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Mars In-Situ Resource Utilization Based on the Reverse Water Gas Shift: Experiments and Mission Applications

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Abstract

This paper discusses approaches to Mars in-situ resource utilization (ISRU) using the reverse water gas shift (RWGS) reaction, which offers a potential means of producing oxygen on Mars at a significantly lower energy cost than the zirconia-electrolysis system. The RWGS also can be used as the first step in a process to produce either ethylene or methanol, both of which are storable fuels on Mars. The advantage of producing ethylene is that it minimizes the amount of hydrogen that needs to be transported to Mars to support in-situ propellant production. The advantage of producing methanol is that it minimizes the power requirement of the in-situ propellant production system. Highly promising preliminary experimental results of research on Mars ISRU systems using the RWGS are reported. Scalings are provided showing power and mass estimates for Mars ISRU systems across the span of potential mission applications. Mission analysis of both the Mars Sample Return and robotic Mars Ballistic Hopper missions are presented, showing strong advantages for those systems utilizing the RWGS. It is concluded that the RWGS system, both by itself or in combination with either ethylene or methanol formation reactors offers great potential for enhancing future Mars exploration and should be researched further.

Introduction

It has long been known that the capability to exploit the Martian atmosphere offers profound advantages for the design of both piloted Mars missions[1,2,3,4,5,6] and robotic Mars sample return missions[7,8,9] as well. For example, in the "Mars Direct[4]" mission plan, a manned Mars mission is accomplished by using a single heavy lift launch vehicle to send an unfueled Earth Return Vehicle (ERV) directly to the Martian surface, where it autonomously manufactures the propellant required for a direct return flight to Earth. After this process is completed, another heavy lift launch vehicle is used to send the crew to Mars in a relatively modest hab module which lands near the now-fueled ERV on the surface of Mars. After conducting operations on the surface for an extended period, the crew leaves the hab module on Mars and returns to Earth in the ERV. Thus, by exploiting the capability for in-situ propellant manufacture, an entire piloted Mars mission can be accomplished without any on-orbit assembly or orbital rendezvous of any type. In addition, as each sequential mission adds a hab to the Mars surface infrastructure, and as the propellant manufacture processes also provide propellant for high powered ground vehicles as well as water and oxygen supplemental consumables for the base, this strategy allows a very substantial capability to be built up on the Martian surface in a fairly short period of time. The attractiveness of such a Mars mission strategy was underlined in a recent study by Johnson Space Center[10], which estimated that a piloted Mars exploration program could be carried out in this way for a cost of $55 billion. This cost was almost an order of magnitude less than that generated by the same costing models for more traditional forms of Mars mission design[11] which ignored the potential of in-situ propellant manufacture, instead employing very large advanced spacecraft constructed on orbit to accomplish the piloted Mars mission. Recent studies of the Mars Sample Return (MSR) mission done with sophisticated costing tools by Lockheed Martin Astronautics[12] and Science Applications International (SAIC)[13] indicate that, if in-situ propellant manufacture technology is available, a MSR mission returning a 1 kg sample could be accomplished with a single launch of a Delta 7925 and a cost in the neighborhood of $250 to $350 million. These costs are a factor of 3 to 10 lower than those projected for more traditional style MSR missions[14], which generally required multiple spacecraft, autonomous Mars orbit rendezvous and dock on the return leg, and Atlas or Titan class launch vehicles.

Technical Background: Related Mars In-situ Propellant Production Research

Because the benefits to be obtained from Mars in-situ propellant manufacture are so large, a fair amount of research and analysis has been done on potential

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techniques for its accomplishment. To date, however, only two techniques have been researched experimentally. The first of these to be researched, known as "zirconia electrolysis," involves the direct dissociation of CO_2 (which comprises 95% of the Martian atmosphere) into carbon monoxide and oxygen gas. The other, known as "Sabatier-electrolysis" reacts hydrogen with Martian CO_2 in two steps to produce methane and oxygen. Each of these techniques has advantages and disadvantages.

The zirconia electrolysis technique was first proposed by Dr. Robert Ash at JPL in the mid 1970's[7]. Ash and his collaborators conducted some fundamental feasibility studies at JPL at that time, and Ash, now a professor at Old Dominion University, has continued to work on the process. However in recent years the center for most zirconia electrolysis research has shifted to the University of Arizona, where it has been led by professors K.R. Sridar and Kumar Ramohali.

Conceptually, the zirconia electrolysis process is quite simple. Carbon dioxide gas is heated to temperatures of about 1000 C, where it partially dissociates into CO and O_2. The gas is run through thin walled zirconia tubes which are porous to oxygen transport. An electrochemical voltage potential is then set up between the inner and outer walls of the tube causing the oxygen molecules to migrate across the tube, allowing pure oxygen gas to be collected in the region surrounding the tube. The waste gas left inside the tube is thus a mixture of carbon dioxide (the majority) and carbon monoxide (the minority). In some of the older literature[2,3] it is frequently proposed that waste gas be recycled sufficiently to allow carbon monoxide concentrations to built up to the point where it is practical to separate bulk quantities of pure CO from the waste gas stream, after which the CO could be liquefied and burned as a fuel with the product oxygen. The advantage of such a scheme would be that a complete propellant combination could be produced using as raw materials nothing but the majority constituent of the Martian atmosphere. The disadvantage, however, is that a CO/O_2 rocket engine is technically difficult, featuring a very high flame temperature and modest specific impulse (~270 s). Thus the only customer supporting such an novel and presumably expensive engine development would be users of Mars ascent vehicles. Furthermore, the power consumption required to produce CO fuel using this technique is very large, making the practicality of such a scheme questionable. For these reasons, most of the recent literature produced by zirconia electrolysis advocates has emphasized using the process to produce oxygen only, with some high performing fuel such as methane transported to Mars from Earth[15]. Since methane only comprises perhaps 22% of the mass of propellant used by a methane/oxygen rocket, the mission leverage resulting from using a zirconia electrolysis system only as an oxygen production machine is still quite large.

That said, there are a number of fundamental disadvantages to the zirconia electrolysis system that have prevented it from being generally accepted as practical in the mission planning community to date. The first is that the oxygen output that can be generated by each of the tubes is quite small, so that hundreds of the tubes would be required to produce propellant on the scale required for a Mars Sample Return mission, while tens of thousands would be needed to support a piloted Mars mission. These tubes would have to be manifolded in large groups, and if a single tube within a group were to crack or develop a leaky seal, the entire manifolded group would be lost to the system. Since the tubes are made of brittle ceramic, and since high temperature/long duration seals are required for operation (with daily start-up/shutdown cycles for hundreds of days if the power source is solar), such failure modes are not improbable. Even worse, for most purposes the required power to produce oxygen using these systems is unacceptably high. Currently, there is ongoing research at the University of Arizona to see if using zirconia plates or other configurations to replace the tubes can remedy these problems, but results to-date are not especially promising. Moreover, given that research on these systems has been going on for nearly twenty years now, significant breakthroughs beyond already demonstrated levels of performance may be regarded as highly improbable.

The other prime candidate technology within the Mars in-situ propellant production community is the Sabatier-electrolysis, or SE system. The subsystem components of the SE system are actually based upon gaslight era chemical engineering, and space-qualified components for the individual required subsystems have been available for some time due to development accomplished under the Air Force 1960's Manned Orbiting Lab and NASA's current Space Station program. Using such systems for Mars propellant manufacture was first suggested by Dr. Robert Ash in his seminal 1976 paper[7], and incorporated as central to Mars mission design by Dr. Robert Zubrin and David Baker in their 1990 paper[4] introducing the "Mars Direct" mission concept. Experimental work on integrated SE systems designed for Mars propellant manufacture did not begin until 1993, however, when, with funding support from the New Initiatives Office at NASA JSC, a

full scale (for a MSR mission application) working unit was built by Zubrin, Steve Price, and Larry Clark at Martin Marietta Astronautics (now Lockheed Martin Astronautics) in Denver. This initial demonstration project was highly successful, obtaining 94% conversion efficiencies within the first two weeks of operation. Furthermore, it was shown that key components of the SE system could be built with masses an order of magnitude less than those estimated in the prior literature[16]. During 1994 and 1995, further funding was provided for this project by JSC and then JPL, and successive improvements implemented including integrating the SE system with a sorption pump based CO_2 acquisition system (all prior Mars in-situ propellant production work had been done with compressed bottled CO_2) allowing the machine to acquire its CO_2 from a Mars atmosphere simulant reservoir held at Martian pressures (~8 mbar), and using a compact Stirling cycle refrigerator to liquefy the machine's oxygen product. Thus using the SE process, for the first time, a complete, integrated, end-to-end, full-scale Mars in-sit propellant unit was demonstrated[17].

The SE process sounds more complex than the zirconia-electrolysis process but in most respects is simpler in execution. The way it works is as follows: Carbon dioxide acquired from the Martian atmosphere is reacted with hydrogen in accord with reaction (1)

$$4H_2 + CO_2 = CH_4 + 2H_2O \qquad \Delta H = -40 \text{ kcal/mole} \quad (1)$$

Reaction (1), known for over a century as the "Sabatier reaction," is highly exothermic and has a large equilibrium constant (~10^9) driving it to the right. It occurs spontaneously in the presence of either a nickel or ruthenium catalyst (nickel is cheaper, ruthenium is better) at temperatures above 250 C. (Typical reactors operate with peak temperatures around 400 C in the forward reaction zone, declining to 200 C at the exit.) Because of the high equilibrium constant and high reaction rate when properly catalyzed, yields over 90% are readily obtained even with very small reactors. Reaction yields of 96% have been achieved in the Lockheed-Martin machine at stoichiometric mixture ratios, and 99.9% conversion rates of lean reagents have been achieved at non-stoichiometric mixture ratios[17].

The methane and water produced by reaction (1) are easily separated in a condenser. The methane is then liquefied and stored, while the water is electrolyzed in accord with:

$$2H_2O = 2H_2 + O_2 \qquad \Delta H = +57 \text{ kcal/mole} \quad (2)$$

The oxygen so produced is liquefied and stored, while the hydrogen is recycled back into the Sabatier reactor to produce more methane and water, and so forth.

It will be noted that reaction (2) only produces two hydrogen molecules to recycle back to reaction (1), which requires an input of four hydrogens. Thus a net input of hydrogen is required to make the system run. This could, in principal, be acquired on Mars at large energy cost by condensing it out of the atmosphere[1,18] in a relatively simple automated system, or mined from Martian permafrost with the aid of human explorers or a very advanced type of automated mining system. Alternatively, (and more practically for early missions) the hydrogen can simply be brought from Earth. In this case, the combination of reactions (1) and (2) will produce 12 kg of CH_4/O_2 bipropellant on Mars for every 1 kg of hydrogen imported.

The primary advantages of the SE system are simplicity, robustness, scalability, and energy efficiency. The Sabatier reactor is basically a simple steel pipe containing a catalyst bed, which can easily be scaled to support a mission of any size. For example, the Lockheed Martin unit demonstrated that a small Sabatier reactor 0.1 liter in volume would be sufficient to support the MSR mission propellant requirement of ~1 kg/day. Based on these results the entire Mars Direct manned mission propellant production could be done in three 10 liter pipe reactors. Operating at ~400 C with a filter to preclude catalyst poisoning by Martian dust, such reactors are basically bulletproof, especially since their small size makes it practical to support virtually any desired level of subsystem redundancy. Available water electrolysis units using solid polymer electrolytes are highly efficient (>90%) and extremely rugged, as they have been designed for nuclear submarine use with specifications that include resistance to depth charge attack. The power advantage of the SE system is illustrated in Table 1, which compares the achieved performance to date of the SE unit at Lockheed Martin with the best results from zirconia-electrolysis units at the University of Arizona. The results shown are for chemical process requirements only, since that is the only issue the University of Arizona machine addresses. It should be noted, however, that the power requirements for the gas acquisition to service the zirconia based system would be about 4 times greater than the SE system, because the zirconia system only removes one oxygen atom from each CO_2 reacted, and only reacts about 46% of input CO_2, while the SE system removes both oxygens from each CO_2 and is more than 95% efficient.

It can be seen that the energy efficiency advantage of the SE process over the zirconia process is enormous. However the SE process has disadvantages of its own.

Table 1 Comparison of Sabatier Electrolysis and Zirconia Electrolysis Results

Parameter	Sabatier/Electrolysis	Zirconia/electrolysis
Operator	Lockheed Martin	Univ. of Arizona
O_2 Production	0.48 kg/day	0.15 kg/day
CH_4 Production	0.24 kg/day	0
Power	120 W	250 W
Power/Propellant	166 W-day/kg	1562 W-day/kg

The primary disadvantage of the SE system is the need to import hydrogen. This requirement is especially painful on the MSR mission, where the relatively small tank sizes employed increases the tank surface area/volume ratio, increasing heat-leak and thus boiloff, making transport of the required hydrogen to Mars difficult. The SE process, operating alone, produces 2 kg of oxygen for every one kg of methane. But the optimal mixture ratio to burn O_2/CH_4 in a rocket engine is not 2/1 but about 3.5/1, where an engine specific impulse as high as 380 s can be achieved. If the SE process is acting alone, the only way to achieve this mixture ratio is to throw away some of the methane produced. This drops the net propellant leverage actually achieved by the system from the theoretical 12/1 (propellant produced to hydrogen imported ratio) to an actual 10.3/1. Since the hydrogen required to produce 10.3 times its weight in CH_4/O_2 propellant actually occupies a volume equivalent to about 14 times its weight in CH_4/O_2 propellant, and at least 20% extra hydrogen will be needed at launch to allow for boil-off losses during flight to Mars, such limited leverage requires that the CH_4/O_2 tanks be drastically oversized if they are to be used to transport the required hydrogen feed stock. Oversizing the tanks to meet this requirement causes tank weights to increase, thereby increasing net propellant requirements, etc., with the net result being a severe negative impact on overall mission performance.

Thus we see that a simple SE system incorporating only reactions (1) and (2) cannot provide a really attractive Mars in-situ propellant production system. This situation changes, however, if a third reaction is introduced which allows the 3.5/1 mixture ratio to be achieved not by throwing away methane, but by adding oxygen. In this case, instead of the propellant production leverage falling from the theoretical SE 12/1 to 10.3/1, it rises to 18/1. Since this leverage is significantly greater than the density ratios of CH_4/O_2 bipropellant to H_2 feed stock, this means that the hydrogen feed stock can be transported to Mars in the ascent vehicles propellant tanks, without any oversizing required. Put more simply, having a third, oxygen producing reaction available nearly doubles the propellant leverage of the SE system, and this doubling of performance is the difference between an attractive system and an inadequate one.

So, in short, what we need is an oxygen machine. The zirconia electrolysis nominally fits the bill, but as we have seen it is inadequate from a practical point of view, with power requirements greatly in excess of anything likely to be available on an MSR mission (a zirconia-electrolysis based MSR mission would need at least 5 RTG's, which are not to be had), and scalability problems that preclude use as a central technology for supporting a piloted Mars mission. What we need is a in-situ propellant production system that combines the simple steel-pipe reactor and high energy efficiency advantages of the SE system with the "infinite leverage oxygen machine" talking points of the zirconia-electrolysis approach. The only system that potentially meets these requirements is the reverse water gas shift (RWGS). In fact, as we shall see, a RWGS system may offer much more.

The Reverse Water Gas Shift

The reverse water gas shift (RWGS) reaction has been known to chemistry since the mid 1800's. While it has been discussed as a potential technique for Mars propellant manufacture in the literature[4], there has been no experimental work done to demonstrate its viability for such application to-date. The RWGS reaction is given by equation (3).

$$CO_2 + H_2 = CO + H_2O \qquad \Delta H = +9 \text{ kcal/mole} \quad (3)$$

This reaction is mildly endothermic and will occur rapidly in the presence of a catalyst at temperatures of 400 C or greater. Unfortunately at 400 C the equilibrium constant K_p driving it to the right is only about 0.1, and even at much higher temperatures K_p remains of order unity. There is thus a significant problem in driving the

RWGS reaction to completion. An additional problem is to insure that then reaction is narrowly catalyzed to reduce CO2 to CO, avoiding the alternative exothermic reactions producing methane or methanol.

However, assuming that reaction (3) can be driven as written, an "infinite leverage oxygen machine" can be created by simply tying reaction (3) in tandem with the water electrolysis reaction (2). That is, the CO produced by reaction (3) is discarded while the water is electrolyzed to produce oxygen (the net product), and hydrogen which can be recycled to reduce more CO_2. Since all the hydrogen is recycled, barring leakage losses this can go on forever allowing the system to produce as much oxygen as desired. The only imported reagent needed is a small amount of water which is endlessly recycled.

The RWGS/electrolysis oxygen machine shares many of the advantages, and indeed can share many of the subsystem components, of an SE system. The RWGS reactor itself is just a simple steel pipe filled with catalyst, much like a Sabatier reactor, except that the catalyst is different. A similar condenser and identical water electrolysis system is also employed. Because the RWGS reaction is only mildly endothermic (9 kcal/mole for RWGS compared to 57 kcal/mole for water electrolysis), system power requirements are dominated by the water electrolysis step, the available technology for which is highly efficient. Moreover, since the thermal power required by the RWGS is less than that produced by the Sabatier reactor and their operating temperatures are comparable, a Sabatier reactor can be used to provide the heat required to drive the RWGS reactor. That is, if a Sabatier reactor running at a rate of 1 unit of equation (1) is lain side by side in direct thermal contact with a RWGS reactor running at a rate of 2 units of equation (3), the net reaction of the combined system will be:

$$3CO_2 + 6H_2 = CH_4 + 4H_2O + 2CO$$
$$\Delta H = -22 \text{ kcal/mole} \qquad (4)$$

"Reaction" (4) is thus exothermic, requiring no net input power to operate. When run in combination with reaction (2), the net result is to produce 4 kg of methane and 16 kg of oxygen for every kg of H_2 imported, for a net propellant leverage of 20/1 and a O_2/CH_4 mixture ratio of 4/1. The energy efficiency of the combined RWGS/SE system is essentially the same as that in a simple SE system. Achieving such performance in a Mars in-situ propellant production system would be superb. The trick, however, is to find a practical way to drive the RWGS reaction to completion.

There are a number of ways that this could be accomplished. These are:

a) Overload the reactor with CO_2 to force the complete consumption of the H_2, and then recycle the excess CO_2 in the exhaust stream back into the reactor.
b) Overload the reactor with H_2 to force the complete consumption of the CO_2, and then recycle the excess H_2 in the exhaust stream back into the reactor.
c) Operate a system that removes water vapor from the reactor, thereby driving reaction (3) to the right. Such a system could either be a desiccant bed or condensing apparatus.
d) Combine approaches (a) and (c).
e) Combine approaches (b) and (c).

Fig 1. schematically illustrates a system capable of operating in any of the modes (b), (c) or (e) listed above. In this case the drying apparatus employed is a condenser bottle kept at a temperature between O C and 10 C. Since water at 10 C has a vapor pressure of about 0.01 atmospheres, cycling reactor gas through this condenser by bubbling it through a small liquid water reservoir will remove the vast majority of steam from the reactor if the reactor pressure is of the order of 1 atmosphere or more. (Freezing the water vapor in the condenser or using a zeolite desiccant bed could reduce the water vapor pressure in the returning stream to much lower values than 0.01 atmospheres, but the engineering complexity and power requirements associated with such options may make them less attractive than the simple liquid-phase condenser proposed here.) A counterflow arrangement is used to minimize heat lost from the system during the condensing process. Assuming the rate of flow through the condenser loop is much (an order of magnitude or more) higher than the rate of net flow through the reactor, the reagent concentrations in the reactor will approach those that would result if the H_2O concentration was physically pegged at 0.01 atmosphere. Hydrogen can be separated from the exhaust stream by means of a hydrogen permeable membrane and a recirculation pump, after which it can be fed back into the reactor. An alternative arrangement in which the exhaust gas is fed through a cooled sorbant bed (Mars' environment makes such cooling very easy) would allow for batch capture of CO_2 from the exhaust, after which it could be recirculated, enabling such a system to operate in modes (a) or (d). Such a system should be able to achieve high RWGS conversion yields. For example, if the reactor was operated at stoichiometric mixture ratios at 400 C (K_p=0.1), we find:

$$[CO][H_2O]/[CO_2][H_2] = [CO][0.01]/[CO_2][H_2] = 0.1 \quad (5)$$

or, since the system is stoichiometric, and $[CO_2] = [H_2] = X$

$$CO = 10X^2 \quad (6)$$

Fig.1. Schematic of RWGS system used as an "infinite leverage" O2 machine. The subsystem drawn inside the dotted lines currently needs experimental verification.

If X=1, CO=10 (i.e. the reactor is operating at 12 atmospheres, or 176 psi) and the conversion rate is 90%. This can be increased by going to higher pressures or increasing the ratio of H2 to CO2 in the input stream. The results for various reactor pressures and for both stoichiometric and 2:1 off-stoichiometric input ratios are shown in Fig. 2.

Fig. 2. Conversion efficiencies in a RWGS system where a 10 C condenser is used to peg water vapor pressure in the reactor at 0.01 atmospheres.

The yields shown in Fig. 2 will only be approached asymptotically as the rate of flow through the condenser loop approach a rate infinitely faster than the reactor net output flow (i.e. Flow2 >>Flow1). Of course, the faster the rate of reactor gas recycle through the condenser loop, the more heat loss will occur, and more heating and loop circulation pump power will be needed. Preliminary analysis indicates, that with efficient counterflow heat exchanger design, that Flow2/Flow1 ratios greater than 10 and possibly as high as 50 may be practical.

However, provided the waste hydrogen is recycled, it really doesn't matter too much whether the real yield in the reactor is 80% or 99%, because CO_2 is available in unlimited quantities on Mars. On the other hand, if the desire for engineering simplicity makes it necessary to eliminate the hydrogen recirculation loop from the system, then real reactor yields are very important. While calculations can be of great assistance in predicting what such yields would be, the system, combining considerations of both chemical equilibrium and kinetics, system geometry, reactor temperature profiles, catalyst activity and surface area, is so complex that an accurate performance assessment can only be done by experiment.

Use of RWGS Reactor to Produce Ethylene

The discussion so far has shown how a RWGS reactor can be used either as the sole component in a loop with an electrolyser as an "infinite-leverage oxygen machine" on Mars, or how it can be used in tandem with an SE based Mars in-situ propellant production system to increase the leverage of such a system from 10.3/1 to 20/1. In addition, it should be obvious that, operating without an electrolyser, a RWGS reactor can be used to leverage imported hydrogen into water on Mars (to augment crew consumables) with a mass leverage ratio of 9/1. However the RWGS reactor opens up additional remarkable possibilities.

Let's say we operate the RWGS reactor with an excess of hydrogen, but we do <u>not</u> recycle the waste hydrogen effluent. As a simplified example, assume that the H_2/CO_2 input ratio is 3/1, and that the CO_2 conversion rate is close to 100%. Then we have 3 units of H_2 and 1 unit of CO_2 going into the reactor, 1 unit of H_2O collected in the condenser, and 1 unit of CO and 2 units of H_2 leaving the reactor. The water is electrolyzed to produce product oxygen for the propellant tanks and hydrogen for recycle into the RWGS. The CO and H_2 mixture can then be fed as input into an ethylene reactor, where in the presence of a iron Fischer Tropsch catalyst they can be reacted in accordance with:

$$2CO + 4H_2 = C_2H_4 + 2H_2O \quad \Delta H=-49.4 \text{ kcal/mole} \qquad (7)$$

A schematic showing how reaction (7) could be operated in series with a RWGS reactor is shown in Fig. 3.

Fig.3. Schematic of RWGS/ethylene system. As an alternative, a methanol reactor could be used in place of the ethylene reactor. The subsystem drawn inside the dotted lines needs experimental verification.

Reaction (7) is strongly exothermic, and so like the Sabatier reaction, can be used as a heat source to provide the energy needed to drive the endothermic RWGS. It also has a high equilibrium constant, making the achievement of high ethylene (C_2H_4) yields possible. However, this system has extraordinary advantages over a Sabatier reactor. In the first place, ethylene has only two hydrogen atoms per carbon, while methane has four. *Thus using ethylene for fuel instead of methane cuts the hydrogen importation requirement in half.* Again, the propellant leverage of a RWGS/ethylene system is nearly double that of a RWGS/SE system, which itself is nearly double that of a simple SE system. In fact, with propellant leverage so high, it may be possible to acquire the required amounts of hydrogen from Mars atmospheric water vapor without too great a power impact, eliminating the hydrogen importation problem altogether. In the second place, ethylene has a boiling point (at one atmosphere pressure) of -104 C, much higher than methane's boiling point of -183 C. In fact, under a few atmospheres pressure ethylene is storable at Mars average ambient temperatures, whereas methane's critical temperature is below typical Mars nighttime temperatures. Thus ethylene can be liquefied on Mars without the use of a cryogenic refrigerator, whereas methane cannot be. This cuts the required refrigeration power for a RWGS based ethylene/oxygen system about in half relative to that of an SE based methane/oxygen production system. It also greatly reduces the need to insulate the ethylene fuel tanks. In the third place, the density of liquid ethylene is 50% greater than liquid methane, allowing for the use of smaller and therefore lighter fuel tanks on Mars ascent vehicles or ground rovers employing ethylene instead of methane fuel. Fourth, an ethylene/oxygen rocket engine should have a specific impulse about two seconds higher than a methane/oxygen rocket[19], thereby slightly increasing overall mission performance. Fifth, ethylene has many other uses besides rocket or rover or welding fuel. It is used as an anesthetic. It is also used as a ripening agent for fruits and as a means of reducing the dormant time of seeds. These features could prove very useful in a developing Mars base which is aiming for self-sufficiency.

However, beyond this, ethylene is extraordinarily useful as the basic feedstock for a range of processes to manufacture polyethylene and numerous other plastics. These plastics can be formed into films or fabrics to create large inflatable structures and well as to manufacture clothing, bags, insulation, and tires, among others. They can also be formed into high-density stiff forms to produce bottles and other watertight vessels, tableware and innumerable other small but necessary objects, boxes, and rigid structures of every size and description, including those that are both transparent and opaque. Lubricants, sealants, adhesives, tapes, can all be manufactured; in fact the list is nearly endless. On Earth, ethylene has been characterized as the basis of the plastics industry[20] that has revolutionized modern life since the 1950's. The development of an ethylene-based plastics manufacturing capability on Mars would offer similar enormous benefits in opening up all sorts of possibilities and capabilities necessary for the human exploration and settlement of the Red Planet.

It may be noted that if Reaction (7) is not narrowly catalyzed, it will also have side reactions yielding methanol (CH_3OH) and propylene (C_3H_6). The later is not a problem, as propylene would be a superior product to ethylene, both as a fuel and a plastic feedstock (to produce polypropylene). Small methanol yields are acceptable, as methanol is miscible with ethylene and propylene and a mixture of the three would still make good storable rocket fuel. If the primary objective is to reduce hydrogen importation, excessive methanol yields would be a problem, however, because methanol molecules have four hydrogens for every carbon atom. However, experiments have shown that if properly catalyzed, the methanol yield of reaction (7) can be kept as low as 2% by weight[20].

Use of RWGS to Produce Methanol

An alternative approach, however, is to send the CO/H2 effluent of a RWGS system into a reactor designed to produce methanol. As the conversion of CO/H2 “syngas” in such copper-zinc catalyst reactors is one of the principle ways of producing methanol today, this approach represents much more mature technology

than ethylene production. While such a strategy may appear to offer no advantages over using an S/E system augmented by a RWGS (because methanol, like methane has 4 hydrogens for every carbon), this is not true. The reason is that while methanol production offers no greater hydrogen leverage than the methane production of a Sabatier reactor, the methanol/RWGS system requires significantly less power. The reason for this is that the primary power requirement of an ISPP plant is to drive water electrolysis to produce oxygen. By reducing the oxygen fraction of the propellant, (methanol burns at between 1/1 and 1.5/1 oxygen/fuel mixture ratio, much less than the 3.5/1 of a methane system.) this power requirement is reduced accordingly. The second largest power requirement for an ISPP unit is for refrigeration of cryogenic propellants. Methanol is not a cryogen, and requires no power for its liquefaction. Thus, to the extent that methanol comprises a large fraction of the total propellant mixture, refrigeration power requirements are reduced as well. By combining these two advantages, a fuel-rich methanol/O2 ISPP system can have its power requirements dropped to half that of a Sabatier/Electrolysis ISPP system (Its nearest competitor) and less than a tenth that of the alternative zirconia/electrolysis ISPP system.

Because power requirements may be decisive in determining the practicality of in-situ propellant production for supporting both robotic Mars Sample Return and human piloted Mars exploration missions, the development of the methanol/RWGS system may offer critical advantages in enabling such missions.

The specific impulse of rocket engines using methanol, kerosene, methane, and oxygen is given in Table 2. Methanol/oxygen rockets have a specific impulse that is about 20 seconds (~6%) worse than those powered by methane/oxygen.

Table 2 Specific Impulse of Rocket Engines

Fuel	O/F Mixture Ratio	Chamber Temperature (C)	Isp
Methanol	1:1	2818	334 s
Methanol	1.5:1	3042	353 s
Kerosene	2.6:1	3331	361 s
Methane	3.5:1	3222	374 s
Ethylene	2.6:1	3521	376 s

Thus, it may be objected that while the methanol/RWGS system produces more than twice as much propellant per unit power expended than the S/E system, it also needs more propellant than the S/E because the methanol fuel produced by methanol/RWGS has a lower Isp than the methane produced by the S/E. However for a spacecraft performing the 4 km/s ΔV needed to go from the Mars surface to orbit in a single stage, the methanol/O2 bipropellant needed (at 334 s Isp) is only about 20% more than the amount of (374 s) CH4/O2 needed. If a two-stage vehicle is used to go from the Martian surface directly back to Earth (ΔV=6.4 km/s), 43% more methanol/O2 than methane/O2 will be needed. So despite the lower performance of methanol fuel compared to methane, the power savings required to accomplish the same mission will still be quite large.

RWGS DEMONSTRATION PROJECT

In order to demonstrate the feasibility and assess the potential of the RWGS for Mars ISRU, a demonstration project has been initated at Pioneer Astronautics under Phase I SBIR funding from NASA Johnson Space Center. The system to be contructed will demonstrate the RWGS as both as a stand-alone oxygen production apparatus and as a first step in a machine that will produce both oxygen and methanol. The Phase I project began March 17, 1997 and is scheduled to run until September 17, 1997. Progress to date (June 6, 1997) has been primarily in three areas:

1) Literature search,
2) Development and production of catalysts, and
3) System analysis, design, procurement, and construction.

1) Literature Survey on RWGS Catalysts

A literature search on Chemical Abstract was performed in order to find catalyst candidates for the RWGS reactor. The focus of this literature search was to determine which catalysts are the most selective towards production of carbon monoxide. For this application selectivity of the catalyst is more important than its activity. Based on this search, three groups of catalysts appear to be suitable for this application:

1. Cu supported catalysts
2. Au supported catalysts

3. Mo compounds

The Cu supported catalysts have shown good activity and outstanding selectivity to produce CO from CO_2. For example, Nozaki et al. (1987)[27] reported that their Cu/alumina catalyst demonstrated 28% CO_2 conversion with 100% CO selectivity when the reactor was operated at 350 °C under atmospheric pressure with SV (space velocity) of 100 ml/min/g-cat and CO_2/H_2 feed ratio of 1/4. The loading of Cu was 12 wt%. Even though they have tested various metal supported catalysts on alumina under the same conditions (Ni, Rh, Ru, Pt, Pd and Re), the Cu catalyst was the only one that exhibited exclusive selectivity to CO. The other metal catalysts tended to produce more methane or, in some cases, only methane.

5 wt% Cu/silica catalyst was also able to give at least 97% CO selectivity (Kitayama, 1997)[26]. The catalyst was evaluated at 350 °C with a feed ratio CO_2/H_2 of 1/4. The conversion to CO was 60% under a pressure of 150 torr. The catalyst activity was improved by adding a little amount of Ni to Cu while maintaining high activity. However, if the catalyst had too much Ni, it started forming more methane. The authors recommend $Ni_{0.1}Cu_{0.9}$/silica as the best catalyst in this series.

When 5 wt% Cu/silica catalyst was operated at 60 bar and 280 °C with a feed mixture (CO_2: 22.7%, H_2: 67.2%, Ar: 10.1%) and SV of 50 ml/min/g-cat , the selectivity to carbon monoxide was decreased and more methanol was produced (Dubois, 1992) [22]. According to their results, the catalyst showed 17% CO_2 conversion and carbon monoxide and methanol selectivities of 76 and 24%, respectively.

The selection of support material for Cu catalysts and the reaction pressure seem to be two critical parameters affecting selectivity. For methanol synthesis process Cu/ZnO catalyst is usually employed under 10 bar with the temperature range of 250 - 350 °C. The Cu/ZnO catalyst is more selective to produce methanol than carbon monoxide even at atmospheric pressure (Fujita, 1992) [25], which implies that ZnO plays an important role in the reaction chemistry.

Au supported catalysts on metal oxides were tested by Sakurai (1993) [29]. They used a hydrogen-carbon dioxide feed mixture with argon (CO_2: 23.4%, H_2: 66.2%, Ar: 10.4%) under 8 atm with a space velocity of 3000 ml/h/g-cat. The temperature range evaluated was 150 - 400 °C. Among those they tested, Au/TiO_2 and Au/Fe_2O_3 were found to have good selectivity and a conversion level close to the thermodynamic equilibrium value. At 400 °C 35% carbon monoxide and 3.3% methane were produced on Au/TiO_2, and 38% and 1.3% on Au/Fe_2O_3. However, the Au/Fe_2O_3 catalyst tended to produce more methanol in the temperature range of 150 - 300 °C than Au/TiO_2.

According to the recent publication by the same group (Sakurai 1997) [30], by decreasing reaction pressure from 50 to 1 bar, CO selectivity of the Au supported catalysts were significantly improved. For example, CO, methanol and methane were produced with selectivities of 86, 4 and 10%, respectively, on 2 atom% Au/TiO_2 at 50 bar while more than 99% of CO was formed at 1 bar on the same catalyst. The most remarkable property of the Au catalysts is that they are able to reach CO_2 conversions that are dose to the equilibrium limit even at temperatures as low as 250 K. The major disadvantage of gold catalysts would be cost compared with copper and other materials.

Mo catalysts have attracted some attention for the RWGS reaction. Saito and Anderson (1981)[28] tested bulk Mo compounds for CO_2 reduction and they found that Mo metal had fairly higher activity than MoS_2. On the other hand, MoS_2 supported on TiO_2 appeared to demonstrate the best performance in the MoS_2 supported catalysts (Taoda, 1991) [32]. 13% CO_2 conversion was achieved with more than 99% selectivity on this catalyst at 400 °C with a CO_2/H_2 feed ratio of 1. The conversion of the catalyst at 400 °C was much lower than that at thermodynamic equilibrium. One advantage of using sulfide catalysts is that the catalyst can't be deactivated by sulfur compounds present in the feed.

If no sulfur exists in the feed stream, use of Mo oxide catalysts is more practical. The MoO_3/ZnO catalyst was tested at 873 K with a CO_2/H_2 ratio of 1 (Suzuki, 1995)[31]. The CO_2 conversion was 30% with close to 100% CO selectivity. The other RWGS catalyst, NiO/ZnO, showed higher activity (38%) but selectivity dropped to 93%. With excess amount of CO in the feed stream at 903 K, NiO/ZnO failed to demonstrate good performance because of carbon deposition and methanation. On the contrary, under the same reaction conditions, the MoO_3/ZnO catalyst maintained close to 100% CO selectivity. The function of the ZnO support in this study was not explained.

From the above information it appears that Cu supported catalysts on alumina or silica are the primary candidates for the RWGS reaction. Au supported catalysts are worth trying if necessary but less desired do to considerations of cost and preparation

procedures. Mo oxide supported catalysts also have a good chance to achieve the requirements for the RWGS reactor.

2) Development and production of catalysts

Catalyst Selection

Based on the literature survey, the Cu supported catalysts on g-alumina and silica were chosen. The loading of Cu was approximately 10 wt%.

Catalyst Preparation

Supports used were g-alumina (Norton, 1/16' spheres, BET surface area = 200 m^2/g) and silica gel (Davison Chemical, Grade 57, crashed into 20/40 mesh, BET surface area = 300 m^2/g). The support materials were calcined at 500 °C overnight to drive off all the adsorbed water. After cooling, the support was impregnated with a solution of cupric nitrate by incipient wetness technique. The impregnated material was then dried at 110 °C overnight and calcined at 500 °C for 2 hours. The pore volume of each support was determined prior to the impregnation, and was fund to be 0.60 ml/g for g-alumina and 1.16 ml/g for silica. To ensure filling of the pores, the impregnation was done under vacuum.

Apparatus

Catalyst evaluation tests were conducted in order to provide kinetic information of the candidates for reactor design purposes. The reactor employed was a continuous down-flow micro catalytic reactor. High purity hydrogen and carbon dioxide cylinders equipped with water removal cartridges were used to feed the reactor. The feed mixture was preheated to 150 °C before flowing over the catalyst bed composed of catalyst and quartz chips as a diluent. The catalyst bed was mounted in 1/2 inch stainless steel tube with a small piece of 100 mesh wire cloth to support the catalyst bed. The bed was located in the isothermal zone of the reactor. A Lindberg furnace heated the reactor. The temperature was monitored in the middle of the bed by a J type thermocouple inserted from the top of the reactor. The reaction products flowed through a heated line to the gas sample valve in an SRI gas chromatograph (GC, thermal conductivity detector). The GC column was 10 ft by 1/8 stainless steel tubing and packed with Porapak N (80-100 mesh).

Equipment Calibration

To ensure accuracy, all major pieces of equipment were calibrated. In addition, a blank run was made on the stainless steel tube containing only quartz chips at 400 °C to verify that it has no activity for the RWGS reaction.

Gas Chromatograph

The compounds expected in the product stream were determined by their relative retention times. To obtain clear peak separation the initial oven temperature of 50 °C was ramped at 20 °C per minute to 150 °C where it was held for 10 minutes. The response factors of the compounds were determined with a gas mixture containing 25% of each, H_2, CO, CH_4, CO_2. Water and methanol response factors were determined with their liquid mixtures. Accurate analysis of hydrogen requires spiking the GC helium carrier gas with hydrogen, therefore, 10% H_2 in He was used as a carrier gas for GC. Water eluted in a very broad peak with poor reproducibility. The water concentration was therefore determined from the concentrations of the other products by using reaction stoichiometry.

Test Procedure

The catalyst bed consisted of 0.5 g of catalyst and 1.5 g of quartz chips. The catalyst was reduced in situ using hydrogen at 400 °C for 2 hours, then, the inlet gas was switched to a hydrogen and carbon dioxide gas mixture at selected flow rates. The H_2 to CO_2 ratio was 1 and reaction temperature was fixed at 400 °C under atmospheric pressure. The operating conditions were maintained constant until a minimum of three consecutive samples of product stream were reproducible (steady state).

Test Results of Cu/g-Alumina Catalyst

The Cu/g-alumina catalyst was evaluated at the total feed flow rates of 10.4, 19.6, and 42.0 ml/min in this sequence. The results are listed in Table 3.

Table 3. Test Results of Cu/g-Alumina Catalyst

Flow rate	CO2 Conversion	CO Selectivity
10.4 ml/min	19.6 %	100 %
19.6 ml/min	13.0%	100 %
42.0 ml/min	8.0 %	100 %

As expected, the lower feed flow rate resulted in a conversion approaching the thermodynamic equilibrium value (24% at 400 °C). It is important to emphasize that no by-products, such as methane or methanol, were detected throughout the entire run. The activity and selectivity of this catalyst were satisfactory.

Based on the above results, it can be projected that a 300 cc copper on alumina catalyst bed should be more than sufficient to perform the chemical synthesis for an RWGS unit supporting a propellant production rate of 0.5 kg/day.

3) System design, procurement, and construction

System design, procurement, and construction to date have focused on the RWGS unit, which will provide feed to the methanol converter. The proposed arrangement of process units is shown in Figure 3: Reverse Water Gas Shift Unit Process Design.

The system consists of a fresh feed inlet from bottled hydrogen and carbon dioxide gas. This fresh feed is mixed with recycled gas, warmed to reactor temperature and passed through the RWGS reactor catalyst bed. Effluent from the RWGS reactor is cooled in the condenser and then phase separated in a vessel. The aqueous phase can be drawn off the phase separator or simply accumulated in the vessel. In the Phase 2 portion of this project, the water will be sent to an electrolysis unit that will produce pure oxygen for liquefaction and hydrogen for recycle to the RWGS unit feed. Vapor from the phase separator is sent to the membrane unit, which recovers hydrogen and carbon dioxide in the low pressure permeate and rejects carbon monoxide in the high pressure residue that is sent to the methanol converter. The permeate is sent to a low flow compressor, which returns it to the RWGS reactor after mixing with the fresh feed.

The stoichiometry of the fresh feed to the RWGS system can be adjusted to allow it to operate in different modes. When producing an oxygen/methanol bipropellant, the molar stoichiometry ideally operates in a 5:3 hydrogen:carbon dioxide ratio. At this ratio and 100% carbon dioxide conversion efficiency, the RWGS unit provides 3 moles of water to the electrolysis unit, and three moles of CO and two moles of H_2 to the methanol converter. The methanol converter feed produces one mole of methanol, with two excess moles of carbon monoxide for venting. This feed ratio provides enough oxygen for an ideal stoichiometric burn for each mole of methanol.

Alternatively, a 1:1 hydrogen:carbon dioxide molar feed ratio can be used to make the RWGS reactor into a high leverage oxygen machine. If the membrane unit recovers hydrogen very efficiently, the mass leverage can theoretically be made as high as desired. Decreasing the hydrogen/carbon dioxide feed ratio below 1:1 will also increase hydrogen mass leverage, but at the expense of additional power to gather the carbon dioxide from the atmosphere.

The system was analyzed with a spreadsheet developed to simulate the process design. The simulation allows different process parameters to be examined to determine the optimum system operation point. Using the spreadsheet analysis tool, it is found that under the preferred 10 bar/400 C operating conditions, in the 5:3 "bipropellant mode" it is possible to achieve CO_2 conversions in this system greater than 99%. As all residual hydrogen is funneled to the methanol reactor in this mode, none of the precious H_2 would be wasted. To achieve this level of performance, a methyl-butadiene membrane of about 1 square meter is required, if 0.5 kg of methanol/oxygen bipropellant is to be produced in a 12 hour day. Although operation of the apparatus during the Phase I project will be exclusively in the oxygen/methanol bipropellant mode, simulations were also performed of the oxygen production mode. According to spreadsheet analysis of this mode, under the preferred operating condition of 10 bar/400 C, it is possible to attain 99% conversion of both CO2 and hydrogen with a oxygen production rate of 0.5 kg per 12 hour day, provided that a 4 square meter methyl-pentene membrane is used.

3.1) RWGS reactor

The heart of the RWGS unit, the RWGS reactor, was analyzed with several different parameters. The spreadsheet simulation makes the simplifying assumption that the RWGS reactor effluent is in equilibrium. To make this assumption true, kinetic data for the desired catalyst (section 2, above) is used to size the reactor large enough to achieve results very close to equilibrium. The equilibrium expression used for the RWGS reaction was developed by Bissett[21].

Using the reactor inlet concentrations and the equilibrium constant, solution for the effluent concentrations is simple. However, since there is a large recycle stream, the inlet concentrations are not immediately known. The inlet concentrations are determined by an iterative procedure using a direct substitution convergence method.

The RWGS reactor unit also requires heat input to allow the reaction to proceed. The heat input has four terms: 1) heat required to raise the temperature of the fresh feed to reactor temperature, 2) heat required to raise the recycle stream to the reactor temperature, 3) heat required to maintain reactor temperature while the

endothermic reaction is occurring, and 4) heat leak to the surroundings.

The equilibrium constant of the RWGS reaction is a weak function of temperature, improving from 0.086 at 400 °C to about 1.7 at 1000 °C. However, above 400 °C, design of the system, with appropriate high temperature components, becomes prohibitive. Increasing the recycle at a lower temperature is more economical than raising the temperature, therefore 400 °C was chosen as the approximate practical upper limit for the temperature. The temperature will be varied after startup to determine the precise optimum. Figure 4 shows the tradeoff of membrane surface area with temperature for a constant carbon dioxide conversion rate. The amount of required area increases as the temperature is lowered because there is a lower per pass conversion in the RWGS reactor, which means that more of the reactants must be recycled. This graph is nearly linear, and shows reasonable membrane areas at temperatures below 400 °C, which indicates that there is no compelling process reason to go above this temperature.

Reactor construction is a simple process. The laboratory in which the apparatus is being built has a large selection of stainless steel vessels in the 200 ml range. The chosen reactor vessel will be fit with 100-mesh solid retaining screen, a layer of inert material and the catalyst. The reactants will flow downward through the catalyst bed to prevent fluidization or channeling. Base mode for reactor operation will be approximately 400 °C and 10 bar absolute, which provides a good balance of various trade-offs according to the simulation results. After the apparatus is operating properly, these parameters will be varied to determine how closely the simulated model agrees with experimental results.

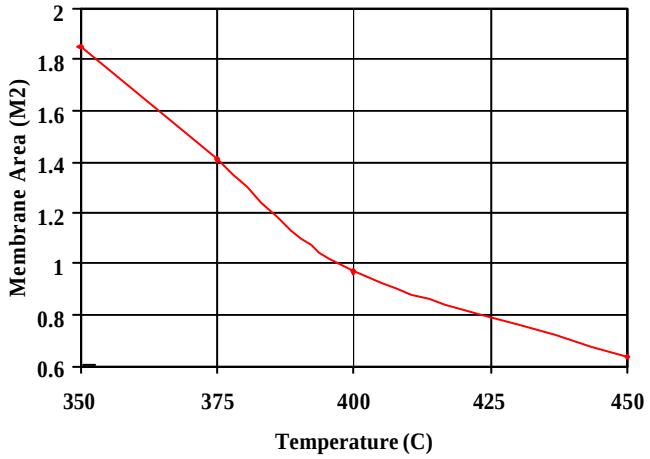

Fig. 4 Tradeoff of Membrane surface area with temperature for constant CO2 conversion rate.

3.2) Water condenser/separator

The water condenser spreadsheet calculation involves calculation of the required sensible and latent heat of the hot reactor effluent, and of the vapor/liquid equilibrium state at the desired final temperature. Several simplifications were also assumed for these calculations, the most important of which is that hydrogen is negligibly soluble in the aqueous phase.

The condenser temperature is set at 10 °C, in order to avoid having to worry about formation of solid ice. Simulation verifies the intuitive conclusion that condenser performance, and therefore RWGS unit performance, improves as temperature is lowered.

The condenser is a simple coiled tube, which straightens and penetrates a 3/8" NPT hole in the top end cap of the separator vessel. The tube goes almost to the bottom of the separator, under the liquid level, where it discharges the two phase stream. Vapor from the separator leaves via a second 3/8" NPT penetration in the top end cap, while the aqueous phase flows out through a 1/16" NPT penetration in the bottom end cap. Cooling duty for the condenser coil and the separator will be provided by an ice bath that will keep the temperature of the separator at approximately 10 °C.

3.3) Membrane separation unit

The vapor from the separator overhead flows to the membrane unit, where carbon monoxide is rejected and hydrogen and carbon dioxide are recovered and recycled to the RWGS reactor. Performance of the membrane unit is calculated by the spreadsheet ("Membrane Unit", Page 1).

While system pressure has a negligible effect on the equilibrium of the RWGS reaction, it has a major impact on membrane unit performance. Higher pressure differences between the feed and permeate side of the membrane increase the amount of gas which permeates. In addition, higher system pressure increases the RWGS reaction rate, decreases volumetric flows, increases heat transfer, and increases the amount of water recovered in the condenser. Thus, higher pressure has a number of benefits for the system. The major drawback of higher pressure is the increased structural requirements for system design. Standard components designed for more than about 10 bar are difficult to find, so this was chosen as the best practical operating pressure.

With a fixed reactor pressure and membrane area, the

permeate pressure determines the amount of gas which permeates and is recycled to the reactor. As permeate pressure decreases, the total CO_2 conversion increases, but the required power to recompress the permeate also increases. Figure 5 shows the relation between permeate pressure, carbon dioxide conversion, and pump power based on a fixed membrane and 10 bar upstream pressure. Based on this diagram, 3 bar was calculated as the optimal permeate pressure for an RWGS reactor pressure of 10 bar. The precise optimum pressures for the membrane unit will be verified during system testing.

Commercial membrane performance is extremely difficult to predict, so simulation calculations were based on public domain data from generic type membrane materials. Rubbery membranes, such as amorphous poly-(1,3-butadiene) or poly-metylpentene typically have a high absolute permeability, but a relatively low hydrogen/carbon monoxide separation factor. Crystalline (glassy type) membrane materials, such as polyimides or cellulose acetate, have excellent separation factors for both hydrogen and carbon dioxide relative to carbon monoxide, but have fairly low absolute permeabilities. Simulation calculations focused primarily on rubbery type polymers. Using the simulation results, a large number of membrane vendors were contacted to see if they would supply a unit that could provide the desired performance.

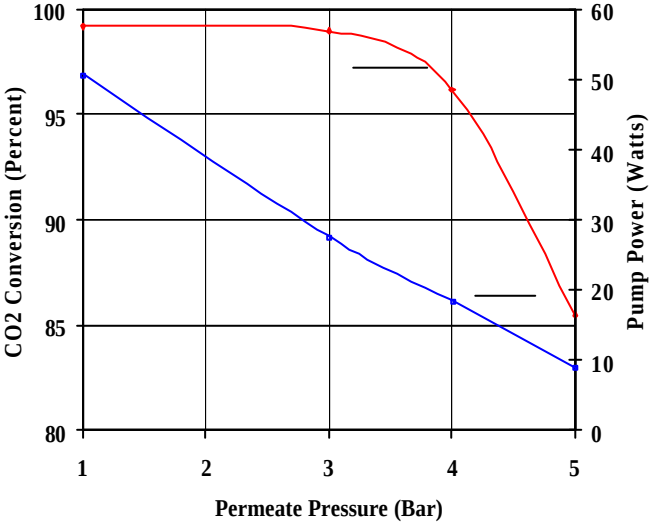

Fig. 5 Relationship between permeate pressure, CO2 conversion, and pump power for RWGS with fixed membrane size.

Three vendors were able to offer potential solutions for the desired application. Permea (Air Products) sells laboratory scale hollow fiber polysulfone membranes, which are typically used for air separation. Separation performance will not be as good as desired, but should be sufficient to allow an efficient RWGS reactor, and Permea has the units in stock and for a reasonable price. This unit was purchased to allow construction and startup of the RWGS unit. MEDAL (DuPont/Air Liquide) does not have a stock unit that provides the desired separation, but is interested in developing such a unit. This will be an ongoing development effort in which the RWGS apparatus will test a number of MEDAL's membranes. W. R. Grace supplies hydrogen recovery membrane modules to resellers, and has a laboratory scale unit which fits the desired application. However, this is a spiral wound unit and will not perform as well as the hollow fiber polysulfone unit.

All membrane units will be supplied with standard 1/4" NPT fittings. Construction will simply be a matter of hooking them up into the piping.

3.4) Pump (Low flow compressor)

The permeate from the membrane is pumped back to feed pressure, during which adiabatic heating from the pump reduces the amount of thermal energy required to reheat the recycle stream before sending it back to the RWGS reactor. The system design requires that the compressor can achieve a pressure ratio of about 3.3 to pump the permeate gas from 3 bar to 10 bar.

The compressor will use standard 1/4" NPT fittings and 110 VAC power.

3.5) Piping

A complete system design was developed based on the system parameters determined during the process design phase. Sizing for system piping is calculated by the spreadsheet. Control systems, instrumentation, valving, and relief systems were developed using the sizing criteria from these sheets.

3.6) RWGS unit power analysis

Total power of the RWGS system is of great interest. The power calculations for production of 500 grams of bipropellant per 12 hour day were calculated using the spreadsheet. If the process parameters are changed, the power requirements will also change, but the current power usage is very close to the minimum. The final results are described below.

Thermal power requirements:	
To provide RWGS heat of reaction	27 Watts
To preheat feed and recycle gas	43 Watts
Electrical power requirements:	
Recycle pump power:	28 Watts
Electrolysis of water produced:	190 Watts

Note that the effluent of the RWGS reactor needs to lose 102 Watts in a temperature range from 400 °C (reactor temperature) to 10 °C (condenser temperature). This available thermal power may be partially recovered by integrating it with the heater required for the RWGS reactor using a small heat exchanger. Calculation shows that a reasonably designed exchanger can recover about 43 Watts, which reduces the required RWGS heating duty to 27 Watts. Integration of these heat duties will be explored during operation of the apparatus. The total required power to run the system is thus estimated to be 27+ 28+ 190 = **243 Watts**. The fact that the highly efficient water electrolysis unit dominates system power requirements provides strong support for the belief that the RWGS should be a power-efficient means of producing oxygen on Mars.

It is of considerable interest to Mars mission planners to know how the mass and power requirements of each of the Mars ISRU systems under current development scales with propellant production rates. The best estimates for such scalings based upon current experimental data are given in Table 4. It may be noted that the production rate of 0.5 kg/day corresponds to the propellant requirements of a well-designed robotic Mars Sample Return mission, 5 kg/day corresponds to the life support oxygen requirements of a 5 person Mars Base, 50 kg/day corresponds to the propellant production requirement of a low-end version of the Mars Semi-Direct human mission plan, while 500 kg/day corresponds to the propellant production needs of a Mars Direct style mission enlarged by about a factor of two over the original baseline.

Scaling Relations for Mars ISRU Systems

Table 4. Scaling Relations for Mars ISRU Systems
(mass in kg, no redundancy. 12 hr daytime power in Watts -night power=0)

	0.5 kg/day		5 kg/day		50 kg/day		500 kg/day	
System	mass	power	mass	power	mass	power	mass	power
Zirconia/Electrolysis (Z/E)								
sorption pumps	12	60	48	600	192	6000	768	60,000
chemical synthesis	3	1170	6	11,700	33	117,000	303	1170,000
controls	2	20	4	40	8	80	12	160
lines, valves, misc	2	0	10	0	50	0	250	0
refrigerator	3	120	12	1,200	48	12,000	192	120,000
Total	*22*	*1370*	*80*	*13,540*	*331*	*135,080*	*1,525*	*1350,160*
Sabatier/Electrolysis (S/E)								
sorption pumps	3	15	12	150	48	1500	192	15,000
chemical synthesis	3	120	6	1,200	33	12,000	303	120,000
controls	2	20	4	40	8	80	12	160
lines, valves, misc	2	0	6	0	18	0	56	0
refrigerator	2	80	8	800	32	8000	128	80,000
Total	*12*	*235*	*36*	*2,190*	*139*	*21,580*	*691*	*215,160*
Reverse Water Gas Shift (RWGS)								
sorption pumps	6	30	24	300	96	3000	384	30,000
chemical synthesis	4	225	8	2250	44	22500	404	225,000
controls	2	20	4	40	8	80	12	160
lines, valves, misc	3	0	9	0	27	0	84	0
refrigerator	3	120	12	1200	48	12000	192	120,000
Total	*18*	*395*	*57*	*3,790*	*223*	*37,580*	*1076*	*375,160*
S/E-RWGS								
sorption pumps	5	24	20	240	80	2400	320	24,000
chemical synthesis	4	150	8	1500	44	15000	404	150,000
controls	2	20	4	40	8	80	12	160
lines, valves, misc	3	0	9	0	27	0	84	0
refrigerator	2.5	105		10	1050	40	10,500	160 105,000
Total	*16.5*	*299*	*51*	*2830*	*199*	*27,980*	*980*	*279,160*
RWGS-Ethylene								

sorption pumps	3	15	12	150	48	1500	192	15,000
chemical synthesis	4	150	8	1500	44	15000	404	150,000
controls	2	20	4	40	8	80	12	160
lines, valves, misc	3	0	9	0	27	0	84	0
refrigerator	2	60	8	600	32	6000	128	60,000
Total	*14*	*245*	*41*	*2,290*	*159*	*22,580*	*820*	*225,160*

Basis for Scalings Shown

The masses and power requirements of the S/E and Z/E systems in the 0.5 kg/day production rate are known with considerable accuracy from the experimental work done at Lockheed Martin and the University of Arizona. Power requirements for larger systems can also be estimated with confidence, since with all subsystems except controls, power requirement will increase linearly with production rate.

Mass of sorption pump systems are estimated to increase by a factor of four for every factor of 10 increase in output rate. This is based upon a relative decrease in parasitic mass as the total sorption pump system becomes larger.

Mass of the chemical synthesis gear is assumed to be linear with respect to the roughly ~0.3 kg of *actual chemical reactors* contained within the 3 kg mass of the chemical reactor system required for the 0.5 kg/day production rate. This is based upon the author's knowledge of the details of the Lockheed-Martin S/E system (0.1 kg Sabatier reactor + 0.2 kg of solid polymer electrolyte contained within the ~3 kg chemical synthesis subsystem) and reports from K.R. Sridhar of the University of Arizona of ~0.3 kg of actual Z/E cells within a ~0.5 kg/day output unit there.

Control system mass and power is estimated to scale up by a factor of two for every factor of 10 increase in output.

Mass of lines and valves for all systems except the Z/E are assumed to scale up by factor of 3 for every factor of 10 increase in output. For the Z/E system, a factor of 5 increase in mass for every factor of 10 increase in output is assumed. This is because the Z/E system is composed of large numbers of small tubes. As the system scales up, more and more manifolds are required. This contrasts unfavorably with the other systems, which can simply employ larger reactor vessels as output rates are increased.

Refrigerator mass is assumed to increase by a factor of four for every factor of 10 increase in output. This is based upon scaling observed in existing Stirling cycle units such as that used in the Lockheed Martin ISRU experiment.

It will be noted that the sorption pump requirement for the Z/E system is four times that of the S/E system. This is because the Z/E system only takes one oxygen from each CO2 molecule ingested, while the S/E system takes two; and because existing Z/E systems have only about a 46% conversion efficiency, compared to 96% demonstrated in the S/E system. In all cases sorption pump power requirements are based upon the assumption that waste heat from the chemical reactors is used to provide ~80% of the total power needed. This level of performance has been demonstrated on the Lockheed Martin ISRU system.

RWGS sorption pump requirements are double those of the S/E system because only one oxygen can be obtained from each CO2 molecule ingested. Provided that the system is run hydrogen rich, however, CO2 conversion to CO should be >90%. Chemical synthesis power per unit propellant produced by RWGS will be about 80% greater than S/E because the S/E system produces 1/3 of its propellant "for free" (from a chemical synthesis power point of view) in the form of methane (disadvantage factor =1.5) and because of the extra energy cost associated with the endothermic RWGS reaction (disadvantage factor=1.15) and power required to run the RWGS system pump (disadvantage factor= 1.05). RWGS/Ethylene systems have similar sorption pump power requirements to the S/E because they also obtain both the oxygens contained in each CO2 molecule ingested. Because it utilizes about 2/3 of the oxygen it obtains through its pump, the S/E-RWGS pump power requirement is intermediate between that of the S/E and the RWGS.

Chemical synthesis power requirements of both the S/E-RWGS and RWGS/Ethylene systems approach that of the S/E in efficiency because both of these systems employ exothermic reactors which provide enough waste heat to meet the power requirements of the endothermic RWGS.

RWGS and Z/E systems have the highest refrigeration power requirements because they have no hydrogen feed stock to use as a coolant to supplement the

refrigerator. In the S/E system, the hydrogen feedstock is sufficient to refrigerate all the methane product, leaving only the oxygen (67% of the output by mass) to be cooled by the refrigerator. The RWGS/Ethylene system has the lowest refrigeration requirement because the ethylene is not a cryogen on Mars and needs no refrigeration, thereby allowing the hydrogen feed stock to be used to cool part of the oxygen product. SE/RWGS refrigeration power requirements are intermediate between those of S/E and RWGS because this system is basically a superposition of the two.

Mars Sample Return Mission Analysis

In order to assess the mission benefits of the RWGS, a study was done of the Mars Sample Return (MSR) mission utilizing both In-Situ Propellant Production (ISPP) and non-ISPP approaches. A common baseline for a MSR mission utilizing each of nine examined ISPP technologies and well as two missions employing propellant hauled from Earth was established. The technology assumptions are shown below:

Assumptions

Mission Mode: Direct entry at Mars, Mars surveyor 2001 derived lander. Direct return from Mars surface, two-stage ascent vehicle, direct entry at Earth. ΔV split: 4.0 km/s 1st stage, 2.5 km/s 2nd stage. This split allows the first stage to reach low Mars orbit, adding flexibility to the mission.
General Technology base: Mars surveyor 2001 class avionics (as described in Lockheed-Martin MSR report to JSC, March 1995).
Sample size: 0.5 kg
Sample Return Capsule: 6.0 kg (chuteless, passive decelerator technology)
Average direct solar incidence: 500 W/m^2
Batteries: Li-ion, 90 w-hrs/kg
Solar array: Fixed, 15% efficient. 3 kg/m^2 = 12.5 W/kg [Ave. 12-hr daytime power]
Trans-Earth Cruise Stage (TECS): 24.0 kg
MAV Stage 2: 9.0 kg + 12 % of propellant mass
MAV Stage 1: 17.0 kg + 17% of propellant (hi-P tanks) or 10% of propellant (low-P tanks)
Lander Avionics: 35 kg
Lander science payload: 15 kg
Landing system: 66% of landed payload (N_2H_4 propulsion, 400 m/s DV, no chute)
Aeroshell: 27% of entry mass
Trans-Mars Cruise Stage: 21 kg + 7% of TMI payload
ISRU system mass and power: As described in MIRUR report for task B1, except when noted otherwise.
Non ISRU lander power requirement: 100 W daytime
Launch Vehicle options: Existing US launch vehicles as described in Isakowitz, "Space Launch Systems," 1996.
Rocket specific impulse: 325 s NTO/MMH, 374 s CH_4/O_2, 376 s C_2H_4/O_2

The technology assumptions given above are either well known or can be justified based upon work presented in detail in reference 12. A noteworthy divergence of technology proposed in that (and this) report compared to that assumed in most MSR mission studies is the use of a completely passive sample return capsule (SRC). That is, since the SRC must be designed to withstand landing shock even if its parachute does not open, it is argued that it is best to eliminate the parachute system altogether, along with its concomitant paraphernalia of pyros, mortars, altimeters, barometers, etc. This allows the SRC mass to be dropped from a typical value of ~17 kg for the conventional approach, to about 6 kg for the approach proposed here. Since the mass is so low, the SRC can be made of a solid combination of balsa wood and styrofoam, and since its ballistic coefficient is very low, impact velocity can be kept to less than 20 m/s. This impact can be cushioned by the shock absorbing qualities of the SRC balsa wood/styrofoam combination even on the hardest surface, and these materials also provide floatation in the event of a water landing. The passive SRC is thus not only much lighter than the conventional variety, but also much more reliable and obviously much cheaper to develop as well. It is therefore clear that conventional active SRC designs are unworthy of further consideration.

Cases Considered

Eleven different mission options were analyzed in the present study. These options studied include:

* Zirconia/electrolysis (Z/E) systems to produce oxygen to be used in conjunction with imported CH_4 in the Mars Ascent Vehicle (MAV) to enable sample return. Two Z/E options were considered. The first option assumes that Z/E chemical synthesis power requirements are those reported by K.R. Sridhar[35] in 1994. These formed the basis for the power scaling relationships for Z/E technology reported in the ISRU scaling section above. The other option, termed "Z/E low" on the accompanying graphs, are based upon the more optimistic Z/E chemical synthesis power estimates

reported by Sridhar to the NASA JSC ISRU technology workshop[36], Feb. 5, 1997.

* Sabatier/Electrolysis (S/E), producing CH_4/O_2 propellant from imported hydrogen and discarding the extra methane to produce a net 10.3:1 ratio (leverage) of produced propellant compared to the hydrogen import requirement. This option was reported in two versions. The first, used conventional MAV tanks to deliver the required hydrogen feedstock to Mars in liquid form This plan assumed that 30% extra hydrogen would be shipped to counter propellant boiloff. The second S/E plan assumed that the required hydrogen was imported to Mars in supercritical form in "hard" graphite overwrapped tanks, as was recommended in reference 12. This version required to extra hydrogen as there would be no boiloff.

* Reverse Water Gas Shift (RWGS) used to produce oxygen to use on a MAV in conjunction with CH_4 imported from Earth

* S/E system augmented by a RWGS reactor to increase system leverage to 18:1. Both normal tank and hard tank options were considered.

* RWGS system combined with an ethylene reactor to produce propellant at 31:1 leverage. Both normal tank and hard tank options were considered.

* Options using terrestrial propellants only (i.e. no ISPP, termed "Ter" options on the accompanying graphs.) Two options were considered. One imported CH_4/O_2 to Mars, to take advantage of the high Isp offered by such propulsion. The other used conventional storables (NTO/MMH)

Study Results

The results of the study are shown in figures 6 through 11.

In figure 6 we see the trans-Mars injection mass of each of the mission options. It can be seen that from a mass point of view the most favorable options are the S/E, S/E-RWGS, and the RWGS/Ethylene.

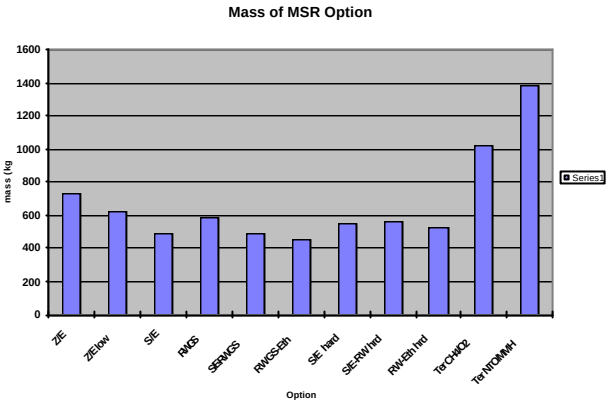

Fig. 6 Mass of Mars Sample Return Missions

In fig. 7, these results are put into perspective by showing the mass margin that each mission would enjoy if launched on a Delta 7925 launch vehicle, which is the most capable US launch vehicle available short of purchasing an Atlas 2A. The Delta costs about $50 million, while the Atlas costs $90 million, and the reliability of the Delta is 95% compared to the Atlas's 87%, so the advantage of being able to achieve Delta launch is considerable[37]. It can be seen that each of the favored S/E, S/E-RWGS, and RWGS/Ethylene options enjoy launch margin exceeding 100% on a Delta 7925. This represents a very high comfort level and should allow major cost savings by avoiding the need for a forceful "weight reduction" program should subsystem component mass exceed study expectations. While not as high, acceptable mass margins are also enjoyed by all other ISRU options, except the nominal Z/E (1994 performance estimates) system, whose 35% mission margin is uncomfortably tight for this stage of the design process. It can be seen that both non-ISRU options fail completely, with nominal mission masses exceeding the capability of the Delta 7925, even if no margin is required. These missions must therefore fly on an Atlas. however it should be noted that with their large Mars-entry masses, both of these missions would be too heavy to allow for entry into Mars' atmosphere protected by a Pathfinder or Mars Surveyor aeroshell, so a new aeroshell would need to be developed. Even if that were done, however, fairing diameter limitations on the Atlas 2A or 2AS (3.6 m diameter fairing) would require a ballistic coefficient 26% higher than that of the Pathfinder mission and about 50% more than the Mars Surveyor lander.

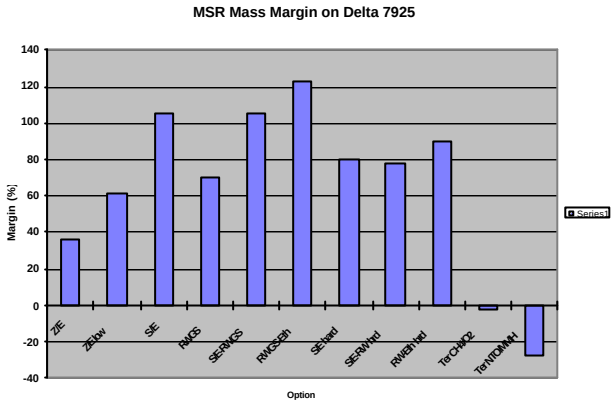

Fig. 7 Mass Margin of Mars Sample Return Missions

The mass distribution of each of the MSR options examined is shown in Table 5. The entry under "MAV2" included the sample (0.5 kg), the SRC (5.5 kg), the trans-Earth cruise stage (TECS, 24.0 kg), as well as the dry mass of the second stage of the MAV. The column under propellant lists the propellant that needs to be shipped to Mars outside of parenthesis, while the propellant used for Mars ascent is given within parenthesis. The mass listed for lander is the wet mass of the lander system, including the science payload (15 kg) but excluding the ISPP system and the photovoltaic power system.

In fig 8 we see the hydrogen importation requirement for each of the options considered. Hydrogen importation requirements are a significant concern because of the difficulty of shipping hydrogen across interplanetary space. Unfortunately, the three best options from a mass point of view are also the three that require hydrogen importation. However, of the three, the RWGS/ethylene system is the one which both requires the least hydrogen and is most attractive from the mass perspective. It is thus clearly the best among the hydrogen consuming options. Since among the non-hydrogen consuming options, the RWGS is the one with the lowest TMI mass, it the data argues strongly for the development of the RWGS-based family.

Table 5. Mass of Mars Sample Return Mission Options (kg)

Option	MAV2	MAV1	Propellant	ISPP	Power	Lander	Aeroshell	TMCS	Total
Z/E	40	47	67 (301)	26	88	259	142	68	736
Z/E low	40	47	67 (301)	26	36	225	119	60	619
S/E	40	47	67 (301)	16	19	187	93	52	488
RWGS	40	47	67 (301)	21	27	216	113	58	588
SE-RWGS	40	47	67 (301)	24	25	186	92	51	486
RWGS-Ethly	40	47	67 (296)	20	21	175	85	49	449
S/E hard	40	74	67 (354)	19	22	206	106	56	556
S/E-RW hard	40	74	67 (354)	28	29	208	107	56	561
RW-Eth hard	40	74	67 (353)	24	24	197	100	54	525
Ter CH_4/O_2	40	47	301 (301)	0	8	344	200	87	1026
Ter NTO/MMH	40	62	445 (445)	0	8	449	271	110	1386

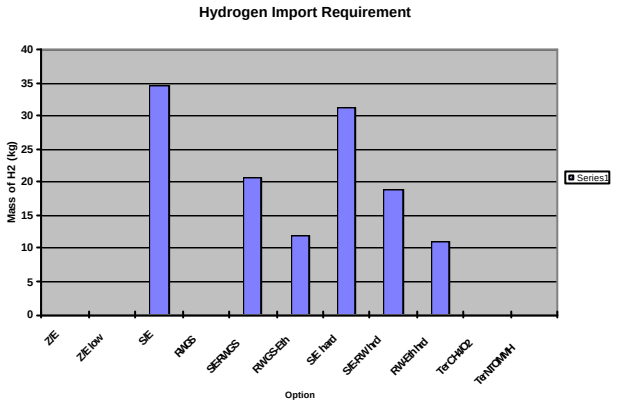

Fig. 8 Hydrogen Importation Requirements of Mars Sample Return Mission Options

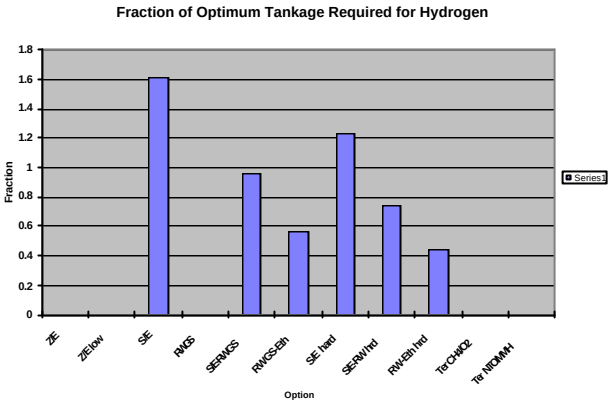

Fig. 9 Fraction of Optimum MAV Tankage Required for Storage of Hydrogen ISPP Feedstock

In fig. 9 we show a comparison of the volume of the required hydrogen needed for ISPP operations with the volume of the available tankage on the MAV. It can be seen that the S/E system requires between 1.25 and 1.6 times as much tankage for hydrogen importation as the MAV actually needs for the CH_4/O_2 propellant that the H_2 feedstock would produce. Considerable tankage oversizing would thus be required for such a pure S/E system. The need to oversize the tanks would cause a mass increase that is not included within the present analysis, and therefore the pure S/E system would be somewhat less favorable from a mass point of view than Figs. 1 and 2 would indicate. If the RWGS system is added to the S/E, oversizing is no longer required, since the hydrogen volume needed is now between 70 and 95% of the tank volume that will be available in any case. In the case of the RWGS/Ethylene system, the vehicle's natural tankage is double what the hydrogen requires, which means that a hydrogen supply 260% that required at Mars arrival could be sent with the ship on TMI. Such a large margin would effectively put to rest concerns about dealing with excessive H_2 boiloff on the outbound trajectory. It is observed that the hard tank approaches require less hydrogen volume than the normal tank approaches. This is because the ability to avoid taking extra hydrogen to counter boiloff losses more than compensates for the extra propellant that the hard tank versions must carry to propel their heavier tanks.

Fig. 10 shows the average required daytime power of each of the options considered. The power requirement of the nominal Z/E system is unacceptable, while the more optimistic "Z/E low" option is still significantly less attractive than all other ISPP options. Of the ISPP options, the S/E has the lowest power requirements, followed by RWGS/Ethylene and S/E-RWGS. The terrestrial importation (non-ISPP) options require far less power than any ISPP system. This avails them little, however, because as we have seen, these options have already been eliminated from the mix on the basis of excessive TMI mass.

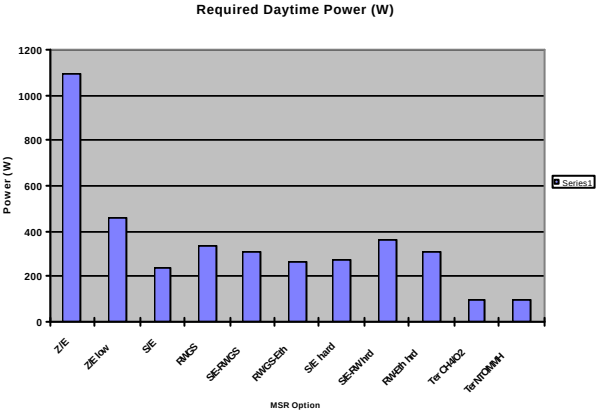

Fig. 10 Required Power of Mars Sample Return Missions

Fig. 11 Shows the required area of the solar array powering each of the options considered. The nominal Z/E option requires 29 square meters, which would be nearly impossible to package and deploy from a lander fitting within the kind of aeroshells that could be

launched by a Delta 7925. The Z/E-low system requires 12 square meters, which may be marginally possible. All the other ISPP systems require between 6 and 8 square meters, which could be accommodated by adding another pair of solar panels to the pair that are presently available on the Mars surveyor lander. It is noted that the "hard" tank options require somewhat more power than the conventional tank approaches. This is to be expected as the heavier tanks increase propellant requirements.

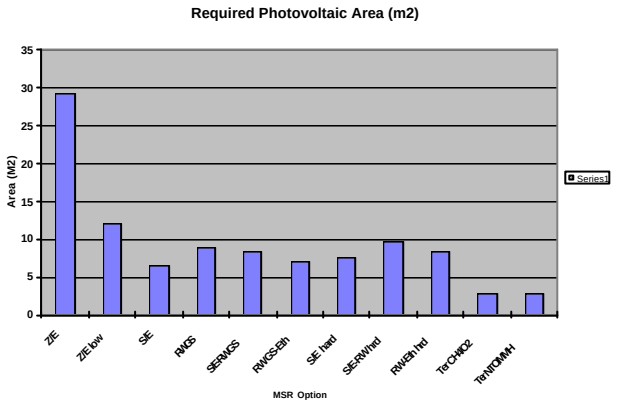

Fig. 11 Area of Photovoltaic Array Required for Mars Sample Return Missions

Mars Sample Return Analysis Conclusions

1. It is concluded that direct return MSR missions utilizing non-ISPP approaches require more than twice the TMI mass of the better ISPP approaches. Under the technology assumptions considered, non-ISPP MSR missions cannot be flown on a Delta 7925. ISPP options including the S/E, S/E RWGS, and RWGS/Ethylene can be flown on the Delta 7925 with greater than 100% mass margin.

2. Of the ISPP options, the Z/E and S/E options suffer because of their excessive power and hydrogen importation requirements, respectively. The S/E-RWGS, RWGS, and RWGS/Ethylene are all attractive.

3. Since all of the attractive ISPP require the RWGS, the development of the RWGS should be made a Mars Sample Return-ISPP program priority.

Mars Exploration Ballistic Hopper Mission Analysis

A common baseline for a Mars Ballistic Hopper (MBH) mission utilizing each of the examined ISRU technologies and well as one mission employing NTO/MMH propellant hauled from Earth. The Technology assumptions are shown below:

Assumptions

Mission Mode: A ballistic hopper is delivered to Mars on an expended lander. The hopper then conducts a series of jumps to distant locations on Mars. Each hopper carries with it all of its propellant or propellant feedstock, ISRU equipment, and power supply. No return to base is required, and no resupply of any materials to the hopper is allowed.
General Technology base: Each hopper is assumed to have a dry mass of 50 kg, including science payload but excluding ISRU system and power system. Such a mass is consistent with Mars surveyor 2001 class avionics (as described in Lockheed-Martin MSR report[1] to JSC, March 1995).
Average direct solar incidence: 500 W/m^2
Solar array: Fixed, 15% efficient. 3 kg/m^2 = 12.5 W/kg [ave 12-hr daytime power]
ISRU system mass and power: Sufficient to allow for a production rate of 0.5 kg per day. Non ISRU lander power requirement: assumed covered within the 50 kg basic hopper dry mass.
Rocket specific impulse: 325 s NTO/MMH, 374 s CH4/O2, 376 s C2H4/O2

Cases Considered

Seven different mission options were analyzed in the present study. These options studied include:

* Zirconia/electrolysis (Z/E) systems to produce oxygen to be used in conjunction with imported CH4 in the Mars Ballistic Hopper (MBH) to enable repeated flights. The Z/E option assumes that Z/E chemical synthesis power requirements are those reported by K.R. Sridhar[35] in 1994. These formed the basis for the power scaling relationships for Z/E technology reported in the scalings section, above.. ISRU power = 1530 W

*Sabatier/Electrolysis (S/E), producing CH4/O2 propellant from imported hydrogen and discarding the extra methane to produce a net 10.3:1 ratio (leverage) of produced propellant compared to the hydrogen import requirement. ISRU Power = 267 W

* Reverse Water Gas Shift (RWGS) used to produce oxygen to use on a MBH in conjunction with CH4 imported from Earth ISRU power = 450 W.

*S/E system augmented by a RWGS reactor to increase leverage to 18:1. ISRU power =343 W.

* RWGS combined with an ethylene reactor to produce propellant at 31:1 leverage. ISRU power =283 W.

* Options using terrestrial propellants only (i.e. no ISPP, termed "Ter" options on the accompanying graphs.) Two options were considered. One imported CH4/O2 to Mars, to take advantage of the high Isp offered by such propulsion. The other used conventional storables (NTO/MMH). ISRU power =0.

Results

The study results are shown if Figs. 12 through 16. In Figure 12, we show the delta-V required by a Mars Ballistic Hopper (MBH) to perform hops of various distances. The lowest curve shows the ideal delta-V required by one-way hops over various distances. The middle curve inflates this number by 15% to allow for gravity and aerodynamic losses. The highest (dashed) curve adds a further 500 m/s to allow for landing after aerodynamic deceleration. This is considered to be the actual delta-V for a given trip. It can be seen that each 1000 km hop requires a delta-V of 2.5 km/s.

In Fig. 12 We show the mass of each MBH option if used to engine in a series of 1000 km hops. The two steepest curves are that for NTO/MMH ("NTO") and terrestrial LOX/CH4 ("ter CH4"), which go to infinity by the third hop. This is because the cumulative delta-V of 7.5 km/s exceeds the practical limits of any system that must carry all of its own propellant. For this reason, the non-ISRU options fail completely in the MBH mission.

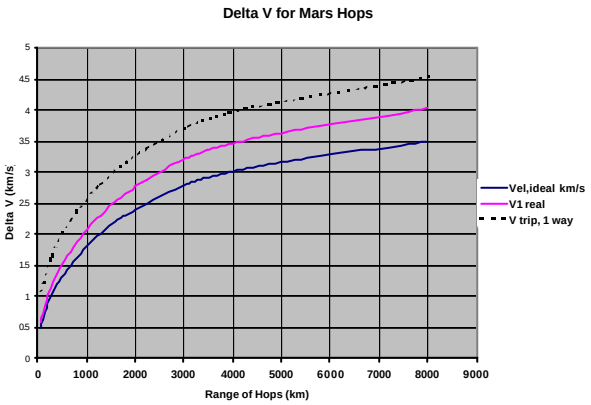

Fig 12. Delta-V required of Mars Hoppers as a Function of Range

The next more favorable option are that employing zirconia cells or the RWGS to produce oxygen, but bringing methane from Earth to supply the fuel. Since these systems have a propellant to feedstock (in this case CH4 fuel) ratio of 4.5, they have an effective specific impulse of (4.5)(374 s) = 1683 seconds. As a result, their mass curves do not hit the steep part of the exponential even after 7 hops. However the very large power supply carried by the zirconia ("Z") hopper sends its mass to rather high values. This is improved considerably the RWGS, whose power needs are on the same order as the fuel and oxygen making options discussed below. However, even the RWGS still suffers in mass compared to these due to the need to carry methane. (The more optimistic assumptions for zirconia power requirements reported by Sridhar[4] in his talk to the Lunar and Planetary Institute in February 1997 would result in a curve between the RWGS and zirconia curves depicted here, with a projected power requirement of 615 W.)

The bottom three lines show the mass of the hopper systems if either a SE, SE/RWGS ("SER"), or RWGS/ethylene ("Eth") system are employed. Because of spectacular effective specific impulses (374*10.3 = 3852 s for SE, 374*18 = 6732 s for SER, 376*31 = 11,656 for RWGS/Ethylene), the mass of these systems hardly rises at all, even after 7 hops. Indeed, it is quite clear that as far as mass is concerned, these systems could undertake a much larger number of hops without significant mass growth.

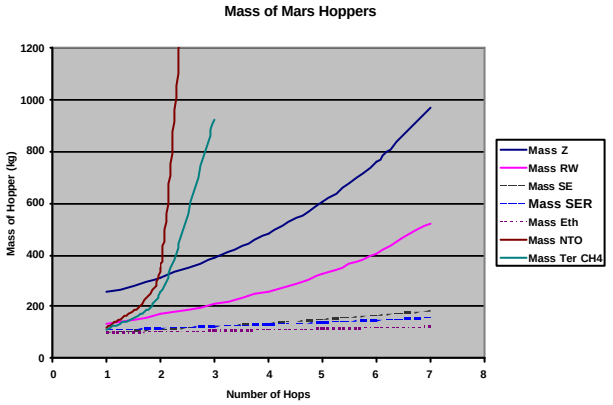

Fig. 13. Mass of Mars Hoppers

In Fig. 14 we show the time required to manufacture the required propellant to prepare the next hop, given our imposed design choice of an ISRU system capable of producing 0.5 kg of propellant per day. Because of its large dry mass, the zirconia system requires the most, ranging from 400 to 900 days per hop as the number of hops increases from 2 to 6. Such long production time

requirements makes this system rather unattractive for the MBH application.

The other options all have ISRU production times of less than 200 days for a 2-hop mission, but this rises to 650 days for the RWGS if 7 hops are attempted. In contrast, because the mass of the SE, SER, and Eth systems do not rise significantly as the number of hops increase, the waiting times of these systems does not increase significantly even after 7 hops. On the basis of both the mass requirements shown in Fig 13 and the time requirements shown in Fig. 14, it can therefore be said that of the options considered, only the SE, SER, or Eth system offer attractive candidates for the MBH mission.

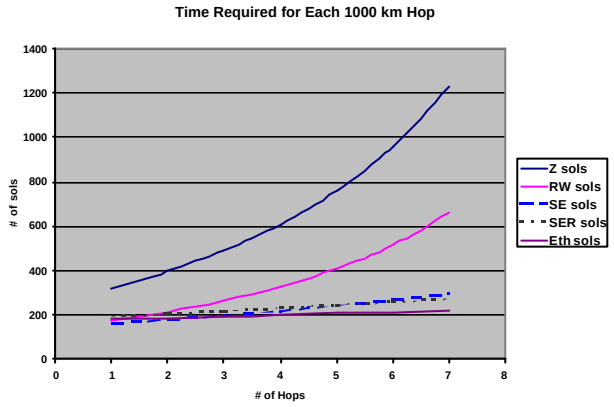

Fig. 14 Time required for each 1000 km Hop

However, the SE, SER, and Eth options all require that hydrogen feedstock be carried to manufacture fuel between flights. The amount of hydrogen required for each hop for each of these systems is shown in fig. 15. Here it can be seen that the SER system requires only about half the hydrogen needed by the simple SE system. The Eth system, in turn, cuts the hydrogen requirement of the SER system in half again.

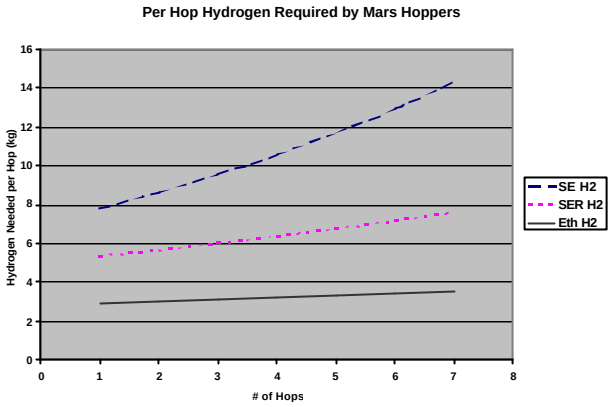

Fig. 15 Per Hop Hydrogen Requirement

In Fig. 16, we show the amount of hydrogen required cumulatively by each of the SE, SER, and Eth hoppers examined. It can be seen that in order to perform a7 hop mission, the SE system requires about 75 kg of hydrogen. If the hydrogen is stored in liquid form, this would require a volume of about 1 cubic meter, which would probably be very difficult to accommodate on a MBH system of the type considered here. On the other hand, the Eth system would require only 22 kg of hydrogen, which would clearly be much more manageable.

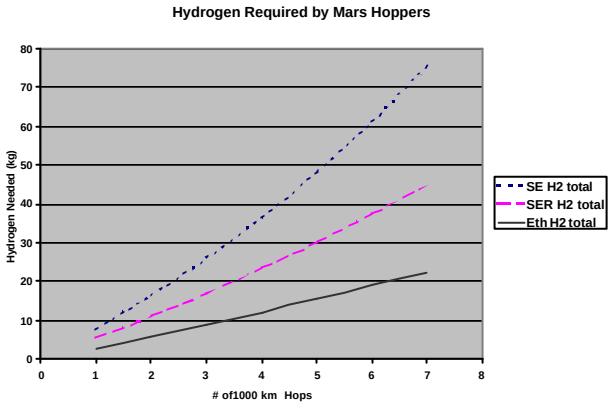

Fig. 16. Total Hydrogen Requirement

Mars Ballistic Hopper Mission Analysis Conclusion

We conclude that the most attractive option for a Mars Ballistic Hopper mission is one employing ISRU using the RWGS/Ethylene system. The second most attractive system is one employing a Sabatier/electrolysis synthesis unit in conjunction with a RWGS reactor. Significantly less attractive are MBH

systems fueled by SE, RWGS, or Zirconia ISRU units, while non-ISRU options fail completely. However, if the RWGS/Ethylene or SE/RWGS systems are employed, it appears possible to develop Mars Ballistic Hoppers that can visit over ten sites separated by thousands of kilometers on Mars. Such capability offers the prospect of increasing the exploratory utility of a Mars spacecraft by an order of magnitude, as it would allow a single lander to visit ten sites instead of one.

Conclusion: Applications and Advantages of RWGS Systems over the State of the Art

To summarize, the development of the RWGS system has many advantages over the state of the art for numerous applications that support NASA's objectives for robotic and human exploration of Mars. These applications include:

1. The ability to manufacture any amount of oxygen on Mars to support human exploration and robotic sample return missions. The only competing system that can do this is zirconia electrolysis. RWGS should be able to do it with a much more rugged and reliable system, on a much larger scale (if desired), with a power consumption about an order of magnitude less. If CO should be desired as a fuel, RWGS has to potential to produce it at least an order or magnitude more efficiently than a zirconia-electrolysis system.

2. It has been found that copper-on-alumina catalyst can be used to catalyze the RWGS reaction in compact reactors operating at 400 C without any side reactions. In other words, RWGS reactors can be built that will reduce CO2 to CO with 100% selectivity.

3. RWGS reactors can also be used in tandem with electrolysis units to provide physical-chemical life support for oxygen regeneration and CO_2 disposal on space stations, Lunar bases, or piloted spacecraft anywhere in space. Compared to zirconia-electrolysis such a system is much more rugged and efficient. Compared to an SE based life support system, it has the advantage of wasting no hydrogen, and thus no water. Compared to a Bosch reactor based life support system, no solid graphite wastes are created.

4. RWGS reactors offer the ability to leverage imported hydrogen into water on Mars with a mass leverage of 9/1. Using a Sabatier reactor for this purpose would only produce a leverage of 4.5/1. Using a Bosch reactor would give 9/1 leverage, but would also produce solid graphite wastes that would be difficult to manage.

5 Used as an adjunct to a SE Mars in-situ propellant system, the RWGS reactor increases net propellant leverage from 10.3:1 to 20:1. This reduces tankage size and mass, and makes the hydrogen importation requirement for the system tractable.

6. Used as the front end of an RWGS/ethylene reactor system, the RWGS enables construction of a Mars in-situ propellant production unit which produces a high-energy propellant combination with a net leverage as high as 31/1. This is more than triple the leverage of a state of the art SE system. Moreover, the fuel produced is both denser than methane and storable on Mars without refrigeration.

7. The product ethylene can be used on Mars for other applications than rocket, rover and welding fuel. It can also be used as an anesthetic, as an aid to crop production, and as the basic feedstock for the manufacture of plastics for structures, fabrics, implements, and many other uses.

8. The RWGS system can be used with a second stage reactor to produce methanol. This enables construction of a Mars in-situ propellant production unit which produces a high-energy propellant combination with a net leverage of 16/1, at an energy cost about half that of the next most efficient system. Moreover, the fuel produced is both denser than methane and storable on Mars without refrigeration.

9. The methanol product of the RWGS system can be used as the fuel in either an expander cycle rocket engine or in fuel cells. Combustion engines burning methanol/oxygen are also possible and would be much easier to cool than those burning any other candidate storable fuel.

10. The RWGS/ethylene or RWGS/methanol systems may have important terrestrial applications as a way to produce relatively storable fuel whose combustion adds nothing to overall atmospheric CO_2 concentrations.

The above list of potential applications and advantages of RWGS based ISRU systems is very impressive, and includes several that may be critical to the successful prosecution of both robotic and human Mars exploration missions. It is therefore recommended that RWGS, RWGS/ethylene, and RWGS/methanol ISPP systems be investigated further.

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