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Combustion of micron-sized aluminum particle, liquid water, and hydrogen peroxide mixtures

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ABSTRACT

The combustion of aluminum particle, liquid water, and hydrogen peroxide (H_2O_2) mixtures is studied theoretically for a pressure range of 1–20 MPa and particle sizes between 3 and 70 μm. The oxidizer-to-fuel (O/F) weight ratio is varied in the range of 1.00–1.67, and four different H_2O_2 concentrations of 0%, 30%, 60%, and 90% are considered. A multi-zone flame model is developed to determine the burning behaviors and combustion-wave structures by solving the energy equation in each zone and enforcing the temperature and heat-flux continuities at the interfacial boundaries. The entrainment of particles is taken into account. Key parameters that dictate the burning properties of mixtures are found to be the thermal diffusivity, flame temperature, particle burning time, ignition temperature, and entrainment index of particles. When the pressure increases from 1 to 20 MPa, the flame thickness decreases by a factor of two. The ensuing enhancement of conductive heat flux to the unburned mixture thus increases the burning rate, which exhibits a pressure dependence of the form $r_b = ap^m$. The exponent, m, depends on reaction kinetics and convective motion of particles. Transition from diffusion to kinetically-controlled conditions causes the pressure exponent to increase from 0.35 at 70 μm to 1.04 at 3 μm. The addition of hydrogen peroxide has a positive effect on the burning properties. The burning rate is nearly doubled when the concentration of hydrogen peroxide increases from 0 to 90%. For the conditions encountered in this study, the following correlation for the burning rate is developed: $r_b[\mathrm{cm/s}] = 4.97(p[\mathrm{MPa}])^{0.37}(d_p[\mu\mathrm{m}])^{-0.85}(\mathrm{O/F})^{-0.54}\exp(0.0066C_{H_2O_2})$.

1. Introduction

Aluminum–water ($Al–H_2O$) mixtures offer promise for various applications, including space and underwater propulsion, hydrogen generation, and fuel cell technology ([1–3]). The combustion of nano-aluminum particles in water has been extensively studied in the recent past ([1,3–6]). The burning rates surpass those of many energetic materials, such as ammonium dinitramide (ADN) and hexanitrohexaazaisowurtzitane (CL-20) ([1,7]). At a pressure of 1 MPa, the burning rate of stoichiometric 38 nm $Al–H_2O$ mixture is 4.5 cm/s, which is nearly twice that of ADN [1]. For a particle size range of 38–130 nm, the burning rate is inversely proportional to particle size and has a pressure dependence of the form $r_b = ap^m$, with the exponent, m, in the range of 0.27–0.68, depending on the consistency of the mixture ([1,5]). The low burning-rate pressure exponents are beneficial for rocket motor performance, since they mitigate combustion instabilities and prevent motor failures [8]. For an equivalence ratio of 0.71, the specific impulse efficiency of 80 nm aluminum and ice (ALICE) mixture varies between 27 and 64%, depending on the motor size (1.91–7.62 cm) [4]. The measured specific impulse is in the range of 56–133 s, significantly lower than theoretical counterparts. This can be attributed to low combustion efficiencies (43–69%), caused by low reaction temperatures, insufficient residence times, and agglomeration of particles [4]. The high oxide (Al_2O_3) content in the particle also contributes the low adiabatic flame temperatures of ALICE mixtures. For example, the oxide layer constitutes ~25% of the particle mass when the particle size reaches 80 nm and the adiabatic flame temperature is ~2850 K at a pressure of 1 MPa [1]. The energy density can be enhanced by replacing a portion of nano-aluminum particles with micron-sized counterparts ([9]), since the active aluminum content of micron-sized particles is nearly 100%. The burning rates, however, decrease by a factor of four when the loading density of micron-sized particles reaches 80% [9]. New methods to promote the performance of aluminum–water mixtures are necessary.

Hydrogen peroxide (H_2O_2) has been used as monopropellant and oxidizer in liquid propellant rocket engines (LPREs) for various applications including rockets, jet-assisted take off (JATO) aircrafts, and attitude control system (ACS) engines [10]. Table 1 shows a

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Nomenclature

A	pre-exponential constant
C	concentration (weight percentage of hydrogen peroxide in oxidizer)
C_p	specific heat
D	diffusivity
d_p	particle diameter
E_A	activation energy
h_{fg}	enthalpy of vaporization
i	stoichiometric fuel-oxidizer mass ratio
k	velocity-to-thermal diffusivity ratio
k_B	Boltzmann constant
L	flame thickness
MW	molecular weight
n	entrainment index
N_A	Avogadro's number
O/F	oxidizer-to-fuel weight ratio
p	pressure
Q_r	heat of reaction
r_b	burning rate
R	gas constant
T	temperature
v	velocity
x	spatial coordinate
X_{eff}	effective oxidizer mole fraction
Y	mass fraction

Greek

ρ	density
δ_v	vapor zone thickness
α	thermal diffusivity
λ	thermal conductivity
τ_b	burning time
ϕ	volume fraction
σ	molecular diameter

Subscript

ad	adiabatic
b	burn
d	diffusion
f	flame, fluid
g	gas
ign	ignition
k	kinetic
l	liquid
m	mixture
O	oxidizer
p	particle
R	reaction zone
u	unburned
V	vapor zone
v	vaporization
L	liquid zone

comparison of the thermophysical properties of hydrogen peroxide and water. They have similar properties; the heat of formation of hydrogen peroxide (−187.80 kJ/mol), however, is greater than that of water (−285.80 kJ/mol). Hydrogen peroxide is thus considerably more energetic than water. One of the main drawbacks of hydrogen peroxide is self-decomposition during storage. It decomposes to form water vapor and oxygen gas

$$H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2. \tag{1}$$

This process is enhanced by heat and catalyzed by impurities, water, and solid particles ([11,12]).

The addition of hydrogen peroxide to aluminum–water mixtures enhances the burning rates ([13,14]). Sabourin et al. [13] packed quasi-homogeneous mixtures of nano-aluminum particles, liquid water, and hydrogen peroxide in a quartz tube and measured the burning rates in an argon environment using an optical pressure vessel. The particle size was 38 nm and the active aluminum content 54.3%. The equivalence ratio was in the range of 0.50–1.25 and the concentration of hydrogen peroxide was varied between 0% and 35%. The concentration is defined as the weight percentage of hydrogen peroxide in oxidizer. For an equivalence ratio of 1.0 and pressure of 3.65 MPa, the burning rate increased by a factor of five, when the H_2O_2 concentration increased from 0 to 32%. Concentrations greater than 35% were not considered, due to an anomalous burning behavior characterized by over pressurization and rupture of the quartz tube. Zaseck et al. [14], similarly, measured the burning rates over a particle size range of 3–36 μm and H_2O_2 concentrations up to 90%. The oxidizer-to-fuel weight ratio was varied between 1.00 and 1.67. For a particle size of 19.86 μm and pressure of 6.9 MPa, the burning rate increased with increasing H_2O_2 concentration, from 0.43 cm/s at 30% to 1.38 cm/s at 90%.

Table 1
Thermophysical properties of hydrogen peroxide and water.

Property	Hydrogen peroxide	Water
Molecular weight (g/mol)	34.01	18.01
Density (g/cm^3)	1.45	1.00
Heat of formation* (kJ/mol)	−187.80	−285.80
Melting point (K)	272.72	273.15
Boiling point§ (K)	423.30	373.13
Heat of vaporization§ (kJ/kg)	1386	2260
Specific heat (kJ/kg-K)	2.36	4.18
Thermal conductivity (W/m-K)	0.46	0.58

* 298 K.
§ 1 atm.

For aluminum–water mixtures, nano-particles must be used to achieve self-sustained flame propagation [1]. The situation becomes substantially different when hydrogen peroxide is used instead of water [14]. The advantages of micron-sized aluminum particles are the high active aluminum content and low cost. The active aluminum content of micron-sized particles is ~100%, which is nearly twice that of 38 nm particles (~54%). As a result, substantial enhancements in the flame temperature are obtained. For example, at a pressure of 3.65 MPa, the adiabatic flame temperature increases from 2500 to 3000 K, when the particle size increases from 38 nm to 1 μm. The cost of nano particles is at least an order of magnitude greater than micron counterparts [14]. It is worthwhile to mention that the reactivity of aluminum particles increases marginally when the particle size decreases below 20 μm [15]. The burning time of nano-aluminum particles is a weak function of particle size; it decreases by a factor of four, when the particle size decreases from 10 μm to 100 nm [15]. For these reasons, micron-sized particles are attractive for energy-conversion applications ([9,14]).

The obtained enhancements in the burning rate can be attributed to the high energy density of an Al–H_2O_2 system,

$$2Al + 1.5H_2O_2 \rightarrow Al_2O_3 + 1.5H_2, \tag{2}$$

$$2Al + 3H_2O \rightarrow Al_2O_3 + 3H_2. \tag{3}$$

The heat of Al–H_2O_2 reaction is −1388 kJ/mol, which is nearly twice that of Al–H_2O counterpart (−813 kJ/mol).