Combustion and Detonation Control
by in-Situ Blending of Liquid Fuels

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Jet propulsion kerosene and hydrogen peroxide are the promising compounds for applications in advanced propulsion systems. Flammability and detonability of sprays and vapors of kerosene and hydrogen peroxide were shown to differ essentially. When mixed with air together and in proper amounts, they can be readily detonated by a relatively weak ignition source. Hybrid combustion of hydrocarbon and hydrogen peroxide droplets has been studied in detail.

1. Introduction

The operational ability of air-breathing propulsion engines (both in deflagration and detonation modes) is considerably dependent on the fuel used. One of the promising solutions to actively control combustion or detonation is to inject several liquid fuels into a combustion chamber. The study particularly implies the use of two liquid fuels: conventional kerosene and hydrogen peroxide. Detailed description of hydrogen peroxide applications in various types of propulsion devices can be found elsewhere [1–3].

The main objective of the research was to analyze the reactivity and performance stability of the fuel blends in terms of the critical initiation energy of detonation, combustion and detonation parameters and their sensitivity to ambient conditions, specific impulse, ignition delay, and combustion of droplets.

2. Previous Accomplishments

Flammability and detonability of air mixtures (both gas-phase and heterogeneous) of hydrocarbon fuels (*n*-heptane, *iso*-octane, and *n*-tetradecane) with hydrogen peroxide was studied theoretically in [4–7]. According to [8], the listed hydrocarbons approximately represent jet propulsion kerosene (It is known that kerosene can be considered to be made up of approximately 79% high *n*-alkanes, 10% cycloalkanes and 11% aromatics). The following results have been obtained:

(1) The flame velocity in suspensions of *n*-heptane droplets in air with addition of H_2O_2 vapor increases with the concentration of H_2O_2 vapor in the mixture, in spite of the fact that the initial concentration of oxygen in the mixture decreases. Addition of H_2O_2 vapor to kerosene–air mixture allows to significantly increase the energy density of the burning material due to increase of the amount of kerosene required for complete burnout in the unit volume.

(2) It has been shown that detonability of kerosene – hydrogen peroxide blends increases significantly with the content of H_2O_2. In terms of the critical initiation energy, the kerosene–air mixtures with 5% and 20% of hydrogen peroxide were shown to be equivalent to stoichiometric ethylene–air and hydrogen–air mixtures, respectively.

(3) Detonation parameters (velocity D_0, temperature and pressure) of kerosene–H_2O_2–air mixtures were shown to be almost independent of the molar fraction of H_2O_2, that is important for performance stability of advanced propulsion systems.

(4) It has been found that addition of H_2O_2 vapor to the hydrocarbon–air mixture results in increase of the specific impulse I_{sp}. This effect becomes apparent at molar concentrations of H_2O_2 exceeding 10%.

3. Combustion Chemistry

To study the behavior of kerosene – hydrogen peroxide blends there is a need in kinetic mechanisms of their mutual oxidation. During previous studies [9, 10], the overall reaction mechanism of hydrocarbon fuel oxidation with regard for addition of H_2O_2 aimed at ignition promotion were developed and verified.

To verify the applicability of the reaction mechanisms to modeling combustion of fuel blends containing considerable amounts of H_2O_2, a set of calculations was made for laminar flame propagation in gaseous mixtures containing H_2O_2 and N_2. As a

reference, a detailed reaction mechanism of H_2O_2 decomposition was used. A reasonable agreement of the predicted results based on the overall and detailed reaction mechanisms was obtained.

The overall reaction mechanism for gaseous mixtures containing a hydrocarbon fuel, H_2O_2 and air is presented in Table 1. The mechanism includes soot, NO and CO formation chemistry.

4. Mathematical Model of Droplet Combustion

The mathematical model considers a single-component liquid droplet in the unconfined initially quiescent gaseous atmosphere. The droplet size is allowed to vary in time due to thermal expansion and liquid gasification processes. Droplet surface is treated as the moving boundary. In general, all physical properties of liquid and gas are pressure and temperature dependent. The constant-pressure approximation with independent diffusion of species in gas phase has been adopted. The set of governing equations includes full equations of thermal conductivity in both phases, continuity and species conservation equations in a gas phase, and the ideal equation of state for gaseous species. Radiation heat loss has been also taken into account.

Two types of droplet ignition procedures were used: (1) ignition by adopting a time-varying activation energy of a rate-controlling gas-phase reaction of hydrocarbon decomposition, and (2) ignition by making a provision of an ignition kernel — a narrow high-temperature zone occupied by combustion products. The behavior of a droplet was found to be fairly independent of the ignition procedure.

5. Combustion of a Single Droplet in Air
5.1 Hydrocarbon Droplet

As reference hydrocarbons, n-tetradecane and n-heptane were considered. Figure 1 shows the comparison of predicted $d^2 - t$-curves for droplets of initial diameter 30 μm. Obviously, n-heptane droplet exhibits higher combustion rate (1.2 mm²/s) than n-tetradecane droplet (0.95 mm²/s). The combustion constant K_{comb} was found to decrease with pressure and with droplet size.

5.2 Hydrogen Peroxide Droplet

Figure 2 shows the predicted histories of the radius of a H_2O_2 droplet of initial diameter 50 μm at pressure p_0 = 5, 10, 20 and 50 bar. The ambient air temperature is T_0 = 1000 K. Initially, the temperature of the droplet is 300 K and no H_2O_2 vapor is present in the ambient air.

With pressure increasing, the droplet lifetime decreases and the rate of droplet surface regression increases, that is different from the behavior of hydrocarbon droplets. At low pressure, the droplet lifetime exceeds 10 ms and the highest attained combustion temperature is 1060 K. Increase in pressure to 10 bar results in shortening the droplet lifetime to 10 ms and increase in the combustion temperature to 1400 K. Further increase in pressure to 20 and 50 bar results in a decrease of the droplet lifetime to 8 and 7 ms and in increase in the combustion temperature to 1700 K and 1800 K, respectively. Examining the $d^2(t)$ plot for the H_2O_2 droplet at $T_0 = 1000$ K and $p_0 = 50$ bar results in the following. Most of the lifetime the droplet evaporates at low rate ($K_{evap} \approx 0.04$ mm²/s). After ignition of H_2O_2 vapor accumulated in the vicinity of the droplet, the rate of surface regression increases by two orders of magnitude and becomes very large ($K_{comb} \approx 3.0$ mm²/s). Note that droplets of hydrocarbons exhibit $K_{comb} \approx 0.6$–1.5 mm²/s depending on droplet size and pressure.

The effect of droplet diameter on combustion intensity of a single H_2O_2 droplet is illustrated by Table 2. Small droplets have shorter lifetime and exhibit smaller combustion rates. A droplet of $d_0 = 10$ μm has low combustion temperatures (less than 1020 K) due to relatively low concentration of H_2O_2 vapor in droplet vicinity. The maximum combustion temperature at $d_0 = 20$ μm is 1340 K. With increasing the initial droplet size to 30 and 50 μm the maximum combustion temperature grows to 1600 K and 1800 K, respectively.

6. Hybrid Combustion

The term 'hybrid combustion' adopted here means (1) combustion of a hydrocarbon droplet in air mixed with H_2O_2 vapor, (2) combustion of a H_2O_2 droplet in air mixed with hydrocarbon vapor, or (3) combustion of a hydrocarbon droplet in hot exhaust gas mixed with H_2O_2 vapor. Such a study is expected to provide a valuable information on the reactivity of the two liquid fuels injected simultaneously into a combustion chamber.

6.1 Hydrocarbon droplet in air–H_2O_2 vapor mixture

Figure 3 shows the histories of the n-heptane droplet radius depending on the volume fraction of H_2O_2 vapor in air. In all the cases, the initial droplet diameter is 50 μm, initial droplet temperature 300 K, and ambient pressure $p_0 = 20$ bar.

It follows from Fig. 3 that addition of H_2O_2 vapor to the gas phase results in a significant transformation of n-heptane droplet behavior. With addition of 5% and 10% (vol.) of H_2O_2 vapor, the lifetime of the droplet decreases from 6 ms to 2 ms and 1 ms, respectively. Moreover, under the specified conditions, the n-heptane droplet simply evaporates rather than burns in pure air.

Figure 4 shows the example of the computed temperature histories during droplet combustion. Droplet ignition is promoted by the localized ignition of H_2O_2 vapor. Ignition of the vapor results in subsequent laminar flame propagation in the gas phase outwards of the droplet surface. The flame has an unusual double-front structure. The forward part of the flame propagates through H_2O_2 vapor. Oxygen formed due to decomposition of H_2O_2 is then consumed in oxidation reactions of n-heptane vapor. The temperature rise in the forward flame is about 400 K. In the subsequent flame, temperature increases by about 2000 K. The apparent flame velocity is 70 to 100 cm/s. The flame propagates in H_2O_2 vapor that gradually decomposes in the bulk. This is indicated in Fig. 4 by the growing level of temperature in front of the flame.

6.2 H_2O_2 droplet in air–hydrocarbon vapor mixture

Figure 5 shows the histories of the H_2O_2 droplet size depending on the volume fraction of n-heptane vapor in air. It follows from Fig. 5 that addition of n-heptane to the gas phase results in a significant transformation of H_2O_2 droplet behavior. With addition of 0.2% and 0.5% (vol.) of n-heptane vapor, the lifetime of the droplet decreases to 5 ms and 3 ms, respectively, that is much less than the lifetime of the H_2O_2 droplet in pure air (about 50 ms). Note that under the specified conditions, the H_2O_2 droplet evaporates rather than burns.

As an example of temperature histories, Fig. 6 indicates violent ignition and combustion of the H_2O_2 droplet in air with 0.5%(vol.) n-heptane vapor. Combustion of the H_2O_2 droplet is characterized by a relatively low combustion temperature (about 1600 K). In Fig. 6, there exists a gas-phase flame propagating outwards of the droplet at the velocity of 30–40 cm/s.

6.3 Hydrocarbon droplet in exhaust gas–H_2O_2 vapor mixture

Figures 7 and 8 show the development of the temperature field around the n-heptane droplet placed initially into the atmosphere of hot combustion products and H_2O_2 vapor. In both cases, the initial atmosphere does not contain free oxygen and is composed of CO_2, CO, H_2O, H_2, H_2O_2 and N_2.

Figure 7 is plotted for the test case when the initial molar concentration of H_2O_2 is 20%. Auto-ignition occurs in less than 10 μm (!) after starting the calculation. This happens due to extremely fast decomposition of H_2O_2 resulting in the formation of free oxygen that then reacts with hydrocarbon vapor. In the following, a hybrid flame is established in the system. The flame front propagates through the H_2O_2 vapor outwards of the droplet. Free oxygen produced in this flame is consumed by combustion reactions of n-heptane vapor delivered by the droplet evaporation process.

Decrease in the initial concentration of H_2O_2 from 20% (Fig. 7) to 10% (Fig. 8) results in a longer development of the hydrocarbon flame. The temperature rise in Fig. 8 is mainly due to combustion of H_2O_2.

A detailed study of such hybrid systems is continued. The objective of this study is to understand the underlying physics and chemistry of the encountered phenomena in order to elaborate the measures to control combustion and detonation of fuel blends.

7. Conclusion

In addition to accomplishments listed in Section 2, the following findings are to be mentioned:

(1) Droplets of H_2O_2 burn with a considerable temperature rise only at elevated pressures (> 5 bar) and at relatively large droplet size (> 30 μm). Combustion of fine H_2O_2 droplets at atmospheric pressure shows low exothermicity.

(2) Hybrid combustion of hydrocarbon fuel and H_2O_2 shows a great variety of phenomena. Three modes of hybrid combustion have been studied, namely, (1) combustion of a hydrocarbon droplet in air mixed with H_2O_2 vapor, (2) combustion of a H_2O_2 droplet in air mixed with hydrocarbon vapor, and (3) combustion of a hydrocarbon droplet in hot exhaust gas (with no free oxygen) mixed with H_2O_2 vapor. Such a study provides a valuable information on the reactivity of the two liquid fuels injected simultaneously into a combustion chamber. It has been proved, that hybrid combustion is much more efficient than combustion of single components in air.

The results will be used for elaborating improved strategies of active and passive control of combustion and detonation in advanced propulsion engines.

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Table 1: Overall reaction mechanism of hydrocarbon–H_2O_2 system

| N	Reaction	H, kcal/mol	Forward			Reverse		
			A, mol, l, s	n	E, kcal/mol	A, mol, l, s	n	E, kcal/mol
1[a]	$C_nH_{2n+2} + (n+0.5)O_2 = nCO + (n+1)H_2O$	614	$7.0 \cdot 10^{14}$	0.0	50.0			
2	$H_2 + H_2 + O_2 = H_2O + H_2O$	114	$7.0 \cdot 10^{13}$	0.0	21.0			
3	$CO + CO + O_2 = CO_2 + CO_2$	134	$8.5 \cdot 10^{12}$	0.0	21.0			
4	$H_2O + CO = H_2 + CO_2$	10	$1.0 \cdot 10^{12}$	0.0	41.5	$7.0 \cdot 10^{13}$	0.0	49.1
5[b]	$R + R + M = H_2O + M$	118	$9.5 \cdot 10^{12}$	-1.0	0.0	$7.0 \cdot 10^{13}$	-2.0	120.0
6	$R + H_2 + O_2 = R + R + R + 0.5O_2$	-4	$4.5 \cdot 10^{14}$	0.0	16.4			
7	$H_2O_2 = R + R + 0.5O_2$	-92	$5.0 \cdot 10^{15}$	0.0	50.0			
8	$O_2 + C_nH_{2n+2} + N_2 = C_nH_{2n+2} + NO + NO$	-43	$2.0 \cdot 10^{14}$	0.0	50.0			
9	$O_2 + N_2 = NO + NO$	-43	$1.7 \cdot 10^{17}$	-0.5	136.0	$7.0 \cdot 10^{13}$	-0.5	93.3
10[c]	$C_nH_{2n+2} + C_nH_{2n+2} = 2nC + (2n+2)H_2$	-2430	$4.0 \cdot 10^{12}$	0.0	50.0			
11	$C + C + O_2 = CO + CO$	394	$2.6 \cdot 10^{14}$	0.0	0.0			

[a]Reaction rate $W = k[C_nH(2n+2)][O_2]$

[b]R is the conditional radical

[c]C denotes soot

Table 2: Calculated values of the combustion constant K_{comb} for H_2O_2 droplets in air at $T_0 = 1000$ K, $p_0 = 50$ bar and initial droplet temperature of 300 K

| Droplet diameter, μm	10	20	30	50
Combustion constant K_{comb}, mm²/s	0.125	0.5	1.1	3.0
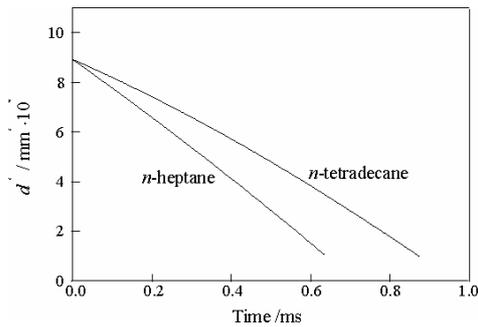
Figure 1: Comparison of predicted $d^2 - t$ plots for the case of combustion of similar n-tetradecane and n-heptane droplets in air ($d_0 = 30$ μm, $p_0 = $ 10 bar, $T_0 = $ 1000 K).
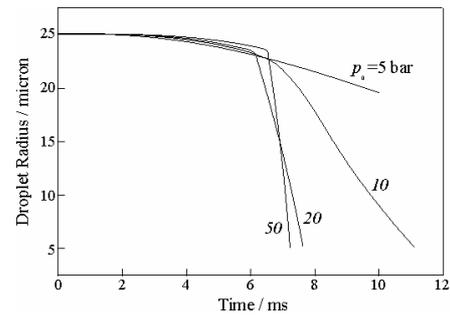
Figure 2: Predicted histories of H_2O_2 droplet radius during combustion at different ambient pressure: $p_0 = $ 5, 10, 20, and 50 bar. Initial droplet diameter 50 μm, ambient temperature $T_0 = $ 1000 K.
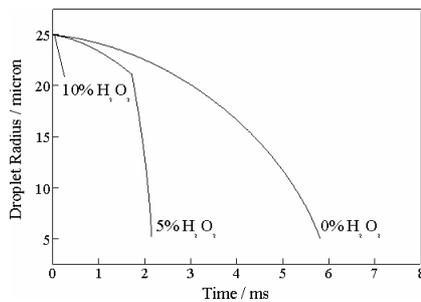

Figure 3: Predicted histories of n-heptane droplet radius during hybrid combustion in air mixed with various amounts of H_2O_2 vapor (10% (vol.), 5% (vol.) and 0%) at pressure $p_0 = $ 20 bar. Droplet diameter 50 μm,, ambient temperature $T_0 = $ 800 K.
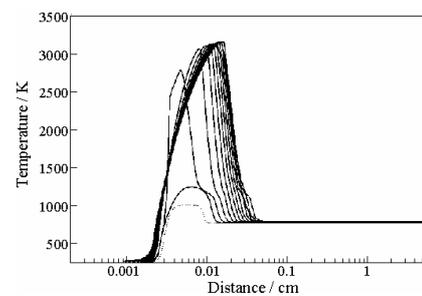
Figure 4: Temperature history for combustion of n-heptane droplet in air with addition of 10% (vol.) H_2O_2 vapor. Droplet diameter 50 μm, pressure $p_0 = $ 20 bar. Dotted line shows initial distribution of ambient temperature.
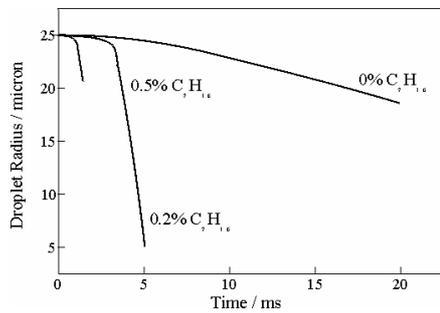
**Figure 5:** Predicted histories of H_2O_2 droplet radius during hybrid combustion in air mixed with various amounts of n-heptane vapor (0.5% (vol.), 0.2% (vol.) and 0%) at pressure $p_0 =$ 20 bar. Initial droplet diameter 50 μm, ambient temperature $T_0 = 800$ K.
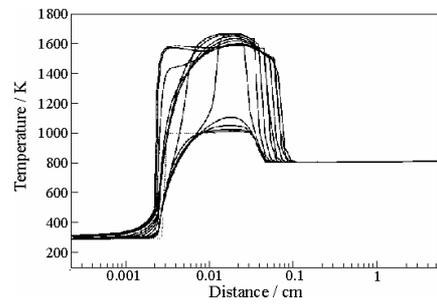
Figure 6: Temperature history for combustion of H_2O_2 droplet in air with addition of 0.5% (vol.) n-heptane vapor. Initial droplet diameter 50 μm, pressure $p_0 =$ 20 bar. Dotted line shows initial distribution of ambient temperature.
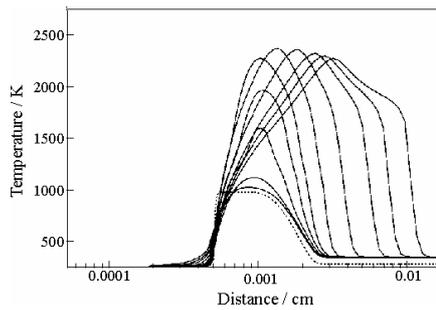
Figure 7: Development of the temperature field around an n-heptane droplet placed initially into the atmosphere of hot combustion products and H_2O_2 vapor (20%(vol.)). Initial atmosphere does not contain free oxygen, droplet diameter 10 μm, pressure $p_0 =$ 20 bar. Dotted line shows initial distribution of ambient temperature.
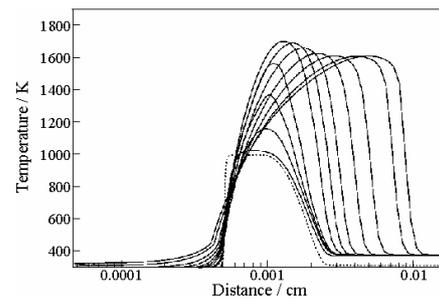
Figure 8: Development of the temperature field around an n-heptane droplet placed initially into the atmosphere of hot combustion products and H_2O_2 vapor (10%(vol.)). Initial atmosphere does not contain free oxygen, droplet diameter 10 μm, pressure $p_0 =$ 20 bar. Dotted line shows initial distribution of ambient temperature.

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