

Hybrid Rocket Propulsion and In-Situ Propellant Production for Future Mars Missions

Adrien J. Boiron¹ and Brian J. Cantwell²
Stanford University, Stanford, CA, 94305

This article shows that a combination of in-situ resource utilization and hybrid rocket propulsion represents a very competitive solution for future medium to large-scale missions to the red planet. A high performance liquid oxygen/paraffin medium-scale hybrid ascent vehicle, of which the oxidizer has been acquired through decomposition of carbon dioxide on the surface of Mars, is estimated to achieve more than 40% mass reduction in respect to the same vehicle brought from Earth, thus outperforming all conventional designs. All the technologies needed are detailed and the in-situ propellant production (ISPP) unit is precisely sized for two selected missions: Mars Sample Return (payload of 36 kg) and the medium-scale case (payload of 500 kg). The many advantages of this design (notably in simplicity, safety and size) over currently dominant in-situ liquid-powered concepts are discussed. The innovative idea described in this article supports renewed interest in hybrid rocket propulsion for space exploration and opens the way for newly ambitious robotic and manned missions to the planet Mars.

Nomenclature

<i>ISPP</i>	= in-situ propellant production
<i>EDL</i>	= entry, descent and landing
<i>MSR</i>	= Mars sample return
<i>MAV</i>	= Mars ascent vehicle
<i>LMO</i>	= low Mars orbit
<i>TRL</i>	= technology readiness level
<i>YSZ</i>	= yttrium-stabilized zirconia
<i>RTG</i>	= radioisotope thermoelectric generator
<i>RPS</i>	= radioisotope power system
<i>ASRG</i>	= advanced stirling radioisotope generator
<i>CO₂</i>	= carbon dioxide
<i>O₂</i>	= dioxygen
<i>CO</i>	= carbon monoxide
<i>LOX</i>	= liquid oxygen (cryogenic fluid)
<i>O/F</i>	= oxidizer to fuel ratio
<i>sol</i>	= martian day

I. Introduction

MARS, an object of fascination since it was first observed by telescope in the 1600s, is the next outward step of human space exploration. Key scientific questions, on the origin of life, the formation of the solar system, and our planet's future are hoped to be answered on the red planet. So far, our knowledge of Mars has remained limited because all experimentation had to be performed remotely and in-situ. Since no landing probe was ever planned to return experiments were restricted to those that were able to fit within the payload constraints, resist the difficult journey and operate autonomously in a harsh extraterrestrial environment.

¹ Graduate Student, Stanford University and ISAE SUPAERO, Toulouse. adrien.boiron@free.fr. AIAA Member.

² Edward C. Wells Professor of the School of Engineering, Department of Aeronautics and Astronautics. cantwell@stanford.edu. AIAA Fellow.

The next stage of Mars exploration, relying on two-way missions, will enable tremendous scientific discoveries. As for the Moon exploration program, firstly sample return and analysis on Earth and secondly manned expedition will constitute and trigger unprecedented scientific and human achievements. Round-trip planetary missions truly are an extraordinary feat of engineering, especially for Mars, where entry, descent and landing (EDL) are known to be particularly challenging¹. In fact, landing high-mass systems safely on Mars, which is definitely the case if you are carrying the propellant needed for the return, is still an active research priority².

In-situ propellant production (ISPP) is a very elegant solution to this problem. By acquiring the propellant for the return flight on the planet being explored, the mass to be liberated from Earth and landed on the planet is reduced, thus greatly lowering mission cost, risk and EDL challenges. Such improvements are so critical that in the long term ISPP could be the only viable solution to enable large-scale round-trip planetary missions. This potential was first acknowledged and considered in 1978 by Ash et al.³ and since then widely studied and discussed for Mars missions.

This article lies within that heritage, making a strong case for in-situ resource utilization. More interestingly, this is the first article to study the use of hybrid rocket propulsion in the ISPP framework. Since the end of the 90s and the discovery of several high regression rate hybrid configurations (liquefying fuels⁴, swirling combustion⁵), hybrid rocket development has started anew and reached such a level of maturity that it can now be competitive with classical types of rocketry and has been considered for space missions to Mars^{6,7}. It will be shown here that a combination of hybrid rocket propulsion and ISPP outperforms conventional designs brought from Earth and presents advantages over liquid-powered in-situ designs for high-mass Mars return missions.

II. Martian Resources

When considering ISPP, we first need to look at the planet's resources, to determine which compounds are available to extract in-situ and could lead to effective propellants for the return flight. Our knowledge of Mars resources comes from NASA's Viking program⁸ in the 70s; soil and atmospheric compositions are shown in table 1.

Atmosphere	Abundance	Soil	Percent by Mass
CO ₂	95.32%	Mg	5.0 ± 2.5
N ₂	2.7%	Al	3.0 ± 0.9
⁴⁰ Ar	1.6%	Si	20.9 ± 2.5
O ₂	0.13%	S	3.1 ± 0.5
CO	0.07%	Cl	0.7 ± 0.3
H ₂ O	0.03%	K	< 0.25
³⁶⁺³⁸ Ar	5.3 ppm	Ca	4.0 ± 0.8
Ne	2.5 ppm	Ti	0.5 ± 0.2
Kr	0.3 ppm	Fe	12.7 ± 2.0
Xe	0.08 ppm	L*	50.1 ± 4.3
O ₃	0.04-0.3 ppm	X**	8.4 ± 7.8

Table 1. Resources on Mars. Adapted from Owen et al.^{8 pp. 4635-4639} and McKay et al.⁹. *L is the sum of all elements not directly determined. **If the detected elements are all present as their common oxides (Cl expected), then X is the sum of components not directly detected, including H₂O, NaO, CO₂ and NO_x.

The composition of the atmosphere at the surface of Mars is very well known, and it is composed almost entirely of carbon dioxide (95.32% by mole). It is the only gas present in reasonably large amount to be interesting for ISPP. This carbon dioxide can be extracted by a dust filter, a CO₂-selective mechanism and a compressor.

The Martian soil presents lots of unknowns and much more challenges for extraction. Even if it is rich in interesting metals (Mg, Al), mining metals on Mars is still far in the future. Also, the presence of water in the soil is for now too uncertain to envisage extraction (for further discussion on water recovery, see McKay et al.⁹).

III. Propellant Production on Mars

Carbon dioxide is by far the most easily accessible resource on Mars. As such, it has always played a key role in Mars mission designs involving ISPP. But its direct use as oxidizer in a rocket system is problematic for two reasons: it is a rather low performance oxidizer, leading to high-mass ascent systems; it can only burn purely metallic fuels in the powder form, but they are strong ignition challenges.

That is why in most designs, CO₂ is used to produce higher energy propellants through chemical reactions realized at the surface of Mars. Two pathways are possible: either decomposition, producing oxidizer such as oxygen, or hydrogenation, producing organic fuels such as methane, ethylene, etc.

In 1978, Ash et al.³ suggested to produce oxygen and methane from water and carbone dioxide, through electrolysis of water (1) and the Sabatier process (2):



This full-ISPP idea (both oxidizer and fuel were produced in-situ) had the advantage that half the water used in the electrolysis cell could be supplied by the methanation reaction, reducing as much the amount of water needing to be extracted. But one year after, Stancati et al.¹⁰, then Ash et al.¹¹, acknowledged that water extraction on Mars was too big a challenge and proposed instead only partial ISPP. They would bring the methane fuel from Earth and produce oxygen on Mars. Oxygen was no longer obtained through electrolysis of water, but through thermal decomposition of carbon dioxide (3):



As early as 1979, the suggested method for that decomposition was solid oxide electrolysis¹⁰. That lead French¹² to propose in 1985 a very simple but lower performance design, that would use CO₂ as monopropellant, i.e. after having decomposed CO₂, the recombination reaction of carbon monoxide and oxygen would be used to propel the rocket. Ramohalli et al.¹³ showed that French's solution, even total in-situ, did not do as well as Stancati et al.¹⁰ partial in-situ solution using methane and oxygen.

In 1991, Zubrin et al.¹⁴ proposed to transport only hydrogen from Earth, make it react upon landing with CO₂ and produce methane through the Sabatier process. But electrolysis of the resulting water could only produce enough oxygen to reach an off-optimum O/F ratio of 2. It would mean a theoretical specific impulse of 340s and propellant mass leveraging of 12 (12 kg of oxygen-methane produced per kilo of hydrogen carried from Earth), that is more than 3 times the mass leveraging of 3.4 achieved by Stancati et al.¹⁰ by bringing methane directly.

In Zubrin's scenario, a higher propellant mass leveraging of 18 can be achieved by producing extra-oxygen in-situ through CO₂ decomposition to get to an optimal O/F of 3.5 and a theoretical specific impulse of 373s. This latter solution, requiring no less than three chemical reactors to be operated at the surface of Mars, was used in 1999 by Thunissen et al.¹⁵ for the design of a potential 2007 Mars Sample Return (MSR) mission.

Pursuing this idea further, Hepp et al.^{16,17} estimated the potential of other organic fuels. Also assuming oxygen is produced on Mars and hydrogen is brought, they calculated the propellant mass leverage of several organic fuels to minimize the amount of hydrogen required. They showed that if methane has a propellant mass leverage around 20, ethane is at 24, ethylene 31 and acetylene 53. Acetylene is very interesting for ISPP thanks to its high in-situ-acquired carbon content and its high energy triple-bond that more than compensates losses due to a higher exhaust molecular weight, leading to a specific impulse still above 400s. But acetylene, besides being a real explosion hazard, needs to be produced in high-energy chemical reactors yet to be miniaturized and developed for Mars in-situ applications.

It is to be noticed that contrary to water electrolysis and the Sabatier process, solid oxide electrolysis was far from a sufficient level of development, when in 1987 Frisbee¹⁸ sized and designed the first Martian ISPP system decomposing CO₂. In the 90s, Sridhar¹⁹⁻²³ led a very successful research and development effort on this crucial technology. By working several years on solid electrolysis in laboratory, he reached two critical thresholds in performance and maturity for its use in space missions. In 1995¹⁹, his design of a Stancati et al.¹⁰ partial in-situ MSR Mission, the first to be based on proof-of-concept, scale-up, and long-term results obtained in laboratory, gave great results. The mass of the in-situ oxygen production unit and of the methane carried was shown to add up only to around 40% of the overall propellant mass, thus generating significant and solid gains.

The promising nature of Sridhar's research led NASA to allow for one module aboard the 2001 Mars Surveyor Mission on ISPP: Sridhar then worked with Baird and Gottman^{22,23} on the Mars In-situ Propellant Production Precursor²⁴ (MIP). It would have been the first ever module to produce oxygen at the surface of Mars, had the mission not been cancelled. This was a real setback for ISPP researchers and believers, since despite its readiness, the module was also not sent on the next missions.

Since then, interest and momentum for ISPP has rather faded away. Most ISPP mission designs carried out so far have concerned MSR missions^{10,15,19}, missions that can now be achieved with much smaller payloads thanks to miniaturization and an Earth return vehicle that now remains in Martian orbit (Mars ascent vehicle (MAV) payload mass of 36 kg in 2010⁶ against 240 kg in 1978³ used until 1995¹⁹). This evolution, as we will see in this article (Part

VII), made ISPP rather irrelevant for MSR missions because it was unnecessarily complex and risky. And even if ISPP has remained very relevant for medium-scale to large-scale future missions to Mars, the recent shrinking of NASA's operational horizon has put it aside.

This article aims to revigorate interest in ISPP, as the authors believe it is the new paradigm in space and planetary exploration, that it will enable newly ambitious missions, manned in particular, to the red planet and beyond. But before explaining how hybrid rocketry emerges as a suitable candidate for ISPP and Mars rocket applications, it is important that we discuss first another stream of research that focused on CO₂/metal powder engines.

IV. CO₂-Metal Powder Rocket Propulsion

If the conventional in-situ research just described was mostly realized in the United States and more specifically by researchers working within the Jet Propulsion Laboratory (JPL) based in Pasadena, CA, CO₂/metal powder engines have been studied all over the world, in Japan, Russia, Europe and the United States.

In 1988 in Japan, Yuasa and Isoda²⁵, pursuing an idea born in the 1960s, started looking at martian CO₂-breathing engines using various metals as fuel. They conducted sample combustion experiments of Li, Mg, B and Al in a carbon dioxide stream. Not late afterwards, Shafirovich and Goldshleger^{26,27} studied more fuel possibilities over the years by running thermodynamic calculations. They looked at pure metallic fuels Li, Be, B, Mg, Al, Si, Ca, Ti, Zr, magnesium and beryllium hydrides, and then at borane and silane liquid hydrides.

Both these studies came to the same conclusions. Magnesium appeared as the most suitable fuel for a CO₂ rocket engine. It could ignite spontaneously close to its melting temperature (1000K), while delivering a relatively high specific impulse for a CO₂ engine, thanks to an elevated heat of reaction and a high rate of vapor phase combustion. Aluminum was another strong candidate; it could provide a better performance but presented severe ignition challenges, because of its alumina protective layer that resists ignition beyond 2000K. Aluminum-magnesium alloys looked promising, as a possible compromise between performance and ignitability.

Shafirovich and Goldshleger also realized combustion experiments and developed a model to explain the combustion of powdered magnesium with CO₂ and CO/CO₂ mixtures^{26,28}. With Gokalp, a researcher working at CNRS in Orléans, France within a group that also investigated magnesium combustion in CO₂ gas²⁹, Shafirovich discussed in 2000 the design of an in-situ MSR mission using CO₂-metal powder propellants³⁰. Their idea was to acquire carbon dioxide from the Martian atmosphere and make it burn with metal powder, first brought from Earth but in the future mined on Mars (magnesium and aluminum are abundantly present in Martian soil, see table 1). This alternative ISPP concept is hoped to be a great solution if one day a long term human colony is established on the red planet. Quite recently in 2007, this idea was experimentally investigated at NASA Marshall Space Center³¹ and extensively studied by Ismail³², chief engineer of Interplanetary Expeditions, a space organization based in the UK.

But despite a promising nature on paper, if nothing else, this international research effort has revealed the shortcomings of CO₂/metal powder propulsion. Because of its weak oxidizing power, CO₂ can only burn metallic fuels in the powder form, leading to a complex propellant feed system such as a pneumatic feed of CO₂ gas carrying metal powder. Also, the performance reached remains rather low (around 200s of specific impulse) and is unhelped by a high condensed phase mass fraction in the exhaust due to the metal oxides. Ignition challenges, on which research is still ongoing, have been hoped to be resolved by using nanoparticles. Reina et al.³³ have shown that aluminum nanoparticles ignite as early as 1000K in CO₂, the same as micron-size magnesium powder. But for high performance rocket applications, these nanoparticles would need to be not oxidized to avoid a high alumina mass fraction in the nano-size fuel, and that is far from easy to manufacture.

At last, Martian CO₂-breathing ramjets, which were the initial interest²⁵, have been proven to be problematic. On top of the issues already discussed, the low density of the Mars atmosphere leads to extremely large and thus impractical inlet designs, and the low pressure is believed to not allow complete combustion of the metal powder⁷.

V. The Hybrid for Mars

A. Presentation

Hybrid rockets, based on a combination of liquid oxidizer and solid fuel (see figure 1), were first tested in Russia by Korolev and Tikhonravov in 1933. Their development continued in France for meteorological rockets in the 60s and also in the United States up to the 80s, notably by the American Rocket Company (AMROC). Their main drawback was the low regression rate of hybrid fuels such as HTPB, imposing multiport designs and complicated injection systems, for a moderate performance. In 1999, Stanford researchers³⁴ proved the existence of high-

regression paraffin-based hybrid fuels, allowing much simpler single port chamber configurations and achieving higher performance. This revolution strongly increased the competitiveness of hybrid rockets with respect to other traditional rocket engines, and started a new era of hybrid rocket development.

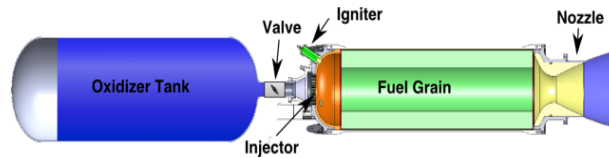


Figure 1. Conceptual schematic of a hybrid rocket.

The concept behind the hybrid, that of storing fuel and oxidizer in two different tanks and phases, one liquid and one solid, presents an important safety advantage. The inert nature of both stored propellants and the one-valve-only throttling and thrust termination capability substantially reduce operational risks such that in hybrid propulsion reduced development and recurring costs are expected in the long run. The physics of hybrid combustion, characterized by flux-driven regression and not pressure-driven regression as in solids, contributes also to this safety feature. Then, the hybrid benefits from an interesting position of compromise between the two classical types of rocketry in terms of performance, manufacture and operation. For example, with respect to liquid engines, hybrids provide a higher fuel density, can be enhanced by solid additives, are mechanically simpler, more tolerant to fabrication errors and have one less liquid to manage; compared to solids, hybrids provide higher specific impulse, are chemically simpler, more tolerant to processing errors and have one more liquid to manage allowing for full thrust modulation. Thanks to these advantages, hybrid rockets have become a suitable and competitive solution in numerous missions, in suborbital flight but also we argue in Mars rocket applications.

B. Previous Research

In fact, a hybrid rocket design was proposed by Chandler et al.⁶ in 2010 for a MAV design, using a paraffin-based fuel and Nytox³⁵ (combination of nitrous oxide (N₂O) and oxygen) as oxidizer. This solution benefits from all the advantages of the hybrid, uses an oxidizer that would be perfectly storable in the Martian temperature conditions, and aluminum additive in the paraffin fuel to increase performance. They showed that a hybrid MAV would be lighter than a solid propulsion design, and therefore a very convenient choice for a MSR mission. But this hybrid rocket solution does not use any in-situ propellants: everything is to be brought ready to fire from Earth.

At the same time, Karabeyoglu⁷ proposed a partial in-situ N₂O-CO₂ hybrid rocket, using carbon dioxide present in Mars atmosphere to diminish the mass needed to be brought to Mars for a given MSR payload. His idea was the following: since CO₂ and N₂O have very similar physical properties, they are perfectly miscible in the entire range of compositions; we can then create a paraffin-fuel with a very high aluminum content (80%), use N₂O to react with paraffin and melt the aluminum oxide protective layer, so that CO₂ can react with aluminum (it was the same idea behind magnesium-aluminum alloys for CO₂/metal powder rockets). Adding oxygen to the mixture would improve performance, allow partial self-pressurization, increase safety and was thus recommended. The resulting rocket turns out to be an in-situ adaptation of Chandler et al.⁶, in which an optimal amount of the brought oxidizers is replaced by Martian CO₂, thus enabling higher performing MSR missions.

C. Objectives

But we can go further. We saw in Part II for example that the oxygen Chandler et al.⁶ and Karabeyoglu⁷ are bringing from Earth for their MAV systems can be produced on Mars. The next logical step is then to investigate maximally in-situ hybrid rocket systems for Mars ascent, and that is precisely the goal of this paper.

The main questions to be answered are the following:

- Which propellants to choose?
- How to acquire them?
- How much mass, space and power would that require?
- How does this hybrid in-situ MAV perform comparatively to other designs?

D. Propellant Combination

Like many before us (see Part III), we assume that carbon dioxide is the only available resource on Mars. For hybrids, carbon dioxide can be used directly as oxidizer, or to produce higher performing oxygen; it cannot realistically be used yet to produce solid hybrid fuels such as HTPB, HDPE or Paraffin. In a future where this could be possible, using the same thinking as Hepp et al.¹⁷, an in-situ produced paraffin/O₂ combination would quite interestingly lead to a very high propellant mass leverage, close to 30 comparable to ethylene.

But in the practical present, we have to bring the hybrid fuel from Earth since only the oxidizer can be acquired on Mars. The O/F ratio then represents the fraction of in-situ propellant over brought propellant (and in-situ propellant mass fraction is then the same as oxidizer propellant mass fraction). That is why for hybrids, a sufficiently high O/F ratio is important to benefit from ISPP.

Like Chandler et al.⁶, we choose a paraffin-based fuel because pure paraffin wax has a low glass transition temperature of about -108°C, much lower than the glass transition temperature of polymeric fuels (i.e. for HTPB the glass transition occurs at -70°C). This makes paraffin a viable fuel for the Martian environment where with a -60°C average, the coldest temperature is for example just -111°C in the winter morning at Holden Crater, the most extreme MSR site of interest. Furthermore, since paraffin is highly crystalline, the fuel glass transition is quite weak and the fuel grain is expected to recover from departures below its glass transition temperature⁶.

For our hybrid in-situ MAV, we choose then to associate the paraffin fuel with liquid oxygen (LOX), for their high joint performance, high O/F ratio (see Section E), and many other combined qualities that will be developed later (see Section F).

E. Operational O/F Ratio

In their 2007 MSR mission design, Thunissen et al.¹⁵ chose an operational O/F of 3.9, which is sensibly higher than the 3.45 optimal O/F of liquid methane and LOX shown on figure 2. That was because thanks to a slow decrease in performance at O/F ratios beyond the optimum, it was possible to replace some brought fuel by in-situ acquired oxidizer and further reduce the brought mass to Mars. For ISPP round-trip missions, one should indeed be careful to choose the configuration that minimizes the lift-off mass from Earth, which is the true aim, and may not be at the same time minimizing the lift-off mass from the extraterrestrial body.

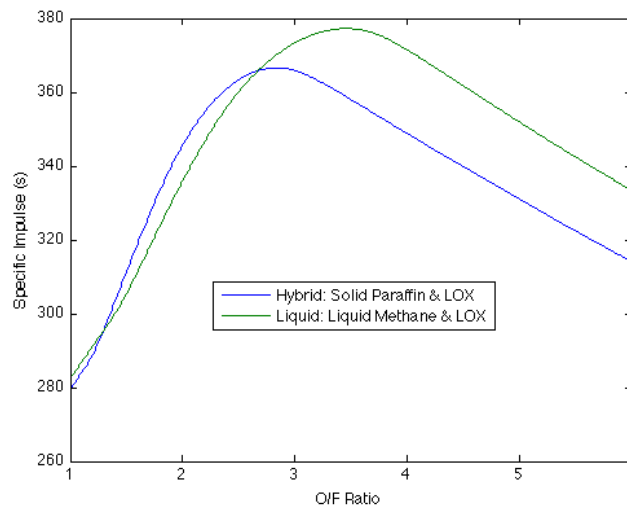


Figure 2. Specific Impulse vs O/F Ratio for Pure Paraffin and Methane with LOX. Results from rocket equilibrium calculations in CEA2³⁶, with the following parameters: chamber pressure 500 psi, nozzle area ratio 70, shifting equilibrium, exhaust in vacuum, paraffin grain at martian average temperature 210K.

On figure 2, we can see that the specific impulse provided by the hybrid decreases rather slowly and in the same manner as the liquid engine beyond its combination optimum O/F, located here at 2.84. There exists the possibility then that operating the hybrid oxidizer-rich could lead to a reduction of the brought mass. To investigate this idea, rocket sizes and staging have to be calculated. For simplicity, we assume that the hybrid MAV has two identical stages (identical means here same structural efficiency ϵ and specific impulse I_{sp}). The targeted orbit is a low Mars

orbit (LMO) at 500 kilometers of altitude, for which the speed increment ΔV required is 4375 m/s⁶. The following relation, derived by one of the authors³⁷, provides the payload fraction Γ for n identical optimized stages (optimization of the staging is carried out with Lagrange multipliers):

$$\Gamma = \left(\frac{1 - \epsilon \exp\left(\frac{\Delta V}{n g_o I_{sp}}\right)}{(1 - \epsilon) \exp\left(\frac{\Delta V}{n g_o I_{sp}}\right)} \right)^n \quad (4)$$

Here g_o is the acceleration of gravity (9.81 m.s⁻²), the structural efficiency is chosen at $\epsilon = 0.18$ and the specific impulse is a function of the O/F ratio, obtained through rocket equilibrium calculations in CEA2³⁶, as shown in figure 2. Since this study is independent of the payload mass, we will use “factor” quantities, noted with X. For example, the brought rocket mass factor is defined as the brought rocket mass (i.e. mass of the fuel and rocket structure) divided by the payload mass. It is equal to the lift-off mass factor (inverse of payload fraction) minus the in-situ acquired mass factor (oxidizer mass fraction over payload fraction):

$$XM_{brought} = XM_{lift-off} - XM_{in-situ} = \frac{1}{\Gamma} - \frac{O/F}{1 + O/F} \frac{1 - \Gamma}{\Gamma} (1 - \epsilon) \quad (5)$$

The overall brought mass we wish to minimize is then the sum of the rocket brought mass, the lander mass and the ISPP unit mass:

$$XM_{overall\ brought} = XM_{brought} + XM_{lander} + XM_{ISPP\ unit} \quad (6)$$

The lander mass, being a monotonic function of other masses, can be removed. The ISPP unit mass, on the contrary, is expected to increase as the O/F increases, thus reducing the benefits of oxidizer-rich engine operation on the overall brought mass. We neglect its effect at first. The minimization of the overall brought mass then reduces to the minimization of the brought rocket mass, which is through the use of CEA2³⁶, an explicit function of the O/F.

As shown on figure 3, the minimum brought mass O/F is 3.42. At that O/F, the ideal specific impulse is 359.5s, the brought rocket mass factor is 2.5543, the in-situ acquired mass factor is 2.6980, and the lift-off mass factor is 5.2523 (payload fraction of 0.1904). For comparison, at the combination optimum O/F of 2.84, the ideal specific impulse is 366.6s (+1.86%), the brought rocket mass factor is 2.5999 (+1.79%), the in-situ acquired mass factor is 2.4655 (-8.62%), and the lift-off mass factor is 5.0654 (-3.56%) (payload fraction of 0.1974 (+3.68%)). Thus, by acquiring roughly 9% more oxygen on Mars, we can reduce the Mass to be delivered on the surface by close to 2% in respect to the system at optimum combination O/F.

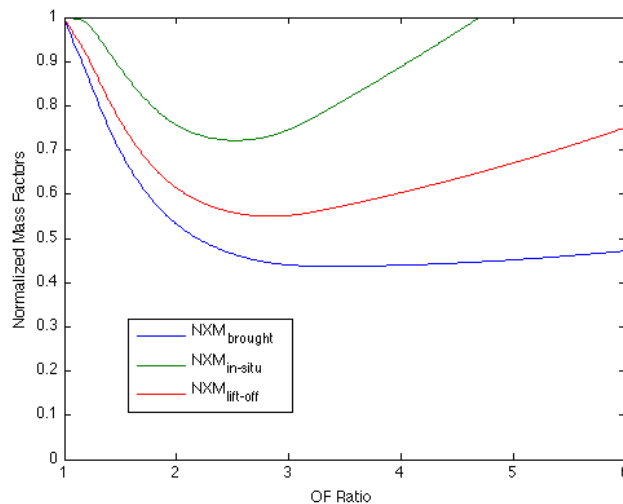


Figure 3. Normalized Mass Factors (NXM) vs O/F Ratio for Pure Paraffin and LOX. Mass factors are normalized to their value at an O/F of 1. Brought rocket mass factor minimum is at O/F of 3.42, lift-off mass factor minimum at 2.84 (corresponding to maximum I_{sp} in figure 2), and in-situ acquired mass factor minimum at 2.52. Results using rocket equilibrium calculations in CEA2³⁶, with the same parameters as in figure 2.

To assess the interest this oxidizer-rich operation, we use the medium-scale case studied later (see Part VIII) as example. The payload mass for that case is 500kg, so we would have a brought mass of 1277kg at 3.42 O/F, instead of 1300kg at 2.84 O/F: 23kg are saved. But at the same time, the oxygen production, and with it the ISPP unit mass, increase by 9%. It is estimated the ISPP unit mass for that case is of the order of 250kg, of which 9% amount also to 23kg, cancelling previous gains.

Thereby, we demonstrate that operating the LOX/Paraffin hybrid oxidizer-rich leads to no overall brought mass reduction, since an increase in ISPP unit mass is estimated to compensate for the decrease in rocket brought mass. Moreover, since the oxidizer-rich configuration leads to a lower density impulse and a larger MAV, it is discarded. The hybrid MAV will hence be operated at the optimal combination O/F of 2.84.

F. Emergence of the Hybrid Solution for Mars

This LOX-Paraffin hybrid solution appears as a suitable candidate for Mars ISPP missions, in the continuity of all streams of research, conventional (Part III), metal powder (Part IV) and hybrid (V.B).

I. Connection to conventional in-situ research

The connection of the hybrid solution to conventional in-situ research is very strong. Precisely, the choice and feasibility of this hybrid ISPP configuration, in fact a Stancati et al.¹⁰ partial in-situ design with methane replaced by a hybrid fuel, is highly indebted to the knowledge and results developed by conventional in-situ research since 1978. For instance, the hybrid benefits directly from years of O₂ production research that have made possible the in-situ production of its LOX oxidizer.

But also, the hybrid goes beyond on many aspects and provides fresh ideas to the debate. Quite significantly, it offers a higher fuel density, overall increased safety and simplicity, and half as much cryogenic liquid handling as Stancati et al.¹⁰. As such, the hybrid solution may represent the next step of conventional in-situ research.

Moreover, the matching of paraffin material properties to the Martian environment removes the need for fuel thermal control at the surface of Mars⁶. Concerning the journey in space, since paraffin can easily recover from its glass transition, and previous tests have shown no paraffin outgassing down to vacuum levels of 0.003 psi⁶, the paraffin fuel is expected to withstand space vacuum. If not, a simple pressure barrier could eventually be implemented. Hence, contrary to liquid methane, the paraffin-based fuel should not need thermal control (and maybe only a modest pressure barrier) at any time of the mission, in space and on Mars, leading to a much simpler fuel casing system with substantial power and mass savings.

The hybrid also has the advantage that its fuel grain composition can be modified easily with diverse metallic and structural additives, providing the possibility to tailor its performance, O/F, regression rate, fuel grain strength and thermal properties to find the right configuration for a given Mars ISPP mission. But metallic additives, for example, are not as attractive in ISPP applications since they shift O/F to lower values.

We saw before that a rocket equilibrium calculation for our hybrid at an O/F of 2.84 (and thus an in-situ acquired oxidizer that amounts to 74% of the propellant) gives an ideal specific impulse of 366.6s, which is very satisfactory. In fact, LOX/Paraffin achieves at a lower O/F ratio and a higher fuel density a comparable specific impulse level to that of Stancati et al.¹⁰ and Zubrin et al.¹⁴ with their LOX/Methane design. Hence, the hybrid rocket will always be substantially smaller (higher density impulse) for a given mission, which can be critical and even mission-enabling since the MAV has to fit within the Mars Lander and the Earth rocket launcher.

Furthermore, the 2.84 O/F hybrid is not so much less interesting for ISPP than the 3.4 O/F liquid Stancati et al.¹⁰ solution: in-situ acquired oxidizer only drops from 77% to 74% of the propellant mass. Mass savings coming from the absence of fuel thermal control and liquid management systems, but also from a smaller ISPP unit since much less oxygen is needed for the hybrid, mostly compensate the 3% propellant mass fraction loss.

The second bi-propellant in-situ liquid-powered concept the hybrid has to relate to is the one provided by Zubrin et al.¹⁴. As explained in Part III, Zubrin's scenario reaches a higher propellant mass leverage than Stancati et al.¹⁰ and the hybrid at the cost of bringing liquid hydrogen and operating three different chemical reactors on Mars. The failed attempt of Thunissen et al.¹⁵ in designing a Zubrin MSR mission has demonstrated the danger of over-complexification when it comes to ISPP. For the same reason that we do not believe that ISPP is relevant for MSR missions, we believe that the Zubrin ISPP presents too many unnecessary challenges for the first stage of medium to large-scale missions to Mars, for which one chemical reactor to be operated in-situ on Mars provides already enough challenges and propellant mass leverage.

Still, for the second stage of long-term missions with established infrastructures on the red planet, the Zubrin ISPP is definitely the most attractive conventional solution. But by then, MAVs should certainly have humans on board, for which safety is a critical factor. The safety increment provided by hybrids over conventional types of rocketry has already directed most of the suborbital tourism companies towards hybrid propulsion, and it might be

the same for future Mars rocket companies. The hybrid solution may therefore have in the future a bigger role to play than has been so far anticipated.

Finally, as we have seen by confronting it with the two dominant in-situ liquid-powered designs, this hybrid LOX-Paraffin is very promising. It dominates others in the crucial areas of simplicity, size and safety, and is expected to be very competitive. In Part VII and Part VIII, we will carefully size this hybrid MAV system, to confirm that impression.

2. Connection to CO₂/metal powder rockets

Even if the LOX/Paraffin hybrid rocket does not use any CO₂, and only maybe a very limited amount of metal powder, its choice owes a lot also to the CO₂/metal powder rocket developments. When studying those (see Part IV), we realize that most concerns originate from the weak oxidizing power of CO₂, which in turn requires metallic fuels to be in powder form. It should be noted that in most research so far the bipropellant engine employing metal powder has been preferred to the hybrid engine because of the absence of any additional bounding or gelling compounds, which may reduce the specific impulse³⁰. But since the discovery of high-performance binders such as paraffin in 1998^{4,34}, this assertion has remained true only when limiting oneself to employ CO₂ as oxidizer.

In other words, the idea is the following: by adding some higher energy oxygen to the oxidizer (acquired in-situ through decomposition of CO₂ as in conventional in-situ research), we can bind and burn the metal powder with paraffin and thus remove all severe issues connected with metal powder handling while also appreciably diminishing the condensed phase mass fraction in the exhaust. We would then have a CO₂/O₂/Paraffin/Al-Mg hybrid engine, quite similar to what Karabeyoglu⁷ suggested, just without N₂O, which cannot be produced on Mars.

Two new issues arise, related to the oxidizer mixture and to, as always with CO₂, ignition. By analogy with Nitrox³⁵, since CO₂ and N₂O have very similar properties⁷, we can imagine realizing a liquid mixture of oxygen and carbon dioxide as oxidizer. The problem is that CO₂, having a freezing temperature actually higher than N₂O (-78°C against -91°C at 1 bar), is even less inclined than N₂O to retain the highly volatile O₂ in their joint liquid mixture. It means that a liquid mixture of O₂ and CO₂, at a reasonable storage pressure which needs to be built on Mars, should not be able to contain more than 15% oxygen.

But 15% oxygen, despite the lack of knowledge on such unconventional hybrid ignition configurations, is not probably enough to ignite paraffin. We can reasonably estimate that 30 to 50% oxygen at least should be sufficient to ignite paraffin and eventually aluminum. But then, one tank cannot suffice anymore to feed both oxidizers into the combustion chamber: we need separate feedlines and storage tanks for oxygen and carbon dioxide.

Fuel \ Oxidizer	Low O ₂ Content (30%)	High O ₂ Content (50%)
High Al content (80%)	- ignition - performance + decomposition needs - condensed phase - optimal O/F + fuel density + oxidizer density + liquid phase exit	+ ignition + performance - decomposition needs - condensed phase - optimal O/F + fuel density - oxidizer density + liquid phase exit
Low Al content (50%)	+ ignition = performance + decomposition needs + condensed phase - optimal O/F - fuel density + oxidizer density - solid phase exit	+ ignition ++ performance - decomposition needs + condensed phase + optimal O/F - fuel density - oxidizer density = liquid/solid phase exit

Table 2. CO₂/O₂/Paraffin/Al hybrid propellant choice. *The left sign indicates the level to which the corresponding feature is optimized and leads to an improvement in the overall hybrid solution, in the following order: ++>+>=>-.*

To assess the interest of this CO₂/O₂/Paraffin/Al-Mg hybrid engine, we ran more than a hundred CEA2³⁶ calculations to cover the entire propellant space, from 30 to 50% O₂ mass fraction in the oxidizer, from 80% to 50% Al mass fraction in the fuel, for O/F ratios ranging from 1 to 3.5. Aluminum was preferred to magnesium for performance, and its presence in the fuel needed to be reduced to diminish the condensed phase mass fraction in the exhaust. Parameters were a chamber pressure of 500 psi, reactants in Martian temperature conditions (210K) and nozzle area ratio of 40 exhausting in vacuum with shifting equilibrium. The results of those thermodynamic rocket calculations are summarized in table 2.

Ultimately, the best CO₂/metal hybrid configuration we found was in the High O₂-Low Al corner, for a good ignitability and a reasonable condensed phase mass fraction in the exhaust (23%). Being operated at an O/F ratio of 3 convenient for ISPP, it provided an interesting 294s of vacuum specific impulse for a composition 50/50 O₂/CO₂ and 50/50 Paraffin/Al. At an O/F of 2.5, it could reach 297s of specific impulse at the cost of a higher condensed phase mass fraction in the exhaust (27%).

However, when moving on to the next phase of launcher sizing for standard Mars missions such as MSR, this rather complex bi-oxidizer hybrid system could not compete with the “fully pushed” right-down corner of table 2, the LOX/Paraffin hybrid. Even for the smallest missions such as MSR, where we would expect using some CO₂ could be interesting to reduce the mass of the ISPP unit while not losing too much performance, it appears that the gap in performance between CO₂ and O₂ is too important for such trade-offs to be effective. In fact, the bi-oxidizer hybrid would need around as much O₂ as the LOX/Paraffin for a standard MSR mission due to the drop in performance implied by CO₂, which is not acceptable. This explains notably why CO₂ was not chosen as oxidizer for the hybrid MAV.

To conclude, the LOX/Paraffin hybrid surfaces as an appropriate solution when trying to alleviate or solve the issues posed by CO₂/metal powder bipropellant rockets.

VI. Enabling Technologies

In this part, we detail all the technologies needed for this hybrid ISPP MAV, their origin, principle and current state of development. The performance metrics to be used later (Parts VII-VIII) will also be provided.

G. LOX/Paraffin Hybrid Rocket

The hybrid rocket chosen for our MAV has been already under development for more than 5 years at Space Propulsion Group, Inc, a rocket company based in Sunnyvale, CA. With their LOX/Paraffin design, they reached a performance level of 340s of vacuum specific impulse for a nozzle area ratio of 70. Their engines benefit from a proprietary LOX passive vaporization system which operates upstream of the combustion chamber, thus enabling injection of gaseous oxygen only. They achieved stable combustion of motors of 11 and 22 inches in diameter with high levels of combustion efficiency (>95%) and are currently continuing the development of this high performance hybrid rocket technology.

This value of 340s of delivered vacuum specific impulse will be used in the MAV sizing study. It is to be noted that for methane/LOX engines, delivered performances of 342s and 350s were assumed for Sridhar's two MSR missions¹⁹. Also, the off-optimal-O/F design from Thunissen et al. lead to a lower delivered specific impulse in the 330-335s range¹⁵. The delivered specific impulse levels for the hybrid and liquid engines used in ISPP mission designs for Mars are therefore of the very same magnitude.

H. CO₂ In-Situ Decomposition

1. Technique Selection

A key aspect of ISPP mission design is the choice of the ISPP technique, since it is responsible for most of the interest, performance and feasibility aspects of the mission. For the hybrid MAV, we need a solution to produce O₂ in-situ on Mars. We saw that in conventional in-situ research the technology selected to carry this out has always been solid oxide electrolysis, which produces O₂ from CO₂ extracted in Martian atmosphere.

Over the last few years, many innovative CO₂ decomposition techniques have been under research, especially as a means to reduce human impact on Earth's climate. Even if most of them concerned producing fuels from CO₂, others have widened the possibilities for oxygen production from carbon dioxide. Also, many alternative solutions for Mars applications have been discussed since the beginning of ISPP research in 1978. Many of these alternative solutions are referenced for the reader, ranging from a zinc-modified zeolite³⁸, to plasma discharge³⁹⁻⁴¹, light-assisted reduction¹⁷ and ionizing radiation^{42,43}. For very long term missions to Mars, photosynthesis, but also pyrolysis of metal oxides, silicates or nitrates contained in the Martian soil could constitute other interesting solutions for in-situ oxygen production⁴⁴.

But among all alternative CO₂ decomposition solutions, none exceeds a Technology Readiness Level (TRL) of 4, since they remain so far laboratory-scale experiments and designs. Solid oxide electrolysis, in comparison, is at least a TRL 6 technology, since this system has achieved the production of oxygen in Martian environment when designed for the 2001 Mars Surveyor Mission²². Because of this huge maturity gap, solid oxide electrolysis is clearly the oxygen production technique for us to choose, benefiting from the confidence of previous ISPP mission designers at NASA and JPL.

2. Principle

Solid oxide electrolysis is the reverse mode of operation of a solid oxide fuel cell. As explained by Frisbee¹⁸, it produces oxygen from direct decomposition of CO₂, using a zirconia (ZrO₂) membrane that selectively captures, transports and extracts oxygen ions when a voltage is applied to it. This decomposition functions in two steps. First, carbon dioxide is thermally and catalytically decomposed into oxygen and carbon monoxide in the vicinity of the zirconia cell. Second, the cell extracts O₂ from the CO₂-O₂-CO mixture. Oxygen is reduced and enters the membrane as ion, to then be recombined as dioxygen after oxidation on the other side. Zirconia is chosen as a material for the membrane because it has the ability as shown on figure 4 to pass oxygen ions O²⁻ in vacancies through the crystal lattice at high temperatures (600K to 1300K) when a suitable voltage is applied across the membrane.

3. Developments

The study of solid electrolysis for ISPP on Mars started in 1987 by Frisbee¹⁸ who, two years after French¹², sized and designed an ISPP system for two applications on Mars: retrieve oxygen and carbon monoxide. But Frisbee's estimated solution was still too heavy and energy consuming for reasonable Mars ISPP applications. K. R. Sridhar worked abundantly in the 1990's with numerous colleagues on solid oxide electrolysis for Mars application, pursuing the work started by Frisbee. He went on to use Yttrium-stabilized Zirconia (YSZ) membranes, which could achieve better behavior than the Zirconia alone. We will try here to sum up the key points of his work on the subject.

In 1995¹⁹, he showed, designing two possible MSR missions with the support of extensive full-scale lab experiments, that an in-situ oxygen plant capable of producing 7kg of O₂ per day would constitute a mass of 108kg and consume 2.9kW of power (and 2.5 kg/day would give 64kg and 1.1kW), with a power penalty of 140kg/kW, provided by an radioisotope thermoelectric generator (RTG). The membrane was operated at high temperatures (1073 to 1273K) to realize the necessary thermal decomposition; it thus required lots of energy, and lead to a big mass penalty. Also, Sridhar could only guarantee 32% conversion efficiency of CO₂ at 1000°C, creating the need for CO₂ recycling in his in-situ oxygen production plant.

In 1996¹⁸, he detailed along with Vaniman their experimental set-up, providing an interesting set of results. His electrolysis cell consisted of a non-porous disk of YSZ (ZrO₂-Y₂O₃ 8 mole %), with platinum electrodes sandwiched between two YSZ crucibles using ceramic cements. Alumina tubes feed and exhaust the gases. The O₂ exhaust is on the left of the cutaway view in figure 4. It was shown that this design could withstand without any noticeable degradation in performance up to 2000 hours of operation, which is crucial: an ISPP solution has to be durable and reliable over a long period, even more if energy is slowly supplied by solar panels. They achieved satisfactory oxygen production results for a range of temperature from 750 to 1000°C, with all current flow in the cell attributed successfully to oxygen ion flow, and none to electron transport.

In 1998¹⁹, Sridhar and Foerstner tested a YSZ based regenerative fuel cell, based on the reversion of the electrolytic system. In that case, the chemical energy is actually used to produce electrical energy, the opposite of the electrolysis. It is interesting because it allows electrolysis operation during the day powered through solar exposure, and fuel cell powered by a little extra oxygen and carbon monoxide decomposed to keep the electrolyzer membranes and stacks warm during the night, and power the spacecraft. This approach saves energy for solar-powered ISPP because it is not necessary to ramp up the temperature of the YSZ cells each Martian morning, an energy larger than that needed to decompose the extra O₂ to sustain the system warm during the night.

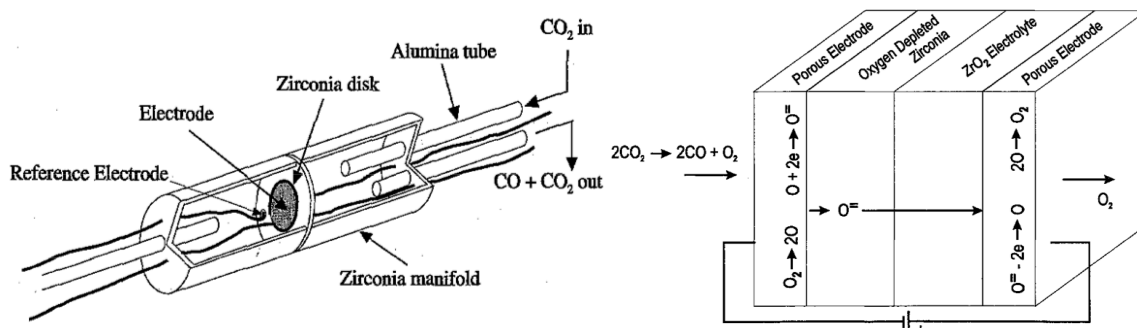


Figure 4. Zirconia cell hardware and electrochemical mechanism, from Sridhar¹⁹

In 1999, Thunissen et al.⁷ used solid oxide electrolysis for the design of a 2007 Mars sample return mission using in-situ propellant production. They revealed that AlliedSignal (under JPL funding) demonstrated operation of a stack of three wafers, achieving at 800°C a conversion efficiency of 80%; a great improvement from Sridhar¹⁹. 90% efficiency was believed feasible and assumed as such in their study, removing the need for CO₂ recycling. This was a significant breakthrough for zirconia cell technology, and it opened the possibility of full-scale zirconia stacks for Mars application. They estimated at 11.4 kg the mass of their zirconia cell system to produce 0.4kg of oxygen per 7 hour operational Martian day, all that with an energy consumption of 420W, provided by solar arrays.

In 1999 also, Sridhar worked with Baird and Gottman²⁰⁻²¹ on the Mars In-situ Propellant Production Precursor (MIP)²², a module that was planned to fly on the 2001 Mars Surveyor Lander Mission, and to realize CO₂ decomposition into O₂ on Mars for the first time. As we already mentioned, this mission was regrettably later cancelled by NASA, and the MIP module was not reused later in any other mission. The module contained an Oxygen Generation Subsystem (OGS) experiment, specifically dedicated to our subject of interest.

This OGS weighed less than a kilogram and fitted in a 3 liters envelope, needing only a few watts to keep it at 750°C steady operating temperature, and was supposed to be the first system to ever extract oxygen out of Mars atmosphere. We can appreciate the confidence, excitement of his creators and the TRL 6 achieved development of zirconia technology in the quote below:

*“Overall, OGS development hardware more than meets its objectives. The OGS has demonstrated its primary function, oxygen generation from input CO₂, in the Mars surface environment and has very successfully demonstrated integrated operations within the overall MIP package. OGS has proven itself ready to proceed to the flight design phase of the project. The OGS has also proven that zirconia ceramic-based oxygen generation devices can be built to be mechanically rugged; capable of repeated, large temperature swing thermal cycling with the new seal and heater technologies; and easily manufactured and expanded with the metal manifold concept. This family of ISRU hardware is ready to support future exploration missions to Mars and beyond.”*²²

After 2001, the frequency of studies on Mars zirconia technology sensibly diminishes. But in 2005, research by Park and Wachsman⁴⁵ led to very interesting results and possibilities for improvement. They looked at other materials for ceramic oxygen generators (such as our zirconia cell) that would allow a more efficient CO₂ decomposition. Rare-earth doped ceria and bismuth oxide are two promising materials since their oxygen ion conductivity at 800°C is higher than that of YSZ at 1000°C, but they present some problems that reduce the system efficiency because of their unfit behavior at low oxygen partial pressures. To correct that, they constructed bilayer electrolytes with stabilizing additives into these two materials, allowing them to reach sufficient conductivity at low temperatures (below 700°C). Their bilayer electrolytes were composed of samarium-doped ceria (Ce_{0.8}Sm_{0.2}O_{1.5}) on the reducing side and erbium-stabilized bismuth oxide (Bi_{0.8}Er_{0.2}O_{1.5}) on the oxidizing side. In these bilayer electrolytes, the oxygen ion conductivity is higher than in zirconia also because it can progress in a channel between the two layers, instead of having to jump from one vacancy to the next in a crystal lattice.

Parameter	Value
Oxygen Production Rate	1 A = 0.325 g/hr of O ₂
Current Density	0.4 A/cm ²
Cell Voltage	1.7 V
CO ₂ Conversion Efficiency	90%
Membrane Temperature	800 °C
Heat Loss	10 W per wafer disk
Stackable Wafer Size	10 cm diameter disk
System Specific Mass*	5.4 kg/440 cm ² of wafer area
CO ₂ Input Pressure	1 bar

Table 3. Zirconia cell operational metrics. Numbers adapted from Thunissen et al.¹⁵.
*including connecting tubes, valves, sensors and controls, and to be used only for systems of the order or above the 440 cm² total wafer area of Thunissen et al..

Park and Wachsman demonstrated the feasibility of oxygen production at lower temperatures, in the 400°C-700°C range. They proved that if going colder diminishes the oxygen production rate, it also diminishes the power needed for that production, such that the oxygen rate per unit power does actually increase slightly when we go from 700°C to 400°C, which is very interesting, even if for now it would lead to very large systems.

Research needs to be pursued in that field for new solid oxide electrolysis improvements to be available for ISPP mission designers. In our study, we will use the demonstrated numbers provided by Thunissen et al.¹⁵ to size the zirconia cell. The relevant metrics of performance are given in table 3.

I. CO₂ Extraction and Pre-Processing

The carbon dioxide to be fed into the zirconia cell needs to be extracted from the atmosphere, compressed and heated. This will be realized sequentially:

1. Dust Filtering

To avoid obstructions and other problems in the compressor feedline of the ISPP unit, an appropriate Martian dust filter needs to be used. This dust filter would capture particles ranging from around 1 to 10 microns in size, and would need to be purged periodically to remain functional³². The dust filter is sized after estimations from Sridhar¹⁹: mass of 0.6 kg per 2.5 kg of O₂ produced per 24.4-hr day.

2. Selective Compression

Extraction and compression of carbon dioxide gas are then realized by a sorption compressor^{32,46,47}. It uses an adsorbent microporous material, that can trap vapour and gas molecules within its pores. This material can be tailored to the gas, and for example capture CO₂ selectively. The compression is realized by temperature swing: at low pressure and low temperature (nighttime), the microporous material is loaded with carbon dioxide from the atmosphere; adsorbed gases are released into the ISPP unit when the bed is warmed to the maximum temperature (daytime), at higher temperature and pressure.

Because of laboratory convenience, and to achieve a satisfactory oxygen production rate (the Nernst equation notably depends on oxygen partial pressure), most zirconia cell developed so far have used a CO₂ input pressure of 1 bar. Since on Mars the average atmospheric pressure is 6 millibars (11.6 millibars at the lowest point), at least two orders of magnitude of compression are needed. For the small flow rates of ISPP, the mechanical solution to provide high compression ratios is a multistage reciprocating compressor⁴⁸, a solution much less suitable for ISPP on Mars than temperature swing adsorption⁴⁶.

Indeed, the important 70K diurnal swing on Mars is enough for the sorption compression work, and could be increased by waste heat from the zirconia cell and RTG. Furthermore, the sorption compressor can select CO₂, has far fewer moving parts, can achieve two orders of magnitude compression with a single-bed adsorption pump and uses no lubricants. For sizing, we will use Thunissen et al.¹⁵ estimations: their 6 kg compressor (including sorbent, housing and connections) provides 175 g/hr of CO₂ for 60 W of electrical power with thermal losses compensated.

3. Heating

Pre-heating of the CO₂ input stream is assured by a heat exchanger transferring heat from the carbon monoxide coming out of the zirconia cell. The RTG waste heat can also be used. The heat exchanger is sized after estimations from Sridhar¹⁹: mass of 0.4 kg per 2.5 kg of O₂ produced per 24.4-hr day.

J. Oxygen Liquefaction

The ideal system to liquefy the oxidizer is an orifice pulse-tube cryocooler⁴⁹. It is a regenerative cooler made of an actuated piston, a regenerator, a pulse-tube equipped with two heat exchanger at its ends and an orifice leading to a reservoir. The working gas, usually Helium, is alternatively compressed and expanded in the pulse tube, and thus transfers heat from the cooling subject to the ambient air. It is convenient for Mars ISPP applications: it can reach temperature ratios above 4 (or 60K) in one stage; it has only one moving part, that is at room temperature; it has the highest reliability, a good intrinsic efficiency and compactness; it only needs modest pressures and pressure ratios for the working gas.

A very promising cryocooler for ISPP has been developed by Olson et al.⁵⁰ at Lockheed Martin. Their design was able to provide 20W of cooling power at 70K with 600W of compressor electrical power, and 26W of cooling at 100K with 400W of compressor electrical power. These are results achieved while rejecting heat at 300K, it could therefore provide more cooling on Mars where the ambient temperature is of 210K on average. Their cryocooler is designed for a high power density (only 7kg), at the expense of a 20% loss in efficiency in respect to a design optimized for the highest efficiency.

Due to a lack of time, the liquefaction requirements for the oxygen are not calculated in this paper. Instead, mass and power assessments extrapolated from Sridhar¹⁹ and Thunissen et al.¹⁵ are used conservatively. Sridhar estimates for example that 10 kg and 70W are needed to liquefy and store 2.5 kg oxygen produced per 24.4-hr day on Mars¹⁹.

K. Power Supply

Two types of power supply are available for Mars: solar panels and radioisotope power systems (RPSs).

1. Solar Panels

On Mars, an average solar flux of 430 W/m^2 is available for the 7-hr day¹⁵. In 1999, Thunissen et al.¹⁵ chose for their MSR mission design advanced silicon solar arrays, which could at the time provide 19% of solar-to-electrical conversion efficiency (81.7 We/m^2). They assumed a power density of 50 We/kg , and panel degradation by dust of 19% over 300 sol (1 sol is 1 Martian day, 24.4 hours), but Spirit and Opportunity showed since then that dust devils could prevent such degradations.

Recent developments in multi-junction solar cells for Mars applications⁵¹ have lead to substantial improvements in the conversion efficiency, which is getting closer to 30%. For the MAV design, we will use conservatively a conversion efficiency of 22% achieved by modern silicon solar arrays (95 We/m^2) and the same power density of 50 We/kg ; per sol, this power density drops to 14.3 We/kg .

To provide electricity during the night, we will use the same batteries as Thunissen et al.¹⁵: lithium-ion batteries with an assumed specific energy density of 100 W-hr/kg and an 80% charge/discharge efficiency.

2. RPSs

Radioisotope power systems have been used by NASA for many years; they convert the heat released by an enclosed decaying radioisotope into electricity. As pointed out by Misra⁵², RPSs are long-lived, compact and relatively insensitive to radiation and other environmental effects and they can operate continuously, providing a stable amount of electricity, independently of orientation to and distance from the Sun, making them ideal for outer planet and space missions in extreme environments, especially in dark regions of Mars and the Moon.

NASA has developed for Curiosity a Multi-Mission Radioisotope Thermoelectric Generator (MMRTG), able to work in space vacuum and in planetary atmospheres; it has a 14-year life, but a specific power of only 2.8 We/kg ⁵². Since the energy source is enclosed in the power system, RPSs have indeed a much lower specific power than solar panels, even with solar power present only 7 out of 24.4 hours.

For future missions, advanced radioisotope power systems with high specific power are investigated by NASA⁵². A promising candidate is the Advanced Stirling Radioisotope Generator (ASRG), which thanks to its use of the Stirling cycle, is more efficient to convert heat into electricity (30-35% instead of 5% for the MMRTG⁵²). A 2007 ASRG design by Chan et al.⁵³, weighing 20.84 kg and delivering 140 We , reached a specific power of 6.7 We/kg , more than twice that of the MMRTG, and above other previous designs (GPHS-RTG reached 5.1 We/kg). They were also confident that by optimizing the existing generator housing and enclosure designs, the specific power could be further improved beyond 7 We/kg .

For the hybrid MAV, the RPS source chosen is the ASRG with 6.7 We/kg of specific power, a value expected to increase with future developments and the scale of the power system.

VII. Small-Scale Case: MSR

L. Case Definition

We will size the hybrid MAV for two missions. The first one is Mars Sample Return (MSR), because of its important place in the ISPP literature. To compare with Chandler et al.⁶, we choose a payload mass of 36 kg , a 500km LMO for which 4375 m/s of speed increment are required, and a nozzle area ratio of 40. To compare with Thunissen et al.¹⁵, we limit the propellant production period to 300 sol.

Thanks to the high performance of the hybrid, two configurations are possible for this MSR mission: one stage ($n = 1$) or two stages ($n = 2$). We will explore both.

M. Methodology

1. Staging

Like in Section E, we assume for simplicity that the rocket has n identical stages, i.e. stages with the same structural efficiency (fixed here at 0.18 close to the values of Chandler et al.⁶) and specific impulse (corrected at 330s due to a smaller nozzle area ratio). Also, the ISPP unit is considered to be either in the payload or remaining on Mars. We use Equation 4 to find the optimal staging and payload fraction. The optimal payload ratio λ (identical for all stages) is similarly given by the following relation³⁷:

$$\lambda = \frac{1 - \epsilon \exp\left(\frac{\Delta V}{ng_o I_{sp}}\right)}{\exp\left(\frac{\Delta V}{ng_o I_{sp}}\right) - 1} \quad (7)$$

From those relations (Eqs. 4,7), knowing the parameters, payload mass and 2.84 operational O/F ratio, we can estimate the mass of all stages, but also structural, fuel and oxidizer masses. It is to be noted that simple sizing such as this is enough to evaluate the interest of the hybrid ISPP idea, considering reasonable performance parameters (ϵ and I_{sp}) are chosen. For future developments, a more precise approach would be needed.

2. ISPP Unit Sizing

Once we know the amount of oxygen that needs to be produced in-situ, the ISPP unit to provide it is sized step-by-step, until we determine the overall mass of the ISPP unit, including the ISPP power supply mass. We use the same sizing approach as Thunissen et al.¹⁵ and Sridhar¹⁹.

3. ISPP Gain Definition

To quantify the gain provided by ISPP for Mars applications, we compare the mass of the ISPP solution (brought rocket mass with no oxidizer + ISPP unit mass) with the mass of the filled rocket entirely brought from Earth (brought rocket mass including the oxidizer). Other components of the mission (lander, communication systems, ...) are here irrelevant because either monotonous or constant functions of the brought mass.

Thus, we define the maximal in-situ gain (i.e. considering the ISPP unit has no mass), in our case simply equal to the proportion of oxidizer in the rocket at lift-off:

$$\text{Max } G_{in-situ} = \frac{O/F}{1 + O/F} (1 - \Gamma)(1 - \epsilon) \quad (8)$$

Secondly, we define the effective in-situ gain, which is the percentage of the lift-off mass saved by using ISPP when taking into account the ISPP unit mass. It is our metric for ISPP performance and it is given by:

$$G_{in-situ} = \frac{O/F}{1 + O/F} (1 - \Gamma)(1 - \epsilon) - \frac{M_{ISPP \text{ unit}}}{M_{lift-off}} \quad (9)$$

4. Margin Policy

Between different MAV designs^{6,15,19}, the margin policies can vary a lot. In this hybrid MAV design, we will use the same margin philosophy as Sridhar¹⁹, that is very little margins. For each technology involved in the design, we utilize demonstrated, referenced and conservative levels of performance to lead to a reasonable design.

N. Results

System	Solid ⁶	Brought Nytrox ⁶	ISPP LOX/Par ($n = 1$)	ISPP LOX/Par ($n = 2$)
Stage 1 Mass (kg)	215.6	128.9	374.3	134.1
Stage 1 ϵ	0.170	0.167	0.18	0.18
Stage 1 AR	53.2	40	40	40
Stage 1 I_{sp} (s)	287	300	330	330
Stage 1 ΔV (m/s)	2530	1675	4375	2187
Stage 2 Mass (kg)	86.2	83.4	-	53.8
Stage 2 ϵ	0.175	0.147	-	0.18
Stage 2 AR	41	41.7	-	40
Stage 2 I_{sp} (s)	287	303	-	330
Stage 2 ΔV (m/s)	1845	2700	-	2188
Lift-off Mass (kg)	301.8	248.4	374.3	223.9
Rocket Brought Mass (kg)	301.8	248.4	169.1	110.0

Table 4. MSR rocket mass estimations. The hybrid ISPP MAV is compared with Chandler et al.⁶ for identical mission requirements and rocket parameters. Brought Nytrox corresponds to their Nytrox/Paraffin-Al configuration with a 20% margin.

On table 4, one-stage and two-stage hybrid ISPP MAV designs are compared with a solid and hybrid solution both brought from Earth⁶. We can see that the high performance and ISPP option of our two designs lead to promising results. As a matter of fact, the maximal in-situ gains are very high and quite comparable: 54.8% for the one-stage versus 50.9% for the two-stage. The next step is to determine the oxygen requirements and size the ISPP unit, using the metrics of performance given in Part VI. For this small-scale application, we choose solar panels for their high specific power, restraining one sol to 7 hours.

Number of Stages	1	2
O ₂ Mass needed (kg)	205.2	113.9
O ₂ per 7-hr sol (g/sol)	684.0	379.7
O ₂ per hour (g/hr)	97.7	54.3

Table 5. MSR oxygen production requirements.

Number of Stages	1	2
Overall current (A)	301	168
Cell power (W)	512	286
Cell area (cm ²)	753	420
Nb of 10cm diameter wafers	10	6
ZrO ₂ system mass (kg)	9	5.4
Stack heat loss (W)	100	60
CO ₂ extraction rate (g/hr)	300	167
Sorption comp. power (W)	105	60
Sorption comp. mass (kg)	10.5	6

Table 6. MSR Zirconia cell sizing.

Mass budget (kg)	1	2	Power budget (W)	1 day	1 night	2 day	2 night
ZrO ₂ system	9	5.4	ZrO ₂ system	612	-	346	-
Sorption comp.	10.5	6	Sorption comp.	105	-	60	-
Cryocooler	10	12	Cryocooler	100	30	70	30
Dust filter	0.6	0.4	Batteries	77	-30	77	-30
Heat exchanger	0.4	0.3	Total	894	0	553	0
Batteries	5.4	5.4					
Other*	16	20					
Solar panels	17.9	11.1	Solar panels area (m ²)	9.5	-	5.9	-
Total	69.8	60.6					

Table 7. MSR ISPP unit mass and power budgets. *plumbing, structure, controls and microprocessor, extrapolated from Sridhar¹⁹.

Some precisions need to be made about the estimations presented in table 7, because if most of them are inspired from previous results, some have been adapted. For example, the two-stage solution, even if it requires less oxygen, has a higher mass in cryocooler, plumbing, structure and controls, because of the two distinct liquid oxygen tanks it has to fill and thermally control. Also, a lower power consumption in the cold night is required since we just need to keep the oxygen liquid. On Mars, by convention the day is 7 hours long and the night 14.4 hours, which explains the very different charge and discharge power levels of the batteries.

Now that the ISPP unit is sized, we can evaluate the effective in-situ gain; results are presented in table 8.

System	Solid ⁶	Brought Nytrox ⁶	1	2
Lift-off mass (kg)	301.8	248.4	374.3	223.9
Rocket brought mass (kg)	301.8	248.4	169.1	110.0
Igloo mass (kg)	50	0	0	0
ISPP unit mass (kg)	0	0	69.8	60.6
System brought mass (kg)	351.8	248.4	238.9	170.6

Table 8. MSR conclusions. Comparison with Chandler et al.⁶.

We can see that the single stage ISPP solution requires approximately the same mass to be delivered on Mars as the Nytrox solution proposed by Chandler et al.⁶, while occupying much more volume due to the supplementary ISPP unit. It is therefore not of a high interest. The two-stage solution, on the other hand, achieves a 23.8% effective in-situ gain (in respect to a brought LOX/Paraffin) and a 31.3% relative in-situ gain (in respect to the Brought Nytrox⁶). But since a 20% margin was included in the Brought Nytrox⁶ design, if we add roughly a 20% margin on the overall system, we reach a more comparable 204.7 kg and 17.6% relative in-situ gain.

This leads to two conclusive remarks. The first is that this hybrid ISPP solution is much more competitive for small-scale missions than the Zubrin-type of Thunissen et al.¹⁵. If Thunissen et al. concluded in 1999 to the unlikelihood of a feasible, practical, entirely ISPP based MSR missions that can be accomplished in 2007-2009¹⁵, we presented here a feasible design that requires less brought mass than the solid and Nytrox advanced solutions of Chandler et al.⁶ entirely carried from Earth. In fact, the hybrid MAV benefits from much lower power requirements than the Zubrin-type MSR, since for a similar propellant performance, it does not need to produce liquid methane and realize water electrolysis in-situ. The solar array surface thus gets reduced: our two-stage design only requires 6m² (slightly more if we were to add margins), to compare with the unpractical and excessive 29m² of Thunissen et al.¹⁵. Here, performance echoes simplicity.

The second remark is that our design, even if it has a lower brought mass on paper, brings too little gain to justify so many risks and complications (solid oxide fuel cell, sorption compressor, cryocooler...). It would be also larger, due to the supplementary presence of the ISPP unit. Thus, it does not appear interesting and suitable in the context of a MSR mission; it makes sense indeed to choose the design with the lowest number of challenges for the first planetary round-trip missions. That is why MSR missions will certainly be realized by ready-to-fire rocket systems entirely brought from Earth.

As mentioned in Part III, ISPP is an outdated solution for MSR missions, and MSR ISPP efforts may very well stop after this article. The promise of ISPP has shifted and now resides in medium to large scale missions, as we shall see in Part VIII.

VIII. Medium-Scale Case

O. Case Definition

The medium-scale mission payload is set to 500 kg, to correspond to a brought mass of the order of the Curiosity mars rover which recently landed on Mars. We keep the same orbit, velocity increment requirements, structural efficiency, O/F ratio as in Part VII. We allow ourselves to increase the nozzle area ratio back to 70, the specific impulse reaches 340s.

P. Results

For this case, we realize the staging of the two-stage and one-stage systems.

Number of stages	1	2
Payload fraction	0.1090	0.1709
Payload ratio	0.1223	0.7048
Lift-off mass (kg)	4587.9	2925.4
Oxidizer mass (kg)	2479.1	1470.9
Fuel mass (kg)	872.9	517.9
Structure mass (kg)	735.8	436.6
Rocket brought mass (kg)	2108.8	1454.5
Maximal in-situ gain (%)	54.04	50.28

Table 9. Medium-scale staging.

In table 9, we can see that the maximal in-situ gain is almost the same as for MSR: the payload fraction only changed slightly because of the higher specific impulse. Since for bigger payloads, the two-stage solution is the most reasonable, we will limit our study to this alternative.

Also, due to the higher weight of the MAV, we choose to use for this medium-scale case the ASRG, providing power continuously and around the clock. Thanks to the high half-life of this radioisotope power system, we can look at longer durations on Mars; we will design the mission for two durations: 300 and 500 sol. The issue for 500 days is then not power availability (14 years of half-life) but the endurance of the zirconia cell. We can now proceed with the ISPP unit step-by-step sizing.

ISPP duration (sol)	300	500
O ₂ Mass needed (kg)	1470.9	1470.9
O ₂ per 24.4-hr sol (kg/sol)	4.903	2.942
O ₂ per hour (g/hr)	200.9	120.6

Table 10. Medium-scale oxygen production requirements.

ISPP duration (sol)	300	500
Overall current (A)	619	372
Cell power (W)	1053	633
Cell area (cm ²)	1548	930
Nb of 10cm diameter wafers	20	12
ZrO ₂ system mass (kg)	18	10.8
Stack heat loss (W)	200	120
CO ₂ extraction rate (g/hr)	617	371
Sorption comp. power (W)	215	130
Sorption comp. mass (kg)	21.5	13

Table 11. Medium-scale Zirconia cell sizing.

Mass budget (kg)	300	500	Power budget (W)	300	500
ZrO ₂ system	18	10.8	ZrO ₂ system	1253	753
Sorption comp.	21.5	13	Sorption comp.	215	130
Cryocooler	20	14	Cryocooler	245	145
Dust filter	1.2	0.8	Total	1713	1028
Heat exchanger	0.8	0.5			
Other*	31	24			
ASRG	256	154			
Total	348.5	217.1			

Table 12. Medium-scale ISPP unit mass and power budgets. *plumbing, structure, controls and microprocessor, extrapolated from Sridhar¹⁹.

If before all component masses of ISPP unit were of the same order (see table 7), now the ASRG mass is clearly dominating: power supply represents 73.4% of the ISPP unit mass for 300 sol. The ISPP performance is therefore highly dependent of the power supply specific power, such that we could have a higher in-situ gain by partially replacing RPSs by solar panels. We have such a situation also because of the high specific power of the zirconia cell. If we want to increase reliability through redundancy, or endurance through successive operation of zirconia cells, we could thus bring several zirconia cells for a relatively low weight penalty.

Developing advanced RPS systems with high specific power appears as a research priority to increase the performance and feasibility of future ISPP missions. For example here, reaching a specific power of 10 We/kg would lead to a 171 kg ASRG and a 25% reduction in the ISPP unit mass for the 300 sol case. It is to be noted that if we were to use solar panels for this medium-scale case, we would restrain operation for 7 hours per sol, need much faster oxygen production, thus a higher power, making the solar panel area too large, above 50m².

ISPP duration (sol)	300	500
Lift-off mass (kg)	2925.4	2925.4
Rocket brought mass (kg)	1454.5	1454.5
ISPP unit mass (kg)	348.5	217.1
System brought mass (kg)	1803.0	1671.6
Effective in-situ gain	38.4%	42.9%

Table 13. Medium-scale conclusions.

For this medium-scale mission with a MAV payload of 500 kg, the hybrid ISPP solution reaches an effective in-situ gain around 40%, which is impressive and, thanks also to its high combination performance, makes this technology outperform by far any rocket system brought from Earth. Indeed, we only need to deliver on Mars system mass of 1671.6 kg for the 500 sol case, which means we obtain a system brought mass factor of only 3.34.

Q. Extension to Large-Scale Missions

These results extend similarly to larger scale missions, as for example manned missions with payloads of several metric tons. The principle is the same, and the energy supply will dominate more and more in the ISPP unit mass. For missions requiring payloads above 500 kg, the effective in-situ gain will be beyond 43% for 500 sol durations, increasing with the mission scale as the ISPP unit gets smaller and smaller in proportion. For this type of hybrid

MAV two-stage solution, and independently of the payload mass, the effective in-situ gain will remain limited by the 50.28% maximal value given in table 9.

IX. Conclusion

A new MAV concept was proposed in this article, relying on high performance hybrid rocket propulsion and in-situ propellant production. From Part II to Part V, we explained the emergence and discussed the promising nature of this hybrid ISPP design, after looking at Martian resources and going over the history of ISPP research. In Part VI, we described the technologies that made this concept possible and provided their metrics of performance. In Part VII and VIII, we estimated the ISPP unit mass and calculated the effective in-situ gain for two configurations: MSR and a medium-scale case with a 500 kg payload.

We demonstrated that the high-performance hybrid ISPP MAV, if not interesting for MSR, can achieve effective in-situ gains beyond 40% for medium-scale to large-scale long duration Mars missions, results that are very promising. This design surpasses by far any solution brought from Earth, and presents many advantages in terms of simplicity, safety, size and certainly cost over conventional and currently dominant in-situ liquid-powered concepts while reaching comparable levels of in-situ performance.

To conclude, this research puts the hybrid on the map for future medium-scale to large-scale Mars exploration, especially manned exploration. It shows the high compatibility and potential of hybrid propulsion and ISPP, and provides motivation for further research and advances in these two fields. More development is in fact needed to ensure the scalability of most enabling technologies and the launching of a new mission carrying a demonstrator of ISPP on Mars is critical to confirm the concept idea as soon as possible.

Acknowledgments

The authors would like to thank Dr. Arif Karabeyoglu, Dr. Ashley Chandler and Gregory Zilliac of NASA Ames Research Center for their persistent support and precious advice on oxidizer mixtures, paraffin properties, hybrid rocket ignition, condensed exhaust nozzle operation and many other key aspects of this research.

The article also benefited from the help of Dr. Thomas F. Jaramillo, who provided great insight on the physics, principles, performance metrics and hardware characteristics of electrochemical systems such as the zirconia solid electrolysis cell.

The authors would also like to thank Pr. Scott Hubbard, Dr. Timothy Szwarc, and the PhD candidates Jonah Zimmerman, Ben Waxman, Elizabeth Jens, Javier Stober and Pavan Narsai of Stanford University for their valued contributions and support.

References

- ¹Hand, E. "7 minutes of terror. The Curiosity rover prepares to plunge down to Mars". 1 Aug. 2012. *Nature* 488, pp. 16-17.
- ²Bakhtian, N. M. Afrosmis M. J. "Analysis of Inviscid Simulations for the Study of Supersonic Retropropulsion". Presented at the 29th Applied Aerodynamics Conference. 27-30 June 2011 in Honolulu, HI. AIAA 2011-3194.
- ³Ash, R.L., Dowler, W. L., and Varsi, G. "Feasibility of rocket propellant production on Mars". *Acta Astronautica* Vol. 5, 1978, pp. 705-724.
- ⁴Karabeyoglu, A. M. "Transient Combustion in Hybrid Rockets". August 1998. Ph. D. Thesis, Stanford University.
- ⁵Knuth, W. H., Gramer, D. J., Chiaverini, M. J., Sauer, J. A. Orbital Technologies Corporation, Madison, WI. "Development and testing of a vortex-driven high-regression rate hybrid rocket engine". Presented at the 34th AIAA/ASME/SAE/ASME Joint Propulsion Conference and Exhibit. 13-15 July 1998 in Cleveland, OH. AIAA 98-3507.
- ⁶Chandler, A. A., Cantwell, B. J., Hubbard, G. S., Karabeyoglu, A. "A two-stage, single port hybrid propulsion system for a Mars ascent vehicle". Presented at the 46th AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit, 25-28 July, 2010 in Nashville, TN. AIAA 2010-6635.
- ⁷Karabeyoglu, A. "Mixtures of nitrous oxide, carbon dioxide and oxygen as oxidizers for Mars applications". Presented at the 46th AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit, 25-28 July, 2010 in Nashville, TN. AIAA 2010-6712.
- ⁸Flinn, E. A., Csanady, G., Siscoe, G. L. (eds.), "Scientific Results of the Viking Project" *Journal of Geophysical Research*, Vol. 82, No. 28, 1977, pp. 3959-4681 (special issue).
- ⁹McKay, C. P., Meyer, T. R., Boston P. J., Nelson, M., Maccallum, T., Gwynne, O. "Utilizing Martian resources for life support" SAE technical paper 941256. Presented at the International Conference on Environmental Systems, June 1994.
- ¹⁰Stancati, M. L., Niehoff, J. C., Wells, W. C. and Ash R. L. "In-situ propellant production – A new potential for round-trip spacecraft". Presented at the AIAA Conference on Advanced Technology for Future Space Systems, May 8-10, 1979 in Hampton, VA. AIAA 79-0906.
- ¹¹Ash, R. L., Richter, R., Dowler, W. L., Hanson, J. A., and Uphoff, C. W. "Autonomous oxygen production for Mars return vehicle". 1982. Paper presented at the 33rd Intl. Astronautical Congress, Sept. 27-Oct. 2, Paris. IAF-82-210.

¹²French, J. R. "The impact of martian propellant manufacturing on early manned exploration". *Case for Mars II*, ed. C. P. McKay. Science and Technology Series 62. 1985.

¹³Ramohalli, K., Dowler, W., French, J., Ash, R. "Novel extraterrestrial processing for space propulsion". *Acta Astronautica* Vol. 15, 1986, pp. 259-273.

¹⁴Zubrin, R. M., Baker, D. A., Gwynne, O. "Mars direct: a simple, robust, and cost effective architecture for the space exploration initiative". Paper presented at the 29th Aerospace Sciences Meeting, Jan 7-10, 1991 in Reno, NV. AIAA 91-0329.

¹⁵Thunissen, D., Rapp, D., Voorhees, C., Dawson, S., and Guernsey, C. "A 2007 Mars sample return mission utilizing in-situ propellant production". Presented at the 37th AIAA Aerospace Sciences Meeting and Exhibit, January 11-14, 1999 in Reno, NV. AIAA 99-0851.

¹⁶Hepp, A. F., Landis, G. A., Kubiak C. P. "Chemical approaches to carbon dioxide utilization for manned Mars missions", in *Resources of Near-Earth Space*, University of Arizona Press. NASA Technical Memorandum 103728, January 1991.

¹⁷Hepp, A. F., Landis, G. A., Kubiak C. P. "A chemical approach to carbon dioxide utilization on Mars". In-Situ Resource Utilization (ISRU) Technical Interchange Meeting, p. 27. February 4-5, 1997.

¹⁸Frisbee, R. H. "Mass and power estimates for Mars in-situ propellant production systems". Paper presented at the 23rd AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit, June 29-July 2, 1987 in San Diego, CA. AIAA 87-1900.

¹⁹Sridhar, K. R. "Mars Sample Return Mission with In-Situ Resource Utilization". *Journal of Propulsion and Power* Vol. 11, No. 6, 1995, pp. 1356-1362.

²⁰Sridhar, K. R., Vaniman, B. T. 1997. "Oxygen production on Mars using solid oxide electrolysis". *Solid State Ionics* Vol. 93, 1997, pp. 321-328.

²¹Sridhar, K. R., Foerstner, R. "Regenerative CO₂/O₂ solid oxide fuel cells for Mars exploration". 1998. AIAA 650:113.

²²Sridhar, K. R., Gottman, M., Baird, R. S. "2001 Mars in-situ oxygen production flight demonstration". 1999. AIAA 99-2413.

²³Sridhar, K. R., Gottman, M., Baird, R. S. "Update on the oxygen generator system for the 2001 Mars surveyor mission". 2000. AIAA 2000-1068.

²⁴D. I. Kaplan, J. E. Ratliff, R. S. Baird, G. B. Sanders, K. R. Johnson, P. B. Karlmann, C. R. Baraona, G. A. Landis, P. P. Jenkins, and D. A. Scheiman. "The Mars in-situ propellant production precursor (MIP) flight demonstration". 2001.

²⁵Yuasa, S., Isoda, H. "Ignition and combustion of metals in a carbon dioxide stream". Presented at the 22nd International Symposium on Combustion, pp. 1635-1641.

²⁶Shafirovich, E. Y., Shiryayev, A. A., Goldshleger, U. I. "Magnesium and carbon dioxide: a rocket propellant for Mars missions". *Journal of Propulsion and Power*. Vol. 9, No. 2, 1993, pp. 197-203.

²⁷Shafirovich, E. Y., Goldshleger, U. I. "Comparison of potential fuels for martian rockets using CO₂". *Journal of Propulsion and Power*. Vol. 13, No. 3, 1997, pp. 395-397.

²⁸Shafirovich, E. Y., Goldshleger, U. I. "Combustion of magnesium particles in CO₂/CO mixtures". *Combustion Science and Techniques*. Vol. 84, 1992, pp. 33-43.

²⁹Legrand, B., Marion, M., Chauveau, C., Gokalp, I., Shafirovich, E. Y. "Ignition and combustion of levitated magnesium and aluminum particles in carbon dioxide". *Combustion Science and Technology*. Vol. 165, No. 1, 2001, pp. 151-174.

³⁰Gokalp, I., Shafirovich, E. Y. "The concept of a rocket engine using CO₂/metal propellants for Mars sample return missions". Presented at the 3rd International Conference on Spacecraft Propulsion, 10-13 October, 2000 in Cannes, France. ESA SP-465.

³¹Foote, J. P., Litchford, R. J. "Powdered magnesium – carbon dioxide rocket combustion technology for in-situ Mars propulsion". Marshall Space Flight Center, NASA/TP 215077. 2007.

³²Ismail, A. M., "Technology requirements for Mars sample return using CO₂/metal powder propellants". Interplanetary Expeditions. 2007.

³³Reina, A., Colombo, G., Maggi, F., De Luca, L. T., Lesniak, I., Lempert, D. B., Manelis, G. B. "Magnesium and aluminum ignition in CO₂ atmosphere". *Aerotecnica Missili & Spazio*, Vol. 89, No. 1, January 2010. *The Journal of Aerospace Science, Technology and Systems*.

³⁴Karabeyoglu, M. A., Cantwell, B. J., Altman, D. "Development and testing of paraffin-based hybrid rocket fuels". Presented at the 37th AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit, July 8-11, 2001 in Salt Lake City, UT. AIAA 2001-4503.

³⁵Karabeyoglu, A. "Mixtures of nitrous oxide and oxygen (nytrox) as oxidizers for rocket propulsion applications". Presented at the 45th AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit 2-5 August, 2009 in Denver, CO. AIAA 2009-4966.

³⁶CEA2, Chemical Equilibrium with Applications. NASA Glenn Web Software. <http://www.grc.nasa.gov/WWW/CEAWeb/>. Version 2. McBride, Gordon, Zeleznik and others.

³⁷Cantwell, B. J., Stanford University. Aircraft and Rocket Propulsion AA283 Course. Lecture Notes 2013. Chapter 8, Multistage Rockets. Available online at http://www.stanford.edu/~cantwell/AA283_Course_Material/AA283_Course_Notes/.

³⁸Wang, J-F., Wang, K-X., Wang, J-Q., Li, L., Chen, J-S. "Decomposition of CO₂ to carbon and oxygen under mild conditions over a zinc-modified zeolite". *Chemical Communications* Vol. 48, 2012, pp. 2325-2327.

³⁹Ash, R. L., Wu, D., Outlaw, R. A. "A study of glow-discharge and permeation techniques for extraterrestrial oxygen beneficiation". *Advanced Space Research* Vol. 14, No. 6, 1994, pp. 259-263.

⁴⁰Savinov, S. Y., Lee, H., Song, H. K., Na, B-K. "Decomposition of methane and carbon dioxide in a radio-frequency discharge". *Industrial and Engineering Chemistry Research*. Vol. 38, No. 7, 1999, pp 2540-2547.

- ⁴¹Matsumoto, H., Tanabe, S., Okitsu, K., Hayashi, Y., Suib, S. L. "Profiles of carbon dioxide decomposition in a dielectric-barrier discharge-plasma system". *Bulletin of the Chemical Society of Japan*. Vol. 72, 1999, pp 2567-2571.
- ⁴²Harteck, P., Dondes, S. "Decomposition of carbon dioxide by ionizing radiation". Part I. *Journal of Chemical Physics*. Vol. 23, No. 5, 1955, pp 902-908.
- ⁴³Harteck, P., Dondes, S. "Decomposition of carbon dioxide by ionizing radiation". Part II. *Journal of Chemical Physics*. Vol. 25, No. 6, 1957, pp 1727-1733.
- ⁴⁴Birch, P. "Terraforming Mars quickly". *Journal of British Interplanetary Society*. Vol. 45, 1992, pp. 331-340.
- ⁴⁵Park, J. Y., Wachsman, E. D. "Lower temperature electrolytic reduction of CO₂ to O₂ and CO with high conductivity solid oxide bilayer electrolytes". *Journal of the Electrochemical Society* Vol. 152, No. 8, 2005, pp. A1654-A1659
- ⁴⁶Finn, J. E., McKay, C. P., Sridhar, K. R. "Martian atmospheric utilization by temperature swing adsorption". *SAE Technical Paper Series*. Presented at 26th ICES in Monterey, CA in 1996. 961597.
- ⁴⁷Iacomini, C., MacCallum, T., Morin, T., StraubLopez, K., Paul, H. "Martian liquid CO₂ and metabolic heat regenerated temperature swing adsorption for portable life support systems". *AIP Conference Proceedings*. Vol. 880, 2007, pp. 863-870.
- ⁴⁸Brown, R., N. "Compressors (Third Edition)". *Elsevier* 1997. Ch.1, p. 3.
- ⁴⁹Flynn, T. N. "Cryogenic Engineering (Second Edition)". *CRC Press*. 2004. Ch. 6, pp. 422-427.
- ⁵⁰Olson, J., Champagne, P., Roth, E., Nast, T. "Very high capacity aerospace cryocooler". *Advances in Cryogenic Engineering. AIP Conference Proceedings*. Vol. 1434, 2012, pp. 161-167.
- ⁵¹Edmondson, K. M., Joslin, D. E., Fetzer, C. M., King, R. R., Karam, N. H., Mardesich, N., Stella, P. M., Rapp, D., Mueller, R. "Simulation of the Mars surface solar spectra for optimized performance of triple-junction solar cells". Presented at the 19th SPRAT Conference in Cleveland, OH on September 20-22, 2005. JPL Technical Report.
- ⁵²Misra, A. K. "Overview of NASA Program on Development of Radioisotope Power Systems with High Specific Power". Presented at the 4th IECEC, June 26-29 2006 in San Diego, CA. AIAA 2006-4187.
- ⁵³Chan, J., Wood, J. G., Schreiber, J. G. "Development of advanced stirling radioisotope generator for space exploration". Prepared for the Space Technology and Applications International Forum (STAIF), held February 11-15 2007 in Albuquerque, NM. NASA/TM-2007-214806.