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Propulsive Performance of a Hypergolic H_2O_2/Kerosene Bipropellant

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Hydrogen peroxide (H_2O_2)/kerosene is a prospective bipropellant due to its high-energy content, high storage density, and environmentally benign properties. The possibility of making it hypergolic renders this option even more attracting. Self-ignitable H_2O_2/kerosene bipropellants were prepared by combining different candidate catalysts and promoters. Preliminary screening evaluations were conducted by using a dropping-test method. Propulsive performances of the combinations having passed satisfying dropping-test requirements were then investigated on a specially designed thrust engine. The results revealed that short ignition delay and reliable propulsion performances could be acquired in both steady-state and pulse-mode operations, and the combination of kerosene with additives and H_2O_2 of 90% concentration could still have good performances after 3 months storage time. It is expected that the combination of H_2O_2 and kerosene can be an efficacious alternative for storable toxic propellants used currently.

I. Introduction

In recent years, interest in green propellants has greatly increased to enhance safety and reduce costs for aerospace propulsion systems.[1] Among the propellants presently in use as well as under research, the combination of hydrogen peroxide with kerosene is promising due to its high-density specific impulse, long-term storage capability, and low toxicity, which are especially suitable for spacecrafts with on-orbit propulsion systems.

Hydrogen peroxide is a high-density liquid oxidizer with the unusual characteristics of being able to decompose exothermically into steam and oxygen.[2] The use of H_2O_2 as a propellant has a long history, which can be traced to the 1930s. With the successes attained in the production, transportation, and handling of high-concentration hydrogen peroxide, the search for green propellants with higher energies has motivated a renewed interest in storable propellants, especially those from combinations of H_2O_2 and kerosene.

A decade ago, the U.S. Air Force and U.S. Navy began to consider the use of H_2O_2/kerosene as a bipropellant in rocket propulsion systems.[3] From then on, extensive studies on the bipropellant technology using high-concentration rocket-grade hydrogen peroxide have been conducted. The operation of such an engine is a two-stage process. That is, H_2O_2 is first decomposed into a high-temperature and oxygen-rich steam as it comes in contact with a catalyst medium, then kerosene is injected, which can then be autoignited to release heat without the requirement of an ignition system. In this mode, heterogeneous catalysts, in particular silver-screen type catalyst systems, were employed. It was reported on the Internet that the forthcoming launching of the X-37 spacecraft by NASA, as well as the advanced technology vehicle (ATV) spacecraft developed by the Boeing Company, will all adopt such a propulsion system.

In addition to the mentioned process, H_2O_2/kerosene bipropellants also tend to be formulated as hypergolic. Additives containing salts of transition metals and combustible organic compounds, the former the catalyst and the latter the promoter, are added to kerosene. The catalyst, the promoter, and the complex formed by them are all soluble in kerosene to make the fuel homogeneous. The fuel is hypergolic with high-concentration hydrogen peroxide, the same as the well-known hypergolic bipropellant of nitrogen tetroxide and monomethyl hydrazine. A diagram of the thruster engines that use the two mentioned bipropellants is shown in Fig. 1.

To now, reports on hypergolic fuels are still rather scarce. The most noted one is the nontoxic hypergolic miscible bipropellant developed by Rusek et al.[4] in 1999. Rocket-grade hydrogen peroxide was used as the oxidant, and the nontoxic hypergolic miscible fuels were mainly based on alcohols and ketones. The fuels prepared in this way have rapid ignition capabilities. During firing tests with an open injector rocket thruster, hypergolicity was demonstrated on all of the oxidizer-to-fuel (O/F) ratios examined, and ignition times varied with the O/F ratio. Morlan et al. also reported on a homogeneous catalyst developed for 98% hydrogen peroxide.[5] The ignition delay for their open-cup test was 11 ms, but no firing test performances were given. In the 1990s, researchers[6] of the 801 Research Institute of the Aerospace Science and Technology Corporation of the People's Republic of China began to explore additives that could make kerosene self-ignitable with H_2O_2. Firing tests on a small test-piece thrust chamber revealed successful performances with normal startup, stable combustion, bright exhaust, and normal shutdown.

Since 1996, our research group at Dalian Institute of Chemical Physics of the Chinese Academy of Sciences has carried out basic catalytic studies on high-concentration hydrogen peroxide propellant systems. Besides developing heterogeneous catalysts with high activity levels, instant reactivities, and long life spans for H_2O_2 monopropellants,[7–11] we have also focused our attention on hypergolic H_2O_2/kerosene bipropellants with short ignition delays and good stabilities.[12,13] In this paper, the various approaches of exploring self-ignitable H_2O_2/kerosene bipropellants are presented, and the ignition and combustion performances by using a dropping-test equipment and a specially designed thrust engine are also reported.

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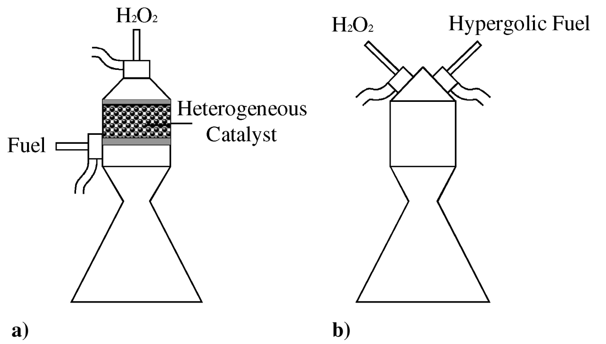

Fig. 1 Diagram of thruster engines for H_2O_2/kerosene bipropellants: a) catalytic ignition and b) hypergolic ignition.

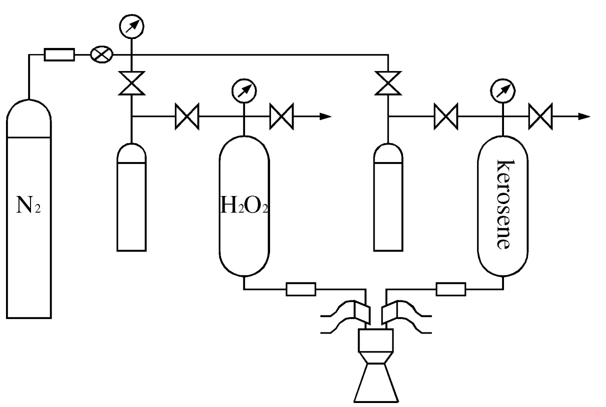

Fig. 2 Layout of bipropellant system.

II. Experimental

A. Bipropellant Composition

Nontoxic bipropellants prepared in this study involved a nontoxic hypergolic fuel and high-concentration hydrogen peroxide. The nontoxic hypergolic fuels consisted of three components, namely, a hydrocarbon fuel, which was the main component of the fuel and derived from Chinese standard 3 aviation kerosene or high-density rocket kerosene; a transition metal salt, which could react to form a catalyst soluble in kerosene; and an organic additive, which had good miscibility with the catalyst and the kerosene. The fuel complex so formed was highly miscible to render the fuel homogeneous. The high-concentration hydrogen peroxide used in our studies had a concentration of 90 or 96%.

B. Open-Cup Test or Dropping Test

Preliminary evaluations of the activities of the fuels were investigated with 96% H_2O_2 in an open-cup test. A small quantity of H_2O_2 was first placed inside a small stainless plate. A drop of the fuel mixture was then added to the H_2O_2, and the reaction phenomena were examined. Those candidate fuel mixtures that exhibited hypergolicities without any delay were then chosen as potential samples for future thruster tests.

C. Firing Tests on Rocket Thruster

Firing tests on a rocket thruster were then conducted to investigate the combustion characteristics of the bipropellants. A flow chart of the firing test process is given in Fig. 2. The evaluation equipment consisted of a pressurized feed system, a hydrogen peroxide tank, a kerosene tank, a bipropellant rocket thruster, and a computer monitoring system. The rocket thruster was specially designed and fabricated by the Aerospace Science and Technology Corporation of the People's Republic of China. The main design characteristics were as follows: The vacuum thrust was 30 N, the chamber pressure was 0.8 MPa, and the characteristic length was 0.8 m. The kerosene fuel and the H_2O_2 were stored in separate tanks. Under the pressure of high-purity nitrogen, the two feeds were compressed to the combustion chamber to contact and ignite. Solenoid valves were used to control the rates of the feeds and their working modes, and three pressure sensors were used to measure the chamber pressure and the feed-line pressure. Accumulative average flow rates were measured with glass tube flowmeters. Two ignition delay parameters, designated separately as T_0 and T_{90}, were defined as the time in which the chamber pressure reached 4 and 90%, respectively, of the steady pressure during the pressure-building period. Rf describes the roughness of the pressure, and q_m represents the flow rate of the feed. The combustion efficiency η is calculated taking the corresponding pure kerosene as the reference. The concentration of hydrogen peroxide used was 90%.

III. Results and Discussion

A. Screening Results on Open-Cup Test

An ideal catalyst must remain in a uniform solution state in kerosene and have good ignition characteristics. In addition, it should also have good chemical stability and should be non-reactive in air. Small amounts of suitable Mn(II), Mn(III), Co(II), Co(III), Fe(III), and Pd(II) salts were selected to add into the kerosene. These salts are soluble, but their solubility is fairly low. Open-cup tests with suspended solutions were conducted first. Among the tested salts, it was found that Mn(II), Mn(III), and Co(II) salts exhibited very high activity levels for ignition. Then the upper layer clear solutions were scrutinized. Decomposition phenomena were observed in all samples, but no combustion occured. These results suggested that the tested Mn(II), Mn(III), and Co(II) salts had suitable catalytic activity, but their solubilities in kerosene had still to be improved. Thus, the next key problem was to select suitable additives to increase the miscibilities of the catalysts and the kerosene.

Organic additives were chosen from compounds of alcohols, amines, and aromatic hydrocarbons. With the addition of these organic additives, homogenous fuels containing a certain amount of Mn(II), Mn(III), and Co(II) salts separately or in combinations were successfully prepared. Open-cup tests were then conducted, and typical results are shown in Table 1. The screening results showed that by choosing suitable catalysts and organic additives, it was possible to make kerosene hypergolic with high-concentration hydrogen peroxide.

B. Firing Tests on Rocket Thruster

Firing tests on a rocket thruster were conducted to obtain the detailed startup and combustion characteristics. A representative steady-state performance approximating the designed chamber pressure is shown in Fig. 3. The startup and ignition were normal, and

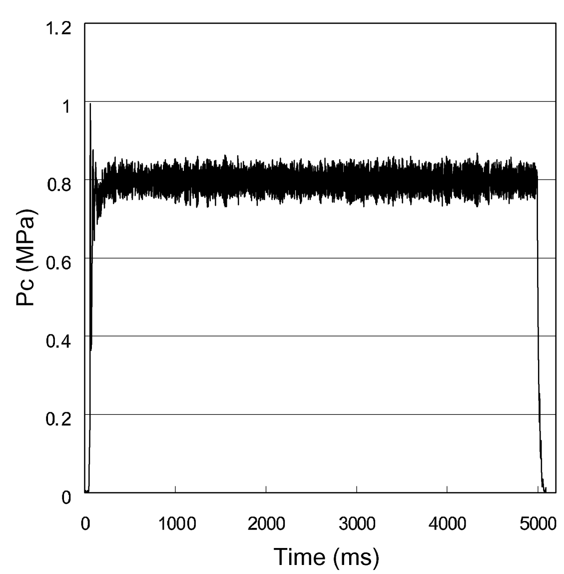

Fig. 3 Steady-state performance of thruster firing test with cold startup: H_2O_2: 90%, q_o = 15.2 g/s, q_f = 2.49 g/s, F/O = 6.1, η = 97%, and Rf = ±7.5%.

Table 1 Screening results of open-cup tests[a]

Fuel number	Active metal	Result
522-4	Mn(III)	Instantaneous ignition, flame stable, loud sound
522-9	Mn(III)	Fast reaction, then ignited a moment later
614-3	Co(II)	Fast reaction, then ignited a moment later
614-4	Co(II)	Fast reaction, instantaneous ignition
614-6	Co(II)	Fast reaction, instantaneous ignition
614-8	Co(II)	Fast reaction, then ignited a moment later
630-1	Mn(III)+Co(II)	Fast reaction, then ignited a moment later
109-17	Mn(III)+Co(II)	Instantaneous ignition, flame stable
108-7	Mn(II) +Co(II)	Fast reaction, then ignited a moment later
1010-26	Mn(III)+Co(II)	Instantaneous ignition, loud sound

[a]High-concentration hydrogen peroxide of 96%.

Table 2 Propulsive performances in steady-state operation[a]

Number	Time, s	q_{mo}, g/s	q_{mf}, g/s	O/F ratio	P_c, MPa	ΔP_c, $\pm$%	η, %	T_0, ms	T_{90}, ms
1	9.8	15.94	2.65	6.0	0.80	6	92.1	35	94
2	8	18.98	2.76	6.9	0.80	9		31	113

[a]Hydrogen peroxide concentration of 90%.

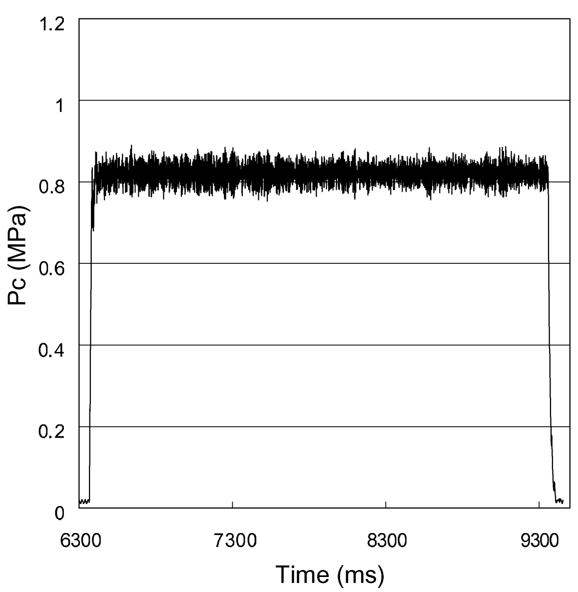

Fig. 4 Hot steady-state performance: H_2O_2: 90%, q_o = 15.7 g/s, q_f = 2.49 g/s, F/O = 6.3, η = 96%, and Rf = $\pm$7.5%.

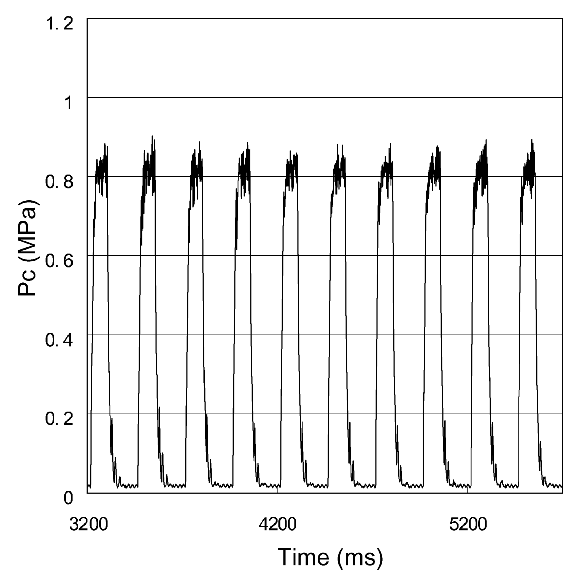

Fig. 5 Following a steady-state operation of 5 s, 100-ms pulse-mode performance.

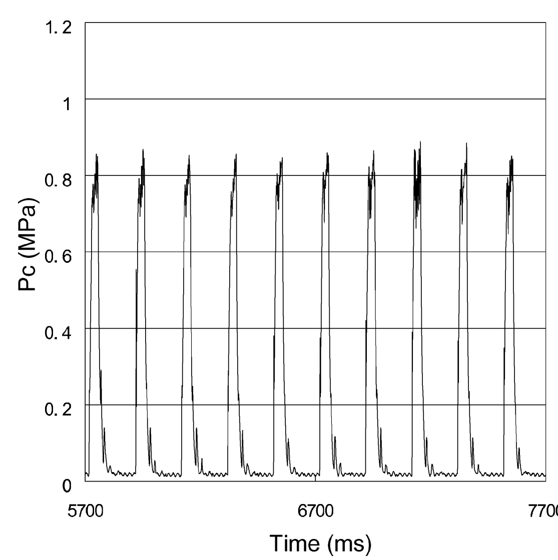

Fig. 6 Following a steady-state operation, 50-ms pulse-mode performance.

only a small startup pressure peak was identified. T_{90}, a key parameter expressing the characteristics of firing tests on thrusters, was quite short, only about 108 ms. The performance was quite good, giving a combustion efficiency of about 0.97. Some other steady-state performances with much longer working times are given in Table 2. It can be seen from these results that reliable ignition and stable combustion performances were also evidenced.

Because one possible application for the present propellant combinations is for attitude control of spacecraft, performance under hot steady-state and short-pulse mode is of great importance. The performance of hot steady-state operation following a steady-state operation of 5 s at the designed pressure is presented in Fig. 4. It can be seen that no startup pressure peaks appeared, and the pressure was stable at the designed pressure. Both T_0 and T_{90} were quite short, equal to about 19 and 35 ms, respectively. The performance under a 100-ms pulse mode is shown in Fig. 5, which signified that the ignition was rather stable and repetitive. The performance of an even shorter pulse mode of 50 ms is shown in Fig. 6. In this case, a pressure flat of about 20 ms emerged on the pressure curve.

Preliminary storage evaluation has also been conducted over a fuel sample after a 3 months storage period. Comparative ignition and combustion characteristics were observed, indicating that the

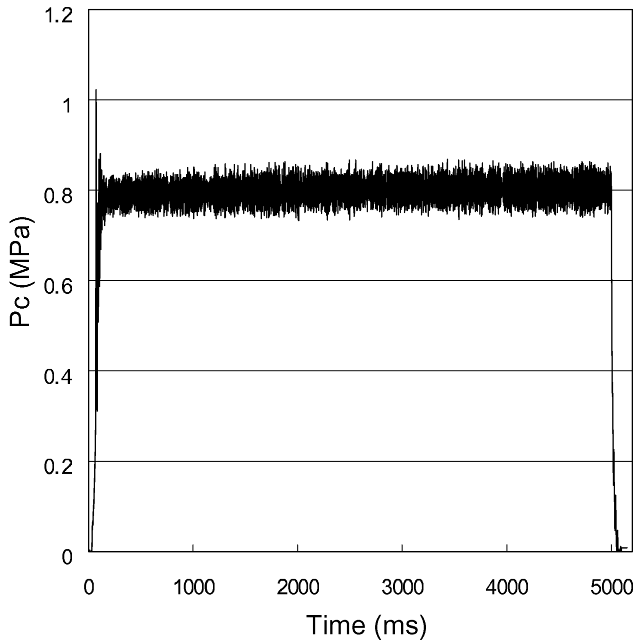

Fig. 7 Ignition performance after three months storage life with cold startup: H_2O_2: 90%, q_o = 16.1 g/s, q_f = 2.54 g/s, F/O = 6.3, η = 93%, and Rf = ±7.9%.

hypergolic fuel did not show any degradation over after being stored for three months, as shown in Fig. 7.

IV. Conclusions

Based on results of open-cup tests and firing tests, it can be concluded that, by utilizing high-concentration (90%) hydrogen peroxide and additive-added kerosene, it is feasible to prepare self-ignitable propellant combinations. Green and nontoxic hypergolic H_2O_2/kerosene bipropellants are promising candidates as effective alternatives for toxic propellants currently in use.

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