Technical Notes

Silanes/H$_2$O$_2$: A High-Performance Synthetic Bipropellant for Chemical Space Propulsion

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I. Introduction

MONOSILANE is today produced industrially in plants with annual capacities of up to multihundred tons. This gaseous silane is to a great extent used to convert metallurgical-grade silicon into highly pure solar grade silicon. However, a comparably small amount of monosilane is also used for ignition of propellant flows in test facilities [1] and was also employed in NASA's ground-breaking X-43A scramjet flights in 2004 [2,3]. This simplest silane SiH$_4$ has proven its applicability as an ignition promoter and piloting fuel in scramjets [4–8] already in the 1980s because of its hypergolic nature.

In contrast, longer-chained, liquid silanes are not produced on a large scale. Nevertheless, this might soon change, due to recent breakthroughs in the production of ultrathin semiconducting films from liquid silane precursors [9,10]. Such films might have considerable impact on space technology, because they open up the possibility of using extremely lightweight, large-area screens or foldable solar panels. Silanes which are liquid at ambient conditions are not only much easier to handle than gaseous silanes, but can also be stored much more effectively because of their higher densities [11–14]. In addition, while lower silanes self-ignite and burn vigorously when exposed to air, their initial reactivity decreases with increasing chain length, rendering silanes above the *n*-hexasilane quasi stable in air at ambient conditions. The term "quasi stability" is used because although the vapor pressure of liquid, longer-chained silanes is low enough to prevent instant ignition with air, their decomposition and oxidation can nevertheless be triggered relatively

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easily. The reason for this behavior can be found in their thermodynamics: although alkanes have negative heats of formation (approximately −20 kJ/mol per CH$_2$ group), the corresponding silanes have positive heats of formation (approximately +40 kJ/mol per SiH$_2$ group). This fundamental difference was (to our knowledge) pointed out for the first time in [10].

Since then, it became possible to estimate the ideal rocket performance of liquid silanes burning with various oxidizers with standard calculation tools, such as NASA CEA2 [15]. We used empirically corrected ab initio calculations to create the necessary computer-compatible data sets for silanes up to the pentasilanes (SiH$_4$, Si$_2$H$_6$, Si$_3$H$_8$, cyclo-Si$_3$H$_6$, *n*-Si$_4$H$_{10}$, iso-Si$_4$H$_{10}$, cyclo-Si$_4$H$_8$, *n*-Si$_5$H$_{12}$, iso-Si$_5$H$_{12}$, neo-Si$_5$H$_{12}$, and cyclo-Si$_4$H$_{10}$) and included them into the master propellant libraries of CEA2, as described in detail in [10] (and references therein). The accuracy of the underlying data is supported by a different ab initio approach [16], and it is planned to extend such ab initio data sets up to heptasilanes as well as to experimentally verify the heats of formation of higher silanes.

The main objective of this paper is to explore the potential (ideal) rocket performance of liquid silanes with highly concentrated H$_2$O$_2$ as rocket bipropellants using the new thermodynamic data. Comparing different oxidizers [11–14] such as atmospheric air, NTO, N$_2$O, LOX, and H$_2$O$_2$, anhydrous high concentration H$_2$O$_2$ turned out to be the best-performing oxidizing agent for silanes in terms of specific impulse I_{sp}. Comparison with the same combustion parameters, but using alkanes/H$_2$O$_2$ and MMH/NTO shows that the silanes/H$_2$O$_2$ system is notably superior to these more common types of bipropellants. In addition, the combination of silanes and rocket-grade hydrogen peroxide (RGHP) is expected to be hypergolic, because both silanes [1–8] as well as H$_2$O$_2$ [17,18] are known to promote autoignition.

This said, it should be noted that the calculated specific impulse of silanes/H$_2$O$_2$ systems overestimates the I_{sp} that can be obtained in reality, mainly because 1) of the shifting equilibrium assumption, used because the kinetics of the decomposition and oxidation of liquid silanes is still unknown, and, 2) significant amounts of condensed combustion products such as Si(l), SiO$_2$(l), and even solid beta-cristobalite SiO$_2$ (b-crt) are predicted to occur: at the oxidizer/fuel (O/F) ratios yielding the maximum I_{sp}, the condensed mole fraction ranges from less than 10% in the combustion chamber up to about 20% at the nozzle exit.

Because the environmental effects of hydrazines/NTO combinations are severe enough to make these toxic propellants unwanted for next-generation reusable rocket-vehicles, there are now renewed efforts to use RGHP [19] as an oxidizer in combination with hydrocarbon fuels [20], for example, to power reaction control systems (RCS). These "green" bipropellants are considered because of their comparable ease of handling and environmental friendliness, properties which cancel out their performance disadvantages when compared to hydrazines/NTO for some applications. Concerning the environmental impact of silanes/H$_2$O$_2$, future studies will have to show to which extent the formation of liquid and solid particles in the exhaust flow compromises the environmental advantage of reduced toxicity. Besides, these particulates may deposit on engine walls: that might affect performance negatively, but may also reduce wall heat transfer drastically [21–23].

Silanes have Si–H ratios ranging from 1:4 (for monosilane) to 1:2 (for cyclic silanes), so that they can be seen as good hydrogen

carriers. Furthermore, because of their high enthalpy of formation, they could in principle also be used as monopropellants. Their good performance is accompanied by quite good storability, high density, and relative lack of toxicity. These are the main reasons suggesting silanes as effective fuels for rockets [11,12,14] or scramjets [11,13,14].

II. Ideal Rocket Performance Calculations

By using the NASA code CEA2, rocket performance of silicon hydrides (from monosilane SiH_4 to pentasilane Si_5H_{12}) with RGHP, as well as of CH_4 and C_5H_{12} with RGHP and of MMH and NTO was calculated. Chamber pressure was assumed 70 bar in all cases. Vacuum-specific impulse I_{vac} and chamber temperature T_c were calculated assuming shifting equilibrium (for the reason mentioned above) and plotted vs the equivalence ratio

$$\Phi = \frac{F/O}{(F/O)_{stoich}} \qquad (1)$$

Figures 1 and 2 show the calculated vacuum-specific impulse and chamber temperature of the high-energy silicon hydrides (from monosilane, SiH_4, to pentasilane, Si_5H_{12}) with RGHP. Figure 1 shows that the maximum of the vacuum-specific impulse is extremely broad, a feature expected because of the strongly positive heats of formation [11–14]. This broad maximum is centered in the fuel-rich region around $\Phi = 3–4$.

The peak theoretical specific impulse that can be achieved with the hydrogen-richest silane, SiH_4, is 3371 m/s at $\Phi = 4$. The hydrogen fraction of the silanes decreases with increasing chain length and the peak shifts toward lower Φ, but still, for example, for trisilane Si_3H_8, which is already liquid at ambient conditions, the specific impulse of 3196 m/s at $\Phi = 3.2$ is significantly high.

The chamber temperature plots in Fig. 2 show combustion temperature also has a broad maximum, with a rather sharp drop beyond $\Phi = 5$. Because of the broad maximum of the I_{vac} and the sharp temperature drop approaching $\Phi = 5$, it is suggested that rich mixtures may considerably reduce temperature with moderate I_{vac} losses.

To compare the rocket performance of silicon hydrides/RGHP bipropellants with hydrocarbons/RGHP, in Figs. 3 and 4 their calculated specific impulses and chamber temperatures are contrasted: a completely different picture arises when calculating rocket performance of CH_4 and C_5H_{12} with RGHP. Their specific impulses and chamber temperatures have sharp, nearly coincident maxima near $\Phi = 1$ due to the negative heats of formation of alkanes. Their positive energy release results from the heat of formation of combustion products alone, which peaks at the stoichiometric equivalence ratio. As far as peak specific impulse, silanes are much better than alkanes, further indicating their potential. Figure 4 compares the chamber temperatures of both combinations. Near the peak specific impulse, temperatures are quite similar for both bipropellants. The silanes/RGHP combinations, however, offer the possibility to significantly lower chamber temperature, with no great loss of I_{vac}, by simply decreasing the O/F ratio a little.

Figure 5 shows a comparison between the specific impulses of silicon hydrides/RGHP and MMH/NTO. Pure (100%) MMH and NTO were assumed. One of the reasons why this bipropellant combination is in widespread use is that its specific impulse is notably higher than, for example, that of hydrocarbons/NTO. In this calculation, the maximum specific impulse of 3076 m/s is reached at $\Phi = 1.1$, with a chamber temperature of 3396 K. Again, temperature and specific impulse have a sharp maximum close to the stoichiometric value $\Phi = 1$. It is remarkable that the maximum theoretically possible specific impulse of SiH_4/RGHP is about 300 m/s higher than that of the MMH/NTO standard at the assigned chamber pressure of 70 bar.

Whereas SiH_4 would have to be stored cryogenically to keep tank size and weight small, Si_5H_{12} is a liquid that is supposed to be nonflammable in air at standard pressure and at temperatures <27°C [11,12], which by far does not require excessive cooling. Even
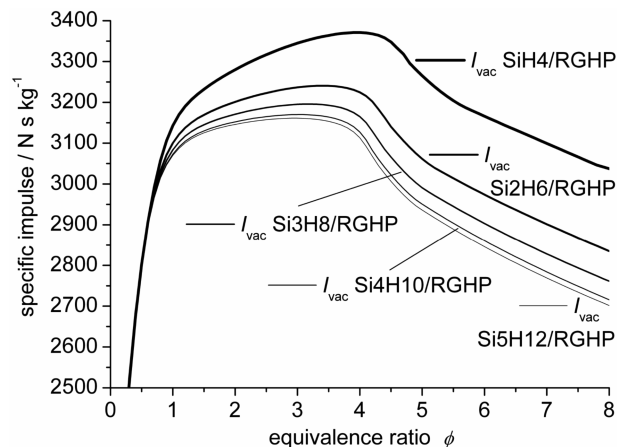

Fig. 1   Calculated vacuum-specific impulse of linear silanes from mono- to pentasilane with RGHP@98% at 70 bar vs equivalence ratio.
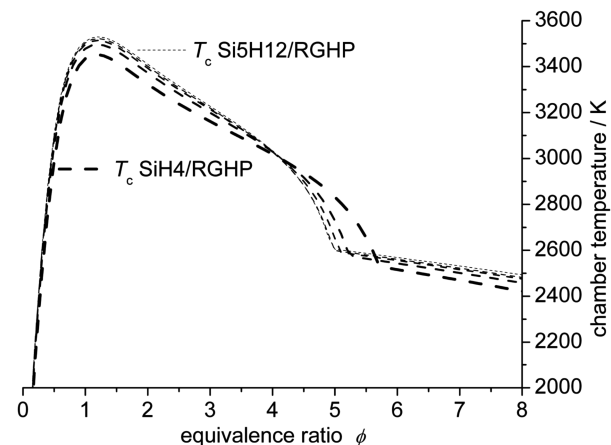

Fig. 2   Chamber temperature with combustion of linear silanes (from mono- to pentasilanes) with RGHP@98% at 70 bar vs equivalence ratio.
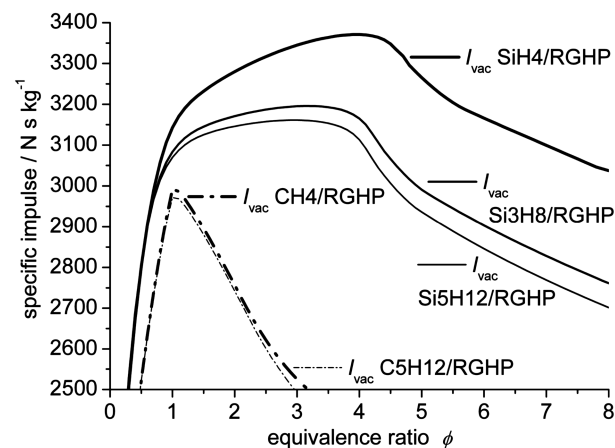

Fig. 3   Comparison of the vacuum-specific impulses of silanes/RGHP and alkanes/RGHP at 70 bar vs equivalence ratio.
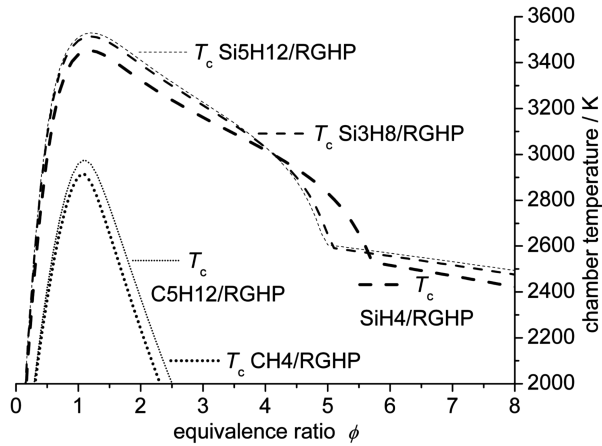
Fig. 4   Comparison of the chamber temperatures of silanes/RGHP and alkanes/RGHP at 70 bar vs equivalence ratio.
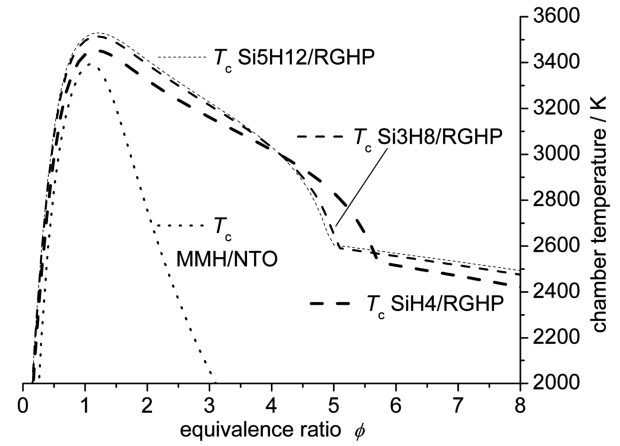

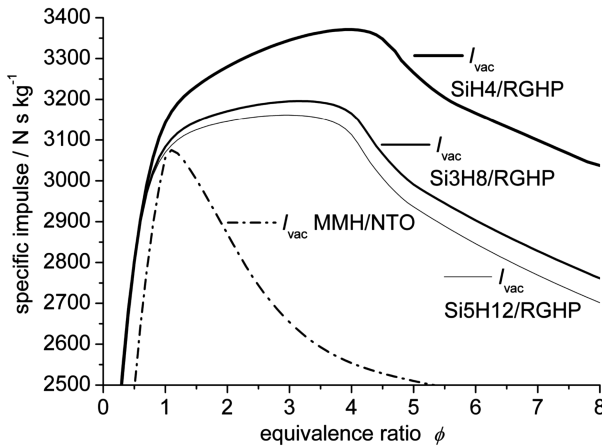**Fig. 6   Comparison between the chamber temperatures of silanes/RGHP and MMH/NTO at 70 bar vs equivalence ratio.**

Fig. 5   Comparison of the specific impulses of silanes/RGHP and MMH/NTO at 70 bar vs equivalence ratio.

Si_5H_{12}/RGHP has a significantly higher calculated specific impulse than MMH/NTO.

At the same time, the chamber combustion temperatures are at least 150 K lower than those of MMH/NTO and can be further decreased by moving the O/F working point to higher equivalence ratios without losing too much I_{vac}, which is a convenient engineering feature. This is shown in Figs. 5 and 6.

III.   Conclusions

Table 1 shows an overview of the calculations presented. The vacuum-specific impulses, combustion temperatures in the chamber, nozzle expansion ratio, and densities of the fuels are given as well as the equivalence and corresponding oxidizer–fuel–mass ratio that would be used to obtain the maximum specific impulse. For this ratio, the average (bulk) density of the bipropellant

$$\bar{\rho} = \frac{(F/O)_{max} + 1}{\frac{(O/F)_{max}}{\rho_{oxidizer}} + \frac{1}{\rho_{fuel}}} \tag{2}$$

was calculated.

Considerable effort has been put in the development of low- or nontoxic propellants with high performance. For example, nontoxic hypergolic miscible fuels (NHMF) have been developed that allow one to obtain up to 93% of the specific impulse of NTO/MMH when used with 98% grade H_2O_2 [18]. In the present work, the ideal rocket performance of the combination of silicon hydrides and 98% pure H_2O_2 (which is probably hypergolic) is predicted to be even higher than that of NTO/MMH at the same conditions.

All of the silanes/RGHP combinations examined yield a better peak I_{vac} than the corresponding hydrocarbons as well as the well-known MMH/NTO. The vacuum-specific impulse of SiH_4/RGHP is about 10% higher than for MMH/NTO, and the peak I_{vac} of Si_5H_{12}/RGHP still exceeds the I_{vac} that can be obtained with MMH/NTO by about 3%. At the same time, the combustion temperatures for all silanes/RGHP are much lower than for MMH/NTO at the peak I_{vac}, the difference amounting to more than 300 K for SiH_4/RGHP. The combustion temperatures of hydrocarbons are lower, but, unlike silanes, hydrocarbons do not offer the additional possibility of lowering the combustion temperatures significantly without sharp losses of I_{vac}.

Although the specific densities of silanes are much higher than those of the alkanes, their bulk densities at the optimal mixture ratios are lower than for alkanes, owing to their O/F ratio and high density of the RGHP oxidizer. Therefore density impulse is somewhat lower for silanes than for MMH/NTO. Finally, to get a more realistic description of silane-fueled rockets, the effect of decomposition and oxidation kinetics as well as the impact of condensed combustion products will have to be investigated.

Table 1   Overview of rocket performance characteristics of the silanes/RGHP bipropellants in comparison to hydrocarbons/RGHP and MMH/NTO

Propellant	I_{vac}, m/s	T_c, K	Φ_{max}	ρ, g·cm^{-3}	$(O/F)_{max}$	$\bar{\rho}$, g·cm^{-3}	a_e/a_t
Monosilane	3371	3019	4.0	0.68	1.05	0.93	11.3
Disilane	3241	3135	3.4	0.686	1.12	0.95	11.4
Trisilane	3196	3180	3.2	0.739	1.15	0.96	11.4
Tetrasilane	3170	3219	3.0	0.795	1.20	1.05	11.4
Pentasilane	3161	3245	3.0	0.827	1.22	1.08	11.4
Methane	2992	2905	1.0	0.4211	8.44	1.14	9.9
Pentane	2972	2960	1.0	0.6213	7.50	1.24	10.1
MMH/NTO	3076	3396	1.1	0.874	2.27	1.21	9.8

Acknowledgments

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