

Kinetic Model for Aluminum-Sensitized Ram Accelerator Combustion

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The chemical nature of the projectile in a ram accelerator device can play a role in the ignition process. We focus here on aluminum. An Al/H/C/O kinetic model is proposed to examine the effect of the vapor pressure of liquid aluminum on the $H_2/O_2/CO_2$ ignition chemistry. These mixtures are of interest for the superdetonative propulsion mode in a ram accelerator device. The vapor pressure of liquid aluminum, as a film or as droplets, in the 1000–1300 K temperature range and in the 30–200 bar pressure range, although very weak (mole fraction of Al in the range 10^{-10} – 10^{-8}), is shown to reduce the $H_2/O_2/CO_2$ ignition delays in some cases by a factor two to three, depending on the conditions of temperature and pressure.

Introduction

NUMEROUS research activities are conducted worldwide on the development of hypervelocity laboratory launchers. One of them deals with an accelerator based on the principle of the airborne ramjet engine, which was first designed in 1983 at the University of Washington.¹

The feasibility of accelerating a projectile by this means was first experimentally demonstrated in 1986 with a 38-mm accelerator at the University of Washington,² followed in 1992 with 90 mm at ISL, French–German Research Institute of Saint-Louis,³ and in 1993 with 120 mm at the U.S. Army Research Laboratory.⁴ This type of launcher is called a ram accelerator (RAMAC). The key feature of this accelerator is that the projectile to be launched behaves as the centerbody of a conventional ramjet that moves at a supersonic velocity down a tube filled with a dense premixed explosive gaseous mixture. The biconical projectile centerbody, smaller than the launch-tube diameter, is coaxially centered in this tube by means of guiding fins for a smooth bore. An alternative configuration was also investigated at ISL, French–German Research Institute of Saint-Louis (hereafter ISL) in which the tube itself is fitted with rails and the projectile is a finless body.⁵ Because the projectile centerbody is undersized, whichever guiding means is used, a flow has to be established around it and combustion initiated and then stabilized on or at the vicinity of the afterbody situated downstream of the throat. This combustion zone results in an increase of pressure on the afterbody, thereby producing a forward thrust. Depending on the ratio of the projectile velocity V_{proj} to the theoretical Chapman–Jouguet detonation velocity of the gaseous mixture, D_{cj} (computed at local initial conditions at rest taken upstream the projectile nose), three basic propulsion modes have been identified,⁶ namely, thermally choked or subdetonative for $V_{proj} < 0.9D_{cj}$, transdetonative for $0.9D_{cj} < V_{proj} < 1.1D_{cj}$, and finally superdetonative for $V_{proj} > 1.1D_{cj}$.

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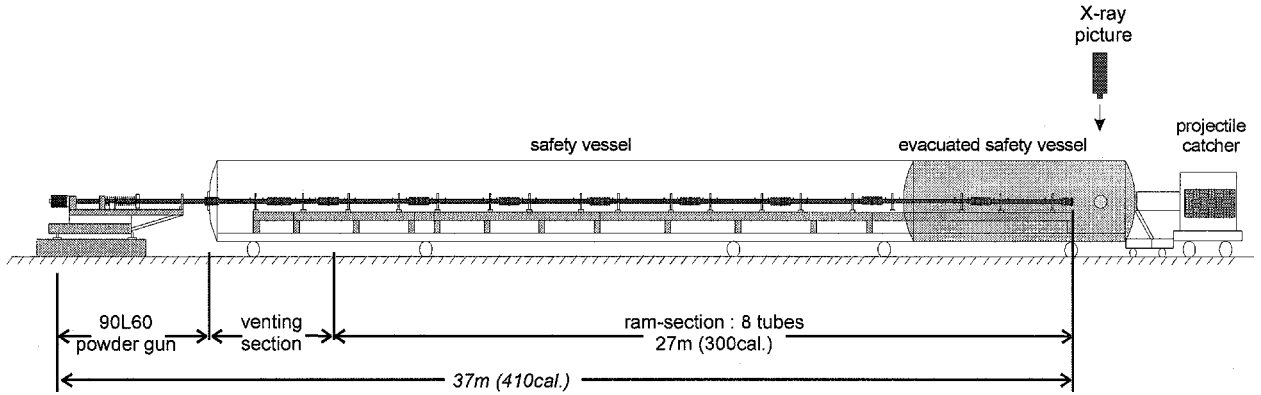
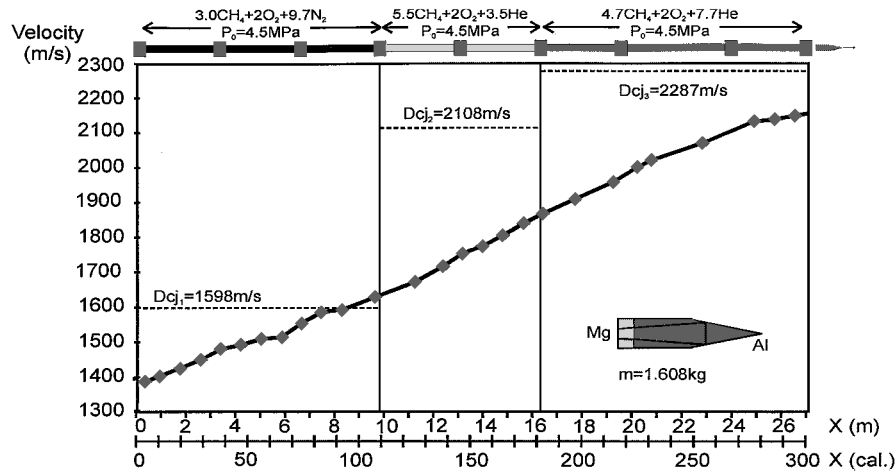
Among the numerous experimental conditions involved worldwide, two fuel types have been primarily investigated both experimentally and numerically, namely, methane and hydrogen. Fuel-rich methane-based mixtures diluted with nitrogen and helium have been successfully used at ISL in the thermally choked propulsion mode with the 90-mm-caliber smooth bore RAMAC 90 (Ref. 7).

A maximum exit muzzle velocity of 2180 m/s has been achieved using three different mixtures staged along a 27-m-long ram section.⁸ Figure 1 shows the latest experimental configuration, whereas Fig. 2 presents the velocity profile along the ram section and Table 1 summarizes the characteristics of the gaseous mixtures involved.

Chemical kinetics models were written for implementation in physical codes to simulate ignition delays and the resulting reacting flows as encountered during RAMAC combustion.^{9–13} Ignition delays, whatever the combustion regime is, have to be compatible with the projectile's speed and length to ensure the coupling between the projectile and the combustion. Yungster and Rabinowitz⁹ proposed a detailed methane/air mechanism. Petersen et al.¹² proposed and validated a kinetic model to simulate the CH_4/O_2 /diluant ignition delays at high pressure and simultaneously moderate temperature conditions,¹⁴ which are representative of the temperature and pressure reached before the ignition. Saurel,¹⁵ Leblanc et al.,¹¹ and Choi et al.¹⁶ followed the ISL experiments of Seiler et al.¹⁷ in the superdetonative regime and used $H_2/O_2/N_2$ or $H_2/O_2/CO_2$ kinetic models. Reduced kinetic models have also been proposed to simulate the RAMAC combustion process.¹⁸ From a chemical kinetic point of view, things are probably more complicated than generally believed. Indeed, it has been recently observed that the chemical nature of the projectile itself can play a role in the RAMAC process. Seiler et al.¹⁹ obtained sustained combustion with aluminum projectiles but not with steel projectiles. Veyssi re et al.,²⁰ based on experimental results obtained with the ISL 30-mm RAMAC, assume that metallic particles ablated from the projectile react with the gaseous mixture and modify the performance of the propellant mixture. Legendre and Giraud,⁸ by using projectiles with afterbodies of magnesium or aluminum or both also assumed that magnesium particles ablated from the projectile are able to provide a significantly greater forward thrust. Therefore, the nature of the projectile not only plays a role during the combustion process, because it has been observed that projectiles made of both aluminum and magnesium are severely damaged in some parts of the afterbody after firing,⁸ but also can play a role for ignition itself.

Table 1 RAMAC 90 experiment 1415/149: characteristics of the gaseous mixtures

Characteristic	Mixture composition		
	$3.0\text{CH}_4 + 2\text{O}_2 + 9.7\text{N}_2$	$5.5\text{CH}_4 + 2\text{O}_2 + 3.5\text{He}$	$4.7\text{CH}_4 + 2\text{O}_2 + 7.7\text{He}$
Initial pressure P_0 , MPa	4.5	4.5	4.5
Detonation velocity D_{cj} , m/s	1598	2108	2287
Sound velocity, m/s	362	478	552

**Fig. 1** ISL's RAMAC 90 experimental setup.**Fig. 2** RAMAC 90 experimental result 1415/149.

The study of the detonation structure around hypersonic projectiles has been extensively studied both experimentally by Kasahara and Arai,²¹ among others, and numerically in Refs. 16, 22, and 23 as have the detonation properties of the gaseous mixtures.^{24–28} The combustion of aluminum particles in various environments was also studied extensively since 1960 (references in Refs. 29–31), as well as the effect of aluminum particles on detonation propagation in H_2/O_2 /diluent mixtures.³² Following Ingignoli,³² the presence of aluminum particles modifies the detonation properties of H_2/O_2 /diluent mixtures. However, up to now, the effect of aluminum is far from clear in the case of RAMACs. Nusca¹³ tried to explain it numerically by assuming that the aluminum surface of the projectile plays a catalytic role, but this attempt was not successful. As noted by Nusca, accurate numerical simulations of RAMACs need a chemical kinetics mechanism. It is, therefore, interesting to investigate the chemical kinetics effects of aluminum on the ignition delays of H_2/O_2 /diluent mixtures, which are considered experimentally and numerically for the RAMAC superdetonativeregime. This superdetonativeregime is the only one that should lead to projectiles traveling at hypervelocities (up to 10 km/s). Detonation properties of dense methane-based mixtures to be used in RAMACs have been studied by Legendre et al.,²⁶ Legendre,³³ and Legendre et al.³⁴ It is also of interest to study the effects of aluminum atoms on the ignition delays of CH_4/O_2 /diluent mixtures.

The aim of this paper is to examine how the presence of aluminum can play a role in the ignition process. We will investigate the effect of the saturated vapor pressure of liquid aluminum as a flat surface, the projectile itself, and droplets of different sizes. For each mixture, it will be assumed that, locally around the projectile or around droplets ablated from the projectile, the temperature of the projectile or of the droplets is equal to the temperature of the surrounding gases. In that case, the pressure of Al in the gas mixtures cannot exceed the saturation pressure P_{sat} , and the mole fraction of Al, X_{Al} , is given by $P_{\text{sat}}/P_{\text{total}}$, where P_{sat} is the saturation pressure at T and P_{total} and where P_{total} is the applied pressure on liquid aluminum. The effect of T and P_{total} on P_{sat} will be examined for liquid Al as a flat surface or as droplets.

Effects of Pressure and Geometry on the Vapor Pressure of Liquid Aluminum

Nusca¹³ shows that the computed properties of the flowfields are essentially the same if the wall of the projectile is considered as catalytic or not. Therefore, we will examine the effect on H_2/O_2 ignition of the vapor pressure of the aluminum liquid surface of the projectile and also the effect of the vapor pressure of aluminum droplets, in the case of surface ablation. The mixtures under consideration are the ones obtained by mixing the vapor pressure of liquid

aluminum with the combustible mixture H_2/O_2 /diluent according to Dalton's law. Temperature and pressure ranges considered here are 1000–1300 K and 30–200 bar, respectively. These ranges are the ones expected to be representative of the conditions inducing ignition of the mixture considered. The saturated vapor pressure of liquid aluminum P^* is given by³⁵

$$\log P^* = 5.006 + 5.911 - 16211/T \quad (1)$$

between the melting point (933 K) and 1800 K, where P^* is in pascal and T in degrees Kelvin. Relation (1) holds above a flat liquid aluminum surface. However, as material removal occurs not only by vaporization but also by the expulsion of molten material, the saturated vapor pressure of liquid Al as droplets has to be considered. The saturated vapor pressure P of a liquid when it is dispersed as droplets of radius r is given by the Kelvin equation (see Ref. 36):

$$P = P^* \exp(2\gamma V_m / rRT) \quad (2)$$

with $V_m = M/\rho$, where $M = 26.9815 \times 10^{-3}$ kg/mol is the molar mass of Al, ρ (in grams per cubic centimeter) is the volumic mass of liquid Al given, between the melting point up to 1473 K, by³⁷ $\rho = 2.370 - 2.8 \times 10^{-4}(T - 933)$, and γ (in millinewtons per meter) = $865 - 0.12(T - 933)$ (Ref. 38) is the surface tension. P^*

Table 2 Effect of applied pressure ΔP on the saturated vapor pressure of a flat liquid Al surface (or as a droplet with a radius above 500 μm) at 1000 K and at 1300 K

Temperature, K	ΔP , bar	Saturated vapor pressure P' , Pa	P'/P^*
1000	1	5.08×10^{-6}	1
1000	100	5.15×10^{-6}	1.013
1000	200	5.22×10^{-6}	1.027
1300	1	2.80×10^{-2}	1
1300	100	2.82×10^{-2}	1.007
1300	200	2.86×10^{-2}	1.021

^a P' is saturated vapor pressure of a flat liquid aluminum surface when a pressure ΔP is applied at T and P^* is saturated vapor pressure of a flat aluminum surface under vacuum at T .

Table 3 Effect of the geometry on the saturated vapor pressure of liquid Al

Temperature, K	Radius r , μm	Saturated vapor pressure P , Pa	P/P^*
1000	500	5.10×10^{-6}	1.004
1000	20	5.72×10^{-6}	1.12
1000	1	5.41×10^{-5}	10.65
1300	500	2.80×10^{-2}	1.003
1300	20	3.06×10^{-2}	1.094
1300	1	0.17	6.097

Table 4 Al/C/O/H submechanism, $k = A \times T^n \exp(-\Theta/T)$ with $\Theta = E/R$ the activation temperature

Reaction ^b	A	n	Θ	Reference
$\text{Al} + \text{CO}_2 = \text{AlO} + \text{CO}$	1.74×10^{14}	0	3221	45
$\text{Al} + \text{O}_2 = \text{AlO} + \text{O}$	9.72×10^{13}	0	80.5	46
$\text{Al} + \text{O} + \text{M} = \text{AlO} + \text{M}$	3×10^{17}	-1	0	Estimated
$\text{AlO} + \text{CO}_2 = \text{OAlO} + \text{CO}$	1.5×10^{10}	0	-400	47
$\text{AlO} + \text{O}_2 = \text{OAlO} + \text{O}$	4.62×10^{14}	0	10008	48
$\text{Al} + \text{H}_2\text{O} = \text{H} + \text{AlOH}$	1.14×10^{12}	0	442.8	49
$\text{Al} + \text{H}_2\text{O} = \text{AlO} + \text{H}_2$	9.6×10^{13}	0	2868.6	49
$\text{AlOH} = \text{Al} + \text{OH}$	10^{15}	0	66431.8	Estimated ^a
$\text{AlOH} = \text{AlO} + \text{H}$	10^{15}	0	57725.2	Estimated ^a
$\text{AlOAl} = \text{AlO} + \text{Al}$	10^{15}	0	67035.7	Estimated ^a
$\text{OAlO} = \text{AlO} + \text{O}$	10^{15}	0	44564.6	Estimated ^a
$\text{AlOAlO} = \text{AlOAl} + \text{O}$	10^{15}	0	52466	Estimated ^a
$\text{AlOAlO} = \text{Al} + \text{OAlO}$	10^{15}	0	74937.1	Estimated ^a
$\text{AlOAlO} = \text{AlO} + \text{AlO}$	10^{15}	0	59335.7	Estimated ^a
$\text{Al}_2\text{O}_3 = \text{AlOAlO} + \text{O}$	3×10^{15}	0	49144.4	Estimated ^a
$\text{Al}_2\text{O}_3 = \text{OAlO} + \text{AlO}$	3×10^{15}	0	63915.4	Estimated ^a

^aRate constant is k_∞ . ^bUnits are $\text{cm}^3, \text{mol}^{-1}, \text{s}^{-1}, \text{K}$.

is the vapor pressure for a flat liquid surface and is numerically given by Eq. (1).

The effect of pressure on the saturated vapor pressure of liquid aluminum, flat surface, or as droplets, is given by

$$P' = P^* \exp(V_m \Delta P / RT) \quad (3)$$

where P' is the saturated vapor pressure of liquid aluminum when a pressure ΔP is applied and P^* the saturated vapor pressure of the liquid in the absence of an additional pressure. P^* is P^* , given by Eq. (1), when a flat liquid surface is under consideration or P , given by Eq. (2), when a droplet is under consideration.

Calculations show (Table 2) that the effect on the vapor pressure of the pressure ΔP applied on a liquid Al surface is rather weak because, whatever the temperature is between the melting point and 1300 K, the vapor pressure at 200 bar is only about 2% (at 1000 K and at 1300 K) higher than the saturated vapor pressure at 1 bar. In fact, the effect on the vapor pressure of the applied pressure can probably be neglected.

Calculations show (Table 3) that, whatever the temperature, the vapor pressure of liquid aluminum as droplets is significantly different, at least 10% higher, from the corresponding one for a flat surface only if the radius of the droplet is below 20 μm .

Real-Gas Effects

Bauer et al.³⁹ showed that real-gas effects have to be considered to improve the modeling of the performance of a RAMAC. This statement in fact does not apply to ignition delays, following Petersen et al.,¹² who only observed a difference of 3–5% between the ignition delays predicted with an ideal-gas solver and the ignition delays predicted with a real-gas solver, even at pressures of hundreds of atmospheres. The effect of Al on the ignition delays of H_2/O_2 /diluent and CH_4/O_2 /diluent mixtures has been studied here by using an ideal-gas version of CHEMKIN⁴⁰ in conjunction with the SENKIN⁴¹ code. For the calculations of ignition delays, the reactive mixture, considered as premixed, is assumed to be at a constant volume over its reaction time. The SENKIN code is used to compute ignition delays in static reactor and ignition delays behind plane detonation waves according to the Zeldovich, von Neumann, Döring (ZND) model. Thaker and Chelliah⁴² also demonstrated that the SENKIN code can be used reliably to predict ignition delays (or induction distance) behind oblique detonation waves.

Al/ H_2 / O_2 / CO_2 Reaction Mechanism and Thermochemistry

This mechanism consists of 53 reversible chemical reactions among 23 species. It is based on an Al/H submechanism proposed by Swihart et al.⁴³ and Swihart and Catoire⁴⁴ primarily devoted to the combustion of aluminum particles in HCl and relevant reactions from the less well-understood Al/C/O/H system. The Al/C/O/H

submechanism used here is given in Table 4 (see Refs. 45–49). It has to be added to one of the numerous H_2/O_2 mechanisms given in the literature. The Al/H submechanism may be found in Ref. 43. Some possible reactions are not included in the model, due to the lack of kinetic data and information on whether they can even occur, and this model cannot be considered as final. However, our goal here is not to examine the amounts of products formed by the reaction between Al atoms and the $\text{H}_2/\text{O}_2/\text{CO}_2$ system, but the influence of the Al atoms in terms of $\text{H}_2/\text{O}_2/\text{CO}_2$ ignition delays. Surface reactions are also not considered here because they are probably not important, as shown by Nusca.¹³

The CHEMKIN-II⁴⁰ and SENKIN⁴¹ codes were used to integrate the time-dependent rate equations derived from the reaction mechanism for a well-mixed mixture initially at a given initial temperature and at a given initial pressure. In the present study, the ignition delay time is numerically defined as the time at which the rate of temperature increase reaches its maximum, that is, dT/dt is maximum. Other criteria (pressure increase, OH formation) lead to the same ignition delay values. The thermodynamic properties for the Al-containing species have been calculated using ab initio quantum chemical methods.²⁹ The data for AlOH and the non-Al-containing species have been taken from the CHEMKIN-II library⁵⁰ or from the thermochemical tables of Burcat and McBride.⁵¹

Results and Discussion

Among all of the H_2/O_2 /diluent mixtures of interest, the mixture $\text{H}_2 + \frac{1}{2}\text{O}_2 + 4\text{CO}_2$ was considered for this study. For the mixture under consideration, it will be assumed that the mole fraction of aluminum, X_{Al} , is given by the ratio $P_{\text{sat}}/P_{\text{total}}$.

The ability of the H_2/O_2 submechanism, implemented in the Al/ $\text{H}_2/\text{O}_2/\text{CO}_2$ model used, to simulate reliable ignition delays has been demonstrated by Catoire et al.⁵² in $\text{H}_2/\text{O}_2/\text{Ar}$ mixtures. As far as we know, no experimental ignition delay data have been reported in the literature concerning the $\text{H}_2/\text{O}_2/\text{CO}_2$ mixtures. Such mixtures have been considered numerically for the superdetonative propulsion mode by Choi et al.¹⁶ following the experimental results obtained at ISL by Seiler et al.¹⁷

Typical temperature profiles computed are shown in Fig. 3. Basically, calculations show (Table 5) that about no effect at 1000–1100 K or a slight one above 1100 K is computed if one considers the saturated vapor pressure originating from a flat Al surface (the projectile itself, for instance, or droplets of liquid aluminum with a radius above 500 μm). This also holds for droplets with a radius above 20 μm . The Al pressures are too low, and the presence of Al atoms do not lead to significant reduction of the delays in the temperature and pressure ranges specified earlier. To focus on the fact that very small droplets can be ablated from the projectile surface, calculations have been performed with saturated vapor pressure consistent with droplets with a 1 μm radius for the mixture $\text{H}_2 + \frac{1}{2}\text{O}_2 + 4\text{CO}_2$ (Table 5). At an initial temperature of 1000 K, the promoting effect of the Al atoms is rather weak and weaker at 100 bar than at 30 bar. Moreover, at this temperature, no coupling between the combustion and a shock wave established on the projectile has to be expected due to too long ignition delays. At 1100 K, the promoting effect of the Al atoms is more important because the

ignition delay is reduced by a factor 1.7 at 30 bar and by a factor about 1.2 at 100 bar. At temperatures equal or above 1200 K, a relatively important promoting effect can be observed. At 1200 K and 1300 K, at 30 bar, the ignition delays are reduced by a factor about three (Table 5) whereas, at 100 bar, the ignition delays are reduced by a factor 1.5 at 1200 K and 1.9 at 1300 K. In fact, the reduction factor appears to increase with temperature, whatever the pressure. This can be of importance for RAMACs, especially for small (less than the order of 10 μs) ignition delays, where the coupling of shock wave and combustion zone is crucial. The proportions of Al in the mixture shown in Fig. 3 correspond to Al droplets of 1 and 20 μm radius. Figure 4 shows that the ignition delays can be reduced by a factor 2.5 at 1500 K and 100 bar. The proportions of Al in the mixture (mole fraction 6.1×10^{-7}) is the one corresponding to Al droplets of 1 μm radius.

Sensitivity analyses have been performed to search for the reactions responsible for the promoting effect observed. A brute force sensitivity analysis has been performed for one mixture by multiplying (and dividing) successively each rate constant by a factor of two. It was here focused on the reactions with aluminumized species. This study shows that the computed ignition delays are sensitive to the kinetics of the reaction $\text{Al} + \text{H}_2\text{O} = \text{AlO} + \text{H}_2$ (Fig. 3). McClean et al.⁴⁹ give for the rate constant of this reaction the following expression: $k(\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}) = (9.6 \pm 4.2) \times 10^{13} \exp[-(2868 \pm 453)/T]$, and therefore the factor two considered for the sensitivity analysis is coherent with the uncertainty reported by the authors. Moreover, the rate expression given by McLean et al. is

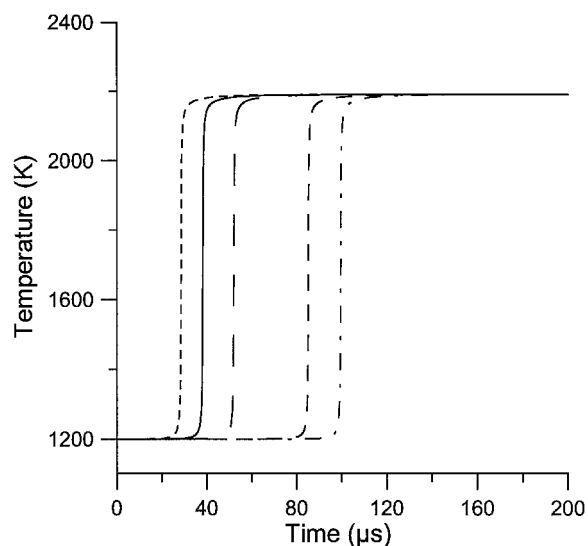


Fig. 3 Ignition delay: ---, no Al, $\tau = 100 \mu\text{s}$; - · -, mole fraction of Al = 9.3×10^{-10} ($r = 20 \mu\text{m}$), $\tau = 84 \mu\text{s}$; —, mole fraction of Al = 6×10^{-9} ($r = 1 \mu\text{m}$), $\tau = 37 \mu\text{s}$, rate constant for $\text{Al} + \text{H}_2\text{O} = \text{AlO} + \text{H}_2$ as given in Table 4; · · ·, mole fraction of Al = 6×10^{-9} ($r = 1 \mu\text{m}$), $\tau = 51 \mu\text{s}$, rate constant for $\text{Al} + \text{H}_2\text{O} = \text{AlO} + \text{H}_2$ divided by two; and - - -, mole fraction of Al = 6×10^{-9} ($r = 1 \mu\text{m}$), $\tau = 28 \mu\text{s}$, rate constant for $\text{Al} + \text{H}_2\text{O} = \text{AlO} + \text{H}_2$ multiplied by two.

Table 5 Ignition delays τ computed for the mixture $\text{H}_2 + \frac{1}{2}\text{O}_2 + 4\text{CO}_2$ with and without aluminum

Temperature, K	Pressure, bar	τ without Al, μs	τ with Al, μs (Al mole fraction) ^a	τ with Al, μs (Al mole fraction) ^b
1000	30	4400	4300 (1.9×10^{-12})	3600 (1.8×10^{-11})
1000	100	2000	2000 (1.7×10^{-11})	1900 (5.4×10^{-12})
1100	30	640	600 (5.5×10^{-11})	375 (4.26×10^{-10})
1100	100	380	380 (1.7×10^{-11})	320 (1.29×10^{-10})
1200	30	100	84 (9.3×10^{-10})	37 (6×10^{-9})
1200	100	88	85 (2.6×10^{-10})	60 (1.8×10^{-9})
1300	30	9	6 (10^{-8})	3.5 (5.6×10^{-8})
1300	100	21	20 (3×10^{-9})	11 (1.7×10^{-8})

^aConsistent with the vapor pressure of a 20- μm -radius droplet.

^bConsistent with the vapor pressure of a 1- μm -radius droplet.

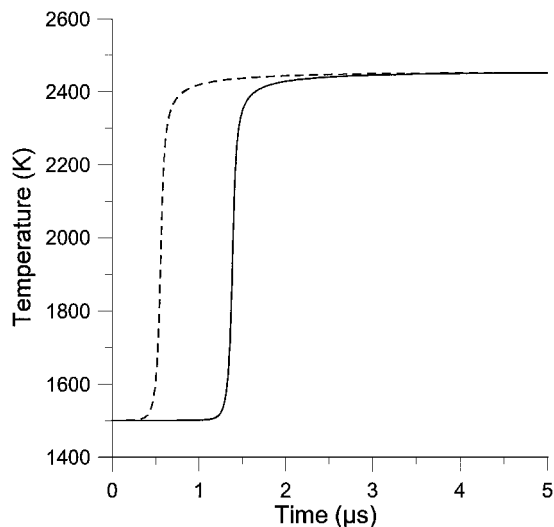


Fig. 4 Ignition delay: —, $\text{H}_2 + \frac{1}{2}\text{O}_2 + 4\text{CO}_2$ at 1500 K and 100 bar without Al and ---, $\text{H}_2 + \frac{1}{2}\text{O}_2 + 4\text{CO}_2$ at 1500 K and 100 bar with Al.

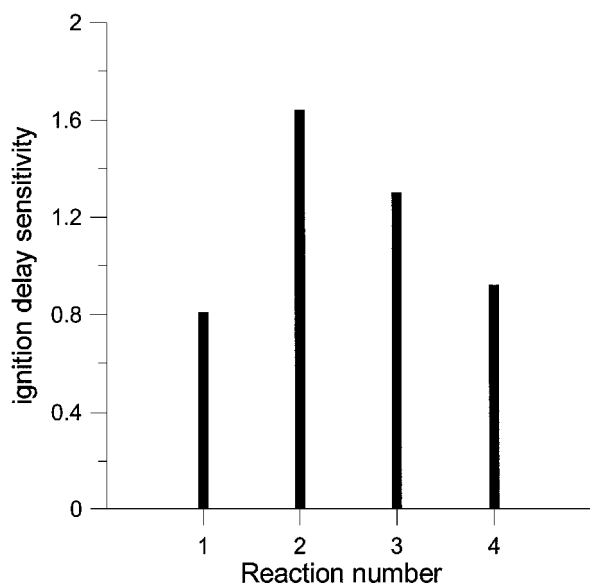


Fig. 5 Ignition delay sensitivity spectrum for the mixture $\text{H}_2 + \frac{1}{2}\text{O}_2 + 4\text{CO}_2$ with Al (mole fraction of Al = 6×10^{-9}) at initial temperature $T = 1200$ K and at initial pressure $P = 30$ bar.

valid (up to 1174 ± 100 K) in the 1000–1300 K temperature range considered here. Above 1300 K, the rate constant has been linearly extrapolated.

To check on the degree to which specific reactions are required, a sensitivity analysis was carried out in which each of the reactions was successively eliminated from the model. Once again, it was focused on the reactions with aluminized species. The corresponding sensitivity spectrum is given in Fig. 5. In Fig. 5 reaction 1 is $\text{Al} + \text{CO}_2 = \text{AlO} + \text{CO}$, reaction 2 is $\text{Al} + \text{H}_2\text{O} = \text{AlO} + \text{H}_2$, reaction 3 is $\text{Al} + \text{O}_2 = \text{AlO} + \text{O}$, and reaction 4 is $\text{AlO} + \text{CO}_2 = \text{OAlO} + \text{CO}$. The ignition delay sensitivity is defined as $(\tau - \tau_0)/\tau_0$, where τ_0 is the ignition delay computed with the full nonmodified model. The following catalytic sequence accounts for the chemistry of Al in $\text{H}_2/\text{O}_2/\text{CO}_2$ mixtures. AlO is produced by



and then reacts with H_2

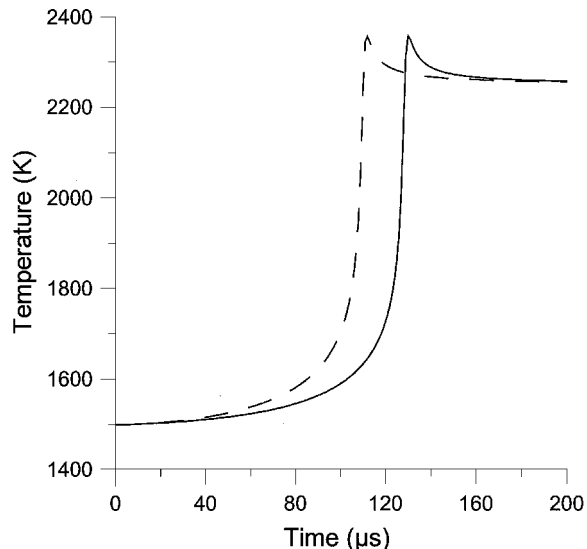
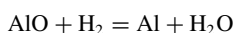


Fig. 6 Ignition delay: —, $3,2\text{CH}_4 + 2\text{O}_2 + 7.5\text{N}_2$ at 1500 K and 30 bar without Al and ---, $3,2\text{CH}_4 + 2\text{O}_2 + 7.5\text{N}_2$ at 1500 K and 30 bar with Al.

to form Al atoms. However, first-order sensitivity analysis shows that some other reactions also exhibit sensitivity toward the Al atoms because the O atoms produced by $\text{Al} + \text{O}_2 = \text{AlO} + \text{O}$ then play a role in the H_2/O_2 ignition kinetics through the important chain branching reactions $\text{H}_2 + \text{O} = \text{OH} + \text{H}$ and $\text{H} + \text{O}_2 = \text{OH} + \text{O}$.

This treatment can be also applied to the $\text{CH}_4/\text{O}_2/\text{N}_2$ mixtures. A significant reduction of the ignition delays can be expected. However, no kinetic data, neither experimental nor theoretical, exist for the reactions $\text{Al} + \text{CH}_4 \rightarrow \text{products}$, $\text{AlO} + \text{CH}_4 \rightarrow \text{products}$, or $\text{Al} + \text{N}_2 \rightarrow \text{products}$. However, the same Al/H/O/C chemistry as implemented in the H_2/O_2 kinetic model has been implemented by the Petersen et al. CH_4/O_2 kinetic model,¹² called RAMEC. This kinetic model has been validated with experimental high pressures and intermediate temperatures ignition delays of $\text{CH}_4/\text{O}_2/\text{diluant}$ mixtures. Computations show that the effect of aluminum on CH_4/O_2 combustion is rather weak in the 1000–1300 K temperature and 1–100 bar pressure range for the mixture $3,2\text{CH}_4 + 2\text{O}_2 + 7.5\text{N}_2$. No very important reduction in the ignition delay is computed at 1500 K and 30 bar (Fig. 6). The mole fraction of Al in the mixture (2×10^{-6}), shown in Fig. 6, corresponds to the saturated vapor pressure of Al droplets with a $1 \mu\text{m}$ radius at 1500 K. This is bound to the fact that the promotion is only due to $\text{Al} + \text{O}_2 = \text{AlO} + \text{O}$, through the formation of O-atoms, without the catalytic reformation of Al as described above for $\text{H}_2/\text{O}_2/\text{CO}_2$ mixtures. However, the kinetics of the $\text{Al}/\text{CH}_4/\text{O}_2/\text{N}_2$ system has to be further studied, both experimentally and theoretically, before one can expect more from this kinetic analysis.

Conclusions

This study shows that the vapor pressure of liquid Al, although very weak in the temperature and pressure ranges considered (up to a mole fraction of 10^{-8}), is able to reduce significantly the ignition delays of the $\text{H}_2/\text{O}_2/\text{diluent}$ mixtures. The nature of this promoting effect is shown to be kinetic more than thermal. However, this effect is much more important if liquid Al is dispersed as droplets of small radius in the hot gaseous mixtures behind the shock wave system established on the projectile. This shortening of the ignition delays is able to ensure the coupling between the oblique wave and the combustion zone needed in the superdetonative combustion regime or to induce an ignition delay compatible with the thermally choked propulsion mode. The kinetic models have to be implemented in physical-chemical models as described by Nusca,¹³ among others. The physical parts of these models need also some refinements (droplet formation, droplet vaporization, and combustion). In their present forms, the two described kinetic models are, however, too big to be implemented “as is,” and they need to be reduced up to a few reactions and species.

The achievement of successful RAMAC experiments with projectiles made of other metals not as convenient, for example, iron, however, can be obtained following the concept of active projectiles as described by Brandeis.⁵³

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