta_{c*} \) = characteristic velocity efficiency \((c^*_{exp} / c^*_{theo})\)
\( \eta_{\Delta T} \) = temperature efficiency \((T_{exp} - T_{amb}) / (T_{ad} - T_{amb})\)

Acronyms
AR = Area Ratio
ECHA = European CHemicals Agency
GEO = Geostationary Orbit
GTO = Geostationary Transfer Orbit
HTP = High Test Peroxide
LAE = Liquid Apogee Engine
LEO = Low Earth Orbit
MEA = mono-ethylamine
MIB = Minimum Impulse Bit
RCT = Reaction Control Thruster


1 INTRODUCTION

PulCheR is the acronym for “Pulsed Chemical Rocket with Green High Performance Propellants”. The project is co-funded by the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement n°313271 ([1-3]).

The project aims at revolutionizing the propulsion for in-space manoeuvres by means of a new type of pulsed concept. The propellants are stored at low pressure inside the tanks and the combustion chamber is fed with the propellants which react in a constant volume approximation. By exploiting the delay time for the propellants to react or decompose, it is possible to inject propellants until the pressure inside the combustion chamber is about the feeding pressure. By this way, the pressure inside the chamber, during the reaction, can reach higher values than the tank pressure and, likewise, the temperature can be higher than expected for a constant pressure operation. The thrust is then generated by many of such pulses repeated during the firing. The PulCheR thruster is conceived to work under transient conditions, with high frequency pulses that allow for a fine control of the minimum impulse bit (MIB), particularly suitable for specific in-orbit missions such as fine attitude control, reaction control and dockings. Moreover, the time averaged thrust generated by the high frequency pulses can be simply modulated only by changing the firing valve re-opening frequency (or, in case of a closed-loop control philosophy, the threshold limit of the chamber pressure at which the firing valves re-open).

As an added value, the new propulsion concept has been investigating the use of green propellants for both mono and bipropellant configurations ([4-5]), after the inclusion of hydrazine in the list of substances of very high concern by the European Chemicals Agency (ECHA, 2011) ([6]).

A preliminary assessment of the candidate propellants to be exploited has identified in the high grade hydrogen peroxide as a valid alternative for monopropellant applications and in the combination of hydrogen peroxide and a light unsaturated hydrocarbon, the propyne, as a possible combination for obtaining a propulsive performance comparable to the current state-of-the-art for future green bipropellant thrusters.

The propulsion concept of PulCheR has been inspired by the defence mechanism of the bombardier beetle ([7-8]). This insect is able to produce an aqueous solution of hydrogen peroxide and hydroquinone, which are stored in a reservoir inside its abdomen. When threatened, the beetle instinctively squeezes its muscles, opening a one-way connecting valve into a reaction chamber (low pressure feeding) where other cells secrete enzyme catalysts (catalase and peroxidase). Extremely fast reactions occur, producing free oxygen and generating enough heat to bring the liquid to the boiling point. Then the valve to the reservoir closes due to the pressure of the released gasses and the hot mixture of water/steam with additional dissolved noxious chemicals is expelled through exit valve at the tip of the abdomen on any predators such as ants, frogs and birds. The flow of reactants into the reaction chamber and subsequent ejection to the atmosphere occur cyclically at a rate of about 500 times per second and with the total pulsation period lasting for only a fraction of a second.

In order to reach the challenging PulCheR objectives, a solid Consortium (see Table 1) has been established. Nine leading companies in space technologies coming from Europe, United States and Japan compose the Consortium. Sitael S.p.A. (formerly ALTA S.p.A.) is glad to coordinate this team.
Table 1 The PulCheR consortium.

The PulCheR project is now in its third year. It has been conceived for both monopropellant and bipropellant thrusters and the activities for the characterization of such a concept are still ongoing. The present paper shows the actual status of the project after 30 months from the beginning.

2 SUMMARY OF THE MAIN RESULTS

During the previous two years many results have been obtained for the PulCheR project ([9]). The main results are summarized in the following list:

- the department of chemistry and industrial chemistry (DCCI) of the University of Pisa has tested many different catalysts with different supports by dropping tests with 30% HTP ([10]). Tests have been performed at different temperatures in order to assess the thermo-mechanical resistance of different catalysts. The results of the tests confirmed the Platinum as the best catalyst for HTP and $\alpha$-$\text{Al}_2\text{O}_3$ as the best carrier. DCCI has proved to be capable of manufacturing catalysts with different size down to 0.2 mm diameter.

- the high temperature due to the combustion reaction of propyne and HTP is not sustainable for most of the commercial materials. DEMOKRITOS has developed some solutions which have been specifically thought for the present application. The materials developed are a SIC based composite and a layered ZrO$_2$ / Ni-based alloy. The preparation procedure of these materials is property. The tests performed, including the exposure to an oxyacetylene flame, demonstrated the capabilities of sustaining temperatures comparable to that of the combustion of propyne and HTP;

- some off-the-shelf valves have been identified by MOOG-Bradford as potentially usable with 98% HTP. In particular, the MOOG valves 51-178 and 52-204B (see Figure 1) demonstrated to be compatible with this substance. Moreover, the latter valve has been identified as a possible candidate also for being used with propyne. The MOOG valve 51-178 has already proved to be compliant with the PulCheR requirements for the monopropellant thruster. Moreover, its wetted material compatibility with 98% HTP has been tested also at IoA with positive feedback;
Figure 1 The MOOG valves: Moog 51-178 (on the left) and Moog 52-204B (on the right).

- An experimental test campaign has been carried out at Sitael on the SD98-SD99 composite catalytic bed produced by DCCI with the main aim of assessing the actual propulsive performance of a green monopropellant thruster powered by 98% hydrogen peroxide. The SD98-SD99 catalysts have been able to decompose up to 1 liter of 98% H2O2 with very good efficiencies ($\eta_c > 95\%$ and $\eta_{\Delta T} \geq 90\%$). The experimental specific impulse reached at sea level with a conical nozzle has been 130 s and the corresponding extrapolated vacuum specific impulse for a bell-contoured nozzle would exceed the target value for the PulCheR project fixed at 185 s. The 98% hydrogen peroxide produced by the Institute of Aviation has proved to reach the desired propulsive performance for the PulCheR project.[10]

- The combination of 98% HTP and propyne is not hypergolic. Tests performed at IoA and then at Sitael confirmed the same results. The combination is not able to spontaneously ignite by reciprocal contact. The two substances are anyway able to be hypergolic if propyne is properly doped with ferric chloride and propargyl alcohol, but the procedure is too difficult for the high vapour pressure of propyne. Some tests performed at Sitael allowed identifying some possible ways to ignite the mixture. The most promising is the named "staged" combustion ([11]), in which HTP passes through a catalytic bed and the hot decomposition by-products meet propyne thus initiating the combustion reaction. The test (a picture of the test is in Figure 2) has shown very interesting results for the combination of these propellants (see Table 2) which are promising for the space application even if they are not hypergolic (specific impulse in vacuum higher than the target value of 320 s);

Figure 2 The test with 98% HTP and propyne at Sitael ([11]).
Table 2 Thrust performance of the bipropellant thruster with 98% HTP and propyne (adapted from [11]).

<table>
<thead>
<tr>
<th>Performance</th>
<th>Units</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>O/F Ratio (O/F) @ Steady-State</td>
<td>--</td>
<td>4.6</td>
</tr>
<tr>
<td>Chamber Pressure (pC) @ Steady-State</td>
<td>bar</td>
<td>10.4</td>
</tr>
<tr>
<td>Specific Impulse (Isp) @ Steady-State</td>
<td>s</td>
<td>213.4</td>
</tr>
<tr>
<td>Vacuum Specific Impulse (Isp vacuum) @ Steady-State (Ae/At=330)</td>
<td>s</td>
<td>324</td>
</tr>
<tr>
<td>Steady-state c* Efficiency (ηc*) @ Steady-State</td>
<td>--</td>
<td>0.955</td>
</tr>
</tbody>
</table>

- the design of the PulCheR monopropellant system has required a non-conventional architecture, without using the stand-off configuration for the firing valve, and properly designing the injectors for reducing the dead volumes which can severely influence the response time of the thruster. The design of the test bench has been particularly demanding in terms of choice of the transducers, and in terms of design, in order to avoid the influence of the pulsating flow inside the feeding line on the thrust measurement ([12]).
- the assessment of the mass flow rate in unsteady conditions, such as those used for PulCheR, is very difficult and no measurement system is capable of reading variations of the mass flow rate within 2-3 ms ([12]). Some measuring systems, such as the turbine flow meter, is capable of giving only some information about firing valve repeatability.

3 SUMMARY OF THE ONGOING MAIN ACTIVITIES

The non-hypergolicity of the combination of HTP and propyne has ruled out the possibility for these substances to be used for the PulCheR concept. Indeed the need of an ignition system imposes a reduced frequency between each pulse thus preventing the exploitation of the advantages of the PulCheR concept. Some dropping tests performed at IoA have shown some "green" substitutes to propyne. The most promising are the propargyl alcohol and MEA (ethanolamine) which become hypergolic with HTP, if doped respectively with ferric chloride (FeCl₃) and Copper Chloride (CuCl₂). Anyway, the best results have been obtained by using MEA with very reduced ignition delay time (26 ms). Unfortunately only dropping tests have been performed with MEA and HTP, whereas no experimental data have been obtained on the injection system for MEA and HTP, as well as no data are available for thruster prototypes.

The use of MEA and HTP has then been considered as a possible alternative to propyne and HTP for the PulCheR thruster. Therefore, some of the expected activities concern with a deeper study of the combination of MEA and HTP in view of a possible future implementation in the PulCheR prototype. To this purpose a series of tests on an injection system with these propellants is expected to be performed at the Institute of Aviation during the third year of the project, as well as some tests with simulant fluids at ZARM will investigate the injection of the selected propellants.

Regardless of the non-hypergolicity of propyne and HTP and, consequently, the impossibility of using the PulCheR concept, the experimental performance of this combination is much more promising than the theoretically calculated for the combination MEA and HTP. This aspect can be positively exploited in conventional propulsive system and so this "green" propellants combination is a valid substitute to actual bipropellant system based on MMH/MON or MMH/NTO. In particular, the advantages of such a system can be evaluated for a realistic case where chemical propulsion is used for geostationary platforms for telecommunication satellites. These satellites typically use a Liquid Apogee Engine (LAE) for orbit transfer, LEO to GEO or GTO to GEO, and Reaction Control Thrusters (RCT) for attitude control.[13-14] The typical characteristics of these types of thrusters are summarized in Table 4.[15-20]
Liquid Apogee Engine (LAE) | Reaction Control Thruster (RCT)
--- | ---
• Thrust level: 400 N (more recently 500 N);
• Operation Mode: long term steady state operation;
• Propellants: MMH/MON or MMH/NTO;
• Vacuum specific impulse (AR=330): 320 s (more recently >325 s);
• Cooling Control: Film and Radiative;
• Single Burn Life: >1.1 hour;
• Accumulated Burn Life: >8.3 hour;
• Cycle Life: >100;
• Type of pressurization: regulated pressure mode

Table 3 Main requirements and characteristics for typical LAE and RCT systems.

The expected performance for the candidate “green” propellants (propyne and HTP, MEA and HTP [20]) is reported in Table 4 at different nozzle expansion ratios. In the same table, also the characteristics of a monopropellant system with HTP are reported.

<table>
<thead>
<tr>
<th>Propellants</th>
<th>LAE (I(_{sp}) vacuum)</th>
<th>RCT (I(_{sp}) vacuum)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_3)H(_4)+H(_2)O(_2)</td>
<td>320 s [AR=330]</td>
<td>290 s [AR=100]</td>
</tr>
<tr>
<td>MEA+HTP</td>
<td>275 s [AR=330]</td>
<td>245 s [AR=100]</td>
</tr>
<tr>
<td>H(_2)O(_2)</td>
<td>N/A</td>
<td>185 s [AR=70]</td>
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</tbody>
</table>

Table 4 Propulsive performance for “green” propellants at expansion ratios typically used for LAE and RCT (MEA and HTP results for LAE assessed on the basis of the results for RCT [20]).

For two geostationary platforms (see Table 5), likewise either Alphabus [13] or Spacebus or Eurostar, with two different orbit manoeuvres, one from LEO to GEO and one from GTO to GEO, and for fixed lifetime (15 years), a calculation of the propellant mass used to the orbit transfer and the N/S station keeping has been performed and used to compare the propellants performance.

<table>
<thead>
<tr>
<th>Geostationary Telecommunication Satellite</th>
<th>GTO to GEO</th>
<th>LEO to GEO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry Mass</td>
<td>3300 kg</td>
<td>1500 kg</td>
</tr>
<tr>
<td>Life Time</td>
<td>15 years</td>
<td>15 years</td>
</tr>
<tr>
<td>N/S Station Keeping</td>
<td>750 m/s (15 x 50 m/s per year)</td>
<td>750 m/s (15 x 50 m/s per year)</td>
</tr>
<tr>
<td>Δv</td>
<td>1800 m/s</td>
<td>4200 m/s</td>
</tr>
</tbody>
</table>

Table 5 Characteristics of the mission requirements.

<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>LAE(C(_3)H(_4)+H(_2)O(_2))+RCT(C(_3)H(_4)+H(_2)O(_2))</td>
<td>3325,86</td>
<td>995,43</td>
<td>4321,29</td>
<td>7621,29</td>
<td>5488,60</td>
<td>452,46</td>
<td>5941,07</td>
<td>7441,07</td>
</tr>
<tr>
<td>LAE(C(_3)H(_4)+H(_2)O(_2))+RCT(H(_2)O(_2))</td>
<td>3862,66</td>
<td>1688,72</td>
<td>5551,38</td>
<td>8851,38</td>
<td>6374,47</td>
<td>767,60</td>
<td>7142,07</td>
<td>8642,07</td>
</tr>
<tr>
<td>LAE(MEA+HTP)+RCT(MEA+HTP)</td>
<td>4277,78</td>
<td>1208,54</td>
<td>5486,32</td>
<td>8786,32</td>
<td>7672,45</td>
<td>549,33</td>
<td>8221,78</td>
<td>9721,78</td>
</tr>
</tbody>
</table>

Table 6 Propellant masses for the two missions.
Table 6 summarizes the main results of the calculation. From the reported data it is apparent the very high performance of the propellant combination propyne and HTP, which justifies the need to go ahead with these propellants, even if the PulCheR concept is not possible for them. So, in addition to study new “green” propellants combinations capable of satisfying the PulCheR requirements, the development of a new conventional bipropellant system which uses propyne and 98% HTP is desirable and probably capable of replacing actual propellants in the future. To this purpose the PulCheR project is focusing with the development of such a thruster for the bipropellant case. The thruster concept is based on the “staged” combustion, with a preliminary injection of HTP through a catalytic bed and following injection of propyne. The bipropellant thruster prototype is shown in Figure 3 and its design has been frozen in the critical design review 2 held during the first part of the third year.

Figure 3 The bipropellant thruster prototype.

The design of the thruster has been chosen in order to take into consideration all the possible features arisen during the preliminary tests on the first bipropellant thruster prototype. In particular the characteristic length of the combustion chamber has been reduced in order to have a faster response of the thruster and the material chosen for the chamber has been properly developed by DEMOKRITOS in order to sustain the very high combustion temperature (a bit lower than 3000 K) for more than 10 s firing. The combustion chamber has been specifically designed to release all the heat by radiation, so film cooling or other coolant techniques are not foreseen. Given the very high temperature of the
thruster, differently to the design of the monopropellant system, a stand-off configuration is used for the valves, whereas the connecting pipes with the thruster have been as short as possible in order to reduce the thruster response time, as well as the use of a bed heater goes in that direction. The valves for both the oxidizer and the fuel have been chosen among the MOOG off-the-shelf valves (model 52-204B). The wetted materials are compatible with the propellants and the valves are under experimental characterization at MOOG-Bradford to find out if they meet also the PulCheR requirements.

The bipropellant thruster has been specifically designed for the “staged” combustion. A complex mechanical component (“Injector Manifold”) has been designed to host the catalytic bed and, at the same time, to allow to centrally inject propyne. The two substances are injected in two separate rooms and they impinge each other inside the combustion chamber by means of a specifically designed injector (see Figure 4).

![Figure 4 The staged combustion for the new bipropellant thruster.](image)

Even if the bipropellant system is now a conventional one, a pulse mode characterization is foreseen. For the characterization a test bench similar to the one already manufactured for the monopropellant system is manufactured for both the oxidizer and fuel lines, as well as the thrust balance is placed on a separate support (see Figure 5). By this way, the dynamics of the two propellants lines and their supporting structures are separate from that of the thruster.
Among the different activities, some tests have been performed to better characterize the response time and the lifetime of the catalytic bed for hydrogen peroxide ([21-22]). The tests have been performed with a 1N thruster designed at SITAEL and tested with 98% HTP produced by IoA. The thruster is visible in Figure 6.

**Figure 5** Test bench for the bipropellant system with three separate supporting structures for the oxidizer and fuel lines and for the thrust balance.

**Figure 6** The 1N monopropellant thruster: on the left a 3D cad rendering, on the right the thruster mounted on the thrust balance.
The tests have been performed at different inlet pressures and in both steady and unsteady conditions in order to characterize the catalyst behaviour in view of its use in both the PulCheR monopropellant thruster and the conventional bipropellant thruster prototype. In steady conditions the results in terms of characteristic velocity efficiency and catalytic bed temperature are good (\(\eta_c > 80\%\) and \(\eta_{\Delta T} \geq 70\%\)) even if lower than in previous experiments. Anyway, the cumulative firing time has been about 500 s with a very short response time for the catalytic bed which results even lower than 100 ms, a value comparable to the current state of the art for monopropellant system. Other tests performed with a pulse mode at different frequency and duty cycle have shown that tests with \(T_{ON}\) of the firing valve equal or higher than 300 ms show a plateau in the thrust profile, corresponding to the steady state thrust value. As expected the catalytic bed temperature influences the bed response time, but the tests clearly show that in a cold start just a few pulses allows the thruster response time to be the same as with a hot start.

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