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Comparison of Potential Fuels for Martian Rockets Using CO_2

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This paper develops a new approach to Mars in-situ resource utilization that is based on using Martian CO_2 as an oxidizer in rocket engines. The recent proposal to use liquid hydrides as fuel in such engines is examined. The performance characteristics of the CO_2-using rocket are calculated thermodynamically for diborane, pentaborane-9, silane, and aluminum boronhydride as fuel. The ideal specific impulse and mass fraction of condensed phase in a nozzle for these fuels are compared with those for magnesium, beryllium, and beryllium hydride. It has been shown that the ideal specific impulse for the liquid hydrides is lower than for beryllium or its hydride, but higher than for magnesium. However, boranes are characterized by the highest content of condensed phase in combustion products, which may result in extremely high two-phase flow losses in specific impulse. The fairly good ignition and combustion characteristics for magnesium with CO_2 and, on the other hand, the lack of information on combustion of the hydrides and beryllium in CO_2 atmosphere allow the conclusion that currently only magnesium fuel can be considered as fitting for rocket engines using CO_2.

Introduction

IT is generally agreed that the architecture of further Mars exploration will require the use of indigenous natural resources of this planet for propellant production. Most of the in-situ resource utilization (ISRU) concepts[1] consider various methods of liquid propellant production with the use of CO_2, which constitutes 95% of Mars atmosphere. An alternative approach has been recently proposed[2,3] that is based on combustibility of some metals in CO_2. Owing to this fact, the metals could be used as fuel in both CO_2-breathing jet engines[2] and rockets using liquid CO_2 as an oxidizer.[3] The latter is especially important for hopper and sample-return missions that could be undertaken in the coming years.[4,5] The use of Martian CO_2 as an oxidizer in rocket engines could decrease the mass of propellant that would need to be transported from Earth. Thermodynamic calculations of CO_2-using rocket performance have been made previously for several metals and their hydrides and mixtures with hydrogen compounds as fuel. The results for Li, Be, B, Mg, Al, Si, Ca, Ti, Zr, BeH_2, MgH_2, and mixtures of Be and Mg with N_2H_4 have been published.[3] It was shown that beryllium or its hydride ensure the highest specific impulse. However, it was concluded that magnesium is the most practical fuel because of a combination of a relatively high specific impulse, appropriate characteristics of ignition and combustion in CO_2, and zero toxicity.

Of course, the main problem in the use of Mg, Be, or BeH_2 is the need for design of a new rocket engine using powdered fuel. The feed of fuel from a storage tank into a combustion chamber is much more complicated for powders than for liquids. Some additional problems, such as clogging of the injectors because of the sintering of powdered metal after engine shutdown or the difficult ignition of powdered fuels in a multiuse engine, must be solved for successful operation of the proposed engine.

Recently, Zubrin[5] has proposed to avoid the problem of new engine design by using boron hydrides, namely, diborane (B_2H_6), that could burn in a relatively conventional liquid bipropellant engine. He does not report data on ignitability of diborane in CO_2 atmospheres, but makes his conclusions on the basis of the thermodynamic specific impulse calculated for the diborane/CO_2 rocket. He assumes the specific impulse of 300 s for his mission analyses and notes that this value is much higher than 190 s for the CO_2/Mg rocket, as was taken to be optimum in Ref. 3. This comparison is not quite valid, since these values were obtained for different nozzle expansions, 600 and 288, and different CO_2/fuel mixture ratios, 2.5 and 4, respectively.

Moreover, two-phase flow losses of the specific impulse were not taken into consideration by Zubrin.[5] The mass fraction of condensed phase in a nozzle for boron is twice that for magnesium.[3] Furthermore, a part of the condensed boron oxide, B_2O_3, forms during its movement through the nozzle. This can cause additional losses of specific impulse (so-called in-nozzle condensation losses). Also, a substantial disadvantage of boron is the fact that the condensed B_2O_3 in a nozzle is not solid but liquid, which can readily adhere to the inner surface of a nozzle, especially in the throat. This feature, and the great two-phase losses in specific impulse, explain why boranes were not employed as fuel for conventional rockets.

However, Zubrin's proposal[5] to use materials that could burn in a conventional liquid bipropellant engine merits further investigation. Several hydrides could be considered apart from diborane. In the present paper we make thermodynamic calculations of performance characteristics for a rocket using CO_2 as an oxidizer, and diborane, pentaborane-9 (B_5H_9), silane (SiH_4), and aluminum boronhydride [$Al(BH_4)_3$] as fuel. Table 1 presents their physical properties. The performance characteristics for these hydrides are compared with those for Mg, Be, and BeH_2, which have been identified previously[3,4] as the most promising fuels for a CO_2-using rocket engine. The goal of this work is to select materials for further experimental studies.

Procedure

All results of this paper have been obtained with software for thermodynamic calculations from the Institute of Structural Macrokinetics, Russian Academy of Sciences. The computer program is based on the method of thermodynamic potential minimization. The software uses a thermodynamic database for more than 2500 compounds including more than 1000 condensed ones. The thermodynamic data for performance calculations of the compounds considered in the present paper

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Table 1 Physical properties of considered fuels

Fuel	Melting point, °C	Boiling point, °C	Density, g/cm^3
B_2H_6	−165.5	−92.5	0.43 (T = −92.5°C)
B_5H_9	−46.8	62	0.62 (T = 25°C)
SiH_4	−185	−112	0.68 (T = −185°C)
$Al(BH_4)_3$	−64.5	44.5	0.54 (T = 25°C)

have been taken from Refs. 6 and 7. The ideal specific impulse, temperatures, and compositions of combustion products in both a chamber and nozzle were calculated under the assumption of equilibrium flow without losses. All of the presented results have been obtained for the chamber pressure of 10 bar and the exit pressure of 10 mb, appropriate for the Martian rocket engine.[3] A simultaneous increase in both values by a factor of 10 affects the specific impulse only slightly.

Results and Discussion

Figures 1 and 2 present the calculated values of ideal specific impulse and condensed phase mass fraction at the nozzle exit section of a rocket engine using CO_2 as an oxidizer and Mg, Be, BeH_2, B_2H_6, B_5H_9, SiH_4, and $Al(BH_4)_3$ as fuel.

It is seen that BeH_2 ensures the highest ideal specific impulse and relatively low fraction of condensed phase in a nozzle. The specific impulse for pure Be is also higher than for the rest of fuels at the mixture mass ratios higher than 4. However, the ignition and combustion of Be and BeH_2 in CO_2 have not been adequately studied because of the toxicity of the combustion products.

Boranes are characterized by the highest fractions of the condensed phase in the nozzle. For diborane this value exceeds 0.8 at the mixture mass ratio of 2.5 that has been selected as optimum in Ref. 5. It is unclear whether a rocket can operate at all at the 80% content of condensed phase in combustion products. The condensed phase fraction decreases with increasing the mixture mass ratio (the specific impulse decreases too), but, regardless, remains steady for boranes twice that for Mg.

It should be noted that the calculations give much more information than is shown in Figs. 1 and 2. Comparison of the calculated product compositions in the chamber and at the nozzle exit section has shown that in the case of boranes about 25% of the B_2O_3 condenses in the nozzle, which may additionally increase two-phase flow losses.

The specific impulse for diborane is higher than for pentaborane, but the difference is noticeable only when the mixture ratio is less than 4. Such mixture ratios seem unacceptable because of the 60–90% content of condensed phase. For the higher mixture ratios, the performance characteristics of B_2H_6 and B_5H_9 are similar and the selection can be made in favor of pentaborane on the basis of its more suitable physical properties (see Table 1).

The specific impulses of $Al(BH_4)_3$ and SiH_4 are close to each other, but the mass fraction of condensed phase is higher for $Al(BH_4)_3$. Taking into consideration the instability[8] of this fuel, we can reject $Al(BH_4)_3$.

The specific impulse for silane is lower than for boranes, but the mass fraction of condensed phase is lower too. In the case of silane the largest fraction of condensed products, SiO_2, forms in the combustion chamber, and the in-nozzle condensation losses are practically nonexistent. Low two-phase losses and solid-state fraction of condensed products might be the deciding point in favor of silane. Silane, as well as the boranes considered previously, is a stable and storable, but toxic, compound. The calculated values of chamber temperature for silane and both boranes are close to each other and fall in the range between 1200–2000 K. Unfortunately, we do not have data on ignition and combustion for gas mixtures of silane and boranes with CO_2.

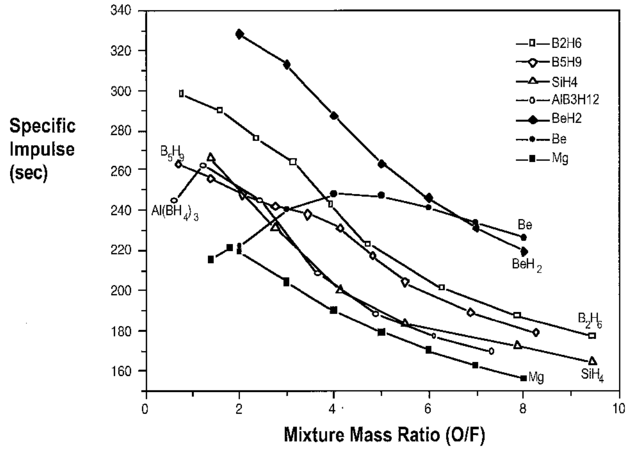

Fig. 1 Ideal (without loss) specific impulse of a rocket using CO_2 as an oxidizer. Chamber pressure is 10 bar, exit pressure is 10 mb.

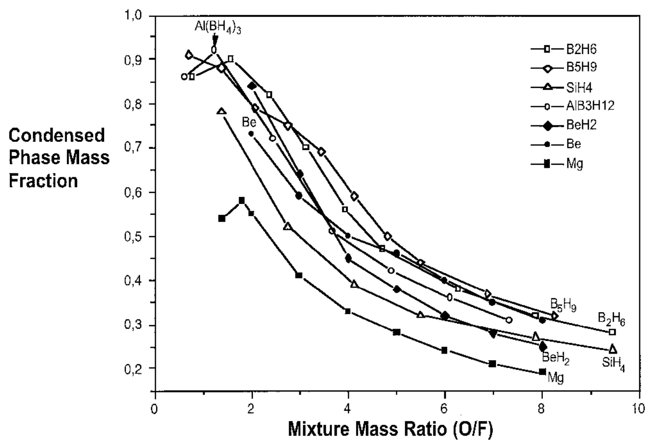

Fig. 2 Mass fraction of condensed phase in a nozzle of a rocket using CO_2 as an oxidizer. Chamber pressure is 10 bar, exit pressure is 10 mb.

The specific impulse of magnesium is the lowest among the considered fuels, but the condensed phase mass fraction is also the lowest for Mg. According to Refs. 9–13, magnesium readily ignites and burns perfectly well in CO_2 and CO_2/CO mixtures, with the maximum flame temperature being equal to 2500–3000 K.

It is also of interest to consider the possibility of replacing pure Mg with Mg/Al alloy. The specific impulse of the CO_2/Al rocket[3] is somewhat higher than in the case of Mg; however, the ignition temperature of Al is significantly higher[14,15] and close to the optimum chamber temperature. This will likely preclude the use of pure Al, because a permanent igniter may become necessary for stable combustion. However, it might be expected that a Mg/Al alloy would be characterized by a lower ignition temperature and a higher burning rate than pure Al. In such a case the replacement of Mg with Mg/Al alloy could result in increasing the specific impulse, while retaining ready ignitability and stable combustion.

Conclusions

Thermodynamic calculations indicate that some liquid hydrides, such as boranes and silane, might be considered as possible candidates for use as fuel in CO_2-using rockets. Their ideal specific impulse is lower than for beryllium or its hydride, but higher than for magnesium. Boranes, however, are distinguished by very high condensed phase fractions in the combustion products, which may substantially decrease the actual specific impulse.

The lack of data on ignition and combustion in CO_2 for the liquid hydrides, as well as for powdered Be and BeH_2, calls for the conclusion that only powdered Mg can be currently considered as an appropriate fuel for the CO_2-using rocket engine. The possibility of replacing pure Mg with Mg/Al alloy for increasing the specific impulse should be also checked experimentally.

Further work on the development of the CO_2-using rocket for Mars missions should be undertaken in two directions. The first one is to perform tests of a model rocket engine using CO_2/Mg propellant. The second one is to perform experiments on ignition and combustion of 1) particles (droplets) of Mg/Al alloy, B_5H_9, Be, and BeH_2 in a CO_2 atmosphere and 2) B_2H_6/CO_2 and SiH_4/CO_2 gas mixtures.

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