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In-Situ-Produced Methane and Methane/Carbon Monoxide Mixtures for Return Propulsion from Mars

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A summary of chemical process routes to produce oxygen, water, methane, carbon monoxide, and other fuels is provided. A conceptual design of a plant for use on a robotic Mars sample return mission is presented that predicts that propellant sufficient for a 500-kg return vehicle (dry) can be produced by a plant having a mass of 2.2 metric tons (MT) and using less than 6 kW. The mass includes the imported hydrogen and the power system. This is lower than the 3.34 mT of propellant it replaces, and provides for a much lower Earth launch mass. This design is based on conservative assumptions and existing hardware. Twice the required amount of hydrogen is imported to simplify the processing and to eliminate the need for a separate means of producing the needed amount of oxygen. The volume of the imported hydrogen does have a significant negative impact. Alternatives to pure methane as a fuel are presented. Mixtures of CO and CH_4 are considered, with their physical properties and propellant performance predicted. The use of such mixtures in place of pure CH_4 in the same sample return mission is analyzed and shown to be competitive.

Introduction

MANY chemical process technologies are available for a Mars mission using indigenous space resource utilization (ISRU) as a means of reducing launch mass. Much effort has centered on the use of the Martian atmosphere for the production of methane and oxygen for a variety of uses at Mars.[1,2] This propellant combination is being considered for the return of both robotic and crewed vehicles.

For a robotic mission, simplicity and power might be the major drivers. For a crewed mission, the desire to produce water for life support may also be a major driver in process selection. Propellant manufacture may turn out to be a small, but significant, "add-on" to a water production plant. Also, oxygen for life support and the recovery of inert gases (N_2 and Ar) from the atmosphere will be factors for a crewed mission. These do not play a part in an ISRU plant for a robotic mission, which will focus solely on making oxygen and fuel using minimal power and mass.

Background

The Sabatier reaction is one of the more discussed processes that could be used on Mars. This reaction, discovered by the French chemist Sabatier nearly a century ago, converts carbon dioxide to methane and water by reacting it with hydrogen at elevated temperatures, as in reaction 1.[3] In a separate step, the water that is produced can be electrolyzed to release oxygen and recover the hydrogen for recycle back to reaction 1, shown in reaction 2. The sum of these reactions (3) converts CO_2 and H_2 into CH_4 and O_2. For ISRU purposes on Mars, this chemistry will allow us to extract oxygen from the atmosphere, to be used as water or to generate oxygen:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \tag{1}$$

$$2H_2O \rightarrow 2H_2 + O_2 \tag{2}$$

$$CO_2 + 2H_2 \rightarrow CH_4 + O_2 \tag{3}$$

Equation (3) is the net of Eqs. (1) and (2).

Since this process recovers oxygen from CO_2, it has been considered for life-support systems.[4] When the process is used in this way, there must also be an efficient way to recover the hydrogen which is in the methane. Otherwise, the resupply of hydrogen will quickly drive the system to higher masses for longer trip-times. This can be accomplished by methane pyrolysis (reaction 4) and can be done with a catalyst, or without a catalyst at slightly higher temperatures. This, along with reaction 2, allows total recovery of the hydrogen in the process. The new net reaction (5) shows that all of the oxygen can theoretically be recovered, while the carbon builds up in the pyrolysis reactor. The carbon that is released can be dense or fluffy. For volume-constrained systems, the dense form is preferred:

$$CH_4 \rightarrow 2H_2 + C \tag{4}$$

$$CO_2 \rightarrow C + O_2 \tag{5}$$

Equation (5) is the net of Eqs. (3) and (4).

When the methane pyrolysis reaction is practiced for life support purposes, carbon must be removed from the system. Difficulty arose in this portion of the early development work done for the space station. Simple sizing equations, along with a desired frequency of change-out, dictated a large but reasonable pyrolysis reactor. While the reaction ran very well in small 2-in.-diam reactors, the larger 6-in. reactors never got to the point where a reliable process was in hand. Also, since manual change-out was required for removal of the carbon-laden reactors, they first had to be cooled. This temperature cycling is not desirable for any system.

On Mars, methane pyrolysis need not be practiced if the desired product is methane. We need the products of the Sabatier reaction plus the water electrolysis reaction (net reaction 3). There were no problems with these in development and confidence in them is high. However, this scheme provides oxygen and methane in a mass ratio of 2:1. If we choose to burn them at the optimum 3.5:1 for higher I_{sp}, we need to obtain additional O_2. Five options present themselves:

Option 1: Produce extra methane and water via the Sabatier process and electrolyze the extra water until the needed amount

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of oxygen is in hand. This also produces additional methane which, in the simplest implementation, could be merely vented. It also requires the importation of more hydrogen, which is a small penalty mass-wise, but has serious volume/tankage implications. No additional production equipment need be delivered, although it might be necessary to size it slightly larger if the production time is critical.

Option 2: A second option is to electrolyze atmospheric CO_2 via zirconia cells to produce the extra oxygen. Much has been written about this.[5–7] Currently, this is less developed and seems to require higher power levels than water electrolysis, but some very good research is being performed in this area. This option requires that an additional piece of equipment be developed and delivered to Mars, but allows smaller Sabatier and water electrolysis units as well as eliminating any extra hydrogen. Another advantage is that it requires no supply of reagents from Earth since its only input is the atmosphere.

Option 3: A third option is to produce extra oxygen by using the reverse water gas shift (RWGS) reaction.[8] This scheme, shown in reaction 6, produces water from CO_2 without the loss of any hydrogen as methane. The water is then split

$$H_2 + CO_2 \rightarrow CO + H_2O \qquad (6)$$

by electrolysis (requiring a separate electrolyzer, perhaps the same one used for the water from the Sabatier reactor) to produce the O_2 and recycle the hydrogen. Eventually, once the required amount of O_2 was in hand, the hydrogen could be sent to the Sabatier reactor to be converted into methane. In its simplest manifestation, the CO is just vented. Since the RWGS reaction is endothermic, chemical engineering tricks must be used to drive the equilibrium reaction to the right.

It is possible that this reaction can be combined with the Sabatier reaction, either in two thermally coupled reactors or within the same vessel, to produce the methane and O_2 (via water) with lower energy requirements.[2] To the best of our knowledge, this "mixed reaction" has not been demonstrated in the lab, but is a reasonable supposition based on known chemical processing technologies.

Option 4: The fourth alternative is to produce extra oxygen by recovering some hydrogen via methane pyrolysis (reaction 4) for recycle to the Sabatier reaction until sufficient O_2 is produced. Although the larger reactors required for space station had trouble in this step, the very successful smaller reactors would be sufficient in this case. The difference is that no change-out of the reactor is required since the carbon can be "burned out" by passing CO_2 from the Martian atmosphere through it, removing the coke as CO, as in reaction 7:

$$C + CO_2 \rightarrow 2CO \qquad (7)$$

This is an option for dealing with deposited carbon that is not available for life support systems because they do not have the enormous resource of the Martian atmosphere. By having two parallel, alternating reactors, one could be cracking methane for hydrogen recovery while the other is being purged of carbon. This allows them to be very small. Because extra CO_2 is required for catalyst regeneration, the CO_2 acquisition system may need to be larger. However, if the CO is retained as fuel, this approach might result in a net reduction in compression requirements. In addition, the pyrolysis unit itself would need to be developed (apparently minor from this point) and delivered to Mars. Once this was done, however, the amount of oxygen available from the atmosphere would be limited only by how completely the hydrogen could be recovered and returned to the process.

Option 5: A fifth option may be possible, as well. Recent work has shown the possibility of using zirconia cells, as in option 2, but with the addition of H_2 to the CO_2 feed.[9,10] The result is that oxygen and methane are the products, with CO being an intermediate that builds up and is later converted into the methane. Some water was also seen during the reaction, but was not well quantified. It, too, can be split to release its oxygen and free its hydrogen for reaction. The net effect is equivalent to performing the Sabatier reaction and water electrolysis in a single reactor. The product methane can have a controllable amount of CO in it if the reduction is not driven to completion, which might have system advantages and even be necessary to avoid carbon deposition in the system. Additionally, it should then be possible to continue feeding just carbon dioxide into the system after the hydrogen is gone to produce any extra oxygen required, with CO as the sole by-product. This would result in the replacement of three reactors with one.

ISRU Recommendations for Mars

Obviously, the production of oxygen and fuel at Mars does not come free. In addition to the imported hydrogen, a small processing plant will be required. This plant will have mass and will need to consume power and reject heat. The energy for liquefaction will also be significant. It is against these needs that one must trade the reduced mass of propellant imported from Earth.

When one chooses to use the atmosphere of Mars, it helps the situation if the ambient pressure at the site is as high as possible. This suggests a lower altitude site, such as the bottom of a canyon or in a large basin, rather than a high altitude site, such as the top of a volcano. This fits in well with other drivers of the mission. For instance, a low altitude will probably be desirable for parachute deceleration of the vehicle. Furthermore, thermal control may be easier with a thicker atmosphere for heat removal from the spacecraft radiators as well as the ISRU plant radiators. The presence of a higher atmospheric pressure may be a significant design factor in both radiator design and compressor sizing. Also, a variety of rock and soil samples from several exposed strata may fall down a canyon wall for retrieval, providing a larger variety of grab samples for easy robotic retrieval. Finally, manned outposts will have more radiation protection with more atmosphere above them.

The amount of imported hydrogen required is directly related to the amount of methane desired. Since hydrogen makes up 25% of the mass of methane, at least this much must be brought from Earth. In addition, anything less than 100% yield and any loss due to boil-off must be considered. The ratio of oxygen to fuel (O/F) will have some affect on the amount of fuel produced, but not as much as one might think since the lower performance will require more total propellant. Finally, one might choose to be wasteful of the hydrogen if this would provide a benefit to the production system as a whole. For instance, the standard routes to methane produce oxygen (as water) and methane in a 2:1 mass ratio. Since engine performance is optimized at ratios approaching 4:1, extra oxygen needs to be produced, which usually means a separate process and plant. If, however, we overproduce the methane (wasting some of the hydrogen), venting the excess until enough oxygen is produced, we can continue to use the same equipment without the need to import a separate piece of hardware. This approach was used in the point design effort for the Mars Sample Return (MSR) mission presented here. Due to its small propellant needs, it was believed that the wasted mass of H_2 would also be small and could be sacrificed for simplicity. This is no longer recommended due to the large volume of H_2 required and its impact on the vehicle's tanks.

Assumptions for MSR ISRU Plant Design

Water electrolysis is certainly technology which is well in hand. Sabatier reactors have been successfully run at Hamilton Standard and at the Johnson Space Center (JSC) for the recovery of oxygen from CO_2 with the consumption of a little hydrogen.[11,12] A large methane pyrolysis unit that was at-

Table 1 Mass, volume, and power of subsystems in a Mars ISRU plant

Subsystem	Mass, kg	Volume, m^3	Power, W
Subatier reactor	221	0.90	—
Compressor	35	0.10	200
SPE electrolysis units	168	0.58	2000
Frame assembly	75	0.12	0
Controller	93	0.46	0
Power system: DIPS[a]	366	2.89	0
Avg: 3221 W Peak: 5772 W			
Thermal control system	142	2.69	1110
Liquefation units	100	2.00	1000
LOX	50	1.00	200
CH_4	50	1.00	800
Structure	169	0.00	0
Avionics	15	0.50	100
Propellant feedstock	639	6.56	400
Hydrogen	371		0
Hydrogen tank[b]	152	5.24	0
H_2O holding tank	5	0.01	0
Plumbing	111	1.31	400
Subsystems total	1854	16.22	4810
Growth 20% (excluding H_2)	371	1.93	962
Total	2225	18.15	5772

[a] DIPS estimates are based on work done for the space exploration initiative; see JSC TM 24101, Conceptual Design of Power Systems, 1990.

[b] Separate H_2 import tanks were included. Reduction of tank volume might be possible if some H_2 can be imported in the dry ascent fuel tanks, but there is not enough volume in these to hold all the H_2.

tached to this did have difficulties, although smaller lab units operated well. Zirconia cell technology is promising, but ceramics might be considered too fragile for launch and landing. This conservative design uses the Sabatier reaction coupled with water electrolysis to produce the propellant needed for a sample return mission. Option 1 is pursued, with no separate means of extra oxygen production. It is not claimed that this point design is the "best" choice. It merely reflects the bias of the authors at the start of the process given the current state of knowledge and their judgment of complexity vs reliability and delivered mass. A complete trade study was not done. This design had as a major intent to "keep it simple." Table 1 shows the masses, volumes, and power requirements for the subsystems. It was not possible to fully explore all the options for production, so conservative, best guesses were made based on the following assumptions:

A payload mass of 500 kg was assumed, which is adequate for a sample canister and return vehicle for a very ambitious mission. Methane/oxygen was the propellant mixture of choice. The design studies resulted in a two-stage return vehicle as optimum, with a total of 3.34 mT of propellant at an O/F ratio of 3.5. Thus, 742 kg of CH_4 and 2598 kg of O_2 were baselined. Production must allow for some losses.

All the methane is produced in the first pass, and this is done in the first 100 days. Thus, the liquid hydrogen could be consumed in the first 100 days, minimizing boiloff. Since no attempt is made to recover the hydrogen incorporated into the extra methane that is vented (required to produce sufficient oxygen), twice the amount of H_2 needs to be imported compared to the case where it is used completely and efficiently in fuel production. Thus, 1 kg of H_2 is required to produce 9 kg of methane and oxygen at the optimum 3.5:1 ratio. The benefit of this approach is that no additional source of oxygen is required, hence, no additional equipment.

The required oxygen is produced by electrolysis of the water produced in the first pass through the Sabatier reactor plus the two subsequent passes of the recycled H_2. All passes through the Sabatier reactor after the first pass provide extra methane, which can either be vented or used to make up any boiloff. Additional oxygen is available by continuing the cyclic process of Sabatier/electrolysis past the first three cycles, if required.

The water from the first pass could be stored for electrolysis after this pass is complete, which would then release the hydrogen for recycle as it is needed, or it could be split as needed to supplement the natural boiloff from the LH_2 tank as required for the Sabatier process. The choice in this work was to begin electrolysis nearly immediately so that a smaller storage volume was required and so that the power demand was spread out over a longer time. Water electrolysis and oxygen liquefaction are big power users, so it helps to spread them out over as long a period as possible. The water is split at half the rate that it is produced, however, thus storage of up to 835 kg of H_2O (0.835 m^3) is required. This can be held in an expandable bladder. After 200 days, the first-pass water has been split to oxygen (which is liquefied as it is made) and hydrogen (for recycle). The second-pass water is split over the next 100 days (same rate, half as much), and that produced in the third pass is split over the next 50 days. Total time for production is thus 350 days. Time remains for additional production, if needed.

Liquefaction requirements are based on a Linde–Hampson cycle.[13] Compressor requirements are based on estimates from Zubrin.[2]

Only a cursory consideration of "overhead" for controllers, structure, and undeveloped scope was done. Avionics, at 15 kg, was included for computer control. Some structure was also included at 169 kg. A 20% growth factor was included in the overall mass and power.

A dynamic isotope power system (DIPS) was provided for power. Efficiencies of 20–25% leave 75–80% of its energy as heat, which could be used to good effect for electrical energy savings, but this was not included. Radiators were sized appropriately.

The Sabatier and electrolysis reactor masses and powers were based on actual laboratory hardware built by Hamilton Standard and are currently being tested at JSC. These are not built to flight hardware requirements, and thus are much heavier than they would be for a real mission. Some double counting of structure is possible since these units have steel support frames and additional structure was included as a separate item. Some extra radiator mass for reactor cooling might be required; the environment on Mars differs from that in a terrestrial lab and fan cooling will not work. The H_2 tank fraction allows for a vacuum jacket.

Alternatives to Methane—Higher Hydrocarbon Fuels

Alternative fuels can also be considered. In place of methane, one can consider the production of higher hydrocarbons as the fuel, either directly from CO_2 or from methane or CO. The process could involve Fischer–Tropsch chemistry with a cobalt-based catalyst.[14] The final product would probably be a mixture of alkanes, and might include olefins and aromatics, thus resembling RP-1 (which is itself merely high purity kerosene, also a mixture). This process is in commercial use in South Africa in syn-fuels plants. Current economics do not favor its use in the rest of the world, but the economic drivers on Mars are quite different. Partially oxygenated products, such as alcohols, can also be made, but their performance as a rocket fuel might not be adequate.[15] Since the technology to produce something akin to RP-1 is nearly in hand, it is useful to consider the systems engineering impacts on Mars missions to decide whether pursuit of this technology is of interest. Since it is to be used for ascent, throttling and engine reusability are not issues. Initial judgment is that the potential benefits outweigh the negatives of such a change. Factors to consider include 1) no liquefaction/refrigeration for fuel, therefore less power and insulation. But it may need to be kept warm to prevent partial or complete solidification; 2) higher leverage of terrestrial hydrogen, less imported H_2; 3) lower I_{sp} (~300 s); 4) lower O/F ratio (2.77 for RP-1 vs 3.45 for CH_4), but more propellant needed, thus roughly the same amount of oxygen is required; 5) production ratio (2.3) more nearly matches optimum O/F, less "extra" oxygen is needed from a separate process; 6) higher propellant mixture bulk density than CH_4/O_2 (1.03 vs 0.83 g/cm^3), therefore, less tankage mass and volume. Possibly smaller launch shroud and aerobrake, too; 7) existing engine technologies; 8) could be used as a rover fuel for an internal combustion engine; and 9) probably need an additional synthesis step, possibly similar to liquid synthetic fuels technology. This should be balanced by simpler separation and liquefaction steps.

Alternatives to Methane—CO

There have been many studies that suggest that carbon monoxide and oxygen be produced at Mars and used for the return to Earth.[16–18] The beauty of this approach is that only one piece of equipment is required, nominally the zirconia cells described in option 2, discussed previously, and no imported H_2 is needed. In reality, a CO separator would be necessary, too. Also, CO_2 produces O_2 and CO at a mass ratio of 0.57 to 1, very close to the optimum I_{sp} O/F ratio of 0.55. A disadvantage is that the performance of CO as a fuel is low, the I_{sp} is only ~260–300 s. Also, the electrolysis of CO_2 is not completely efficient, so recycling or additional compression and/or processing is required. Nevertheless, as the size of the return vehicle gets smaller, the penalty of the poorer propellant mixture is less a factor than the importation of H_2, and CO may be favored. In this study, the ascent vehicle dry mass of 510 kg is already beyond the range where CO would be preferred as a fuel.[17] Work at Lewis Research Center is in progress to evaluate this approach, however. Their efforts include the development of engines that burn CO and O_2, with the addition of low levels of H_2 to the fuel to assist ignition.

Alternatives to Methane—CH_4/CO Mixtures

An option that has not yet been considered builds on the realization that we need not produce absolutely pure CH_4 or CO. Looking at the processes involved, one might predict that some carbon monoxide and even trace hydrogen may end up in any methane produced. Given that some level of these impurities will be allowed, it is interesting to explore how much we might tolerate and what this does to the performance of the fuel. If the impact is minor, it may not be worth driving the process to provide high-purity fuel, especially if accepting moderate (but known) amounts of this "impurity" can simplify the process and reduce the mass and power requirements. Importantly, by including CO in the fuel, the optimum O/F ratio goes down, although the total amount of propellant goes up to compensate. Also, by using the CO (which is a by-product of most oxygen production routes from CO_2) rather than just venting it, we utilize the energy we have expended in collecting the atmosphere. Another desired result is to have an effectively higher leverage on the amount of imported hydrogen, trading it for slightly lower engine performance. Also, whereas pure methane is a solid at the boiling point of liquid O_2, and thus needs to be protected against freezing, the addition of CO will lower the freezing temperature. Thus, the two tanks could be in thermal equilibrium with no need for insulation between them. This may provide options for reducing the amount of vacuum jacketing necessary to prevent dry-ice buildup on the tanks. The clever design of such a system offers mass reduction possibilities.

These mixtures are especially relevant if option 5, the one-step route from CO_2 to O_2 and CH_4 via CO, is used, since only one reactor is required. This separation of the oxygen directly, without isolation of water as an intermediate, should result in lower energy demands since condensation is not required and thermodynamic energy is not "wasted" as heat in at least a portion of the oxygen formation (as water), just to be added back via electrolysis. Considering compressor requirements, using the entire mass of the collected atmosphere for production of propellant, rather than just a portion as in the standard zirconia route, is a major advantage of this scheme.

It might also be possible to make CO/CH_4 mixtures from separate Sabatier and CO production reactors, the latter using either a zirconia cell approach (as in option 2), a reverse water gas shift reactor (option 3), or a carbon/CO_2 reactor (option 4). These approaches suffer from the need to have at least three reactors plus a means of mixing the products in the correct proportion. If a reactor can be produced that can accept CO_2 and hydrogen in some intermediate ratio and produce CH_4 and CO in the desired ratio, the situation is improved. The intermediacy of liquid water still requires a water electrolyzer and costs extra energy due to its separation and electrolysis as a liquid, however. This Sabatier-plus-RWGS "mixed reaction approach" has been discussed by Zubrin with researchers in the field and is thought to be possible.[2] Hydrogen would also need to be recycled unless a wasteful approach was desired for simplicity. This approach to a more flexible propellant production/consumption tradeoff seems promising enough to flesh out some specific possibilities more completely.

Properties of CH_4/CO Mixtures

Figure 1 shows the predicted boiling points (at 1 atm) for mixtures of CO in methane. Storage at other pressures can

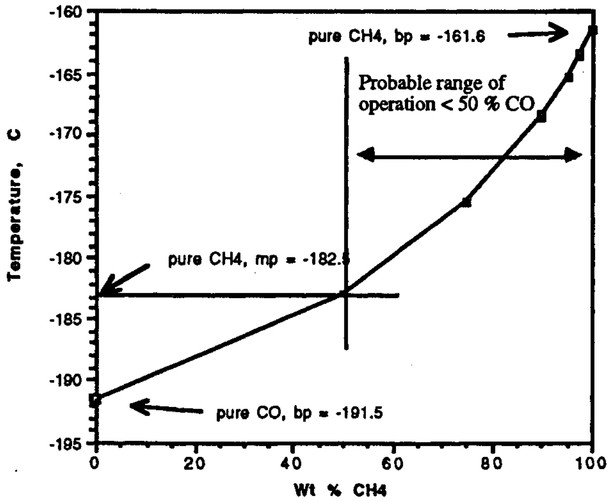

Fig. 1 Normal boiling point of mixtures of CO in CH_4 vs weight % CH_4.

be considered, but since the boiling point temperature increases with increased pressure, the bulk density decreases, resulting in higher volume and structural impact at higher pressures. Since the tanks need to be sturdy enough to survive launch loads they should easily be able to contain propellant at 1 atm. It can be seen that even fairly high levels of CO have only minor impact on the normal boiling point. This change is not likely to drastically affect the liquefaction or refrigeration system that is required. We would be most interested in mixtures that have boiling point temperatures above the freezing point of methane, so that no solid plugs would form in the system if pure methane were to somehow collect in a spot. Note that melting points are relatively insensitive to pressure. This guideline would limit the composition to greater than 50% methane, although higher pressures would expand the possible range of CO content due to the effect on the boiling point of the mixture. Since it is likely that pressure-fed systems will be used due to their simplicity, the propellant tanks will be designed to withstand this pressure. Thus, it is worth considering the entire range of CO/CH_4 mixtures.

The performance of such mixtures in rocket engines can be predicted using various programs that evaluate I_{sp} using thermodynamic data and engine parameters. Over the entire range of CO in CH_4, the optimum vacuum I_{sp} drops from almost 400 to ~305 s (assuming a 500-psia chamber, expansion ratio of 300:1, and one-dimensional equilibrium expansion, actual flight performance will be lower than this but the trend will be similar). This is shown in Fig. 2. The optimum O/F ratio also decreases, the net result being a need for an increasing amount of fuel and a relatively constant amount of oxygen. The bulk densities of the optimum mixes of propellants stay roughly constant, resulting in an increasing volume (as well as mass) of propellant as the CO content increases. One would probably choose to operate above 50% methane since the I_{sp} has not degraded too much from pure methane, and since the performance at this point is roughly equal to that of pure methane at an O/F of 2.0, but the entire trade space could be considered. It is assumed at this point that the two liquids are miscible so that storage in the same tank is feasible and thus no mixing is required. This needs to be tested. The unknown trade at this point is how much simpler, lower mass, and lower power a production process would need to be to justify accepting a lower grade fuel at its optimum O/F as propellant. Conversely, unless the performance with the methane improved the system enough, one might just choose to use CO alone as the fuel, and forego the need to import any H_2 at all from Earth (with all of the demands that would impose on the system), or to use pure CH_4 and oxygen at an O/F of 2.0, as they are produced, without additional O_2 production.

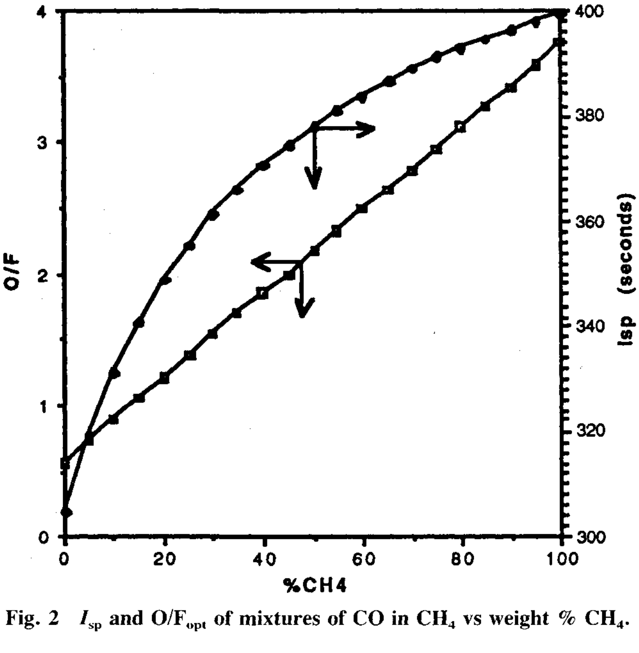

Fig. 2 I_{sp} and O/F_{opt} of mixtures of CO in CH_4 vs weight % CH_4.

Effect of CH_4/CO Mixtures on the MSR Mission

Using the above data on methane-CO fuel mixtures for the baseline payload, the analysis of ΔV, propellant mass, and Mars Ascent Vehicle (MAV) structural mass (again using a two-stage approach) was repeated. The results were put into a spreadsheet and some key requirements of an ISRU plant to make CO, CH_4, and O_2 were estimated for each propellant mixture requirement. While not all design parameters could be determined, several key results were calculated. In the following graphs, the pure methane case was the base case for the study. Figure 3 shows that, as methane is replaced with CO, the total propellant mass increases only slowly at first. The amount of O_2 stays essentially constant due to the declining O/F ratio. The drop in imported H_2 is not linear due to the increase in total fuel mass. The rise in fuel mass is not too great in the regime of >50% methane, and other systems factors, such as reaction yield or separation steps, could drive a system design to this propellant choice.

Figure 4 shows how the volume of the propellant and the increased mass translates into a larger structure for the MAV.

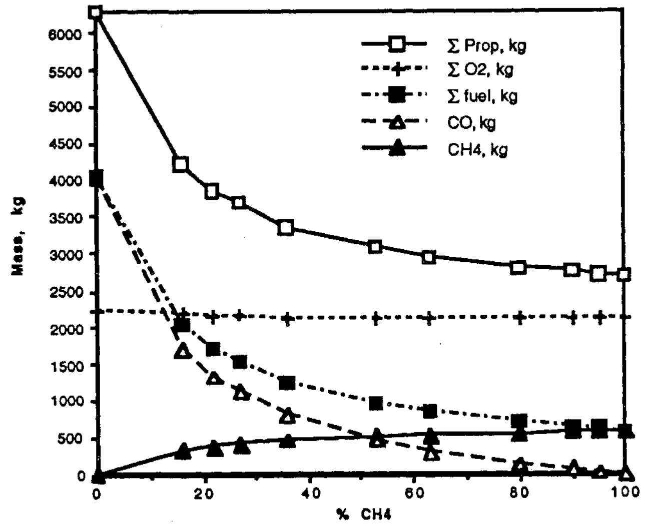

Fig. 3 Propellant masses vs weight % CH_4 for the MSR mission.

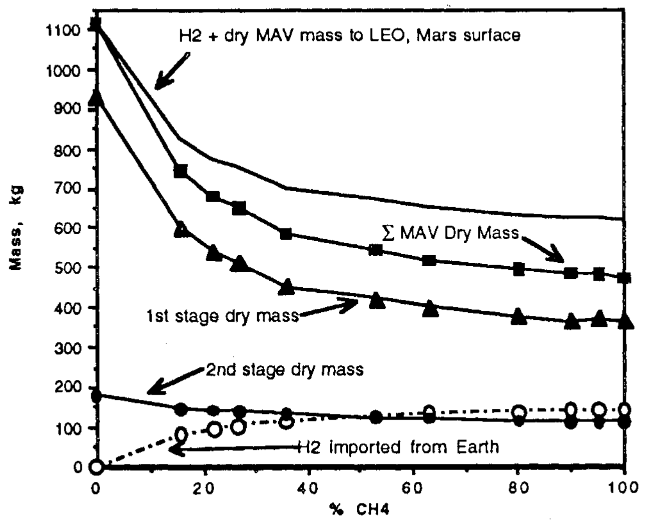

Fig. 4 Weight % CH_4 vs dry masses of MAV stages and imported hydrogen.

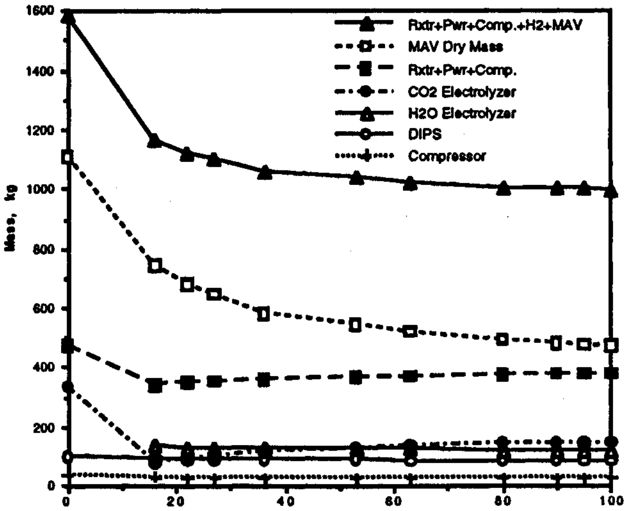

Fig. 5 Weight % CH_4 vs ISRU plant components, dry masses of MAV stages, imported H_2, and total Earth launch mass (excluding constant mass items).

Since the dry mass of the vehicle plus the amount of hydrogen brought to Mars represents an increased liftoff mass from Earth, it is important to look at how this changes with the fuel composition. As can be seen, this total is only mildly sensitive to the composition above 50% methane. This is not the whole story since the mass of the ISRU plant must also be delivered from Earth.

The mass of the ISRU plant was estimated as a function of the composition of the fuel. Many components change only slightly. Some were not calculated due to lack of information on sizing, but would be relatively constant. The key components of the plant thought to be most sensitive to the composition of the fuel are shown in Fig. 5. Also shown is the mass of the MAV structure, imported H_2, and the sum of all the items. Given the assumptions in this analysis, pure CH_4 always provides the lowest mass. This is certainly reasonable, but the increase due to modest amounts of CO is small and within the uncertainty of our assumptions. Furthermore, many components could not be scoped out and may "flatten the curve" even more.

It should be noted that all of these calculations assume standard water electrolyzers and separate CO_2 electrolyzers and Sabatier reactors. Recall that, if option 5, the one-step route from CO_2 to O_2 and CH_4 via CO, is used, only one reactor is required. This separation of the oxygen directly, without isolation of water as an intermediate, should result in lower energy demands and lower reactor masses. Indeed, without the need to provide "pure" methane, it is likely that the plant can be designed to be far lighter since the last few percent conversion of CO_2 is likely to take a disproportionate share of the mass.

A comparison can be made between the performance of these CO/CH_4 mixtures at their optimum O/F ratios and the use of pure CH_4 at an O/F of 2.0, the ratio at which they are produced without any extra oxygen production. The I_{sp} of the latter mixture, at 352 s (calculated using the same assumptions as for the CO/CH_4 mixtures), is the same as that of a 78/22 CO/CH_4 mixture (see Fig. 2). The total mass of propellant would thus be the same as this mixture, namely 3852 kg, as can be seen in Fig. 3. Of this, 2568 kg would be oxygen and 1284 kg methane. The methane made for this case requires 321 kg of imported hydrogen, with no extra CH_4 produced and vented to provide extra oxygen as in the original schemes, and with no allowance for boil-off losses. Thus, more H_2 must be imported from Earth than even the highest of the previous cases: 100% methane (571-kg CH_4, requiring 143-kg H_2 for the fuel with an equivalent amount wasted in order to produce the extra oxygen for the optimum O/F). Furthermore, due to the low density of methane, the propellant bulk density of the new propellant mixture results in a total volume of 5263 l, higher than all but the pure CO case in the CH_4/CO mixture analyses. The tank size increases would cause the dry masses of the two stages of the MAV to go up, also. Ascent vehicle size was the largest factor in the total mass increase calculated for various CO/CH_4 mixtures. The change in ISRU plant masses was relatively insensitive to the composition of the fuel in the mixed fuel cases. The mass of the CO zirconia electrolysis unit would be avoided for a pure methane case, but the mass of the Sabatier and water electrolysis reactors would increase slightly. Depending on the exact process(es) used and the amount of purification of the CH_4 that was required, it is possible that a small advantage in plant mass would exist in favor of the single fuel approach, but the net effect on the Earth launch mass (including the extra hydrogen and MAV mass) is likely to favor the optimum O/F with pure methane or some CO/CH_4 mixture. At the level of study warranted by our current understanding of the requirements of the ISRU plants for these approaches, an advantage for either route is, at best, uncertain.

Summary and Conclusions

A preliminary design of an ISRU plant for use on a Mars sample return mission predicts that sufficient return propellant can be produced by a plant having a mass of roughly two metric tons and using less than 6 kW. The mass includes the imported H_2 and power system. This is lower than the 3.34 mT of propellant it replaces, and provides for a much lower Earth launch mass. This design is based on a number of conservative assumptions and can probably be improved with a concerted development effort. Many variations on this approach are possible.

The Sabatier and water electrolysis reactors proposed for the plant are well along in development and are quite reliable. A low-cost, near-term technology effort could be initiated that would use only these two processes to produce oxygen and methane from the Martian atmosphere for a sample return mission. Twice the required amount of hydrogen (185 kg of additional hydrogen) was imported in order to simplify the overall processing and to eliminate the need for a separate means of producing the needed amount of oxygen. Because of this, the total mass of the process plant plus imported hydrogen may be lower and will probably be simpler. Since hydrogen contains significant chemical energy, the power situation might be improved as well.

The volume of the imported hydrogen does have a significant negative impact. Note that over one-third of the volume and nearly that fraction of the mass is due to the H_2. Because of this, this approach is no longer considered as favorably as at the beginning of the study, despite some advantages. It is likely that bringing only the required amount of H_2 would result in a better overall design. This should be investigated further by a more complete trade analysis against systems that import less or even no hydrogen.

Due to potential systems-wide benefits, the conversion of CO_2 and hydrogen into storable hydrocarbon fuels should also be pursued. Such a process could resemble existing commercial routes to syn-fuels used in South Africa and studied in the U.S. during the energy crisis of the 1970s.

Due to the very high leverage possible, the new technology presented in option 5, namely the direct conversion of CO_2 and hydrogen into methane and oxygen within a zirconia cell, with the possibility of making additional oxygen from straight CO_2, should be pursued. The potential for having one reactor replace three separate systems is exciting. Furthermore, with only minor changes, this one system should be flexible enough to produce the entire range of $CO/CH_4/O_2$ mixtures, whatever that optimum happens to be after future spacecraft and subsystem optimizations.

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