Use of Silane-Methane Mixtures for Scramjet Ignition

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Calculations have been made to demonstrate the use of silane-methane liquid mixtures as an ignition promoter and flame stabilizer in hydrogen- (or other) fueled scramjet applications. The calculations show that mixtures initially nonflammable undergo rapid methane evaporation to produce drops capable of spontaneous inflammation. This technique may be expanded to other spontaneously flammable materials. It was assumed that the liquid silane-methane mixture was sprayed into the combustion chamber upstream of the main fuel-flow positions. Drop size, flow velocity, temperature, and initial liquid mixture composition were varied.

Nomenclature

A = $0.6Pr^{1/3}Re_0^{1/2}$
B = drag parameter, 1/s; = $3\pi\mu_g D_0/m_0$
C_D = drag coefficient
C_1 = $\pi D_0 k_g M_b/m_0 \bar{C}_{pb}$
C_2 = $M_{si} p_R \bar{C}_{psi}/M_b \bar{C}_{pb}$
C_3 $M_{si} p_R L_{si}/L_b M_b$
$\bar{C}_{pb}, \bar{C}_{pa}$ = average specific heat of methane and silane, respectively; cal/g-mole-K
D_0 = initial droplet diameter, μm
$\bar{D}$ = local/initial diameter, dimensionless
H_b = $\bar{C}_{pb} T_0/L_b$, dimensionless
k_g = thermal conductivity, cal/s-cm-K
L_b, L_{si} = latent enthalpy of evaporation of methane and silane, respectively; cal/g-mole
M_b = molecular weight of methane, = 16
M_{si} = molecular weight of silane, = 32
m = droplet mass/m_0
m_b = mass of liquid methane/m_0
m_0 = initial mass of droplet, g
N_{bL} = mole fraction of methane in liquid phase
Nu = Nusselt number based upon diameter
p^0 = vapor pressure of pure phase, atm
p = actual vapor pressure, atm
Pr = Prandtl number
p_R = ratio of actual vapor pressure of silane and methane
R = gas constant, cal/g-mole-K
Re = Reynolds number based upon local diameter and relative velocity
Re_0 = Reynolds number based upon initial diameter and gas velocity
T_0 = ambient temperature, K
$\bar{T}$ = local droplet temperature/T_0
T_1 = T_0/boiling-point methane, = $T_0/111.5$
T_2 = RT_0/L_b
U = droplet velocity/gas velocity
u_g = gas velocity, cm/s
x = distance, cm
μ_g = viscosity coefficient of gas, g/cm-s

Subscripts

b = methane
si = silane

Superscript

0 = pure phase

Introduction

HYDROGEN, because of its rapid flame propagation and excellent cooling capability, is a very desirable fuel for supersonic combustion ramjet (scramjet) use. Hydrogen-air mixtures, however, do not necessarily ignite easily under conditions existing within a scramjet combustor. For this reason, some form of igniter or ignition promoter may be necessary.

One approach to the ignition problem has been the use of a spontaneously flammable mixture injected upstream of the hydrogen injection ports. The use of silane-hydrogen mixtures for this purpose is reported in Ref. 1. Mixtures containing 20% silane and 80% hydrogen were found to be ignitable and to burn in a stable manner. These mixtures, because they are spontaneously flammable and stored as a high-pressure gas, are difficult to handle.

Research at the University of Southern California[2] has shown that programmed ignition can be achieved through the use of liquid mixtures of a sensitive ignition promoter and a volatile diluent. By careful control of the choice of diluent, principally its vapor pressure, and initial mixture composition, a mixture that is not spontaneously flammable initially becomes flammable after the preferential evaporation of the diluent.

In order to examine this concept for scramjet applications, mixtures of silane and methane were examined theoretically. Silane was chosen as the ignition promoter because of existing data on its performance in Ref. 1. It is not necessarily the best promoter from either a handling effectiveness or cost consideration.

This paper is concerned with the behavior of silane-methane mixtures injected as a liquid spray into an environment typical of a supersonic combustor. It is assumed that the mixture is stored as a cryogenic liquid. Calculations are made to illustrate the conditions under which a transition occurs from a vapor that does not inflame rapidly to one which does and, therefore, acts as an ignition promoter and flame stabilizer.

Technical Discussion

In Ref. 1, data are presented that show the relationship between the silane-hydrogen ratio and the time delay for ignition. These data are reproduced in Fig. 1. The data show that the ignition delay increases slowly as the silane-hydrogen ratio decreases until a ratio of 0.02 is reached. At this point, the ignition delay increases very rapidly as the silane-hydrogen ratio is decreased further. In a sense, the silane-hydrogen ratio acts as a switch, being on at values above

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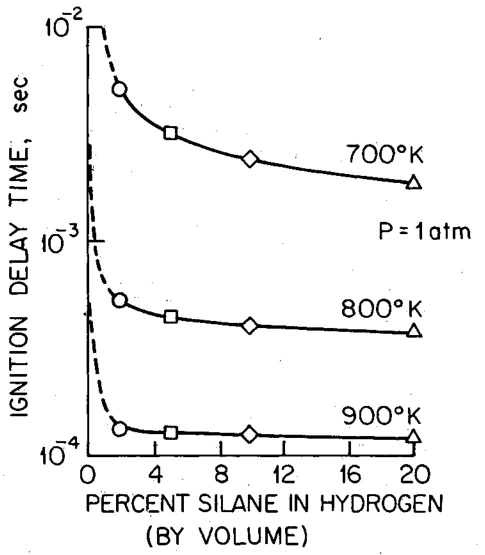

Fig. 1 Ignition delay time as a function of silane concentration. (Reproduced from Ref. 1.)

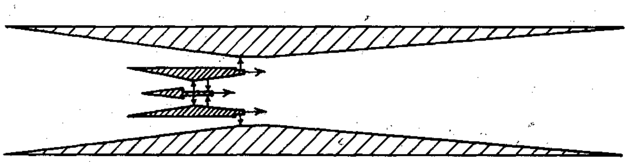

Fig. 2 Sketch of the system where silane is injected into the gas stream. (Reproduced from Ref. 1.)

0.02 and off at values below 0.02. Although, as shown in Fig. 1, the actual value of the ignition delay changes with ambient temperature, the critical value of 0.02 is relatively insensitive to temperature. Gases other than hydrogen would likely alter this critical value; however, it is not clear which direction. The use of diluents with a lower thermal conductivity than hydrogen would tend toward a lower critical value, while those of higher heat capacity would lead to a higher critical value.

Methane has a lower thermal conductivity than hydrogen and a higher heat capacity. In the absence of experimental data on silane-methane mixtures, we have selected 0.02 as the critical value for rapid ignition of silane-methane mixtures.

It is assumed that a liquid mixture of silane and methane is sprayed into the combustor airflow upstream of the primary fuel injection. The primary fuel may be hydrogen or any other suitable scramjet fuel, since only ignition of the additive stream and not the main fuel is considered in this paper.

As the silane-methane mixture evaporates, the methane evaporates first because its boiling temperature is 50 K lower than that of silane. If the initial mixture is chosen properly, the initial vapor concentration has a silane-methane ratio below 0.02. As methane evaporates the silane-methane ratio increases until it exceeds 0.02 and rapid ignition is assumed to occur. There is, of course, an ignition delay, but the mixtures with a silane-methane ratio below 0.02 have had an opportunity to sensitize the environment and, possibly, reduce this delay.

Once the drops ignite, the methane is quickly burned off and, effectively, a spray of burning silane serves as both an ignition source and flame stabilizer.

A schematic of a combustion chamber based on Ref. 1 is shown in Fig. 2. It is assumed that the liquid silane-methane spray is injected into the first injector station; typical injector stations are indicated by arrows. The spray is injected normal to the flow. It is possible that the point of spray injection could be moved further upstream since the initial cooling action of the spray prior to ignition would inhibit choking of the flow.

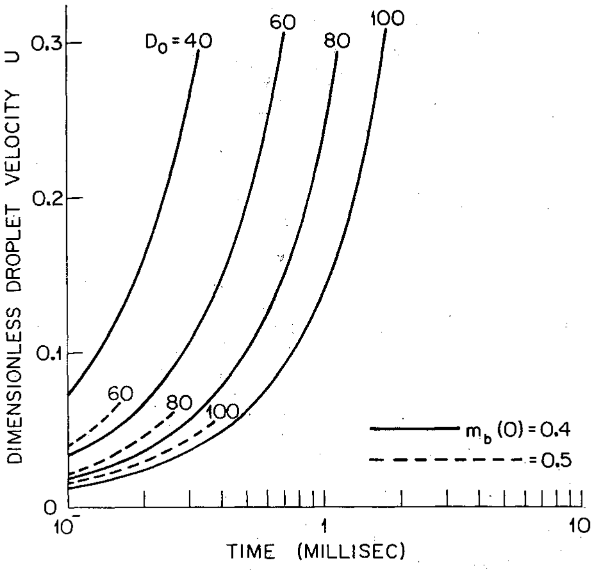

Fig. 3 Velocity history of droplets; 2000 m/s, 900 K, $C_D = 24/Re$.

Analytical Model

The model considers a single droplet of the methane-silane mixture undergoing evaporation in a one-dimensional moving medium. The ambient state and freestream velocity are typical of a scramjet combustor environment. The following assumptions are made:

1) The droplet evaporates at the saturation temperature of the ideal mixture remaining in the liquid phase. Thus, a quasi-steady-state evaporation follows.

2) The evaporation rate is given by the Ranz-Marshall correlation equation and, hence, depends upon the local relative velocity and the temperature difference between the droplet and the freestream.

3) Stokes' drag ($C_D = 24/Re$) is applicable for calculating the acceleration of a droplet. Since, strictly speaking, Stokes' drag is not applicable, drag coefficients 100% larger and half as small as that of Stokes' were also considered for studying the effect of drag.

4) The droplet retains its spherical shape even under a very large accelerating force.

5) Rapid ignition occurs when the mole fraction of *silane vapor* at the droplet surface exceeds 0.02.

6) The ambient condition is not affected by the process of evaporation.

7) Shock-wave interactions due to the presence of either the droplet or the combustor are ignored.

Using dimensionless variables (except for time and droplet location), the following equations describe the behavior of the system:

Energy:

$$\frac{\mathrm{d}m_b}{\mathrm{d}t} = -C_1\left\{\bar{D}[2 + A\sqrt{\bar{D}(1-\bar{U})}]/(1+C_2)\right\} \times \ln[1 + H_b(1-\bar{T})(1+C_2)/(1+C_3)] \quad (1)$$

X momentum:

$$\frac{\mathrm{d}U}{\mathrm{d}t} = B\bar{D}(1-U)/m \quad (2)$$

Droplet location:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = Uu_g \quad (3)$$

Droplet diameter:

$$\frac{\mathrm{d}\bar{D}}{\mathrm{d}t} = \frac{\bar{D}\mathrm{d}m}{\mathrm{d}t}\Big/ 3m \tag{4}$$

Droplet mass:

$$\frac{\mathrm{d}m}{\mathrm{d}t} = (1+2p_R)\frac{\mathrm{d}m_b}{\mathrm{d}t} \tag{5}$$

Equation (1) describes the evaporation of methane from the droplet at the mixture saturation temperature and includes the energy required to superheat the vapor from the saturation temperature to the ambient gas temperature. It incorporates the Ranz-Marshall correlation equation, $Nu = 2 + 0.6\, Re^{1/2}\, Pr^{1/3}$. The rate of change of mass of the entire droplet depends upon the individual rates of evaporation of both methane and silane [Eq. (5)]. The proportion of methane and silane in the vapor phase depends upon the actual vapor pressures of the components, their mole fractions in the liquid phase, and the ratio of the molecular weights.

The vapor pressures of pure silane and methane are calculated from the data of Ref. 3.

$$p^0_{\mathrm{si}} = \exp\,(-1485.06/T_0\bar{T} + 9.177) \tag{6}$$

$$p^0_b = \exp\,(-1044.85/T_0\bar{T} + 9.365) \tag{7}$$

The mole fraction of methane in the liquid phase is given by

$$N_{bL} = 2m_b/(m_b + m) \tag{8}$$

Therefore, the actual vapor pressure ratio p_R can be expressed as

$$p_R = (p^0_{\mathrm{si}}/p^0_b)(1 - N_{bL})/N_{bL} = p_{\mathrm{si}}/p_b \tag{9}$$

For a given mixture total pressure of the vapor (1 atm for the present case) and N_{bL}, the equilibrium mixture saturation temperature can be obtained by solving Eq. (9) along with the condition that $p_{\mathrm{si}} + p_b = 1$. This is done easily by iterating on temperature. A simple correlation equation applicable in the range of our interest where liquid methane evaporation predominates is as follows:

$$\bar{T} = 1/(T_1 + T_2 \ln N_{bL}) \tag{10}$$

Equation (10) is accurate to 0.2 K for N_{bL} values from 0.95 down to 0.34.

There are six unknowns (m_b, m, $\bar{D}$, U, x, and $\bar{T}$) in Eqs. (10) and (1-5). Equations (6-9) help us evaluate p_R and check the mixture total pressure, which is assumed to be 1 atm in this study. Equations (10) and (1-5) are solved by a fourth-order Runge-Kutta scheme with the following initial conditions:

$$\bar{D}(0) = 1, \quad U(0) = 0, \quad x(0) = 0, \quad m(0) = 1, \quad m_b(0) = m_{b_0}$$

$\bar{T}_0$ is defined by m_{b_0} and the ambient temperature. Ambient states of 1 atm and 900 and 700 K were assumed. Two free-stream velocities, 2000 and 1000 m/s, were chosen to illustrate the effect of velocity on the system behavior.

Results and Discussion

Calculations have been made to illustrate the ignition process for different initial silane-methane mixtures, various initial drop sizes, and two air velocities.

Some typical results illustrating the drop velocity after the drop was injected initially at an axial velocity of zero are shown in Fig. 3. Since the most rapid evaporation occurs when the greatest difference in velocity exists between the particles and the stream, the relative drop velocity is an important parameter in the calculation of the time or distance to rapid ignition. Plotted in the figure is the nondimensional drop velocity U vs time after injection. As one would expect, the smallest drops reach larger values of U soonest. Other parameters, such as the drop composition, have a minor effect since the drop density is not sensitive to changes in composition.

Some typical evaporation results with an initial methane mass fraction of 0.9 are illustrated in Fig. 4. The mole fraction of silane in the vapor at the drop surface is plotted against the distance from the injector. The flow velocity is assumed to be constant at 2000 m/s and the ambient temperature is assumed to be 900 K. Drop diameters ranging from 40 to 100 μm are plotted in the figure. A critical concentration of 0.02 is assumed for the separation criterion of transition from slow to rapid ignition, as explained in the discussion of Fig. 1. It is seen that 40-μm drops reach the transition ratio at a distance of about 0.15 m at 2000 m/s, while 100-μm drops require about 0.4 m. As a rough approximation, the distance to reach the critical concentration is directly proportional to drop size. The effects due to a 100% increase in drag coefficient are also shown in this figure. An increase in C_D increases the distance required for ignition. The use of smaller drops, below 40 μm, for example, still permits the critical concentration to be reached at short distances. The critical distance can also be controlled by changing the initial methane concentration. For illustration, an initial methane mass fraction of 0.7 was chosen. Mixtures containing more methane would ignite later, while those containing less methane would ignite sooner. A mixture containing a methane mass fraction of 0.3 would have the critical silane vapor concentration for rapid ignition immediately upon injection. The value of the critical distance is very sensitive to the initial methane concentration in the droplet.

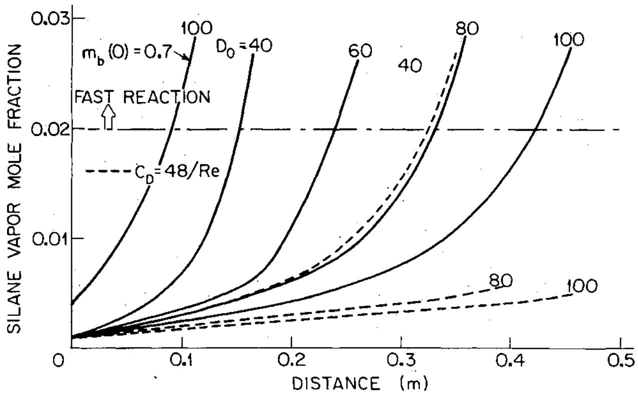

Fig. 4 Mole fraction of silane vapor as a function of distance; 2000 m/s, 900 K, $C_D = 24/Re$, $m_b(0) = 0.9$.

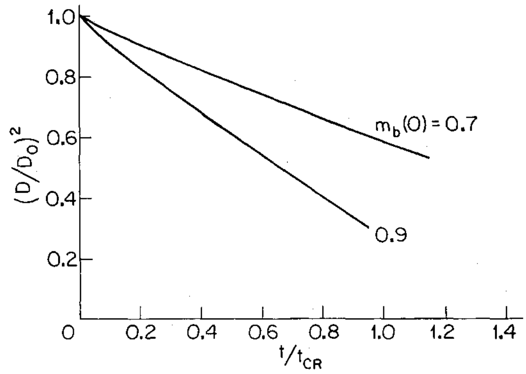

Fig. 5 Diameter history of droplets; 900 K, all diameters.

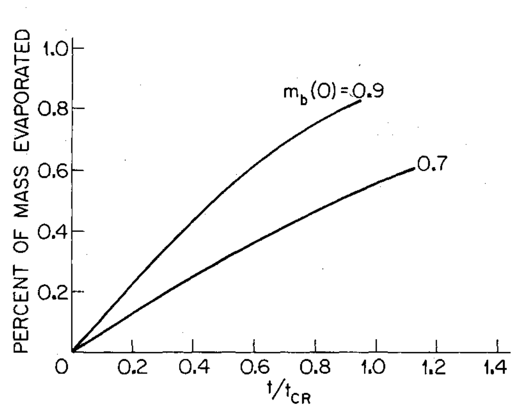

Fig. 6 Fraction of droplet mass actually evaporated; 900 K, all diameters.

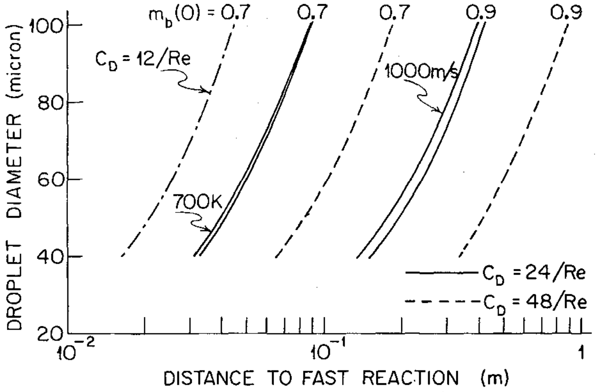

Fig. 7 Effects of initial methane concentration, drag coefficient, velocity, temperature, and droplet size on distance to fast reaction; 900 K, 2000 m/s.

The so-called "D^2 law" is commonly used to represent evaporation data. A plot of $(D/D_0)^2$ vs t/t_{cr}, where t_{cr} is the time to reach rapid ignition, is shown in Fig. 5. It is evident that the relationship is not linear although the various drop sizes and two velocities (1000 and 2000 m/s) are correlated by a single curve. The deviation from linear behavior is due primarily to the changing drop properties as evaporation proceeds, as well as the dependence of the convective heat transfer on drop diameter. A value of 1.0 on the abscissa represents the transition from slow to rapid ignition. The data are replotted in Fig. 6 in terms of mass evaporated. Note that for an initial $m_b = 0.7$ the transition $(t/t_{cr} = 1)$ occurs when about 55% of the mass has evaporated and that this quantity is independent of drop size. As shown in the figure, it does depend on the initial mixture ratio. The actual time for transition, however, also depends strongly on drop size.

The results are summarized in Fig. 7 where the distance to rapid ignition is plotted as a function of initial drop diameter. Two initial methane mass fractions are shown parametrically. The data are shown for a stream velocity of 2000 m/s except for the case of 90% methane where a curve for 1000 m/s is also shown. The effects due to changes in C_D and ambient temperature are also shown.

It is evident that drop sizes representative of a typical spray and containing methane concentrations that make the liquid mixture relatively safe to handle are capable of evaporation to produce rapid ignition after short distances in supersonic flow. The mixtures safer to handle, of course, contain the higher methane concentrations so that there must be a compromise between time to ignition and the relative effectiveness of the diluent.

Although silane-methane mixtures were not chosen as an optimum mixture for ignition, it has been shown that these mixtures are capable of providing the necessary environment for ignition, while the initial liquid mixture is not ignited easily. There are other factors that make the injection of an inerted liquid that becomes flammable after evaporation a desirable ignition promoter. In an actual spray, the smallest drops in the distribution would ignite first and serve as an ignition source for the remainder of the spray. In addition, the larger drops continue to evaporate and serve as ignition promoters even if they have not contacted the flame produced by the smaller drops. In this manner, the distribution of drop sizes produces a distribution in liquid-phase composition as evaporation proceeds, providing a distributed ignition source. The methane continues to evaporate in all of the drops so that almost pure silane is burning shortly after ignition of the drop, serving as a very active center for ignition of the primary fuel and for flame stabilization.

The use of spontaneously flammable materials for ignition and flame stabilization under supersonic flow conditions in a combustor is not without precedent. In Ref. 4, it was shown that aluminum borohydride would ignite and burn after wall injection as a spray in a supersonic tunnel. In a later work,[5] it was shown that aluminum borohydride-jet fuel mixtures containing as much as 41% jet fuel could be ignited in a supersonic tunnel. Jet fuel could be made to burn in the presence of an aluminum borohydride pilot flame.

It seems evident that further theoretical and experimental investigation could lead to promoter-fuel combinations that provide ignition and stable combustion and relatively convenient handling conditions.

References

[1] Beach, H. L. Jr. et al., "Use of Silane in Scramjet Research," 17th JANNAF Combustion Meeting, NASA Langley Research Center, Hampton, VA, Sept. 1980, Chemical Propulsion Information Agency Publication, Vol. 329, Nov. 1980, pp. 639-659.

[2] Gerstein, M. and Choudhury, P. R., "Timed Ignition of Explosives and Flammables from Desensitized Solutions," 9th International Colloquium on the Dynamics of Explosions and Reactive Systems," Poitiers, France, July 1983.

[3] *Handbook of Physics and Chemistry,* 48th Ed., Chemical Rubber Co., Cleveland, OH, 1967-1968.

[4] Fletcher, E. A., Darech, R. G., and Gerstein, M., "Combustion of Aluminum Borohydride in a Supersonic Wind Tunnel," NACA RM E55D07a, 1955.

[5] Allen, H. Jr. and Fletcher, E. A., "Combustion of Various Highly Reactive Fuels in a 3.84 by 10-inch Mach 2 Wind Tunnel," NACA Memo 1-15-59E, 1959.