

# An experimental study on the hypergolic ignition of hydrogen peroxide and ethanolamine

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## ABSTRACT

This paper presents the hypergolic ignition test results of a potential environmentally friendly liquid propellant consisting of hydrogen peroxide oxidizer (with a concentration of 85%) and ethanolamine fuel for use in rocket engines. Open cup drop tests were conducted to study the effect of amount of metal salt catalyst in fuel and the initial temperatures of fuel and oxidizer on the ignition delay time. To test the hypergolic ignition of bipropellant formulation in a real rocket engine environment, a pressure-fed liquid propellant rocket engine (LPRE) was designed and developed. During the tests it was found that the amount of catalyst and the initial temperature of the fuel had a significant effect on the ignition delay of hypergolic bipropellant. However, the oxidizer temperature seemed to have almost no effect on the ignition delay. There was also significant difference between the ignition delay times from open cup tests and those from rocket engine static firings.

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## 1. Introduction

Due to their unique advantages such as active thrust regulation, on-off control capability, and high specific impulse, liquid propellant rocket engines (LPRE) are commonly used in long-range applications like space launch operations. With the increase of number of space launches from year to year, there have been continuous efforts in developing environmentally friendly liquid propellants with low emissions but yet with good ballistic performance in terms of high specific impulse and low ignition delay.

Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) is a non-cryogenic, very strong, storable oxidizer/monopropellant with a high density specific impulse. Being non-toxic,  $\text{H}_2\text{O}_2$  is considered as a green propellant and its popularity is increasing due to the increase of environmental awareness since 1990.

Extensive researches have been done in the past on the use of hydrogen peroxide as a monopropellant, and catalytic decomposition studies comprises a significant percentage of these efforts. Ref. [1] presents an excellent review of the many catalyst which have been considered for hydrogen peroxide decomposition.

In hypergolic bipropellant rocket engines, hydrazine fuel and nitrogen tetroxide oxidizer is the most commonly used combination. However, this combination, being highly toxic, poses great health hazards. Since 1990's, researches have been done on the development of non-toxic, hypergolic bipropellants containing

hydrogen peroxide. US Naval Air Warfare Center Weapons Division at China Lake (NAWC-WD) developed a non-toxic, storable fuel, named block 0, which was hypergolic with and completely miscible in rocket-grade hydrogen peroxide [2]. The fuel is a colloidal suspension of manganese oxide ( $\text{Mn}_3\text{O}_4$ ) in methanol. Experimental results showed that reliable hypergolic ignition was achieved for bipropellant containing this fuel and the hydrogen peroxide, but the aging characteristic of the fuel was found to be very poor [3].

The research group at the Purdue University has extensively studied the hypergolic ignition of block 0 fuel, developed by NAWC-WD, and hydrogen peroxide. In Refs. [4,5], they studied the effects of initial ambient pressure, initial ambient gas properties, and hydrogen peroxide concentration on ignition delay. Drop tests showed that reducing the pressure from atmospheric to 48 kPa (7 psia) led to a 30% increase in the ignition delay for block 0 fuel/98% hydrogen peroxide combination. Ignition delay increased by 50% when hydrogen peroxide concentration was reduced from 99% to 92% at atmospheric pressure. In Refs. [6,7], the effect of catalyst concentration on the ignition delay of block 0 fuel and rocket-grade hydrogen peroxide was studied. The ignition delay times obtained from experiments were about 30 ms for 10% catalyst in methanol and 10 ms for 30% catalyst, showing a decrease in ignition delay with the increase of catalyst percentage.

In Ref. [8], a wide variety of fuels were tested with 90% hydrogen peroxide and the only practical hypergolic fuel with hydrogen peroxide was found to be ethanolamine catalyzed with copper II chloride ( $\text{CuCl}_2$ ). Kerosene, a commonly used liquid fuel in rocket

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engines, did not ignite upon contact with hydrogen peroxide, even with the addition of catalyst. Ethanolamine was found to be the best fuel among the 21 fuels tested due to its high density, low toxicity, respectable performance, and rapid ignition with hydrogen peroxide [8]. Therefore, in this study  $\text{H}_2\text{O}_2$  was chosen as the oxidizer and ethanolamine, which is hypergolic with  $\text{H}_2\text{O}_2$ , as the fuel in the LPRE.

In this paper, the experimental results on the ignition delay of this potential environmentally friendly hypergolic bipropellant are presented.

## 2. Experimental

### 2.1. Open cup drop tests

Open cup drop tests were conducted at atmospheric pressure to measure the ignition delay times of different mixtures of ethanolamine/ $\text{CuCl}_2$  with hydrogen peroxide. In drop tests, 30 mL fuel/catalyst mixture was put into a steel cup. Then, a drop of hydrogen peroxide was added into this cup using a glass pipette. The tests were recorded with a high-speed (500 fps) camera and the time passed from the moment that the first  $\text{H}_2\text{O}_2$  drop touched the fuel surface to the moment that the first flame appeared was defined as the ignition delay time.

### 2.2. Liquid propellant rocket engine tests

The LPRE designed and developed in this study used nitrogen gas-pressurized feed system, which is less complex, lighter, cheaper, and more reliable than the turbopump feed systems [9,10]. An unlike triplet impinging jet type injector shown in Fig. 1 was de-

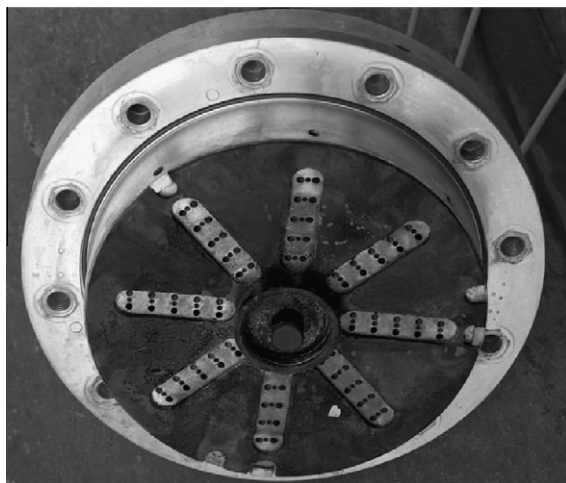


Fig. 1. Unlike triplet impinging jet type injector.

signed to mix the liquid fuel and liquid oxidizer. The impinging angle of the injector was  $30^\circ$ . The injector had 40 injection ports for the fuel and 80 ports for the oxidizer.

A bell type nozzle was designed and manufactured to accelerate the combustion product gases and to produce thrust. Cavitating venturis were used in both fuel and oxidizer lines to control the flow rates. As the temperature of the combustion chamber reaches up to 2500 K, an ablative cooling system was used to protect the rocket engine body from high temperature products. Ablative cooling is cheaper and its application is simpler than the other cooling techniques (i.e., regenerative and radiative) and it has been used in solid propellant rocket motor cooling for many years. It has been also used in several recently developed LPREs such as 2.89 MN-thrust Low Cost Pintle Engine of TRW [11], Korea Sounding Rocket (KSR)-III Engine [12], and Falcon Engine of Space Exploration Technologies [13]. The LPRE flow diagram is presented in Fig. 2.

Fifty percent  $\text{H}_2\text{O}_2$  without stabilizers is available commercially. However, the specific impulse of 50%  $\text{H}_2\text{O}_2$  is very low. To overcome this problem, distillation of  $\text{H}_2\text{O}_2$  from 50% to up to 85% was done using a distillation system in this study. The great danger of high reactivity posed by this high concentration  $\text{H}_2\text{O}_2$  is eliminated by using proper materials (i.e., 316 SS) in the oxidizer tank and oxidizer feeding lines and cleaning the system according to the specifications. Fuel used in the LPRE was compatible with any kind of metal, so fuel tank material was selected as 4140 steel. Manufactured tanks were hydrostatically tested against an internal pressure of 150 bar. For the pressurization of the hydrogen peroxide and fuel tanks, a steel nitrogen tank of proof pressure 300 bar was used for the ground tests.

The designed engine, with the specifications given in Table 1, was manufactured and its ground tests were conducted.

## 3. Results

### 3.1. Open cup drop test results

As explained above, ethanolamine fuel was found to be hypergolic with hydrogen peroxide [8]. To decrease the ignition delay, Melof and Grubelich added  $\text{CuCl}_2$  catalyst to ethanolamine [8]. Although they did not measure ignition delay times, they reported an “instant” ignition when ethanolamine with 1% mass addition of  $\text{CuCl}_2$  contacted with hydrogen peroxide. In this study, 5% addition of  $\text{CuCl}_2$  to ethanolamine gave an ignition delay time of 200 ms (ms) with hydrogen peroxide whereas 10% addition gave a 30 ms ignition delay, which is sufficiently low in rocket engine applications.

The initial temperatures of the fuel and the oxidizer could significantly affect the ignition delay times. To obtain the temperature sensitivity of the ignition delay times for the liquid propellant mixture, drop tests were conducted at different initial temperatures as shown in Table 2 and Fig. 3. In these tests, 90% ethanolamine/10%

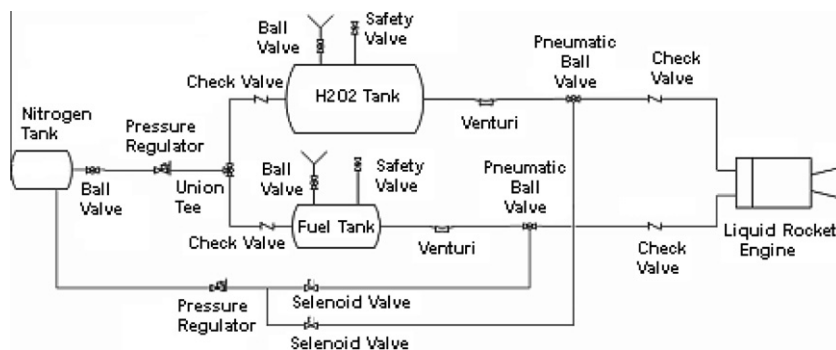


Fig. 2. Flow diagram of the liquid propellant rocket engine.

**Table 1**

Liquid propellant rocket engine specifications.

Parameter	Value
Combustion chamber pressure (bar)	30
Ideal thrust (kN)	25
Mixture ratio	4.12
Fuel mass flow rate (kg/s)	1.96
H <sub>2</sub> O <sub>2</sub> mass flow rate (kg/s)	8.06
Characteristic length, L* (m)	2.3
Combustion chamber diameter (m)	0.14
Throat diameter (m)	0.07
Nozzle exit diameter (m)	0.23
Nozzle expansion ratio	11
Fuel tank pressure (bar)	100
Oxidizer tank pressure (bar)	100
Nitrogen tank pressure (bar)	230
Total working time (s)	~2

**Table 2**

Temperature sensitivity of the ignition delay time for the liquid propellant.

Test #	T <sub>f</sub> (°C) <sup>a</sup>	T <sub>ox</sub> (°C) <sup>b</sup>	t <sub>d</sub> (s) <sup>c</sup>
1	38	34	0.027
2	36	36	0.027
3	38	38	0.028
4	45	12	0.033
5	23	5	0.034
6	29	14	0.035
7	41	10	0.036
8	39	10	0.037
9	24	7	0.040
10	45	4	0.040
11	35	22	0.046
12	24	6	0.047
13	25	14	0.053
14	24	14	0.054
15	32	4	0.055
16	19	11	0.065
17	17	4	0.067
18	7	7	0.093
19	7	7	0.104

<sup>a</sup> Fuel/catalyst mixture initial temperature.<sup>b</sup> Oxidizer initial temperature.<sup>c</sup> Ignition delay time.

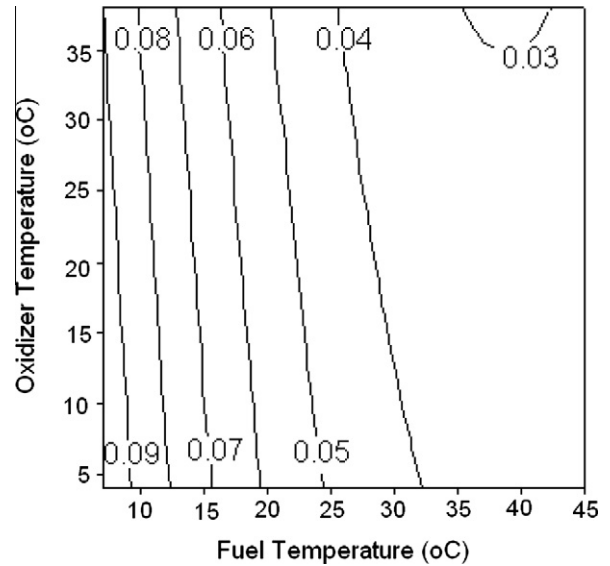
Catalyst mixture was tested and for safety reasons, fuel and especially hydrogen peroxide were not heated to more than 50 °C, as the decomposition rate increases with temperature.

These tests showed that the fuel/catalyst temperature has a strong effect on the ignition delay time. From the contour plot in Fig. 3, for a fixed fuel/catalyst temperature, the ignition delay time is almost constant when the oxidizer temperature is varied from 5 to 35 °C, indicating that the oxidizer temperature has almost no affect on the ignition delay. Therefore, if one wants to keep the ignition delay time less than 50 ms, fuel/catalyst mixture should be heated to an initial temperature higher than 25 °C while the oxidizer is at ambient temperatures. Therefore, for low ignition delay times, initial heating of the oxidizer is not required, only the heating of the fuel is sufficient. The data in Table 2 was correlated with the following equation, which is valid for temperatures in the range of 7 °C < T<sub>f</sub> < 45 °C and 4 °C < T<sub>ox</sub> < 38 °C.

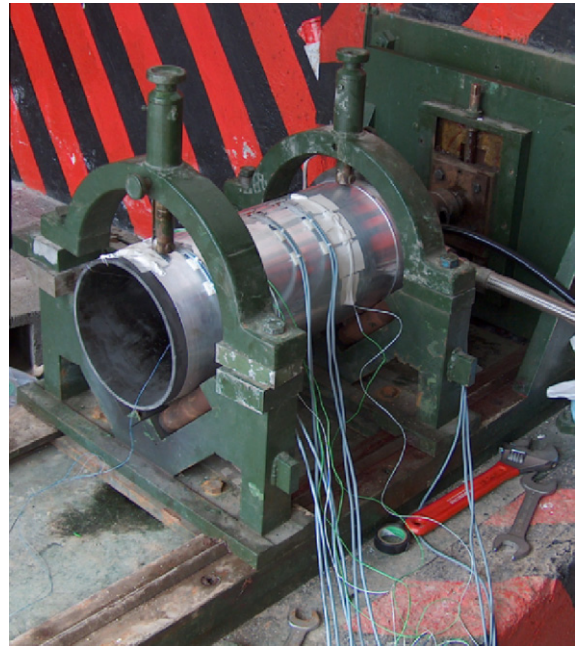
$$t_d(s) = 0.0432 - 0.0293T_f(^{\circ}\text{C}) - 0.004T_{ox}(^{\circ}\text{C}) + 0.0216[T_f(^{\circ}\text{C})]^2 \quad R^2 = 0.87 \quad (1)$$

### 3.2. Open atmosphere tests using the actual full-scale injector

Open atmosphere tests using the actual full-scale injector were conducted before the rocket engine tests. Injector tests provide a

**Fig. 3.** Temperature sensitivity of the ignition delay time for the liquid propellant from open cup drop test.

testing condition (i.e., enhanced mixing of the fuel and the oxidizer) that is closer to the combustion chamber of the actual rocket engine than that provided by open cup drop tests. In these tests, 20 L of Hydrogen Peroxide (85%) and 4 L of ethanolamine/10% CuCl<sub>2</sub> were fed through the unlike triplet impinging jet type injector into the open atmosphere and the ignition delay time (which is the time difference between the impinging of the propellant and the onset of the visible flame) was measured as 190 ms using high-speed camera. This unexpected long ignition delay with the full-scale injector could be a serious problem during the ignition stage of the rocket engine. Since there was no propellant flow rate throttling capability of our engine, as soon as the ball valves were opened, the engine would be fed with high propellant flow. There could be a significant amount of propellant accumulation in the engine during the ignition phase and the ignition of this propellant in

**Fig. 4.** LPRE mounted on the static test ramp.



the engine could cause over-pressurization, even a catastrophic failure. To prevent this in the actual engine firings, electrical blanket heaters were wrapped around the fuel tank for preconditioning the fuel to an initial temperature of 40 °C. In addition, a pyrotechnic igniter attached to the injector was used to prevent any over-pressurization.

### 3.3. Liquid propellant rocket engine tests

In the first engine checkout test, the operation of the hypergolic ignition supported with a pyrotechnic igniter was tested. Therefore no instrumentation was installed on the engine and no measurement was taken. Only a high-speed camera was used to see how LPRE operated. Overall, the test was very successful; the hypergolic ignition of the fuel and oxidizer was successfully achieved.

In the following ground tests (Test 2 and 3), the LPRE was instrumented with load cell and pressure transducers. The LPRE mounted to static test ramp is shown in Fig. 4. One pressure transducer was used to measure the combustion chamber pressure. Another pressure transducer was mounted at the cavitating venturi

exit. A load cell of 200 kN measuring capacity was used to measure the thrust generated by the LPRE.

Similar results were obtained from Tests 2 and 3. The measured pressure–time traces at the venturi exit and engine combustion chamber during Test 2 is given in Fig. 5. The thrust–time curve of the LPRE is given in Fig. 6. The test lasted about 1.7 s and during the test the average chamber pressure and thrust were about 30 bar and 18 kN, respectively.

An ignition delay time was defined as the time in which the chamber pressure reached 90% of the average chamber pressure during the initial pressure rising portion of the P–t trace. Based upon this definition, ignition delay time was deduced as about 130 ms from Fig. 5, which showed that there was a significant difference between this value obtained from rocket engine firings and the values from drop tests (~30 ms) when the fuel initial temperature was about 40 °C.

## 4. Conclusions

In this study, the hypergolic ignition of ethanolamine fuel catalyzed with  $\text{CuCl}_2$  and 85% hydrogen peroxide was demonstrated for the first time in a rocket engine application. The drop tests showed that the amount of catalyst and initial temperature of the fuel have a significant effect on the ignition delay of hydrogen peroxide/ethanolamine hypergolic bipropellant, whereas the oxidizer temperature seemed to have almost no effect on the ignition delay. Ignition delay time could be kept less than 50 ms if the fuel/catalyst mixture is heated to an initial temperature higher than 25 °C while the oxidizer is at ambient temperatures. A liquid propellant rocket engine using this green, non-toxic, and storable hypergolic bipropellant has been developed, manufactured, and successfully ground tested in this research project. The results from open cup drop tests and rocket engine static firings showed that there is a significant difference in the ignition delay times obtained from these two methods.

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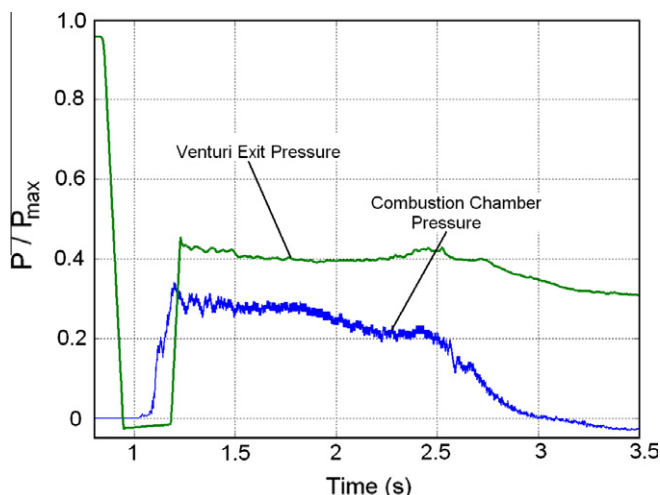


Fig. 5. Measured pressure–time traces in the combustion chamber and at the venturi exit (pressure values are normalized with respect to tank pressure of 100 bar).

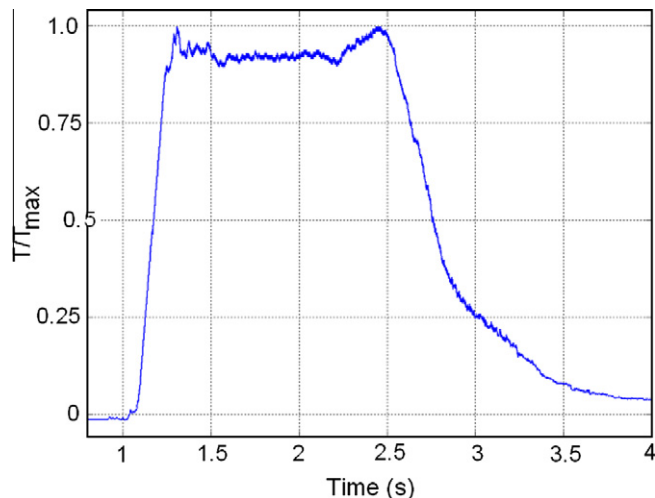


Fig. 6. Measured thrust–time curve of the LPRE (thrust values are normalized with respect to peak thrust value of 20 kN).