High concentration hydrogen peroxide for rocket fuel applications

George PELIN*,[1], Cornel STOICA[1], Cristina - Elisabeta PELIN[1], Raluca BALASA[1]

*Corresponding author
[1]INCAS – National Institute for Aerospace Research "Elie Carafoli",
B-dul Iuliu Maniu 220, Bucharest 061126, Romania,
pelin.george@incas.ro*, stoica.corneliu@incas.ro, pelin.cristina@incas.ro,
balasa.raluca@incas.ro

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Abstract: *This paper presents the experimental study of the distillation of hydrogen peroxide to increase the concentration of the solution, in order to use it as rocket fuel in space applications. The process of obtaining the desired concentration required for the operation of the wind tunnel model rocket engine was obtained using the vacuum distillation method. The process consists in removing a calculated value of the water content from the hydrogen peroxide solution with a concentration of 35%, thus increasing its concentration up to the value of 90%. The key factors that contribute in obtaining the desired concentration were evaluated and experimental results were compared with the calculated values.*

Key Words: *Hydrogen peroxide, rocket fuel, vacuum distillation process, concentration increase*

1. INTRODUCTION

A major interest in the development of eco and green engine technologies can be noticed in the last decade. Low toxicity storable liquid propellants have become considerably more attractive as possible substitutes for oxides of nitrogen and hydrazines. The main benefit of these alternative propellants is the significant cost saving associated with the drastic simplification of the health and safety protection procedures necessary during the propellant production, storage and handling [1].

The most promising high-energy green propellants like ammonium dinitramide (AND), hydroxyl ammonium nitrate (HAN) and hydrazinium nitroformate (HNF) require expensive materials and manufacturing processes for the thrust chamber [1]. Hydrogen peroxide does not show this requirements, so it has been reconsidered as a promising green propellant for low and medium thrust applications. Thus, the interest in hydrogen peroxide (H_2O_2) used as a propellant has been renewed due to its low toxicity, high density impulse and increased versatility which allows it to be used as an oxidant in both two-engine liquid rocket engines and in hybrid rocket engines [2, 3]. It can be used as monopropellant for generating turbine drive gases and as an oxidizer in bipropellant systems [2, 3]. The earliest research on hydrogen peroxide based rockets was initiated in Germany during the 1930s [4]. In the 1950s, United Kingdom, USA and Soviet Union showed interest in hydrogen peroxide as rocket fuel for different applications. US X-1 and X-15 space planes, as well as Mercury and Gemini manned spacecrafts used hydrogen peroxide in their reaction control systems [1]. In the 1960s NASA developed a hydrogen peroxide turbojet engine exhaust simulator for powered model testing in wind tunnels with air exchange. The compact and small propellant lines system showed to provide a hot jet with characteristics that correspond closely to the exhaust of a turbojet engine [5]. Hydrogen peroxide propulsion systems have been developed since 1975. Juan Manuel Lozano is the inventor of the world's most popular machine for producing organic hydrogen peroxide used as a green propellant for next generations of rockets [6].

Later on, in 1997, USA developed small monopropellant satellite thrusters using hydrogen peroxide of 85% concentration [7].

Nowadays, Italy and UK are carrying out a joint activity, funded by ESA, for the development of hydrogen peroxide monopropellant thrusters based on the use of advanced catalytic beds [1]. Recent research at Delft University, also funded by ESA, presents the design of a fully modular 1N thruster to provide the capability of testing and comparing the performance of different concentrations of hydrogen peroxide, different catalysts as well as new technologies in an attempt to resolve the disadvantages associated with the use of catalyst beds [8].

Hydrogen peroxide is a simple inorganic compound but a remarkably versatile one [9], as it is an environmentally friendly chemical bleach used in oxidation processes, especially in the pulp industry, water and air treatment and in various disinfection applications.

The most common process for the industrial production of hydrogen peroxide is through the anthraquinone self-oxidation process which forms an aqueous solution of hydrogen peroxide (~ 40% by weight) [10, 11].

Although hydrogen peroxide is found in the environment in low concentrations, it is commercially manufactured in concentrations of 35, 50, 70 and 85%, solutions that are usually diluted for different applications [12]. 35% is the most common concentration available on the market, while higher concentrations are generally available on request.

Distillation process represents the operation of separating a liquid into two or more products to concentrate the liquid mixtures [9]. Although it consumes a large amount of energy, distillation is a well-known and efficient method of concentration in the process industry [13].

By distillation, theoretically, water can be completely separated from hydrogen peroxide because they do not form an azeotropic mixture [10].

By distilling lower concentrations hydrogen peroxide, the obtained H_2O_2 solutions are cleaner than industrial ones (that have to be stabilized for transport with different stabilizing agents), therefore they are more suitable to be used in special applications [14] such as in space rocket launches and as mono-propeller in various underwater ships [6].

The performance of propellants that use hydrogen peroxide as an oxidizer and gas generator is greatly influenced by its concentration, as the available oxygen content and decomposition temperature increase with increasing concentration [15].

The present paper illustrates a study aimed at processing hydrogen peroxide provided by Evonik, by eliminating water content for increasing the solution concentration to produce model rocket fuel.

The optimal concentration of hydrogen peroxide necessary for the operation of the rocket engine was achieved by vacuum distillation.

The high prices of hydrogen peroxide solutions used for rocket fuel (90% concentration) as well as the difficulties of transporting it over long distances have increased interest in searching for simpler alternatives. Therefore, the chosen solution was to process lower concentrations hydrogen peroxide into much higher concentration solutions by the distillation process [9].

2. EXPERIMENTAL

2.1 Materials

This paper describes the process of distilling hydrogen peroxide at high concentrations from an experimental point of view. Hydrogen peroxide with a concentration of 35% was purchased from provider, having the technical specifications presented in table 1.

Table 1. Information on basic physical and chemical properties of 35% hydrogen peroxide [16]

Substance name	Hydrogen peroxide 35% - Content KMnO4
Chemical formula	H_2O_2
Physical state	fluid
Color	Colorless
pH	1,5 – 4
Density at 25°C	1,1279 g/cm^3
Oxidizing properties	Strong oxidant

The concentration increase was obtained through the hydrogen peroxide distillation plant that is illustrated in figure 1.

2.2 Obtaining method

The process of producing high concentrations (~ 90%) with low cost and high production rate is shown in Figure 1, it is used by NASA, and evaluated as the most efficient process taking into consideration the factors mentioned [17].
A high vacuum pump is required in the production process to maintain a constant vacuum pressure (680 mbar vacuum) throughout the distillation process. In order to obtain a concentration of ~ 90% hydrogen peroxide starting from a concentration of 35%, it is necessary for the distillation process to be carried out in 2 stages, due to the excessive volume of wastewater to be removed.

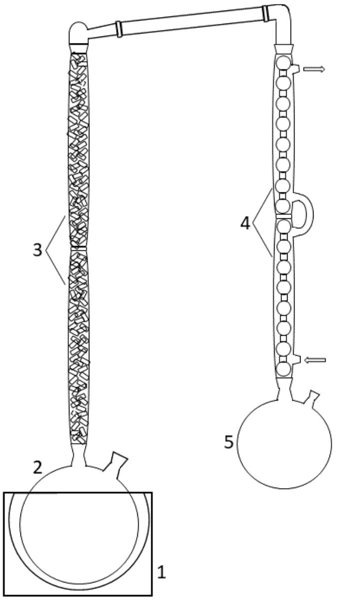


Fig. 1 Scheme of the hydrogen peroxide distillation equipment
1 – electric oven, 2 – glass balloon for hydrogen peroxide, 3 – columns with glass cylinders for water vapor flow, 4 – refrigerants, 5 – glass balloon for wastewater

In the first step, from a quantity of 15l of hydrogen peroxide with a concentration of 35%, 7,5l of hydrogen peroxide of 70% concentration will be obtained according to equation 1.

$$C_1V_1 = C_2V_2 \tag{1}$$

C_1 – initial concentration of the hydrogen peroxide solution,
V_1 – volume of the initial hydrogen peroxide solution,
C_2 – obtained concentration of the hydrogen peroxide solution,
V_2 – volume of the obtained hydrogen peroxide solution.

Thus, a quantity of 15L of hydrogen peroxide of 35% concentration is introduced into the 20l volume glass flask (fig. 1 – 2). The heating nest (fig. 1 – 1) will keep heating temperature constant (approximately 74- 77ºC) throughout the distillation process. When the mentioned temperature is reached, due to the vacuum pressure, water vapor is eliminated and moved through the columns with glass cylinders (fig. 1 – 3). Water vapor condenses on the surface of the interior walls of the refrigerants (fig. 1 – 4) and is collected in the 10l volume glass flask (fig. 1 – 5). The first stage of the distillation process ends when 7.5l of waste water is collected in the 10l glass flask.

In the second step, this time a volume of 15l hydrogen peroxide of 70% concentration is added and according to equation (1), 11.6l of 90% hydrogen peroxide will be obtained at the end of the distillation process. The distillation process ends when 3.4l of liquid is collected in the glass flask for the collection of waste water.

2.3 Results and discussion

In fig. 2 it can be seen that the heating speed to reach boiling temperature is 1.2 degrees/ min. The time required to collect the volume of wastewater by condensation, corresponding to each initial concentration of the hydrogen peroxide solution is about 4 hours.
The vacuum pressure was set at 680 mbar vacuum from the beginning of the distillation process. With temperature increase and by reaching the set temperature domain, a slight increase in vacuum pressure (~ 20 mbar vacuum) was observed. Finally, when the wastewater has started to condense, the vacuum pressure tends to stabilize at the initially set value.

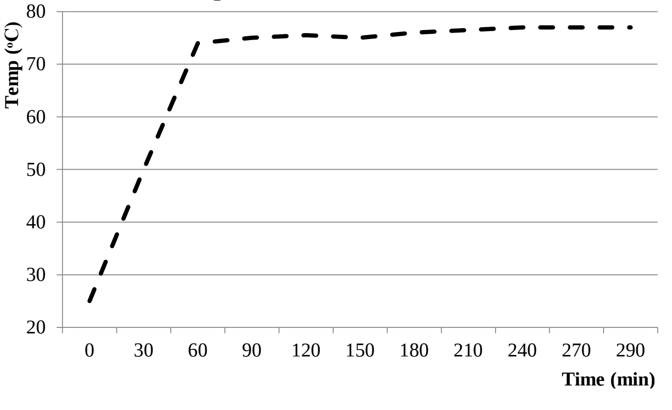
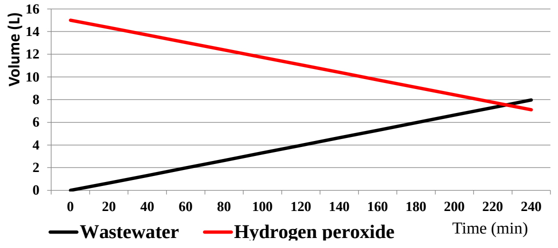
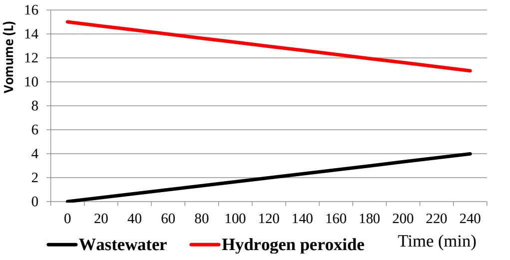


Fig. 2 Temperature / time evolution graphic in the condensation process

As expected in the vacuum distillation process, when the volume of hydrogen peroxide decreases, the volume of wastewater increases. In the first stage (figure 3- left) the resulting volume of hydrogen peroxide is equal to that of the wastewater, as calculated in equation 1. For stage 2 (figure 3 - right) the volume of wastewater to be removed is only 3.4l, calculated by equation 1.



Graph for time/ volume of collected liquids – the first phase



Graph for time/ volume of collected liquids – the second phase

Fig. 3 Volume/ time evolution graphic in the condensation process

After each step, the density of the distilled solution was calculated. Density can be determined using the densimeter, but the most accurate way to calculate density is experimentally. The experimental method was chosen to determine the density at ambient temperature and, for this, an analytical balance and a graduated cylinder of 50 ml were used. A known volume of water was weighed, the result being the weight of a density equal to 1. This was the constant for the tests. The same volume of hydrogen peroxide solution was weighed and the resulting mass was multiplied by the previously obtained constant, thus obtaining the density of the peroxide solution.

The density value was used to determine the obtained concentration [18, 19] (table 2.). Observing lower values of the concentration of the resulting hydrogen peroxide solutions compared to the calculated values, it was decided to determine the wastewater density as well.

Table 2. The solutions concentration values according to density [18]

Liquid solutions	Stage 1		Stage 2	
	Density (g/ml)	Concentration (%)	Density (g/ml)	Concentration (%)
Hydrogen Peroxide	1.2782	68.83	1.3583	84.68
Wastewater	1.0124	4.42	1.0492	14.67

Thus, as it can be observed also from figure 4, there are losses of hydrogen peroxide in the wastewater of 4% in the case of the first distillation step and up to 15% in the second distillation step.

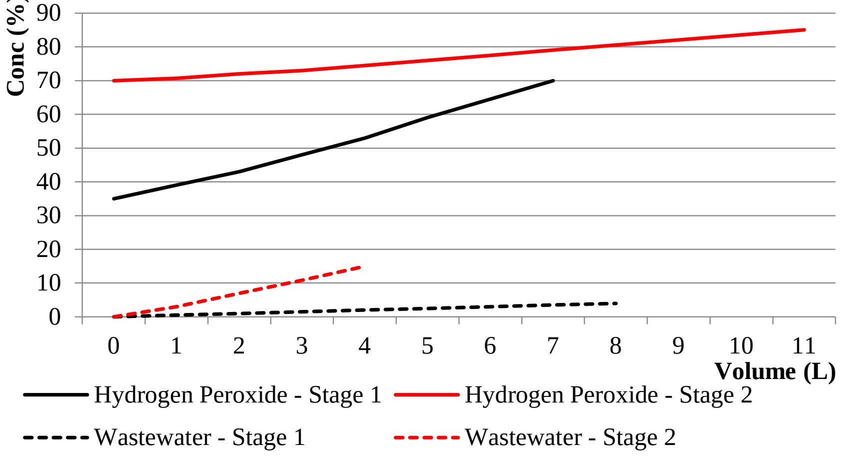


Fig. 4 Concentration/ volume evolution graphic in the condensation process

This issue could be attributed to process parameters control during the distillation. Temperature is automatically controlled with the aid of a thermostat, with a minor fluctuation of ±2ºC for the first stage and ±5ºC for the second stage. Both temperature and pressure parameters become more difficult to control and stabilize as the solution concentration is higher, explaining the higher hydrogen peroxide losses in the second distillation stage.

3. CONCLUSIONS

The preliminary results presented in this paper showed that the decisive factors in increasing the concentration of hydrogen peroxide after the distillation process are to maintain a constant temperature and vacuum pressure throughout the chemical process.
At the beginning of the process the temperature is increasing by 1.2ºC/min and the heating rate of the oven remained constant after reaching the set temperature.
Although the vacuum pressure was set at 680 mbar vacuum, a slight increase in vacuum pressure was observed after reaching the set temperature. The value was stabilized when the wastewater began to condense.
After calculating the densities and implicitly the concentration of the resulting solution, peroxide losses were observed in the wastewater. This was expected to happen, as obtaining higher concentration solutions in the distillation process generates important fluctuations in the process parameters, both in pressure and temperature. Future research takes into consideration equipping the facility with automatic control for the pressure parameter, in order to decrease the peroxide losses, especially for the second stage of the distillation.

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