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# Silanes as Fuels for Scramjets and Their Applications

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**In the light of recently revived interest in scramjet propulsion, a new look is being given at unconventional new fuels. Among the latter are, or could be included, hydrides. These contain hydrogen in variable amounts, suggesting their use for airbreathing applications in which a much higher density compared to that of $LH_2$ would be beneficial. In particular, this paper deals with silicon hydrides ("silanes"), because of their interesting combustion and energetic properties as fuels for scramjets. Silanes in combination with air seem, at this preliminary stage of analysis, an interesting conceptual alternative to $LH_2$ and, perhaps, also to $LCH_4$ for scramjet application. Accordingly, this paper explores the practical limits of application of silanes and their performance along cruiser and accelerator trajectories. Equilibrium composition of the combustion products of silanes, from monosilane up to pentasilane, were calculated. Ideal scramjet performance (specific thrust and specific impulse) were evaluated along a constant dynamic pressure trajectory from 21,350 to 30,500 m and compared to that with $CH_4$/air and $H_2$/air mixtures. High specific thrust is obtained as the equivalence ratio is increased; the $I_{sp}$ trend is the reverse, but still very appealing when weighted with the bulk density of silanes.**

## Nomenclature

| | | |
|---|---|---|
| AFR | = | air-to-fuel mass ratio |
| $C_F$ | = | thrust coefficient |
| $c_p$ | = | specific heat at constant pressure, J/kg · K |
| $F_n$ | = | thrust, N |
| $F/O$ | = | fuel to oxidizer mass ratio |
| $M$ | = | Mach number |
| $m_a$ | = | air mass flow rate, kg/s |
| $m_f$ | = | fuel mass flow rate, kg/s |
| $I_{sp}$ | = | specific impulse, m/s |
| $I_v$ | = | volumetric impulse, N · s/cm$^3$ |
| $P_t$ | = | total pressure, Pa |
| $q$ | = | flight dynamic pressure, Pa |
| $T_t$ | = | total temperature, K |
| $V$ | = | velocity, m/s |
| $\Delta H_f^\circ$ | = | standard enthalpy of formation, J/kmol |
| $\Phi$ | = | equivalence ratio |
| $\Psi$ | = | specific thrust, N · s/kg |

## I. Introduction

IN the light of recently revived interest in scramjet (SCRJ) propulsion, a new look is being given at traditional and unconventional fuels. Among the latter are hydrides, because of their hydrogen content and density. Among hydrides, silanes are of interest because of their combustion and energetic properties.

Silanes have been the subject of chemical research for a long time. They are silicon hydrides organized in molecular chains similar to those of hydrocarbons; due to their position within the periodic table of elements, there are many similarities between silicon and carbon and therefore it is also reasonable to compare silicon hydrides to hydrocarbons. However, little attention has been given to the combustion of higher silanes (higher silanes are silicon hydrides which contain five or more silicon atoms). In fact, monosilane ($SiH_4$) has already been considered and successfully tested as an ignition promoter in SCRJ, and its chemical kinetics with air is fairly well understood [1–5]. In particular, [6] contains chemical mechanisms, reaction-rate parameters, and a list of references on $SiH_4/H_2$ combustion. However, monosilane has little appeal as a potential fuel, because it is gaseous at standard temperature and pressure (STP, i.e, $T = 298.15$ K, $P = 1$ bar); on the other hand, the kinetics of higher order silanes has yet to be explored and no data are currently available. This fact makes estimating their combustion properties inevitably based on chemical equilibrium. In fact, ideal performance of silanes/LOX-fueled rockets was recently calculated using the standard NASA CEA2 program [7,8]. At STP, lower silanes ($SiH_4$, $Si_2H_6$) are gaseous and extremely pyrophoric; with increasing chain length, silanes become liquid. Whereas alkanes are liquid only from pentane on, due to their much higher molecular mass, silanes are liquid and therefore easily pumped from trisilane ($Si_3H_8$) on. When compared to alkanes, the liquid state temperature interval of silanes is shifted to higher temperatures and a little broader, enabling their storage in compact tanks. A fundamental difference between silanes and hydrocarbons is their heat of formation: alkanes have negative heats of formation (approximately $-20$ kJ/mol per $CH_2$ group), whereas the corresponding silanes (Table 1) have positive heats of formation (approximately $+40$ kJ/mol per $SiH_2$ group). Thus, in a combustion chamber the decomposition of silanes yields usable energy [9].

Another important feature of the thermal decomposition of silanes is the large amount of hydrogen theoretically available; in fact, at moderate temperatures (about 500 K) the chains begin to break, and at 700 K their decomposition is complete, yielding silicon and gaseous hydrogen useful for propulsion in combination with air nitrogen and oxygen [10]. This last feature, if confirmed, could identify silanes not only as energy carriers but also components in bifuel systems. Finally, silanes may be considered "green propellants": they are nontoxic and noncarcinogenic, as their combustion products with oxygen are only water, SiO, and $SiO_2$.

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**Table 1 Densities and heats of formation of silanes**

| | Specific gravity | $\Delta H_f^\circ$ at STP, kJ/mol | Physical state at STP |
|---|---|---|---|
| $SiH_4$ | 0.681 | +34.05 | Gas |
| $Si_2H_6$ | 0.686 | +79.76 | Gas |
| $Si_3H_8$ | 0.739 | +120.95 | Liquid |
| $Si_4H_{10}$ | 0.795 | +160.64 | Liquid |
| $Si_5H_{12}$ | 0.827 | +206.00 | Liquid |

**Table 2 Conditions at the combustion chamber entrance**

| $M_o$ | $P_o$, kPa | $T_o$, K | $V_o$, m/s | $P_2$, kPa | $T_2$, K | $V_2$, m/s | $M_2$ |
|---|---|---|---|---|---|---|---|
| 6 | 3.42 | 220.4 | 1785 | 65 | 549.4 | 1589 | 3.4 |
| 8 | 1.92 | 224.3 | 2402 | 75 | 726.1 | 2182 | 4.0 |
| 10 | 1.23 | 226.9 | 3020 | 90 | 937.1 | 2773 | 4.5 |
| 12 | 0.85 | 230.3 | 3650 | 108 | 1191.9 | 3376 | 4.9 |
| 14 | 0.62 | 235.4 | 4305 | 130 | 1501 | 3999 | 5.1 |

## II. Test Cases

To investigate the behavior of silanes as SCRJ fuel, performance was evaluated along a trajectory at constant dynamic pressure $q = 86.14$ kPa; 5 M numbers from $M = 6$ to $M = 14$ were selected, corresponding to a flight path ranging from 21,350 to 30,500 m.

In this work the ideal performance of scramjet was expressed via parameters common in airbreathing propulsion systems. Assuming the fuel mass flow rate to be small in comparison with the air mass flow rate, and complete expansion of the combustion gases in the exhaust nozzle to ambient pressure, the net thrust of the propulsion system is

$$F_n = m_a(V_e - V_0) \tag{1}$$

To eliminate dependence on engine size, the specific thrust is introduced:

$$\Psi = \frac{F_n}{m_a} = V_0\left(\frac{V_e}{V_0} - 1\right) \tag{2}$$

where $V_0$ is the flight speed, and $V_e$ is the exhaust velocity. The nondimensional thrust coefficient is then

$$C_F = 2\left(\frac{V_e}{V_0} - 1\right) \tag{3}$$

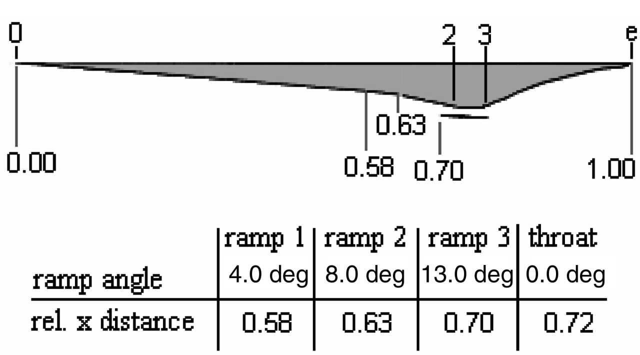


**Fig. 1 Generic variable geometry inlet; design point configuration at $M = 12$.**

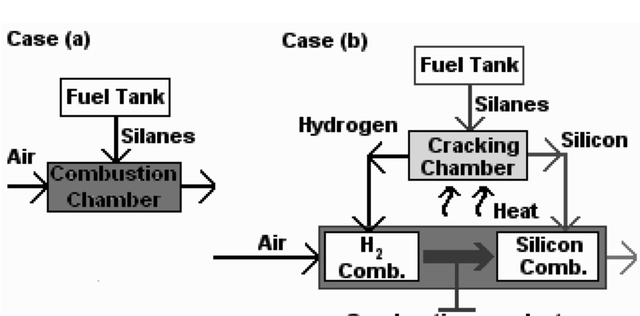


**Fig. 2 Test cases.**

Finally the specific impulse is

$$I_{sp} = \Psi \mathrm{AFR} \tag{4}$$

Conditions at the entrance of the combustion chamber were calculated at each flight Mach number, assuming the flow compressed in a variable geometry hypersonic inlet. Figure 1 shows as example the inlet geometry assumed as design configuration at $M = 12$.

Using values in Table 2 as combustor entrance conditions, equilibrium compositions and adiabatic temperatures in the combustion chamber were evaluated by means of NASA's CEA2 program.

The conditions at the nozzle entrance were calculated assuming constant pressure in the combustion chamber and frictionless flow; in fact, from the Euler equation ($\mathrm{d}p = -\rho V\,\mathrm{d}V$) one obtains

$$V_2 = V_3 \tag{5}$$

and for the Mach number ratio in the combustion chamber

$$\frac{M_3}{M_2} = \sqrt{\frac{T_2}{T_3}} \tag{6}$$

Finally ideal exhaust conditions were calculated assuming isentropic frozen flow through the nozzle with

$$V_e = \sqrt{2c_pT_{t3}\left[1 - \left(\frac{P_0}{P_{t3}}\right)^{(\gamma-1)/\gamma}\right]} \tag{7}$$

where $P_{t3}$, $T_{t3}$ are total pressure and temperature of the burnt gases at the nozzle entrance.

Using these assumptions, two test cases were simulated as shown in Fig. 2.

In case a, combustion of silanes with air was simulated by varying the equivalence ratio from 0.2 to 5. Performance was then compared with that of $CH_4$/air and $H_2$/air mixtures at the same conditions. In case b a silane cracking chamber wrapped around the combustion chamber was assumed present. Gaseous hydrogen and silicon, produced by thermal decomposition of silanes at 1800–2000 K were assumed separately collected in the combustion chamber. The combustion of silicon (the fuel) in the hot stream of $H_2$/air combustion products (the oxidizer) was then simulated varying for each $H_2$/air equivalence ratio (from 0.2 to 5) the fuel (silicon) to oxidizer (burned gases) ratio, from $F/O = 0.005$ to $F/O = 1$. Performance was then compared with that obtained for a $H_2$/air mixture at the same flight conditions.

## III. Results

In case a, high specific thrust was predicted over the whole range of Mach numbers and air/silanes combinations examined; when compared with air/$CH_4$ mixture, silanes enhance the scramjet performance at low Mach numbers, as shown in Fig. 3 for $\Phi = 1$.

This behavior can be explained by observing Fig. 4 where adiabatic flame temperatures as function of Mach number are plotted for the same equivalence ratio, and recalling that specific thrust depends on the exhaust gas velocity and therefore on the combustion chamber exit temperature.

Figure 5 shows specific impulse as a function of Mach number; the detrimental influence of the high average molecular weights of

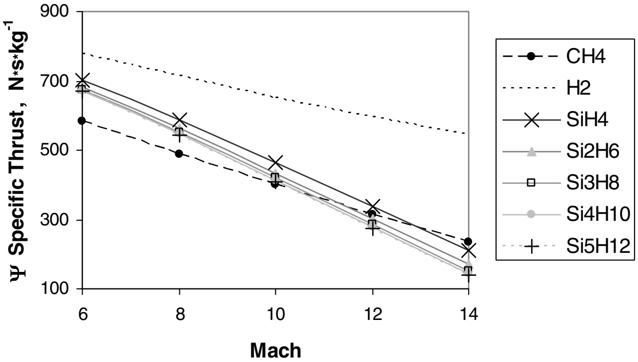

**Fig. 3 Specific thrust (Φ = 1).**

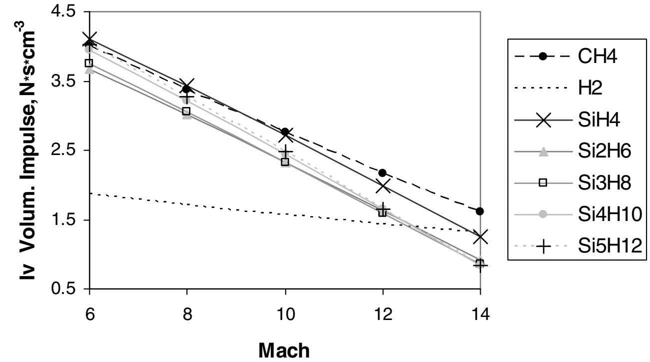

**Fig. 6 Volumetric impulse (Φ = 1).**

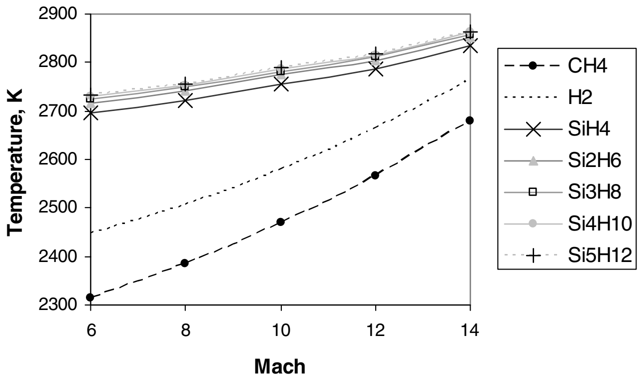

**Fig. 4 Combustion temperature (Φ = 1).**

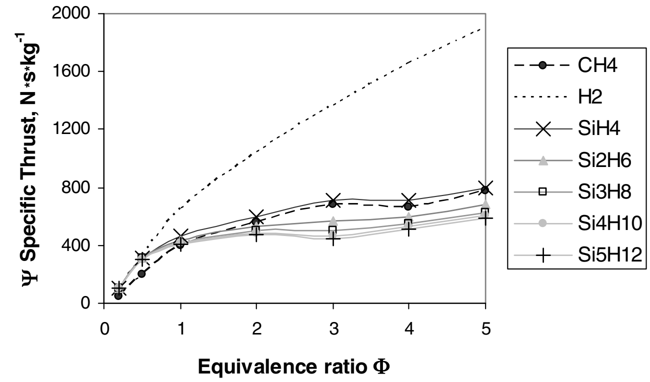

**Fig. 7 Specific thrust (*M* = 10).**

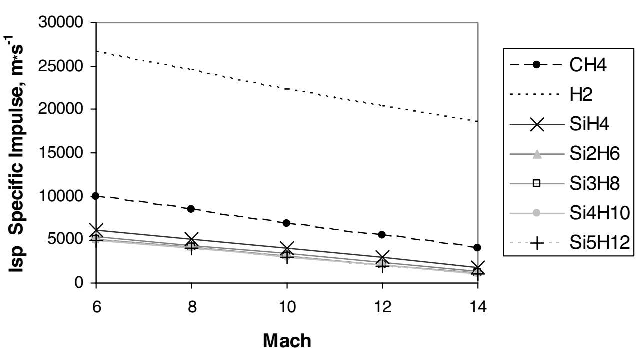

**Fig. 5 Specific impulse (Φ = 1).**

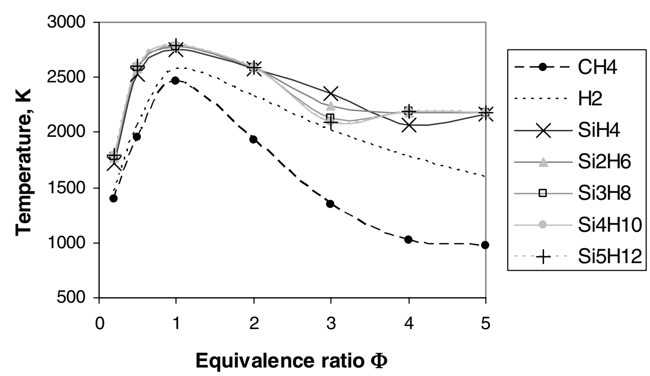

**Fig. 8 Combustion temperature (*M* = 10).**

exhaust gases is evident compared to $H_2$ or $CH_4$, despite the high combustion temperatures.

However, as shown in Fig. 6, the volumetric impulse is high, suggesting silanes as potential competitor fuels when onboard space is limited.

The influence of the equivalence ratio is shown in Figs. 7–10 at $M = 10$.

High specific thrust was obtained (Fig. 7) over the whole range of Mach numbers and air/silane combinations examined. At $M = 10$ silanes enhance scramjet performance for $\Phi < 1$ when compared with $CH_4$/air. Of interest are combustion temperatures (Fig. 8), their value higher and peak broader than that of $CH_4$/air and $H_2$/air systems.

As a result, both the theoretical specific impulse and the volumetric impulse are significant (Fig. 9); overall, the volumetric impulse plotted in Fig. 10 makes lean silanes mixtures very interesting.

As predicted by the present parametric analysis, at the same flight Mach number and equivalence ratio, all the combinations silanes/air examined have practically the same equilibrium composition. For this reason, to investigate the influence of Mach number and equivalence ratio on the chemical composition of burned gases, $Si_3H_8$/air was selected as reference case. In particular, Figs. 11–13 show the mass fractions of the combustion products (nitrogen bars are nonrepresented) for three equivalence ratios ($\Phi = 0.5, 1, 2$), with the flight Mach number as parameter.

Thermal decomposition of $Si_3H_8$ and high reactivity of silicon in the presence of oxygen are the key factors to understand its combustion process. In fact, a considerable part of the overall Gibbs energy comes from fuel decomposition with its positive heat of formation. After decomposition, free silicon reacts with oxygen faster than hydrogen, forming liquid $SiO_2$ ($\Delta H_f^\circ = -910.5$ kJ/mol), gaseous $SiO_2$ ($H_f^\circ = -322.5$ kJ/mol), and gaseous SiO ($H_f^\circ = -98.84$ kJ/mol) and releasing heat; as a result,

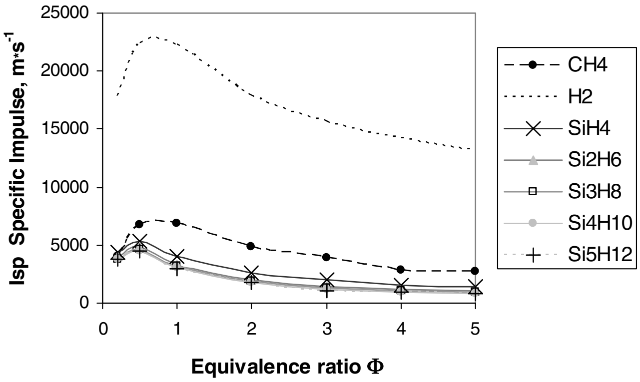


**Fig. 9 Specific impulse ($M = 10$).**

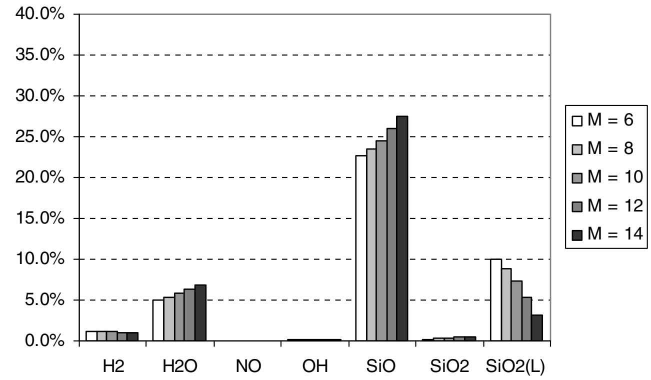


**Fig. 13 $Si_3H_8$/air combustion products mass percentages ($\Phi = 2$).**

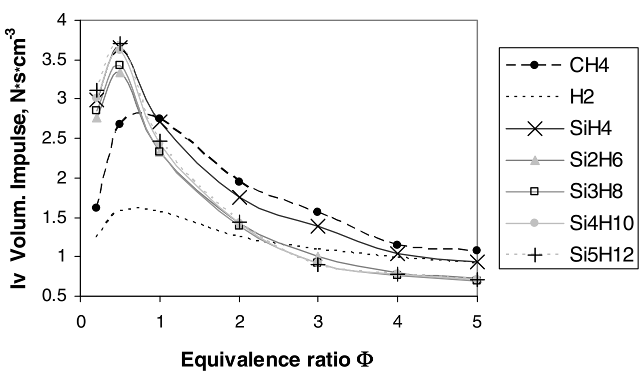


**Fig. 10 Volumetric impulse ($M = 10$).**

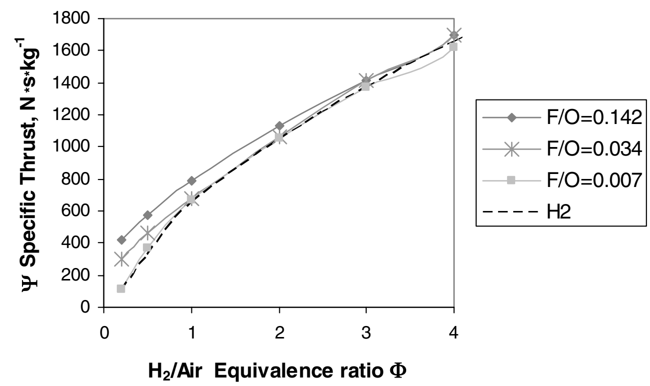


**Fig. 14 Specific thrust ($M = 10$).**

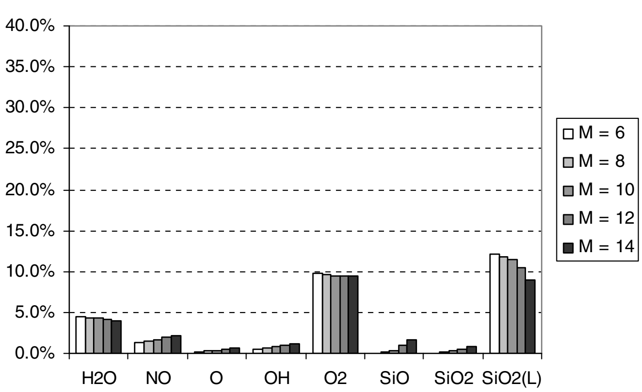


**Fig. 11 $Si_3H_8$/air combustion products mass percentages ($\Phi = 0.5$).**

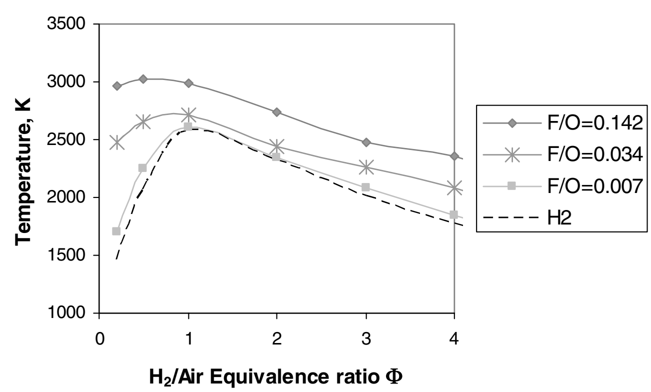


**Fig. 15 Combustion temperature ($M = 10$).**

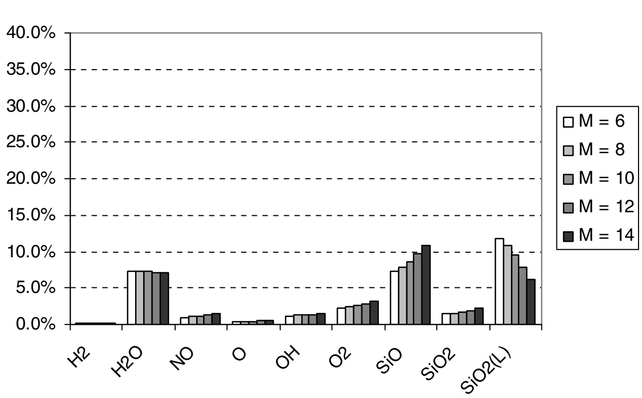


**Fig. 12 $Si_3H_8$/air combustion products mass percentages ($\Phi = 1$).**

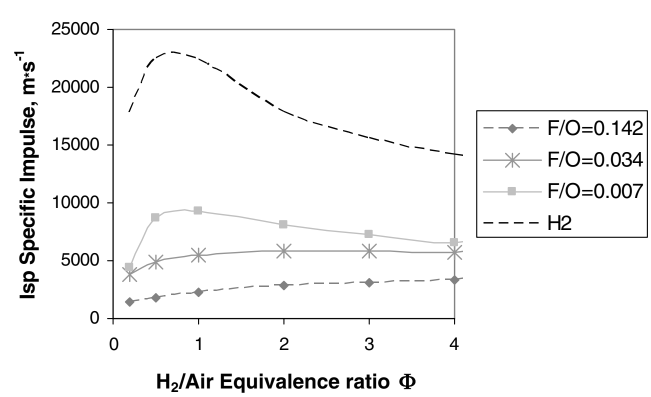


**Fig. 16 Specific impulse ($M = 10$).**

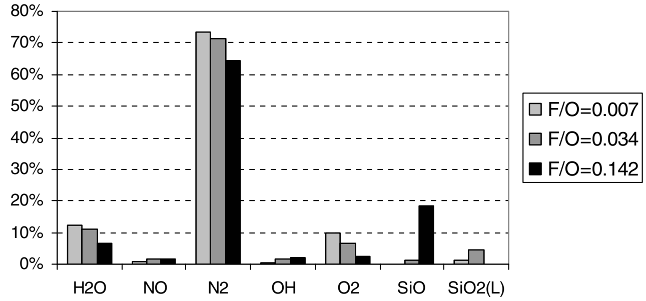


**Fig. 17 Mass percentages; $\Phi(H_2/air) = 0.5$.**

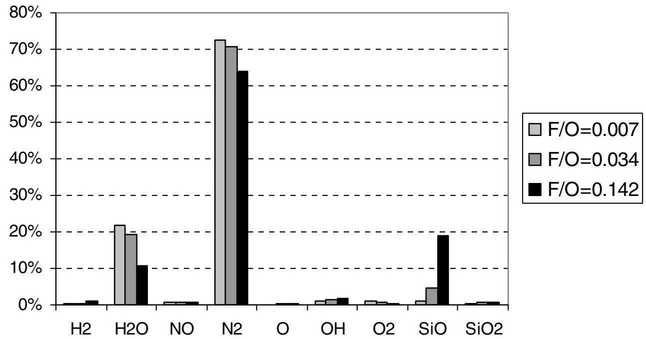


**Fig. 18 Mass percentages; $\Phi(H_2/air) = 0.1$.**

the temperature does not decrease significantly for moderately rich mixtures. At increasing flight Mach numbers, due to the higher temperatures of the incoming air flow, the equilibrium between liquid $SiO_2$ and SiO shifts towards SiO. Finally, at large $\Phi$ (low air oxygen fraction), only SiO is present and the mass fraction of hydrogen increases. In this case temperature decreases and liquid and solid phases appear, raising the average molecular weight of the mixture and thus lowering the specific impulse. It is important to point out that in these calculations there is no evidence of silicon and nitrogen compounds formation.

Results of case b are shown in Figs. 14–16 at flight Mach number $M = 10$.

Figure 14 shows that the injection of silicon into the hot stream of a burned $H_2$/air mixture enhances specific thrust; in particular, high $\Psi$ was obtained for both hydrogen-lean ($\Phi < 1$) and -rich ($\Phi \gg 1$) mixtures. Changing the fuel (silicon) to oxidizer mass ratio affects performance only for $\Phi < 1$, raising the specific thrust when the fraction of silicon is also raised. Combustion temperatures (Fig. 15) are higher than those obtained burning $H_2$, growing with growing silicon injection in the combustion chamber.

Figure 16 shows also the specific impulse to be significant, due to high combustion temperatures and to the average molecular weight of the exhausting gases.

To support this explanation, the equilibrium composition of products following injection of silicon inside the combustion chamber is shown for two values of the equivalence ratio of $H_2$/air (Figs. 17 and 18), with the Si/burned gases ratio ($F/O$) as parameter.

The reactivity of silicon in the presence of oxygen plays again an important role in this process. For oxygen-rich mixtures ($\Phi < 1$) silicon reacts forming SiO and $SiO_2$, releasing energy and increasing combustion chamber temperature; thus good performance is possible at high $F/O$ ratios. For intermediate values of the equivalence ratio ($1 < \Phi < 3$), formation of silicon and oxygen compounds continues, whereas for oxygen-lean mixture ($\Phi > 4$), hydrogen, liquid silicon, and tens of other substances, present in very small mass fractions, are formed. All these results suggest that silanes could act as dense hydrogen "carriers" liquids, and enhancing specific thrusts and combustion temperatures by injecting in the combustor the silicon formed in a cracking chamber. This strategy is made plausible by observing Fig. 19, where volumetric impulse of case b is compared

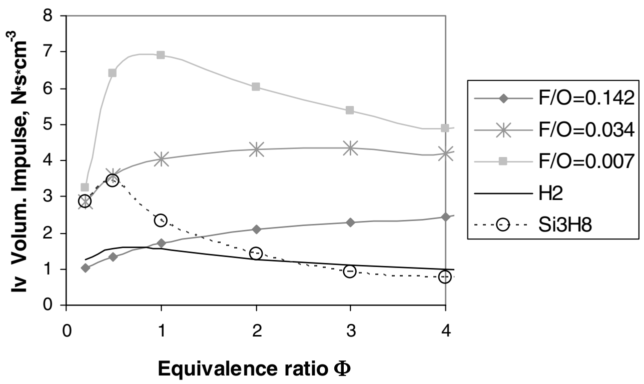


**Fig. 19 $I_v$; comparison with $H_2$ and $Si_3H_8$.**

with two volumetric impulses of case a (hydrogen-fueled scramjet and $Si_3H_8$ fueled scramjet).

## IV. Conclusions

The results of this preliminary investigation suggest further analysis of the applicability of silanes as possible SCRJ fuels. High specific thrust and specific impulse were obtained for all the combinations $Si_nH_{2n+2}$/air investigated, mainly because of their endothermic heats of formation: values are comparable to those of methane/air mixtures, in spite of the higher average molecular weight of the combustion products. The high volumetric impulse make silanes (conceptually at least) an interesting alternative to $LCH_4$ and perhaps $LH_2$, also because their endothermic decomposition may also be exploited for active cooling. As for their safety, there is no danger of forming detonating gases; additionally, they are hypergolic, a desirable feature in SCRJ applications. As shown by the equilibrium analysis, silanes with air oxygen do not produce toxic exhausting gases. Although the equilibrium analysis does not predict gas phase formation of compounds between silicon and air nitrogen, the issue of exothermic catalytically assisted formation of such compounds remains open. The best performance was obtained by using the products of the thermal decomposition of silanes separately. In fact, injecting silicon produced by cracking silanes into the combustion products of air and hydrogen (obtained also by cracking), the specific thrust and combustion temperature are higher than those obtained in a simple $H_2$/air scramjet. Silanes act as "energy carriers," enabling safe storage of hydrogen in compact tanks and enhancing, at least theoretically, the performance of an $H_2$/air scramjet, the technical challenge being the cracking process and separation and feeding system for the two streams of silicon and hydrogen.

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