

1N-44  
11696  
p11

## Material Processing With Hydrogen and Carbon Monoxide on Mars

Aloysius F. Hepp  
*National Aeronautics and Space Administration*  
*Lewis Research Center*  
*Cleveland, Ohio*

Geoffrey A. Landis  
*Sverdrup Technology, Inc.*  
*Lewis Research Center Group*  
*Cleveland, Ohio*

and

Diane L. Linne  
*National Aeronautics and Space Administration*  
*Lewis Research Center*  
*Cleveland, Ohio*

Prepared for the  
Tenth Biennial Conference on Space Manufacturing  
Princeton, New Jersey, May 15-19, 1991

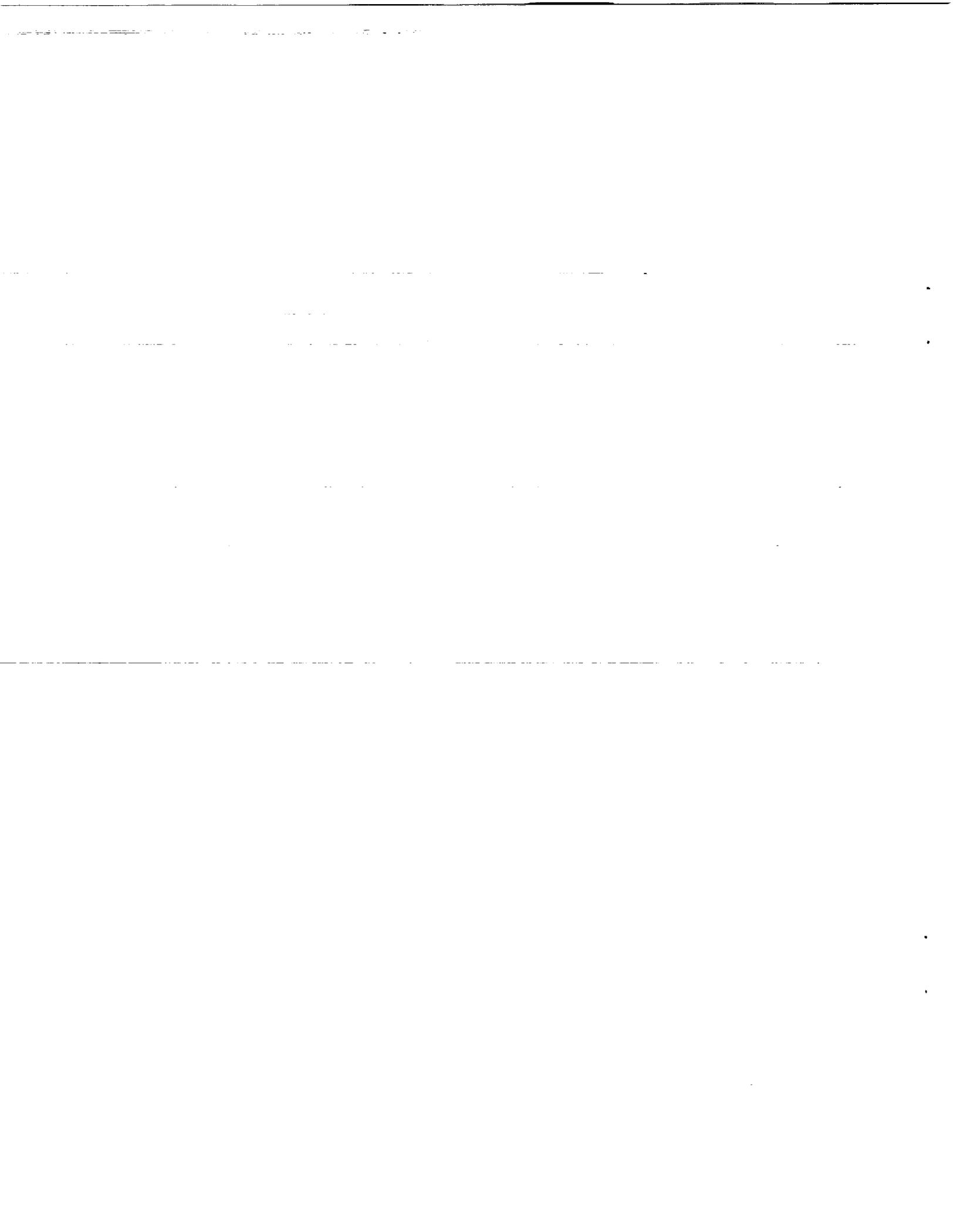
**NASA**

(NASA-TM-104405) MATERIAL PROCESSING WITH  
HYDROGEN AND CARBON MONOXIDE ON MARS (NASA)  
11 p CSCL 10B

N91-23616

Unclas  
0011696

G3/44



# MATERIAL PROCESSING WITH HYDROGEN AND CARBON MONOXIDE ON MARS

Aloysius F. Hepp,\* Geoffrey A. Landis\*\* and Diane L. Linne\*  
National Aeronautics and Space Administration\*  
Sverdrup Technology, Inc.\*\*  
Lewis Research Center  
Cleveland, OH 44135

## ABSTRACT

This study examines several novel proposals for propellant production from carbon dioxide and monoxide and hydrogen. We also examine potential uses of CO as a fuel or as a reducing agent in metal oxide processing as obtained or further reduced to carbon. Hydrogen can be reacted with CO to produce a wide variety of hydrocarbons, alcohols, and other organic compounds. Methanol, produced by Fischer-Tropsch chemistry may be useful as a fuel; it is easy to store and handle because it is a liquid at Mars temperatures. The reduction of CO<sub>2</sub> to hydrocarbons such as methane or acetylene can be accomplished with hydrogen. Carbon monoxide and hydrogen require cryogenic temperatures for storage as liquids. Non-cryogenic storage of hydrogen may be accomplished using hydrocarbons, inorganic hydrides, or metal hydrides. Non-cryogenic storage of CO may be accomplished in the form of iron carbonyl (Fe(CO)<sub>5</sub>) or other metal carbonyls. Low hydrogen-content fuels such as acetylene (C<sub>2</sub>H<sub>2</sub>) may be effective propellants with low requirement for earth-derived resources. The impact on manned Mars missions of alternative propellant production and utilization is discussed.

## INTRODUCTION

Utilization of resources available *in situ* is a critical enabling technology for a permanent human presence in space. A permanent presence on Mars, for example, requires a tremendous infrastructure to sustain life under hostile conditions (low oxygen partial pressure,<sup>1</sup> ultraviolet radiation,<sup>2</sup> low temperatures,<sup>3</sup> etc.). Consequently, there have been numerous studies on the most accessible of Martian resources: atmospheric carbon dioxide.<sup>4-9</sup> Atmospheric CO<sub>2</sub> is: abundant (the atmosphere of Mars consists of 95% carbon dioxide,<sup>1</sup> table 1); available at all points on the surface; of known presence -- requires no precursor mission to verify; chemically simple -- requires no precursor missions to verify composition or properties; and can be obtained by simple compression, with no requirements of mining or beneficiation equipment operation. Many studies focus on obtaining oxygen and the various uses for oxygen including life support and propellant; discussion of carbon monoxide, the co-product from CO<sub>2</sub> fixation revolves around its use as a propellant, being oxidized back to CO<sub>2</sub>.<sup>8,9</sup> In this study, we examine reaction schemes for processing *in-situ* resources; we highlight chemistry with hydrogen and carbon monoxide to produce propellants and other necessities of manned exploration.

TABLE 1.  
COMPOSITION OF MARTIAN  
LOWER ATMOSPHERE\*

GAS		VOLUME FRACTION (%)
Carbon Dioxide	(CO <sub>2</sub> )	95.32
Nitrogen	(N <sub>2</sub> )	2.7
Argon	(Ar)	1.6
Oxygen	(O <sub>2</sub> )	0.13
Carbon Monoxide	(CO)	0.07
Water Vapor	(H <sub>2</sub> O)	0.03

\* - Source: NASA Technical Memorandum 82478.

## PRODUCTION OF HYDROGEN AND CARBON MONOXIDE ON MARS

### Water as a Source of In-Situ Hydrogen

Since the hydrogen/oxygen reaction is the highest specific impulse rocket fuel, production of hydrogen on Mars has been an important research topic and the subject of a considerable number of propulsion suggestions. Hydrogen is available on Mars primarily in the form of water. Water can be electrolyzed to produce the hydrogen required for fuel production and oxygen.

Water is available on Mars in the form of water ice in the polar caps.<sup>10</sup> If the polar regions are the only regions to be exploited, polar ice will provide an abundant and comparatively pure source of hydrogen. For sites far removed from the poles, however, transportation of hydrogen from sources at the polar caps will likely be a difficult task until such a time as a global transportation system is established.

Some amount of water is also believed to be present in the form of permafrost beneath the surface<sup>10</sup> at high-latitude locations. The depth at which permafrost may be found increases as the location approaches the equator. Use of permafrost as a resource, however, would require both precursor missions to locate the resource, and mining and refining equipment to dig out and purify the water.

Like carbon dioxide, the atmosphere of Mars is a convenient but low-density source of water. The Viking orbiter mapped the water vapor content of the Martian atmosphere<sup>1</sup> and as a result we now know the atmosphere to be nearly saturated with water vapor, about 0.03% composition by volume, varying with location and season. This results in an amount of precipitable water

between 1 and 100 microns.<sup>10,11</sup> Water can be precipitated out of the Martian atmosphere by either of two relatively simple mechanical processes: adiabatic expansion,<sup>12</sup> or isothermal compression.<sup>13</sup> Water could be produced from the atmosphere at a rate on the order of one kilogram per 10<sup>6</sup> m<sup>3</sup> of atmosphere processed.

In near-Mars space, it has also been suggested that water may be present on the moons of Mars, Deimos and Phobos, either in the form of hydrated minerals or as buried ice. Such water would most likely be buried some depth below the surface. Because of the low surface gravity of these moons, this could be an important source of hydrogen for operations in space; it is not likely to be an important resource for Mars surface operations.

Except near the poles, hydrogen is likely to be a considerably scarcer resource, as well as one requiring more effort and energy to remove and refine. It is likely that initial missions will bring hydrogen from Earth. For this reason, our analysis of resource use on Mars will focus on systems that minimizing hydrogen requirements, using instead resources derived from carbon di- and monoxide to the greatest extent practical.

#### Solar-Powered Carbon Dioxide Reduction

The "splitting" of CO<sub>2</sub> to CO and O<sub>2</sub> is thermally demanding ( $\Delta H^\circ = 566 \text{ kJ mol}^{-1}$ ,  $\Delta G^\circ = 514 \text{ kJ mol}^{-1}$ ):



The "splitting" of CO<sub>2</sub> to CO and O<sub>2</sub> can be effected at temperatures in excess of 1000K over zirconia,<sup>5</sup> but only by the significant expenditure of a nonrenewable energy source and at low efficiencies.

Of the various chemistries for CO<sub>2</sub> reduction to CO examined to date,<sup>14</sup> the reduction of CO<sub>2</sub> by nickel cluster electrocatalysts<sup>15</sup> holds the greatest promise for a useful device. The proven ability of nickel cluster compounds to electrocatalyze the reduction of CO<sub>2</sub> to CO very near the expected thermodynamic potential can be coupled with photocatalytic and photoelectrochemical systems for oxygen evolution to accomplish the overall "splitting" of CO<sub>2</sub> to CO and O<sub>2</sub>.

The solar power density on the surface of Mars is ~250 W m<sup>-2</sup>, approximately one-fourth that on Earth,<sup>16</sup> and more than adequate to power the direct photochemical or photoelectrochemical deoxygenation of CO<sub>2</sub>. We have proposed the development of energy self-sufficient photochemical systems for the production of oxygen and carbon monoxide from carbon dioxide on the surface of Mars. The approach involves coupled catalytic cycles to simultaneously produce oxygen and carbon monoxide. Efficient metal catalysts and photocatalysts are to be used for both half-reactions: i) the deoxygenation of CO<sub>2</sub> to CO; and ii) the evolution of O<sub>2</sub>. An example of a proposed device is shown in figure 1. The details of this approach and the rationale for such systems are addressed in earlier work.<sup>17</sup>

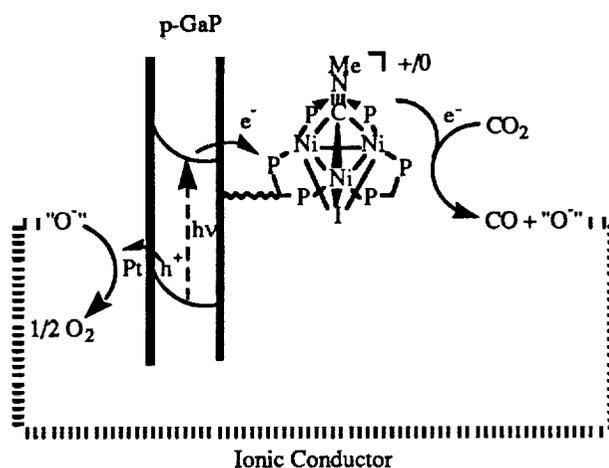


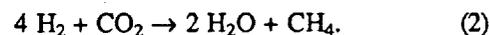
Figure 1. A semiconductor photoelectrochemical system for splitting carbon dioxide. See text for discussion regarding energy requirement of absorbed photon.

Functioning of such a direct photoelectrochemical reaction on the surface of Mars requires the presence of UV photons of energy greater than 2.26 eV. Although the solar spectrum has not been measured at the surface of Mars, the Martian atmosphere, with no ozone layer, allows penetration of solar UV to the surface. The integrated space (AM0) solar spectrum, i.e., total number of photons with energy greater than the photon energy listed, is known for the distance of Earth from the sun.<sup>18</sup> On Mars, the portion of the solar spectrum with  $h\nu > 2.26 \text{ eV}$  represents an electrolysis current equivalent to ~3 mA per cm<sup>2</sup> of solar-exposed surface.

#### RAW MATERIAL PROCESSING WITH HYDROGEN AND CARBON MONOXIDE

##### Methane Production from Carbon Dioxide and Hydrogen

Synthesis of methane and oxygen from indigenous Martian materials has been discussed by Ash<sup>4</sup> and others. A Mars mission involving processing of methane propellant is detailed by Zubrin and Baker.<sup>19,20</sup> The processing module uses the Sabatier reaction to react hydrogen with atmospheric carbon dioxide to produce methane and oxygen:



This is a highly exothermic reaction; the rate of methane production will be limited primarily by the ability to remove the heat produced. The evolved water is recycled to hydrogen and oxygen by electrolysis. Additional oxygen can be produced by reduction of carbon dioxide as discussed in the previous section.<sup>7,19,21</sup> Alternately, if the desired product is oxygen, the methane produced can be pyrolyzed to carbon, and the hydrogen recycled in reaction (2) to reduce further carbon dioxide.<sup>20</sup>

### Production of Alcohols and Higher Hydrocarbons

Carbon monoxide as a resource on Mars, derived from CO<sub>2</sub> fixation, is most often discussed as a propellant.<sup>4,6-9</sup> Used as a rocket fuel, a specific impulse of about 300 seconds could be produced. However, exothermic reaction with O<sub>2</sub> to produce CO<sub>2</sub> is only one potential use for CO. Once CO is produced on Mars, further reactions by Fischer-Tropsch chemistry can be used to synthesize alcohols and higher hydrocarbons, as shown in table 2.

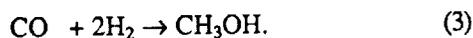
Fischer-Tropsch chemistry can be used to produce almost any organic compound of interest, including hydrocarbon fuels, polymers, and processing feedstock for further use. Methane itself can be used to produce acetylene and higher hydrocarbons. Acetylene can also be used as a feedstock for a wide variety of synthetic polymers and other materials of interest.<sup>22-25</sup> This will be discussed in more detail in a later section.

TABLE 2.  
THERMODYNAMIC VALUES FOR  
CO/H<sub>2</sub> REACTIONS\*

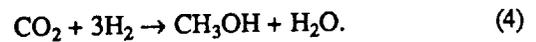
PRODUCT	REACTION	ΔH (kJ mol <sup>-1</sup> )
<b>Methane</b>		
CO + 3 H <sub>2</sub>	→ CH <sub>4</sub> + H <sub>2</sub> O	- 206
2 CO + 2 H <sub>2</sub>	→ CH <sub>4</sub> + CO <sub>2</sub>	- 248
<b>Alkanes</b>		
CO + 2 H <sub>2</sub>	→ (-CH <sub>2</sub> -) + H <sub>2</sub> O	- 165
2 CO + H <sub>2</sub>	→ (-CH <sub>2</sub> -) + CO <sub>2</sub>	- 207
3 CO + 2 H <sub>2</sub> O	→ (-CH <sub>2</sub> -) + 2 CO <sub>2</sub>	- 249
<b>Methanol</b>		
CO + 2 H <sub>2</sub>	→ CH <sub>3</sub> OH	- 90.8
<b>Alcohols</b>		
n CO + 2n H <sub>2</sub>	→ C <sub>n</sub> H <sub>2n+1</sub> OH + (n-1) H <sub>2</sub> O	- 124.8

\* - Adapted from text reference 22.

A potential use for alcohols produced by Fischer-Tropsch chemistry is for propellants. The energy content of alcohols is lower than that of the corresponding hydrocarbons, and thus as rocket propellants they have a specific impulse lower by ~8 to 12% than the corresponding hydrocarbons. The advantage of alcohols is the great ease of storage. With melting points of -97°C and -115°C respectively, methanol and ethanol are liquid over nearly the entire Mars temperature range. Once CO has been produced as discussed above, methanol can be produced with high selectivity by catalytic hydrogenation:<sup>22</sup>



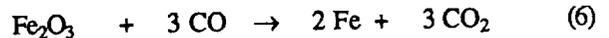
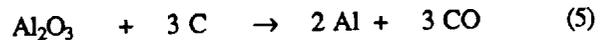
This reaction (see table 2) is currently done on a worldwide production scale on the order of 15 Mtons/yr. Alternatively, methanol can be produced directly from carbon dioxide:<sup>22</sup>



This direct reduction of CO<sub>2</sub> is less exothermic than (3); removal of the water from the methanol produced requires an additional step.

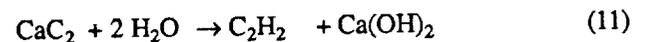
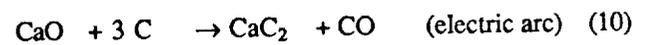
### Carbon Monoxide and Carbon in Oxide Processing

Other applications of CO on Mars take advantage of the CO as a reducing agent or as a source of carbon.<sup>26-30</sup> Typical examples for the production of materials useful for structures and power systems are shown below.



Equation (5) describes a patented process<sup>27</sup> for producing aluminum using carbon and electricity. For each kg of aluminum produced, 3.45 kg of carbon and 32.7 MJ of electrical energy are required. The carbon could be obtained from processes such as (8) or (9) or by electrolysis of CO. Electrical energy could be obtained from solar cells. Equation (6) describes a low temperature reduction of iron oxide that produces iron and carbon dioxide. This system has been studied using mixtures of CO and H<sub>2</sub> as a reductant.<sup>28</sup> Equation (7) summarizes a two-step process for reducing SiO<sub>2</sub> to SiC at temperatures of 1100°C under a CO atmosphere.<sup>29</sup> Equations (8) (25°C) and (9) (200°C) describe relatively low-temperature methods for producing carbon. The sulfuric acid and iron oxide can then be recycled to produce O<sub>2</sub> at elevated temperatures<sup>30</sup> or processed further to produce other materials (i.e. (6) to produce iron). Recycling the products from (8) and (9) results in a process to disproportionate CO into carbon and CO<sub>2</sub>.

Reduced carbon can be used to produce acetylene. The standard terrestrial method for producing acetylene uses calcium carbide in a two-step process starting with carbon and calcium oxide:



While calcium oxide is available on Mars (table 3), it is likely in a silicate form which would have to be refined before use. In order to utilize hydrogen efficiently, the calcium hydroxide would have to be recycled back to calcium oxide. Manufacture of acetylene by this process requires an electrical power for the CaC<sub>2</sub> step of about 10 to 11 kW-hr/kg of acetylene produced.<sup>24</sup> It has the advantage of producing high purity acetylene with few byproducts. Alternative acetylene production methods are discussed below.

**TABLE 3.**  
**APPROXIMATE ELEMENTAL COMPOSITION AND**  
**CHEMISTRY OF VIKING 1 LANDER SITE\***

<u>ELEMENT</u>	<u>(%)</u>	<u>COMPOUND</u>	<u>(%)</u>
Oxides of H, C, N, Na	40	SiO <sub>2</sub>	40
Si	21	Fe <sub>2</sub> O <sub>3</sub>	18
Fe	13	MgO	8
Unknown	9	SO <sub>3</sub>	8
Mg	5	Al <sub>2</sub> O <sub>3</sub>	6
Ca	4	CaO	6
S	3	TiO <sub>2</sub>	1
Ti	1	K <sub>2</sub> O	0.3
Sr, Y, K, Zr, Rb (total)	1		

\* - Source: NASA Technical Memorandum 82478.

**TABLE 4.**  
**ALTERNATIVE MEDIA FOR STORAGE OF HYDROGEN AND CARBON MONOXIDE\***

<u>COMPOUND</u>	<u>MASS<sup>b</sup></u> <u>FRACTION</u>	<u>MASS PER<sup>c</sup></u> <u>VOLUME</u>	<u>M.P.</u> <u>(°C)</u>	<u>B.P.</u> <u>(°C)</u>	<u>REACTION</u> <u>FOR GAS REMOVAL</u>
<u>Hydrogen Liquid Storage</u>					
Liquid H <sub>2</sub>	100 %	0.075	-259°	-253°	
CH <sub>4</sub>	25 %	0.10	-183°	-163°	CH <sub>4</sub> + H <sub>2</sub> O → CO + 3H <sub>2</sub> <sup>d</sup>
NH <sub>3</sub>	18 %	0.14	-78°	-33°	2 NH <sub>3</sub> → 3H <sub>2</sub> + N <sub>2</sub> <sup>e</sup>
SiH <sub>4</sub>	12 %	0.08	-185°	-112°	Catalytic decomposition
H <sub>2</sub> O	11 %	0.11	0°	100°	H <sub>2</sub> O → H <sub>2</sub> + O <sub>2</sub> <sup>f</sup>
C <sub>6</sub> H <sub>12</sub>	7 %	0.05	7°	81°	C <sub>6</sub> H <sub>12</sub> → C <sub>6</sub> H <sub>6</sub> + 3H <sub>2</sub> <sup>g</sup>
<u>Hydrogen Solid Storage</u>					
LiH	13 %	0.11		Solid <sup>h</sup>	Decomposes > 1119°C <sup>i</sup>
MgH <sub>2</sub>	8 %	0.10		Solid <sup>h</sup>	Decomposes > 287°C <sup>i</sup>
CaH <sub>2</sub>	5 %	0.10		Solid <sup>h</sup>	Decomposes > 1074°C <sup>i</sup>
TiH <sub>2</sub>	4 %	0.16		Solid <sup>h</sup>	Decomposes > 400°C <sup>i</sup>
FeTiH <sub>2</sub>	2 %	0.10		Solid <sup>h</sup>	Decomposes > -8°C <sup>i</sup>
LaNi <sub>5</sub> H <sub>6</sub>	1 %	0.09		Solid <sup>h</sup>	Decomposes > 13°C <sup>i</sup>
<u>Carbon Monoxide</u>					
Liquid CO	100 %	0.79	-205°	-190°	
Fe(CO) <sub>5</sub> <sup>j</sup>	71 %	1.03	-21°	103°	Decomposes > 100°C <sup>i</sup>
Ni(CO) <sub>4</sub> <sup>k</sup>	66 %	0.87	-25°	43°	Decomposes > 200°C <sup>i</sup>
CuAlCl <sub>4</sub> (CO) <sup>l</sup>	11 %			Solid <sup>h,m</sup>	Loses CO above 40°C

\* - Mass per unit volume, melting point and boiling point under Earth ambient conditions for temperature and pressure. Bold type denotes possibility of synthesis using materials available *in situ*, see text. <sup>b</sup> - Mass of gas as a percentage of the total mass of the compound. <sup>c</sup> - Grams of gas per cubic centimeter of material. <sup>d</sup> - Steam reformation (Eva-Adam) process. Occurs on a catalyst at 500 - 1200°C. Reference 26 and Kugeler, L., *Nucl. Eng. and Design* 34, 65, 129 (1975). <sup>e</sup> - Haber process occurs at 400 - 550°C at 100 - 1000 atm. over a catalyst. See page 312 in text reference 26. <sup>f</sup> - Reaction occurs by electrolysis. <sup>g</sup> - Catalytic dehydrogenation over oxide catalyst occurs at 560°C, 20 atm. Other hydrocarbons could be used as well, see page 286 in text reference 25. <sup>h</sup> - Solid over ambient temperature range on Mars. <sup>i</sup> - Produces metal and hydrogen or carbon monoxide. <sup>j</sup> - Text reference 33. <sup>k</sup> - Text reference 34. <sup>l</sup> - Walker, D.G., *Chemtech* 308, May 1975 and discussion in text reference 22. <sup>m</sup> - Used as a toluene solution.

## STORAGE OF HYDROGEN AND CARBON MONOXIDE ON MARS

For rocket fuels and for transportation from the Earth, it is important that storage of reactants be in a form which has the highest ratio of usable reactant to mass. In general, this is accomplished by storage of the material as a cryogenic liquid (or, occasionally, in a solid or slush form.) For use on Mars, however, storage as a cryogenic liquid may not be the best solution. Storage on Mars will be required for CO and H<sub>2</sub> for several purposes: storage of rocket fuel during the stay on Mars, storage of reactants, and storage of intermediate products during materials processing. In this section we discuss alternate methods of storage for CO and H<sub>2</sub>.

### Non-cryogenic Storage of Hydrogen

A significant issue for use of cryogenic gases is that of long-term storage. Magnesium and magnesium (nickel) hydrides are considered excellent candidates for both terrestrial<sup>31</sup> and space<sup>32</sup> storage of hydrogen. A number of candidate materials for storage of both hydrogen and carbon monoxide are listed in table 4. The materials in bold print are those that could be produced from elements found *in situ*. A striking property of the gas storage compounds is that except for cyclohexane (C<sub>6</sub>H<sub>12</sub>), all of the listed compounds store more gas per unit volume than cryogenic liquid H<sub>2</sub>.

The metal hydrides are superior to liquid hydrogen in mass of hydrogen stored per unit volume, due to their relatively high density. Although the storage density (mass of hydrogen per volume) of hydrides can be higher than that of liquid hydrogen, the mass fraction (percentage of hydrogen by mass) of hydrogen storage materials is typically very small. Thus, hydride storage is only practical if the storage material is easily available from materials available on Mars.

Hydrogen storage materials can be classified as reversible or irreversible<sup>31</sup> depending upon the difficulty of storing and retrieving gas. Using this criterion, all of the metal complexes are reversible. The organic complexes<sup>25</sup> and ammonia<sup>26</sup> require high temperatures for catalytic production and decomposition. Silane can be easily decomposed to Si and H<sub>2</sub>; the production reaction, however, is quite difficult. Methane has an advantage due to its utility as a fuel but is more difficult to store due to its low boiling point.

Another issue to consider is the ease of handling. Among the non-metallic hydrides and hydrocarbons, ammonia would be the easiest to handle as it is a liquid over much of the temperature range of Mars. Water is a special case since it can be electrolyzed to produce hydrogen and oxygen; there would be no need to produce water if it can be obtained *in situ*. The electricity to produce hydrogen could be derived from a renewable source such as solar cells.

Of the metal hydrides, TiH<sub>2</sub> has the highest storage density, with a hydrogen content more than twice that of liquid hydrogen. However, recovery of hydrogen from TiH<sub>2</sub> requires high-temperature processing. FeTiH<sub>2</sub> has

the most desirable properties in terms of processability. It can be produced from *in-situ* materials. The gas storage density is comparable to other metal hydrides. The most attractive feature of FeTiH<sub>2</sub> is the ease of hydrogen desorption. Unlike the hydrides of Li, Ca, Ti and Mg, FeTiH<sub>2</sub> gives off hydrogen at a temperature that does not require excessive heating.<sup>31,32</sup> The best hydrogen storage strategy therefore may be to use one compound for long-term storage (FeTiH<sub>2</sub>) along with another compound that produces hydrogen as a by-product of decomposition and has other uses (water and hydrocarbons). Both Fe and Ti are available in oxide form on Mars; Fe in abundance and Ti as a minor component of the soil.

### Non-cryogenic Storage of Carbon Monoxide

Carbon monoxide is a tasteless, odorless, and toxic substance with a melting point of - 205°C (68K) and a boiling point of - 190°C (83K);<sup>26</sup> it is a minor component of the Martian atmosphere, see table 1. For CO storage, both iron and nickel carbonyl are superior to liquid CO for gas storage density per unit volume. The gas can be easily removed by heating.

Iron carbonyl (Fe(CO)<sub>5</sub>)<sup>33</sup> is more difficult to produce than nickel carbonyl (Ni(CO)<sub>4</sub>)<sup>34</sup> but it has superior gas storage density, a lower decomposition temperature, and is a liquid over a larger temperature range, improving handling properties. Iron carbonyl is light sensitive, which allows for the possibility of photolytic decomposition. It can also be used as a catalyst in Fischer-Tropsch chemistry.<sup>26</sup> Most important, Fe is available on Mars, and can be produced by reactions such as (9) above.

## PROPELLANT PRODUCTION ON MARS

Tremendous advantages in chemical propulsion missions can be achieved by using Martian resources for propellants. Mars-derived carbon monoxide can be used directly as a fuel, at a specific impulse of about 300 seconds.<sup>8,9</sup> For higher specific impulses it is necessary to synthesize hydrocarbon fuels.

This approach could result in producing a large mass of rocket fuel on Mars from a small amount of hydrogen brought from Earth. For high energy return missions such as manned Mars missions, most of the initial mass required to be placed in low-Earth orbit (IMLEO) is propellant. Of this, a large fraction comprises the fuel for the return trip and the fuel in LEO required to boost the return fuel to Mars. A mission where the return propellant need not be shipped to Mars would greatly reduce the required mission mass. Thus, production of rocket propellant from available resources is an extremely high-leverage approach to reducing mission mass.<sup>35</sup>

### Propellant Mass Leverage

If carbon dioxide is the only resource assumed to be used from Mars, then production of hydrocarbon fuels requires hydrogen brought from Earth. It is desirable to maximize the total impulse of fuel produced and

minimize the amount of hydrogen required. Thus, it is optimal to burn a fuel with a minimum hydrogen content. We can define the *propellant mass leverage* as the mass of propellant produced divided by the mass of earth derived components (in this case, hydrogen). The propellant mass leverage of several fuels (for stoichiometric combustion) is shown in table 5.

TABLE 5.  
IN-SITU PROPELLANT MASS LEVERAGE\*

FUEL	REACTION STOICHIOMETRY	LEVERAGE
Hydrogen	H <sub>2</sub> + 1/2 O <sub>2</sub> (Earth)	1
Hydrogen	H <sub>2</sub> + 1/2 O <sub>2</sub> (Mars)	9
Methane	CH <sub>4</sub> + 2 O <sub>2</sub>	20
Ethane	C <sub>2</sub> H <sub>6</sub> + 7/2 O <sub>2</sub>	24
Ethylene	C <sub>2</sub> H <sub>4</sub> + 3 O <sub>2</sub>	31
Acetylene	C <sub>2</sub> H <sub>2</sub> + 5/2 O <sub>2</sub>	53
Methanol	CH <sub>3</sub> OH + 3/2 O <sub>2</sub>	20
Ethanol	C <sub>2</sub> H <sub>5</sub> OH + 3 O <sub>2</sub>	24
Carbon monoxide	CO + 1/2 O <sub>2</sub>	∞

\* - See discussion in text.

It is important to note that the mass leverage is not the only factor to be considered in a figure of merit; the specific impulse ( $I_{sp}$ ) is also quite important, since it determines the amount of fuel required. Hydrogen/oxygen can produce a specific impulse of up to 500 sec.; the hydrocarbon fuels about 375 sec., the alcohols slightly less, and carbon monoxide about 300 sec. Carbon monoxide contains no Earth-derived hydrogen, and so has a hydrogen leverage of infinity, but the low specific impulse is a drawback.

Since stoichiometric hydrogen/oxygen propellant is nearly 90% oxygen by mass, a mass leverage of a factor of nine can be achieved simply by using oxygen derived from carbon dioxide reduction as the oxidizer for hydrogen produced on Earth. As discussed above, use of liquid hydrogen as a fuel is problematical because it is extremely difficult to store.

An additional increase by a factor of two in propellant leverage is obtained by use of Mars-derived methane. The most detailed analysis of a Mars mission utilizing methane production from atmospheric carbon dioxide is that discussed by Zubrin and Baker,<sup>19,21</sup> using reaction (2) as discussed in an earlier section. The purpose of this chemistry is to produce a large amount of return fuel from a small amount of hydrogen. The required hydrogen is about 5% of the mass of the fuel produced. Hydrogen brought from Earth is converted into methane and water by reaction (2) within two days of arrival on Mars, thus eliminating the significant difficulties of long-term cryogenic storage of hydrogen, as discussed below.

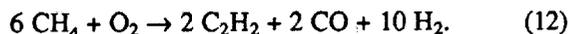
The Baker/Zubrin proposal involved an unmanned preliminary mission to bring to Mars: (1) the return spacecraft, (2) a quantity of liquid hydrogen, and (3) an atmospheric processing module, followed two years later by a manned mission. Their proposal envisioned completion of propellant manufacture, resulting in a fully fueled return vehicle on Mars before the manned crew is launched, and contained several safeguards to ensure that the manned crew would reach the fueled return vehicle despite any credible worst-case.

Additional gains in propellant leverage can be obtained by synthesis of higher hydrocarbons. Ethane and ethylene produce only modest improvements over methane. Of the hydrocarbon rocket fuels, the minimum hydrogen content fuel is acetylene, C<sub>2</sub>H<sub>2</sub> (H-C≡C-H). Despite the higher exhaust molecular weight, acetylene has a theoretical vacuum specific impulse ( $I_{sp}$ ) similar or better to that of methane. The higher exhaust molecular weight is offset by the energy content of the triple bond, resulting in a high combustion temperature.

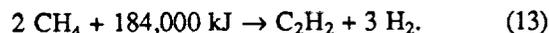
#### Mars-Derived Acetylene/Oxygen Propellant

Acetylene is a gas at room temperature, but has a boiling point of -82°C (assuming pressure > 1.2 atm. to maintain the liquid phase), making it even easier to store than methane, which boils at -163°C. The density of liquid acetylene is 0.62 g/cm<sup>3</sup>, compared to liquid methane at 0.41 g/cm<sup>3</sup>. While acetylene is thermodynamically unstable, decomposition is not a problem for liquid acetylene stored at low temperature.<sup>23</sup> Dilution of acetylene with CO, a co-product of reaction (12), also will stabilize the material. Use of acetylene instead of methane decreases the requirement for hydrogen by another factor of four at no reduction in specific impulse.

A standard production sequence for acetylene is the partial oxidation of methane, or Sachsse process,<sup>23,24</sup> where combustion of the methane with oxygen provides the energy required for pyrolysis:

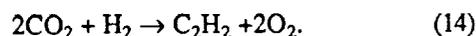


This is an industrial reaction with production of over 50,000 tons/year.<sup>23</sup> The hydrogen can be recycled to methane and reused in reaction (2). The yield of acetylene produced by this process is about 31%. Acetylene can also be produced by thermal or electric arc pyrolysis of methane at around 1250°C:<sup>23</sup>



Conversion to acetylene is about 50% per pass. The energy efficiency is typically about 50%, and thus the energy required for this process is about 8.9 kW-hr per kilogram of acetylene, not including energy required for purification and gas handling.<sup>24</sup>

Chained together, reactions (2), (13), and the electrolysis of water to hydrogen and oxygen produce acetylene by the net reaction:



which produces oxygen and acetylene in a ratio O:F of 2.46. This is slightly on the oxygen-rich side of the maximum specific impulse mixture ratio. Thus, if this chain of reactions is used, no additional oxygen production is required.

Figure 2 (from Ref. 35) shows the specific impulse produced by a liquid acetylene/liquid oxygen rocket engine calculated as a function of the oxygen/fuel mixture ratio for various rocket engine area ratios (AR) using a one-dimensional equilibrium computer code.<sup>36</sup> For the highest performance case, at an expansion ratio of 500, peak  $I_{sp}$  is 425 sec. at a mixture ratio (oxygen:acetylene by mass) of 2.25. Used as a monopropellant, the specific impulse of acetylene is about 350 sec.. In some applications the simplicity of a monopropellant system may justify a lower  $I_{sp}$ . The high combustion temperature of the oxygen-acetylene flame may require development of rocket engine technology.

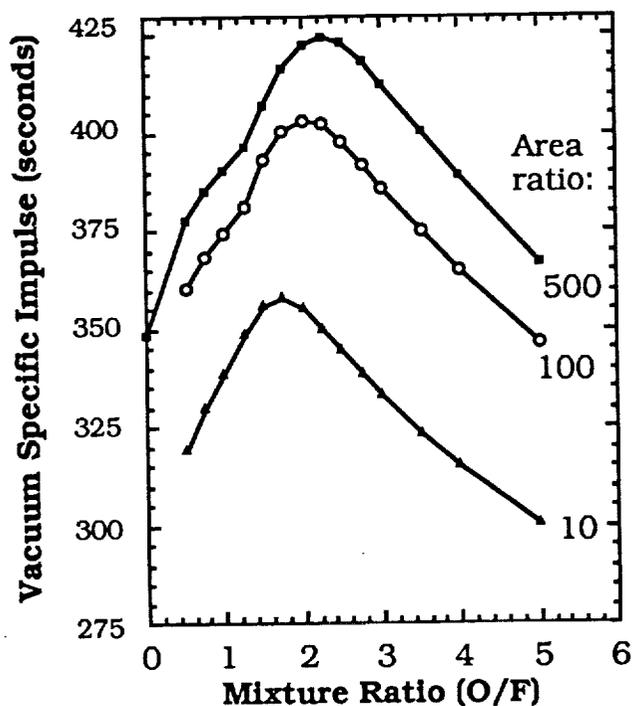


Figure 2. Calculated vacuum specific impulse as a function of the oxygen:fuel mixture ratio for nozzle area ratios of 10, 100, and 500 at a chamber pressure of 3000 psia.

Higher leverage can be achieved by adding an additional component into the fuel mixture. One attractive possibility is carbon monoxide, CO. CO is formed as a byproduct of the reactions used to produce acetylene, so no additional chemical process would be necessary. An equal-mass mixture of acetylene and CO would produce a theoretical specific impulse of about 380 sec. This represents a slight penalty in  $I_{sp}$  over the ~415 sec. of acetylene/oxygen alone, but the mixture has only half the requirement for hydrogen brought from Earth and

a 200° reduction in flame temperature, comparable to that of an acetylene/oxygen engine.

With such high leverage of hydrogen, it becomes possible to consider use of Mars sources of hydrogen, as discussed earlier. The oxygen produced would be sufficient to eliminate the need for reaction (1) above, assuming a stoichiometric fuel ratio. In this case, no reactants need be brought from Earth at all for fuel production on Mars.

#### Effect on Mission Mass

One figure of merit for savings is initial mass in low Earth orbit, IMLEO. Clearly, mission mass savings will depend on the details of the mission architecture, including such details as use of aerobraking and aerodynamic decelerators, whether a Venus swingby is used, whether a habitat is placed in high or low Mars orbit, etc.

Under the most optimistic assumptions, assuming aerobraking at Mars and Earth arrival at no cost in added mass, an  $I_{sp}$  of 450 sec. (LH<sub>2</sub>/LOX), and no allowances for fuel tank mass and engines, every ton of mass injected from Mars to Earth requires 2.6 tons of fuel on Mars. Shipping this fuel to Mars would require an additional 4.3 tons of fuel in LEO. Manufacturing return fuel on Mars will thus reduce the IMLEO by nearly a factor of seven. More pessimistic assumptions adding weight for tanks, aerobrake mass, etc. will increase the advantage of Mars-manufactured propellant even further. Lower values of  $I_{sp}$ , as would be required for space-storable propellants, will also increase this factor, while habitats or vehicle mass left in Mars orbit or left behind on the surface will decrease the factor. In any case, however, manufacturing fuel from in-situ resources on Mars results in large savings in IMLEO.

#### CONCLUSIONS

Relatively simple and well-understood chemical reactions can be used to produce hydrocarbon rocket fuels on Mars from hydrogen. Use of such a process allows an amount of fuel to be produced on Mars which is nearly 100 times the mass of hydrogen brought from Earth. If such a process produces the return propellant for a manned Mars mission the required mission mass in LEO is reduced significantly over a system using all Earth-derived propellants. A further decrease in the requirement for Earth-derived hydrogen is found if the carbon monoxide produced as a by-product of acetylene production is also used as a fuel component. Propellant brought from Earth could be entirely eliminated if a convenient source of hydrogen on Mars such as atmospheric water could be used. Even the simplest processing sequence, manufacturing oxygen, would reduce fuel requirements on Mars by a factor of four if CH<sub>4</sub> propellant is brought entirely from Earth.

If only one single idea is to be emphasized, it is that the carbon dioxide atmosphere of Mars is a significant, abundant resource for manufacturing critical materials on Mars. There are many possible chemical sequences to utilize the CO<sub>2</sub> and reduced by-products CO

and carbon. The processes discussed for making hydrocarbons and alcohols from CO<sub>2</sub> and reducing metal oxides with CO and carbon are thermodynamically feasible but may not be practical. There are likely to be other sequences that are more useful. The applicability of several of these to a Mars processing facility can be found in a recent review by Zubrin.<sup>20</sup>

At this stage in the definition of manned Mars missions, it is important to explore the full range of the known chemistries of simple carbon compounds. A more thorough exploitation of easy-to-obtain resources will enhance the potential for *in situ* resource utilization. Further progress in simplifying *in situ* manufacturing technology will provide for lighter, less-expensive missions and increase the likelihood of manned planetary exploration in our lifetime.

## REFERENCES

- [1] Meyer, T.R. and McKay, C.P., *J. Brit. Interplan. Soc.* **42**, 147 (1989).
- [2] Oro, J. and Holzer, G., "The effects of ultraviolet light on the degradation of organic compounds - A possible explanation for the absence of organic matter on Mars", in *Life Sciences and Space Research XVII: Proceedings of the Open Meeting of the Working Group on Space Biology*, Pergamon Press: Oxford, U.K., 1979, pg. 77.
- [3] Jakosky, B.M. and Haberle, R.M., *J. Geophys. Res.* **95**, 1359 (1990).
- [4] Ash, R.L., Dowler, W.L. and Varsi, G., *Acta Astronautica* **5**, 705 (1978).
- [5] Richter, R., "Basic Investigation into the Production of Oxygen in a Solid Electrolyte Process", in *AIAA 16th Thermophysics Conference*, Palo Alto, CA, AIAA Paper 81-1175, June 1981.
- [6] Johnson, S.W. and Leonard, R.S., "Manned Mars Missions and Extra-terrestrial Resource Engineering Test and Evaluation," AAS Paper 87-263, in *The Case for Mars III: Strategies for Exploration - Technical*, Univelt, Inc.: San Diego, CA, 1989, pg. 455.
- [7] Ash, R.L.; Werne, J.A., and Haywood, M.B., "Design of a Mars Oxygen Processor", AAS Paper 87-263, in *The Case for Mars III: Strategies for Exploration - Technical*, Univelt, Inc.: San Diego, CA, 1989, pg. 479.
- [8] Galecki, D.L., "In-Situ Propellant Advantages for Fast Transfer to Mars," in *AIAA/ASME/SAE/ASEE 24th Joint Propulsion Conference*, Boston, MA, AIAA Paper 88-2901, July 1988.
- [9] Frisbee, R.H., "Mass and Power Estimates for Mars In-Situ Propellant Production Systems," AIAA Paper 87-1900, June 1987.
- [10] Duke, M.B., "Mars Resources," *Manned Mars Missions, Working Group Papers*, Vol. 2, NASA M-002, June 1986.
- [11] Kaplan, D., *Environment of Mars 1988*, NASA Technical Memorandum 100470, Johnson Space Center, 1988.
- [12] Jones, D., "Isentropic Processing for In-Situ Propellant Production on Mars, *Case for Mars Conference IV*, Boulder, CO, June 1990.
- [13] Meyer, T.R., Brown, L., and Tarantino, J., "Atmospheric Water on Mars: Energy Extraction Estimates", *Case for Mars Conference IV*, Boulder, CO, June 1990.
- [14] Ratliff, K. S. and Kubiak, C. P., *Organometallics*, in press.
- [15] Darensbourg, D.J. and Kudaroski, R.A., *Adv. Organomet. Chem.* **22**, 129 (1983).
- [16] Appelbaum, J. and Flood, D.J., "Solar Radiation on Mars, Update 1990," NASA Technical Memorandum 103623, Oct. 1990.
- [17] Hepp, A.F., Landis, G.A., and Kubiak, C.P., "Chemical Approaches to Carbon Dioxide Utilization for Manned Mars Missions", in *Resources of Near-Earth Space*, University of Arizona Press: Tuscon, AZ, in press; also, NASA Technical Memorandum 103728, January, 1991.
- [18] "Solar Constant and Air Mass Zero Solar Spectral Irradiance Tables," ASTM Standard E490-73a (Reapproved 1981), ASTM: Philadelphia, PA, 1985, pg. 428.
- [19] Zubrin, R. and Baker, D., "Humans to Mars in 1999," *Case for Mars Conference IV*, Boulder, CO, June 1990; also Baker, D., and Zubrin, R., *J. Brit. Interplanetary. Soc.* **43**, 519 (1990).
- [20] Zubrin, R.M., Baker, D.A., and Gwynne, O., "Mars Direct: A Simple, Robust, and Cost-Effective Architecture for the Space Exploration initiative," AIAA Paper 91-0326, 29th Aerospace Sciences Meeting, Reno, Nevada, Jan. 1991.
- [21] Clapp, W.M. and Scardera, M.P., "Applications of In-Situ Carbon Monoxide-Oxygen Propellant Production at Mars," AAS Paper 87-212, in *The Case for Mars III: Strategies for Exploration - Technical*, Univelt, Inc.: San Diego, CA, 1989.

[22] Sneed, R.P.A., in *Comprehensive Organometallic Chemistry*, Vol. 8, Chapter 50.1, Pergamon Press: Oxford, U.K., 1982, pp. 1 - 100.

[23] Duncan, D.A., Detz, C.M., and Sargent, H.B., "Acetylene," in *Kirk-Othmer Encyclopedia of Chemical Technology, Third Edition, Volume 1*, John Wiley and Sons, New York, 1973, pp. 192-237.

[24] Copenhaver, J.W., and Bigelow, M.H., *Acetylene and Carbon Monoxide Chemistry*, Reinhold Publishing, New York, 1949, pp. 1-6.

[25] Morrison, R.T. and Boyd, R.N., *Organic Chemistry, Third Edition*, Allyn and Baker, Inc.: Boston, MA, 1973, pg. 252.

[26] F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry, Fifth Edition*, John Wiley and Sons: New York, 1988.

[27] U.S. Patent 4,299,619, issued 1981.

[28] Hughes, R., Kam, E.K.T., and Magadam-Zadeh, H., *Thermochimica Acta* 59, 361 (1982).

[29] Japanese Patent 62 72,113, issued 1985.

[30] Martin, L.R. and Webb, H.M., "Transportable Fuels Via A Carbon Resource Recovery Technique," in *AIAA/ASERC Conference on Solar Energy: Technology Status*, Phoenix, AZ, AIAA Paper 78-1780, November 1978.

[31] Bogdanovic, B., Ritter, A. and Spliethoff, B., *Angew. Chem. Int. Ed. Engl.* 29, 223 (1990).

[32] T-Raissi, A., Slattery, D.K., Zidan, R. and Axelrod, M.J., "Hydrogen Storage Research at Florida Solar Energy Center", preprint.

[33] Shriver, D.F. and Whitmire, K.H., in *Comprehensive Organometallic Chemistry*, Vol. 4, Chapter 31.1, Pergamon Press: Oxford, U.K., 1982, pp. 243 - 329.

[34] Jolly, P.W., in *Comprehensive Organometallic Chemistry*, Vol. 6, Chapter 37.2, Pergamon Press: Oxford, U.K., 1982, pp. 3 - 36.

[35] Landis, G.A. and Linne, D.L., "Acetylene Fuel from Atmospheric CO<sub>2</sub> on Mars," *J. Spacecraft and Rockets*, in press.

[36] Gordon, S., and McBride, B.J., NASA SP-273, 1976.

1. Report No. NASA TM -104405		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle Material Processing With Hydrogen and Carbon Monoxide on Mars				5. Report Date	
				6. Performing Organization Code	
7. Author(s) Aloysius F. Hepp, Geoffrey A. Landis, and Dianne L. Linne				8. Performing Organization Report No. E -6230	
				10. Work Unit No. 506-41-11	
9. Performing Organization Name and Address National Aeronautics and Space Administration Lewis Research Center Cleveland, Ohio 44135 - 3191				11. Contract or Grant No.	
				13. Type of Report and Period Covered Technical Memorandum	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546 - 0001				14. Sponsoring Agency Code	
15. Supplementary Notes Prepared for the Tenth Biennial Conference on Space Manufacturing sponsored by the Space Studies Institute, Princeton, New Jersey, May 15-19, 1991. Aloysius F. Hepp and Dianne L. Linne, NASA Lewis Research Center. Geoffrey A. Landis, Sverdrup Technology, Inc., Lewis Research Center Group, 2001 Aerospace Parkway, Brook Park, Ohio 44142 (work funded by NASA Contract NAS3-25266). Responsible person, Aloysius F. Hepp, (216) 433-3835.					
16. Abstract This study examines several novel proposals for propellant production from carbon dioxide and monoxide and hydrogen. We also examine potential uses of CO as a fuel or as a reducing agent in metal oxide processing as obtained or further reduced to carbon. Hydrogen can be reacted with CO to produce a wide variety of hydrocarbons, alcohols, and other organic compounds. Methanol, produced by Fischer-Tropsch chemistry may be useful as a fuel; it is easy to store and handle because it is a liquid at Mars temperatures. The reduction of CO <sub>2</sub> to hydrocarbons such as methane or acetylene can be accomplished with hydrogen. Carbon monoxide and hydrogen require cryogenic temperatures for storage as liquids. Non-cryogenic storage of hydrogen may be accomplished using hydrocarbons, inorganic hydrides, or metal hydrides. Non-cryogenic storage of CO may be accomplished in the form of iron carbonyl (Fe(CO) <sub>5</sub> ) or other metal carbonyls. Low hydrogen-content fuels such as acetylene (C <sub>2</sub> H <sub>2</sub> ) may be effective propellants with low requirement for earth-derived resources. The impact on manned Mars missions of alternative propellant production and utilization is discussed.					
17. Key Words (Suggested by Author(s)) Extraterrestrial resources; Carbon dioxide; Photoelectrochemistry; Carbon monoxide; Hydro- gen; Mars; Propellants			18. Distribution Statement Unclassified - Unlimited Subject Categories 44 and 28		
19. Security Classif. (of the report) Unclassified		20. Security Classif. (of this page) Unclassified		21. No. of pages 10	22. Price* A02