PRE-MIXED LIQUID GREEN PROPELLANT FOR USE IN ROCKET ENGINES

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Abstract. *Brazil is developing technology for liquid propellant rocket engines, both for use in satellites and launch vehicles. Liquid propellants currently used in Brazil are restricted to use in attitude control of satellites and orbital injection, and are hydrazine and nitrogen tetroxide, both imported, extremely expensive and highly toxic. The pre-mixed propellants based on hydrogen peroxide and ethanol are proving an innovative and very promising taking into account the following factors: The hydrogen peroxide and ethanol are produced in large scale in Brazil for a very low cost. The simulation results show us that the thermochemical premixed propellant has superior performance to the hydrazine. The combustion of premixed propellants using low cost catalysts, and can use those already developed catalysts for hydrazine. The mixture of hydrogen peroxide/ethanol ratio suitable for use as a propellant is safe in terms of his explosiveness. The pre-mixed propellant behaves as a monopropellant, simplifying the whole propulsion system. The toxicology of propellant premixed proved very tolerable and handling much safer compared to hydrazine. We can characterize the propellant pre-mixed as a propellant innovative and totally produced in Brazil, classified as a green propellant, which uses substances produced in Brazil on a large scale and low cost advantage and may substitute with hydrazine and its derivatives.*

Keywords*: rocket, hydrogen peroxide, ethanol, propulsion, propellant.*

1. INTRODUCTION

Rocket engines are fundamentally different from other types of self moving devices due to their reaction behavior, and to launch a rocket a huge quantity of fuel is needed (Sutton 1986). Although the exhaust velocity of burnt gas is high, the gases themselves are light, so a huge amount of propellant is needed to overcome Earth’s gravity and lift a small payload into space. Of course, these gases rest in the atmosphere and, if not properly worked, contribute to pollution.

In order reduce this air pollution during rocket launches we present our research to develop space propellants that are green (“environmental friendly”) and contribute towards non-toxic propellants. The proposals in this work also reveal to be easier and safer to handle this kind of propellant than the conventional ones, and are expected to bring down the costs associated with propellant transport and storage, on-ground operations and in spacecraft development.

Considering green concerns, hydrogen peroxide (H_2O_2) has some features that make it a very promising choice for use in propulsive systems. Among the desired characteristics the most important are: 1) Very versatile and can be used as a monopropellant and bipropellant systems as oxidizers in propellant systems and pre-mixed; 2) With a higher density than most of the propellants, requires a smaller volume of the reservoir and hence a smaller mass of the satellite or launch vehicle; 3) Less toxic than other propellants, such as hydrazine or nitrogen tetra oxide; 4) High fuel oxidizer ratio, thus minimizing the need for greater amounts of fuel; 5) Storable for long periods of time; 6) Compatible with low cost materials such as aluminum and stainless steel; 7) Low cost compared to other propellants, in addition to being produced in Brazil.

Hydrogen peroxide has been historically used very successfully as a propellant in monopropellant and bipropellant propulsive systems, as an example we can cite the German rocket engines of World War II and the successful British space program, presented in the tables 1 and 2. The higher the density of the propellant and the specific impulse, the greater its propulsive efficiency. Table 3 shows a comparison of some commonly used propellants and hydrogen peroxide used as monopropellant, bipropellant and especially in pre-mixed propellants.

It is worth noting that the systems pre-mixed oxidant and fuel are mixed inside the propellant tank, behaving as a monopropellant system.

Table 1. German rocket engines of World War II.

Engine	Kind	Propellants	Thrust (N)
Walter HWK 109-509	Monopropellant	H2O2 (80%)	5000
Walter RII-211	Bipropellant	H2O2 (80%) + "C-Stoff"	17000
Walter HWK 109-507	Monopropellant	H2O2 (80%)	6000

Obs.: C-Stoff (Metanol 57 % + hydrazine monohydrate 30% + water 13%)

Table 2. British rocket engines (1946 to 1971)

Engine	Kind	Species	Thrust (N)	Use
Alpha	Bipropellant	H2O2 (80%) + "C-Stoff"	4000	"Vickers" transonic plane
Beta 1	Bipropellant	H2O2 (80%) + "C-Stoff	8000	"Fairey" high altitude flight
Sprite	Monopropellant	H2O2 (85%)	22680	"Valiant" plane
Beta 2	Bipropellant	H2O2 (80%) + "C-Stoff"	11340	"Delta 1" supersonic plane
Gamma 1	Bipropellant	H2O2 (85%) + Kerosene	36300	Experimental interceptor aircraft
Spectre	Bipropellant	H2O2 (85%) + Kerosene	36300	Interceptor SR-53
Gamma 201	Bipropellant	H2O2 (85%) + Kerosene	74390	"Black Knight" rocket
Stentor	Bipropellant	H2O2 (85%) + Kerosene	97522	Blue Steel missil
Gamma 301	Bipropellant	H2O2 (85%) + Kerosene	95250	"Black Knight" rocket
Gamma Type 2	Bipropellant	H2O2 (85%) + Kerosene	95250	"Black Arrow" rocket second stage
Gamma Type 8	Bipropellant	H2O2 (85%) + Kerosene	95250	"Black Arrow" rocket first stage

Obs.1: English bipropellant engines used pre-catalytic combustion chamber.
Obs.2: The rocket "Black Arrow" is a satellite launch vehicle, and on October 1971 placed a satellite in orbit, enabling the placement of satellites in England.

Table 3. A comparison of some propellants and hydrogen peroxide.

Kind	Propellant	Specific impulse (s)	Density (g/cm^3)
Monopropellant	Hydrazine	178	1.01
Monopropellant	H_2O_2 (80 %)	123	1.30
Monopropellant	H_2O_2 (85 %)	132	1.33
Monopropellant	H_2O_2 (90 %)	140	1.35
Pré-mixed	H_2O_2 (50 %) + Ethanol	180	1.11
Pré-mixed	H_2O_2 (60 %) + Ethanol	200	1.13
Pré-mixed	H_2O_2 (70 %) + Ethanol	217	1.14
Bipropellant	H_2O_2 (85%) + Kerosene	249	1.28

Obs.: Combustion chamber pressure: 500 psi, and expansion to 14.7 psi, engines at sea level.

2. THERMO CHEMICAL EVALUATION OF PRE MIXED PROPELLANTS

2.1. Ethanol + Hydrogen peroxide

The choice of the pair ethanol/hydrogen peroxide is due to the following facts: 1) Hydrogen peroxide is very versatile and can be used as a monopropellant and bipropellant systems as oxidizers in propellant systems and pre-mixed; 2) With a higher density than most of the propellants, hydrogen peroxide requires a smaller volume of the reservoir and hence a smaller mass of the satellite or launch vehicle; 3) Less toxic than other propellants, such as hydrazine or nitrogen tetra oxide; 4) High fuel oxidizer ratio, thus minimizing the need for greater amounts of fuel; 5) Storable for long periods of time; 6) Compatible with low cost materials such as aluminum and stainless steel; 7) Low cost compared to other propellants; 8) Brazil produces large quantities of ethanol (16 million ton per year) and hydrogen peroxide (220,000 ton per year).

We evaluated some pre-mixtures of ethanol/hydrogen peroxide with relative concentration of H2O2 ranging from 50% to 80%. For the selected mixtures we evaluated the optimum fuel oxidizer ratio. For the simulations we used the thermochemical software Propep GDL version 1.2 derived directly from NASA SP273 (Gordon & McBride 1976). The choice of this simulation program was based on the results reliability, and to be open source.

As a first step we optimize the fuel oxidant ratio (O/F) to obtain the maximum specific impulse (Isp), whose results are presented in the table 4. The chart presented in figure 1 provides in a condensed form, a number of simulations used to find the optimized Isp.

Table 4. Stagnation pressures and temperature for various combinations of hydrogen peroxide and ethanol.

Mixture	O/F	Isp (s)	*Tc* (K)	*Pc* (atm)	*Pe* (atm)	ε
H_2O_2 (50%) + Ethanol	8.85	169.1	1461	20	1	3.47
H_2O_2 (60%) + Ethanol	7.35	188.8	1828	20	1	3.56
H_2O_2 (70%) + Ethanol	6.25	204.1	2154	20	1	3.62
H_2O_2 (80%) + Ethanol	5.29	215.9	2424	20	1	3.65

Obs.: *Tc* denotes the stagnation temperature in the combustion chamber, *Pc* denotes the stagnation pressure in the combustion chamber, *Pe* denotes the pressure at the nozzle exit section, and the nozzle optimal expansion ratio is represented in column ε.

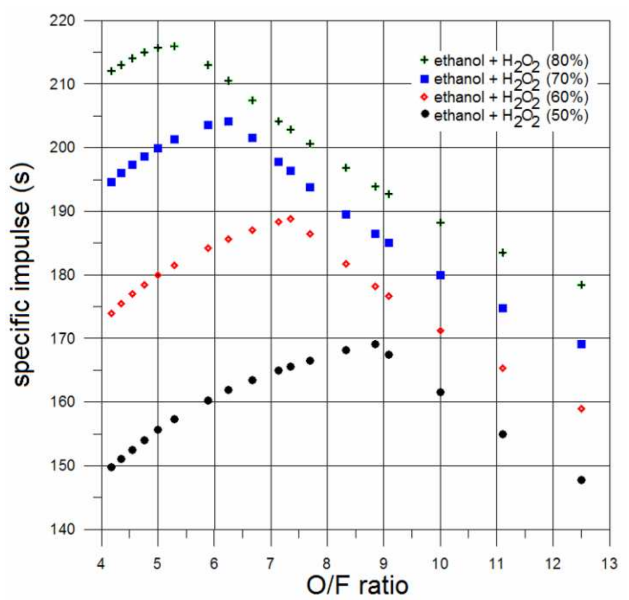

Figure 1. Simulations used to find the optimized Isp.

2.2. Comparisons with Hydrazine

We evaluated the performance of pre-mixed propellants (hydrogen peroxide/ethanol) and hydrazine. The simulations were performed under the same condition of previous calculations, with the exit nozzle pressure of 1 atm. The summarized results are presented in figure 2.

We can characterize the propellant pre-mixed as a propellant innovative and that uses substances 100% produced in Brazil on a large scale and low cost advantage and may substitute with hydrazine. Specific information on explosive properties can be obtained in the extensive work of Schumb et al. (1955), with many data about hydrogen peroxide ant its reactions.

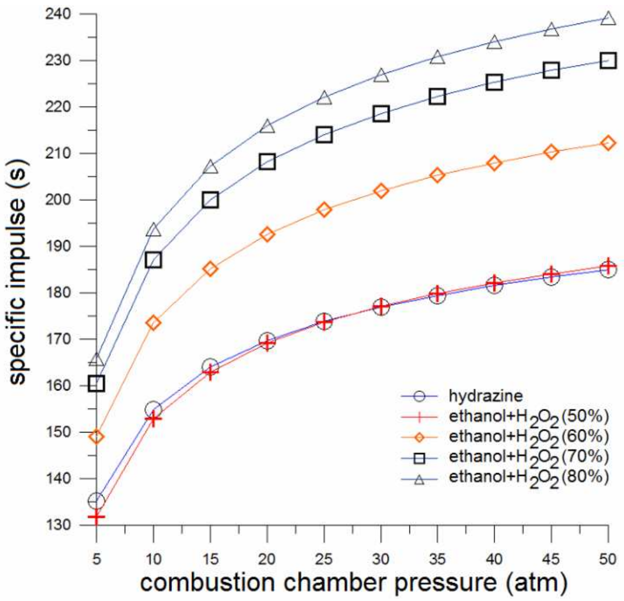

Figure 2. Specific impulse of mixture ethanol + hydrogen peroxide compared to hydrazine.

2.3. Catalysts

The decomposition of hydrogen peroxide occurs under the following reaction

$$H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2 \quad (1)$$

The decomposition process can occur in both liquid and gas phase as five identified forms of decomposition:

1. Homogeneous liquid phase reaction between hydrogen peroxide and the catalyst dissolved;
2. Heterogeneous reaction between hydrogen peroxide in liquid phase with the surface of solid catalyst;
3. Heterogeneous reaction between hydrogen peroxide in the liquid phase and vapor phase at high temperature;
4. Heterogeneous reaction between hydrogen peroxide vapor and dry surface of the solid catalyst;
5. Reaction homogeneous decomposition of hydrogen peroxide vapor.

We use in this work, a ceramic solid catalyst developed for the following purposes: 1) Low cost; 2) Thermal stability; 3) Large contact surface; 4) Large surface porosity; 5) High catalytic activity; 6) Insensitivity to contaminants that alter their catalytic activity.

In a rocket engine one needs controlled catalytic decomposition, which can occur in two distinct ways: thermal decomposition or catalytic decomposition. As a first step when the propellant is injected into the catalytic chamber the decomposition is exclusively catalytic. With the gradual increase of catalyst temperature of the combustion chamber, the thermal decomposition begins to compete with the catalytic process.

Using pre-mixed propellant, one has a mixture of hydrogen peroxide and ethanol, injected into the catalyst. With the decomposition of hydrogen peroxide and the release of excess heat from water and ethanol will become a vapor, then one shall have a mixture of water vapor, ethanol vapor and oxygen at high temperature. The mixture of gases enters the chamber combustion after the catalytic chamber where it spontaneously ignites and starts the combustion reaction between oxygen and ethanol. The ignition is greatly facilitated by the high temperature components and also of those being in the vapor phase. After a few seconds the system reaches a thermal stabilization and the initial firing, provided by an electric spark can be deactivated (Hearn 1982).

Three types of catalysts have been developed, the first type is based on a refractory ceramic composition impregnated with manganese dioxide (MnO_2), a second type is based on the first type of pottery, but is also impregnated with potassium permanganate ($KMnO_4$) and a third consisting of refractory material impregnated only with $KMnO_4$. The refractory ceramic substrate was prepared with a combination of oxides: Al_2O_3 (51%), SiO_2 (42%), Fe_2O_3 (1,6%) and CaO (5,4%). The catalysts obtained can be used until a temperature of 1450 °C and have a maximum density of 2.13 g/cm^3. It should also important to emphasize that we used a maximum concentration of MnO_2 in 10% of the total weight of the ceramic, because its presence at concentrations above this value significantly alter the mechanical characteristics of refractory ceramics obtained.

3. ROCKET ENGINE FOR TESTING THE PROPELLANT

For testing the pre-mixed propellant we build a rocket engine in scale with a 10 N thrust. This engine was designed, based on results of numerical simulation techniques and computational fluid dynamics (CFD), as presented in Hetem et al. (2011 SUBMITTED).

3.1. Mathematical Model and CFD Simulation

The mathematical model for the rocket engine was developed based on Miraglia (1994). The ideal thrust catalytic chamber model must be based on the following assumptions (Himmelblau 1984): 1) ideal gases; 2) the temperature inside the combustion chamber is uniform; 3) the thrust chamber is adiabatic; 4) the propellant is injected, gasified and decomposed instantly; 5) one-dimensional flow; 6) the decomposition reaction is an exclusive function of the catalytic; 7) the thermo chemical properties of gases decomposition are functions uniquely of the chemical compositions of the propellant and the catalytic; 8) the catalyst is incompressible. Some constants were obtained in Griffinand & French (1991).

The mathematical models are based on first order ordinary differential equations, and all the system were modeled by a single system of differential equations. The numerical method chosen for solution of this system were the Runge-Kutta fourth order. This method proved to be very robust and perfectly reliable, providing a fast and effective generation of the numerical results. The algorithm was developed and implemented in C++ language.

We use techniques of Computational Fluid Dynamics (CFD) for simulation of the combustion chamber and nozzle of the rocket engine. The program used was COSMOS, more specifically the package "FLOWORKS" of SOLIDWORKS (DASA 2011), which is suitable for simulating compressible flow at high Mach number. The combustion chamber and nozzle were modeled and simulated. Figure 3 presents the gas speed at the nozzle of the model. The conditions used in them simulation CFD: Structured mesh type, steady state, 3D Navier-Stokes equations using the standard k-epsilon turbulence model, pressure in the combustion chamber 20 Bar, temperature in the combustion chamber 1461 K, mass flow rate 6 g/s, environment pressure 1 atm.

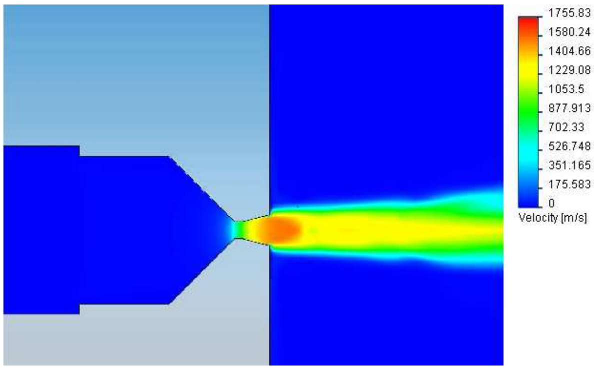

Figure 3. Velocity gradient: the combustion chamber is stagnant; the maximum ejection velocity of the gases is 1755.83 m/s, which represents an Isp of 178 s of pre-mixed propellant with hydrogen peroxide (50%) and ethanol.
Expansion 20 to 1 Bar.

3.2. The engine and static test bench

All components of the propellers were designed program Autodesk INVENTOR 10, because it is a renowned worldwide and enable CAD work directly with solid modeling efficiently. All components were produced in conventional and CNC machines and welding was outsourced to companies specializing in TIG and MIG. Table 5 presents some design details and figure 4 some visualizations of the engine.

The test bench consists of two separate sets, which are the backbone of the pre-mixed propellant tank and support the load cell where we fixed the rocket engine. The propellant tank allows working with a volume of up to 3.5 l (approximately 3.5 kg) of pre-mixed propellant with hydrogen peroxide (50%) and ethanol.

We used a load cell with capacity of 50 N and constant linearity 2mv/V, sourced by a 9 volt alkaline battery, in order to minimize electrical noise caused by external sources of supply. The cell signal was transmitted to an amplifier circuit and sent to the data acquisition system. Measurements of buoyancy were stored in real time on a microcomputer for further analysis.

Table 5. Detailed technical description of the test engine.

Type of injector	distributor plate with holes of 1 mm
Catalytic Chamber Diameter	22 mm
Length	40 mm
Retainer Catalyst	distributor plate with holes of 1 mm 2 mm e screen mesh 30
Combustion Chamber Diameter	22 mm
Combustion Chamber Length	29 mm
Nozzle Throat Diameter	2.1 mm
Exit of Nozzle Diameter	4 mm
Expansion Ratio	3.63
Total mass of Catalyst (thick)	16 g
Total mass of Catalyst (fine)	2 g
Total Propellant Mass	392 g
Ignitor Type	NGK CM-6
Nominal thrust	10 N
Specific Impulse	169,1 s
Nominal Pressure in Combustion Chamber	20 Bar
Nominal Temperature on Combustion Chamber	1461 K
Propellant	H_2O_2 (50%) + Etanol
Mass Flow	6 g/s
Oxidizer Ratio Fuel	8.85

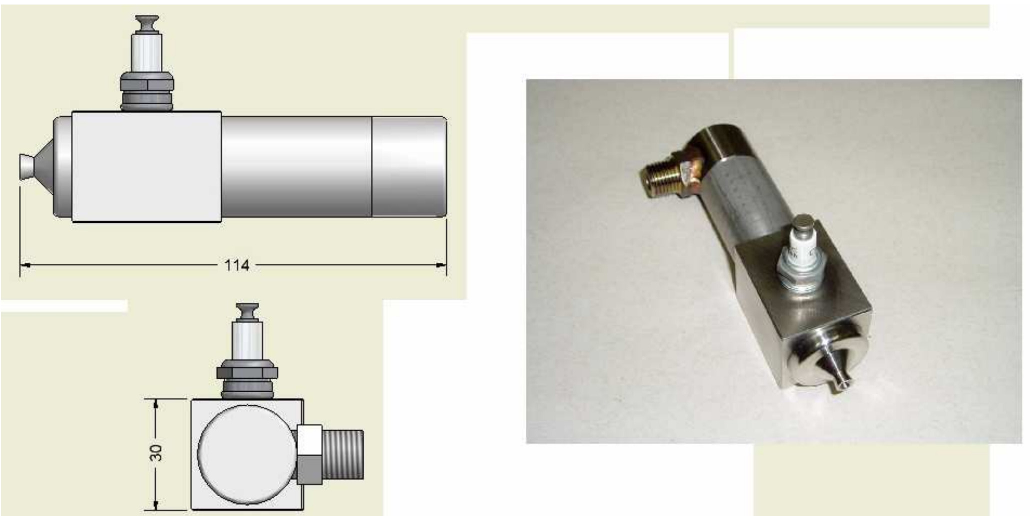

Figure 4. Designs of the test rocket engine (left) and photograph of the final prototype.

4. TESTS

We tested the complete 10 N engine on the bench with the catalyst with better performance, propellant type 2 and pre-mixed hydrogen peroxide and 50% ethanol. The engine shows rapid ignition in the combustion, but some instability that was resolved with the change and calibration of mass flow of propellant.

The procedure for starting the engine followed the following steps: 1) Ball Valve Flow Control open and previously adjusted to the appropriate flow; 2) Opening of solenoid valve supply of propellant; 3) Verification of steam heating of the propellant and catalyst; 4) Drive the ignition circuit. Figures 5 and 6 show images of the tests without and with the nozzle.

The data acquisition system used is the model DI-148U with 8 analog input 0 to ± 10 volts, an acquisition rate of 14,400 samples per second, 10 bit resolution USB connection. The acquisition software used was "Windaq Lite" and "Windaq Waveform Browser”.

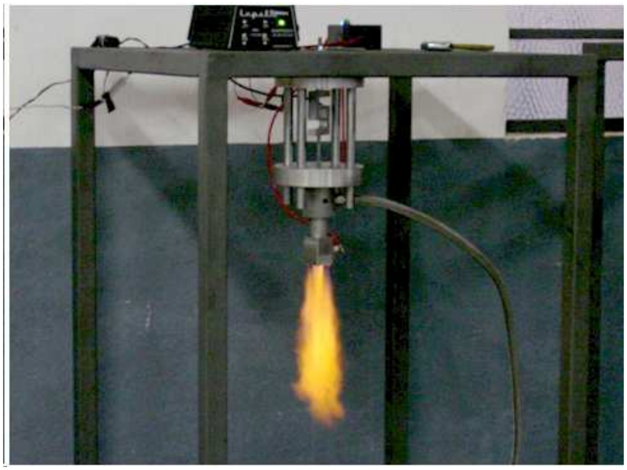

Figure 5. Test of the combustion chamber without nozzle for verification of the electric ignition. The engine was feed with a ethanol + hydrogen peroxide (50%) mixture.

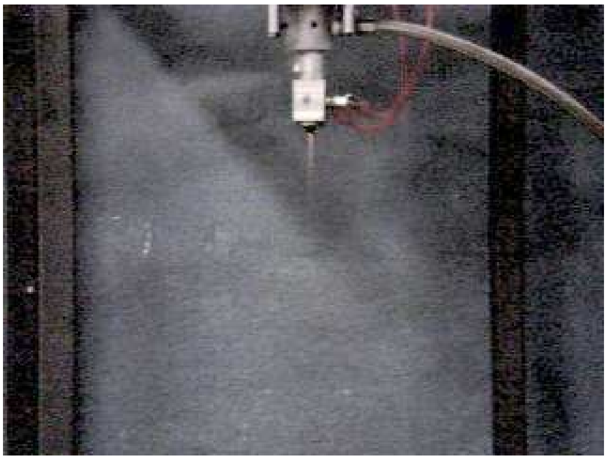

Figure 6. Test of the complete engine with nozzle. The engine was feed with an ethanol + hydrogen peroxide (50%) mixture. As combustion gases are not visible, one notes the lack of flame at the exit of the nozzle after ignition.

5. RESULTS

The tests showed the engine built for testing is stable, and the ignition mechanism is reliable and efficient. Figure 7 presents a plot from raw data from the first test with the engine, with the evolution of thrust with time.

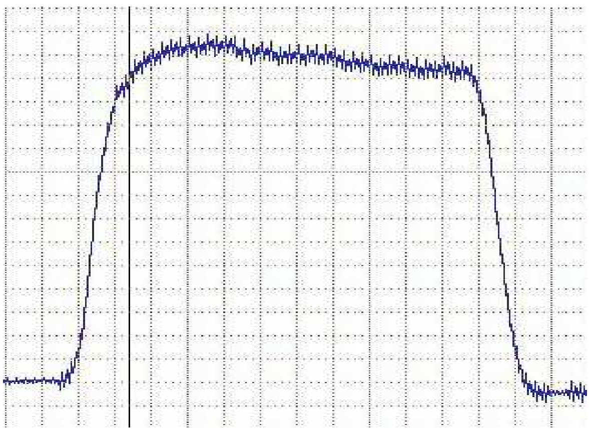

Figure 7. Plot from raw data from the first test with the engine, with the evolution of thrust with time. The total simulation test was about 36 s and the mean thrust after ignition (the vertical thick line) was 9.6 N.

We can observe in the table 6 a comparative of some obtained results.

Table 6. Some comparative results between the simulation and the experiment.

	Simulation	Experimental
Thurst (N)	10.68	9.6
Isp (s)	178	163
Chamber Pressure (Bar)	19.38	19
Mass Flow Rate (g/s)	6	5.8
Chamber temperature (K)	1461	1472

6. CONCLUSIONS

The experimental and simulation results showed that the thermo chemical pre-mixed propellants have higher performance than hydrazine in most conditions, and the pre-mixed propellant behaves as a monopropellant, simplifying the whole propulsion system. The preparation of the propellant mixture consisting of ethanol and hydrogen peroxide (50%) proved to be quite safe.

The toxicological characteristics of the propellant premixed proved very tolerable and handling much safer compared to hydrazine. Other mixtures were not tested because the tests were not made of explosives which will run in a second phase of the research project. Ignition of the propellant is very easy with an ignition delay imperceptible and combustion stability with oscillations occurred with a negligible amplitude.

The aim of demonstrating the technical feasibility of the propellant premixed catalyst and was fully achieved. The propellant Ethanol - Hydrogen Peroxide fits in so-called "Green Propellants" ecological and low cost. The hydrazine has an estimated cost of $ 17.00/Kg while the propellant pre-mixed in the order of $ 1.00/Kg. Improvements in the data acquisition system, specifically the electromagnetic shielding is necessary in the second phase of the project. Tests with explosive peroxide in concentrations above 60% are necessary to continue the experiments safely, that these tests will be performed in the second phase of the project. For our proposed second phase will test the continuity of these drivers and the construction of engines of 100 N and 1000 N for assessment including bipropellant as Ethanol and Hydrogen Peroxide (80% - 85%). The handling of hydrogen peroxide in concentrations 50%, 60% and 70% proved to be quite safe. Hydrogen peroxide is an oxidant shows great versatility, and low cost, and is again arousing great interest in their use in propellant systems from the attitude control thrusters for satellites to launch vehicles. Demonstrating the technical feasibility of the project shows the relevance and importance to the technological development of Brazil in this area.

7. ACKNOWLEDGEMENTS

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