A SURVEY OF RESOURCE UTILIZATION PROCESSES FOR MARS AND ITS MOONS

Robert D. Waldron Canoga Park, California

Abstract

Although information on the compositions and mineralogies of Mars or its moons is fragmentary at best compared to the moon, sufficient information is available to formulate processing options propellants and by-products for Cis-Mars applications. There are four (4) generic classes of accessible source materials: A) Mars atmosphere, B) damp soil/rock, C) Mars dry soil/rock, and D) Phobos, Deimos dry soil/rock. (The last two (2) classes are separately listed since very little is known about the compositions of the martian moons.) Class B could refer to either Mars or its moons and would constitute a viable resource if about 1% or more water content is locally recoverable. We have generated a list of 17 propellant combinations grouped into four (4) functional classes: 1) cryogenic, 2) H-Containing storables, 3) CNO storables, and 4) non-combustion storables. and identified their applicability for manufacture from 6 combinations of the four (4) resource classes listed above. Where manufacture is possible, we have identified one or more processing (synthesis) methods and will discuss available options for both propellant selection and production.

Introduction

Resource utilization studies for Mars and its moons are governed by fundamental constraints and informational deficiencies which differ markedly from those applicable to lunar materials processing. While information on elemental composition at both lunar and Mars landing sites is available, the lunar data extends over the entire range of natural elements and concentration ranges down to a few parts per billion and, in addition, the compositions can be related to mineralogical, structural, and textural features of soils and rocks. For the Mars data, significant gaps occur in light element and trace element abundance information, and geologic differentiation between soils and rocks can only be estimated with considerable uncertainty. However, enough is known about Mars and its moons to provide an outline of resource utilization opportunities for each of four (4) possible scenarios related combinations of practical to input

resources which will have to be verified by additional exploration activities.

Summary of Present Composition Knowledge

The moons of Mars (Phobos & Deimos) are superficially similar to the Moon and are characterized by a hard vacuum, absence of free volatiles and presence of a deep regolith. The low density and albedo were suggested as indicating compositions similar to carbonaceous chondritic meteorites, but recent infrared measurement give no indication of hydrated minerals in the surface layers. In all probability, even in the absence of practical quantities of recoverable water, processes designed to refine lunar silicate minerals could also be applied to Phobos or Deimos plants if suitably modified to operate at milligee gravity levels.

The composition of the Mars atmosphere is known with fairly good precision¹, and the soil and duricrust samples for the two (2) Viking Lander sites are remarkably similar.² Major and minor element concentrations are known for elements of atomic number 12 through 39. These values are given in Tables I & II. Even though light element data is absent from soil analyses, we know from atmospheric data that practical recoverable quantities of carbon, nitrogen, and oxygen are available, and on a global basis, there is a vast reservoir of hydrogen present as frozen water in the polar caps.

General Considerations

From a resource processing or refining standpoint, the local availability or lack of same of water is less important than the relative difficulty or "equivalent cost" of water recovery by various means. For example, the equivalent water content of the martian atmosphere is lower than that of lunar soil. Although the processing of atmosphere for water recovery is somewhat simpler than soil, it is likely that in the absence of simpler water production systems on Mars, one would be driven to "lunar-like" processing schemes in which water would be carefully recycled,

and viable alternatives to hydrogen containing propellants would be favored.

A striking difference between Mars and the Moon is the vast presence and diversity of actual or potential locally derived volatiles on Mars. The global inventory of atmosphere and polar caps³ on Mars are estimated to contain in excess of 10¹³ and 10¹⁶ tonnes respectively. While this is "volatile-poor" compared with earth, the resource is sufficient for any reasonable scale of commercial processing activity.

One other feature of Mars chemistry is of appreciable interest. If water proves to be readily accessible, the availability of C & N from the atmosphere in combination with H & O from soil water and S & Cl from the soil can furnish a broad range of commercial acids, bases and other common reagent or solvent materials for synthetic chemical purposes. A few of such compounds are listed in Table III.

The diversity of such locally derivable resources augmented by calcium, magnesium, ammonium, (and probably sodium) bases & salts opens up a wide vista of potential production chemistry opportunities, and furthermore, can uncouple production and reagent requirements for propellants or fuels from those of metals and other by-products.

Even if locally derivable water requires a prohibitive effort to extract, all of the above chemicals can be used if needed based on imported hydrogen. The distinction of importance then becomes that closure or efficient recycling of the hydrogen content and regeneration of all of the hydrogen containing compounds in Table III is required.

An additional convenience to processing operations is that partially or totally refined intermediates can be stored as sulfate, carbonate, chloride or nitrate salts if desired without burdening the original chemical import inventory, whereas for lunar processing, only elements, oxides or silicides are similarly useful.

Resource Accessibility

For Cis-Mars applications, there are four (4) generic classes of possible resource materials: A) Mars atmosphere, B) damp soil/rock, C) Mars dry soil/rock, and D) Phobos, Deimos dry soil/rock. (The last two (2) classes are separately listed since very little is known about the compositions of the martian moons.

In particular, Mars soil is known to contain useful quantities of sulfur and chlorine whereas Phobos or Deimos regolith <u>may</u> be more "moon-like" in composition.) Class B could refer to either Mars or its moons and would constitute a viable resource if about 1% or more water content is locally recoverable.

The resource (accessibility) classes available for Mars are then A, B, C, A+B and for Phobos/Deimos B or D.

Propellant Selection

For Cis-Mars propellant and fuel production primarily from local resources, a rational selection process should be based on a balance of factors including performance, ease of manufacture, storability, capital and power requirements, etc. The ease of manufacture in turn depends on the accessible local resource classes or scenarios.

The high specific impulse and mature rocket engine technology of H₂/O₂ systems would tend to favor this propellant system as a leading candidate for in-situ propellant production for Cis-Mars travel and Earth return requirements. This system can be useful to provide all of the propellant mass if water is recoverable by straightforward means, but even if hydrogen importation is required, in-situ production can provide from 85-90% of total propellant mass from local resources.

The preferred methods of production given reasonable accessibility of soil or rock water are water recovery by thermal methods followed by water electrolysis.

Regardless of the availability of water, there may be valid reasons to prefer alternative fuels or propellants based on storability, tankage volume, or product density, safety or other considerations. In particular, for small energy applications including vehicular use, fully storable systems may be preferred to cryogenic systems.

We have generated a list of 17 propellant combinations grouped into four (4) functional classes: 1) cryogenic, 2) H-containing storables, 3) CNO storables and 4) non-combustion storables and identified their applicability for manufacture from 6 combinations of the four (4) resource classes listed above. These are shown in Table IV.

The cryogenic class has relatively simple chemistry but requires more complex insulation and refrigeration equipment. Storable class 2 is particularly useful for propellant and fuel manufacture where local water is easily accessible, while class 3 can be produced solely from the Mars atmosphere without either soil processing or access to water.

The 4th class may be less important as a conventional rocket propellant but could play a major role in energy storage, exploration and specialty power systems.

Propellant Production Processes

The 13 combustion propellant combinations and the monopropellant H_2O_2 involve 6 chemical elements for fuel production: C, N, H, O, Si, and Al, of which the first two will probably most readily be derived from the atmosphere and the last two from martian soil. H & O will be recovered from soil moisture, if practical -- otherwise H may have to be imported and O derived from the atmosphere.

The corresponding oxidizers require only the three elements: O, N, & H, if we exclude CO₂ for propellant combination PC-8. For the oxidizers, O & H would be derived from soil moisture when available – otherwise both O & N could be extracted from the atmosphere with H imported. (Oxidizer CO₂ used for PC-8 can be supplied by simple atmospheric compression.)

Where manufacture is possible, we have identified one or more processing (synthesis) methods for all fuels, oxidizers or non-combustion systems listed. These are shown in matrix Table V. The abbreviations TI, PI, F & O indicate total or partial import, fuel or oxidizer components respectively. (* indicates applicability to martian moons only).

The complete matrix has not been exhaustively analyzed for available process chemistry -- in fact, a prior study of lunar processing options indicated more than 100 million process variations are available for separation of oxygen and major element by-products and the number is far greater for Mars.

Propellant Precursors

Fuels for the 13 combustion propellant combinations require the constituent elements listed below for the indicated number of cases: C=9, H=9, O=5, N=3, metals (Si/Al)=3. The corresponding original

resources will be CO₂, H₂O, N₂, and silicate/aluminate minerals respectively for the case of local water access.

Only 4 oxidizers or non-combustion materials are involved in the propellant combinations listed. These are: 1) O_2 , 2) NO_x , 3) H_2O_2 , and 4) CO_2 which appear in 3, 4, 6, an 2 cases respectively.

It is convenient to compile a list of precursor compounds of general utility for propellant production. Thus, carbon dioxide will generally have to be reduced for production of carbon containing fuels and elemental nitrogen requires fixation prior to incorporation in nitrogen containing fuels and oxidizers. Table VI gives a list of precursor compounds of general utility for propellant and non-propellant production processes.

The precursors selected and production methods listed are for the most part obsolete or non-competitive for production of specific materials in terrestrial practice. This is to be expected given the differences in economic factors for source supplies, transportation, energy and capital equipment between Mars and Earth.

Details of Process Chemistries

The process abbreviations given in Tables V & VI total 26 members which may be divided into 3 classes:

- I. Thermal/Mechanical (4) AC, HR, HCR, WR
- II. Single step chemical (11) CDR (1-5), CO, ER (1-4), WG
- III. Multi step chemical (11) AHS, CCS, CP, CS, CSS, CYP, FAL, HAS, NS, PS, SS

Thermal/Mechanical

Atmospheric Compression, (AC), is used to concentrate and liquefy the CO_2 fraction from the martian atmosphere. The minor constituents, Ar and N_2 can be separated by physical absorption methods.

Water Recovery, (WR), is assumed to be by heating mined martian soil. The temperatures and soil masses required will depend on whether permafrost, physically absorbed water or chemical hydrates are involved. Hydrocarbon Recovery, (HR), is only specified as a candidate process for carbonaceous chondrite analog sources at Phobos or Deimos.

The Thermal Recovery process of kerogen compounds is analogous to terrestrial shale oil recovery.

Hydrocarbon Reforming, (HCR), with or without catalysts is a thermal process class designed to produce low molecular weight hydrocarbons from higher molecular weight feedstocks and is of enormous importance in petroleum refining.

Single Step Chemical

To obtain carbon containing fuels from carbon dioxide it is necessary to reduce CO₂ either electrochemically or pyrochemically. We have listed 5 reduction processes of which 3 are electrochemical. These may be described as: CDR(1) vapor phase hydrogen reduction, CDR(2) sodium reduction, CDR(3) fused carbonate electrolysis, CDR(4) solid oxide electrolysis, and CDR(5) aqueous electrolysis. Other reduction methods are also possible. Process CDR(1) is commercially practiced in several versions as Sabatier, Bosch or in 2 or more stages as Fischer-Tropsch, water gas, and shift reactions.

Processes CDR(3) and CDR(4) are closely related to high temperature fuel cell technology. Processes CDR(2) and CDR(5) have been studied⁶ as possible routes to formic acid synthesis by indirect or direct electrolysis. End product carbon compounds can be CO, elemental carbon, hydrocarbons, alcohols, formic acid or other organic compounds, while the oxygen extracted from CO₂ usually appears as H₂O or O₂.

Elemental carbon is usually undesirable as a starting point for carbon containing fuels which do not contain nitrogen, but is extremely useful for fixation of nitrogen and to develop feedstocks for a general industrial organic chemistry. For fuels from PC's 5, 12, & 14, a convenient method of manufacturing cyano compounds is via the cyanamide process. Details will be discussed in a later section.

Combustion, (CO), is used only to provide carbon monoxide on martian moons where atmospheric CO₂ is not available as a starting material and assumes carbonaceous meteoritic composition as feedstock.

Electrochemical Redox, (ER), is a generic class of single stage processes. [Within this class we exclude those electrochemical steps previously listed as CDR (3-5)]. For propellant purposes; ER-1 or aqueous

electrolysis is primarily used for electrolyzing water⁷ to $H_2 \& O_2$.

ER-2 or magma electrolysis is primarily used to recovery oxygen from silicate rocks when easily accessible soil water is absent (as on the Moon) as well as recovery of iron and silicon from cathode deposits.

ER-3 or vapor phase electrolysis is useful for production of ozone $(O_3)^8$ from oxygen, or nitric oxide from O_2/N_2 mixtures. Nitric oxide can also be obtained from the elements by direct combination using intense heating and quenching. NO will oxidize at low temperatures to $NO_2(N_2O_4)$ in the presence of excess oxygen.

Water Generation, (WG), is used as a precursor to formation of hydrogen peroxide where soil moisture is unavailable using locally derived oxygen and imported hydrogen. The water can be made by burning hydrogen or from effluent of a H₂/O₂ fuel cell.

Multistep Chemical

It is convenient to separate the 11 members of this class into 6 sub-groups as shown below:

A.	Precursors	CP, CYP, FAL
B.	Carbon Suboxide	CSS
C.	Cyano Fuels	CCS, CS, HAS
D.	Metal Hydrides	HS,SS
E.	Nitrogen Oxides	NS
F.	Peroxide	PS

<u>Class A, Precursors</u>. The carbide process (CP), is a useful precursor for fixation of nitrogen using the cyanamide process (CYP), for generation of cyanide chemicals and ammonia, and also for production of acetylene (C_2H_2), a synthetic intermediate needed for carbon suboxide synthesis (CSS), carbonyl cyanide synthesis (CSS), and useful for production of a broad range of organic chemicals.

Calcium carbide requires lime (CaO) and elemental carbon (produced from CO₂ by CDR(3) or other means. These are heated to 2000-2200°C in an electric arc furnace giving the reaction:

$$CaO + 3C \rightarrow CaC_2 + CO$$
 (1)

The carbon monoxide can be recycled to the carbon generator.

The cyanamide process, (CYP),12 reacts calcium carbide with elemental nitrogen at 1000-1100°C to form calcium cyanamide according to the equation:

$$Ca C_2 + N_2 \rightarrow Ca CN_2 + C \tag{2}$$

Calcium cyanamide may be converted to calcium cyanide Ca(CN)₂ or hydrolyzed to CaCO₃ and NH₃ in subsequent reactions. It may also be converted to cyanamide (H₂CN₂) by carbonation in aqueous media.

Fluoroacid Leach, (FAL), is a whole soil refining process originally described for lunar materials. 13 It is useful for recovering metals and oxygen from dry silicate minerals. Where individual metals such as Al or Si are not needed, other processes such as ER(2) are probably preferable for oxygen production from dry sources.

Class B, Carbon Suboxide. The carbon suboxide synthesis, (CSS), is most readily performed by dehydration of malonic acid¹⁴ [CH₂(COOH)₂]. Malonic Acid, in turn can be synthesized by several multistep processes. Perhaps the simplest is direct reaction of potassium carbonate and carbon monoxide15:

$$K_2 \stackrel{.}{CO}_3 + CO + H_2O \rightarrow CH_2(COO)_2 K_2 + 2CO_2$$
(3)

Acidification then yields the free acid.

Class C, Cyano-Fuels. Hydrocyanic acid synthesis, (HAS), can be accomplished in a two-step process, starting with calcium cyanamide. By adding NaCl to the product mix from the cyanamide process and heating and quenching, CaCN2 is converted to calcium cyanide¹⁶ according to the following equation:

$$Ca CN_2 + C \rightarrow Ca(CN)_2 \tag{4}$$

The output product is known as black cyanide and contains some excess carbon.

In the second step, the calcium cyanide is acidified with mineral acid and HCN removed by distillation.

Cyanogen synthesis, (CS),17 can be achieved by mild oxidation of HCN or electrolysis of cyanide solutions at the anode.

Carbonyl cyanide [CO(CN)₂] can be synthesized by mild oxidation of tetracyanoethylene

TCNE, in turn, can be synthesized from dibromo malononitrile by reacting with copper. Malononitrile can be made by successive dehydration of ammonium malonate → malonamide or by direct synthesis. The overall synthesis follows the sequence described below:18

$$CH_2(COOH)_2 + 2NH_3 \rightarrow CH_2(COONH_4)_2$$
 (5)

$$CH_2(COONH_4)_2 \rightarrow CH_2(CN)_2 + 4H_2O \tag{6}$$

$$CH_2(CN)_2 + 2Br_2 \rightarrow CBr_2(CN)_2 + 2HBr \tag{7}$$

$$2CBr_2(CN)_2 + 2Cu \rightarrow$$

$$(CN)_2$$
-C=C- $(CN)_2$ [TCNE] + 2CuBr₂ (8)

$$[TCNE]+H_2O_2 \rightarrow (CN)_2-C-C-(CN)_2[TCNEO]+H_2O(9)$$

$$[TCNEO] + (CH_3)_2 - S \rightarrow CO(CN)_2 + (CH_3)_2 - S - C - (CN)_2$$
(10)

Regeneration of reagents can be performed by conventional means.

Class D, Metal Hydride Synthesis. The metal hydrides AlH₃ and SiH₄ can be synthesized by several routes. Aluminum hydride is a polymeric material which could be useful for hybrid rocket applications. It can be most readily formed by treating aluminum trihalides [AlX₃] (where X=Cl or F) with sodium hydride [NaH]. [NaH] can be synthesized by direct combination of the elements. ¹⁹ An overall sequence may be written as:

$$2NaCl^{Electrolysis} \rightarrow 2Na + Cl_2 \tag{11}$$

$$Cl_2 + H_2 \rightarrow 2HCl$$
 (12)

$$Al(OH)_3 + 3HCl \rightarrow AlCl_3 + 3H_2O \tag{13}$$

$$2Na + H_2 \rightarrow 2NaH \tag{14}$$

$$AlCl_3 + 3NaH \rightarrow AlH_3 + 3NaCl \tag{15}$$

$$AlCl_3 + 3NaH \rightarrow AlH_3 + 3NaCl$$

$$3H_2O^{Electrolysis} \rightarrow 3H_2 + \frac{3}{2}O_2$$
(15)

The overall materials balance may be written: (From mineral)

$$Al_2O_3 + 3H_2O \rightarrow 2AlH_3 + 3O_2$$
 (17)

Silanes may be synthesized by a similar route, or alternatively from reduced silicon compounds or intermetallics²⁰ (Si, SiO, SiF₂, or Mg₂Si).

For the first case, we have:

$$SiX_4 + 4NaH \rightarrow SiH_4 + 4NaX$$
 (18)

SiF₄ is directly recoverable from lunar soils treated with HF and the fluoroacid leach process describes reagent regeneration. Acid hydrolysis of SiO or SiF₂ gives partial yields of silanes as:

$$4SiO + 8HX \rightarrow SiH_4 + Si(OH)_4 + 2SiX_4 \tag{19}$$

$$4SiF_2 + 4H_2O \rightarrow SiH_4 + Si(OH)_4 + 2SiX_4$$
 (20)

$$Mg_2Si + 4HX \rightarrow SiH_4 + 2MgX_2$$
 (21)

Class E, Nitrogen Oxide Synthesis. Nitric oxide, (NO), can be made directly from the elements by vapor phase electrolysis or alternatively by heat and quench methods as previously described (e.g. ER-3). NO may be oxidized to NO₂(=N₂O₄) by addition of oxygen at ambient temperatures.

Nitrous oxide, (N₂O), is an alternative oxidizer and is most frequently made by pyrolysis of ammonium nitrate (NH₄NO₃). NH₄NO₃, in turn can be made from ammonia and nitric acid or by oxidation of ammonia using ozone²² according to the equation:

$$6NH_3 + 4O_3 \rightarrow 3NH_4NO_3 + 3H_2O$$
 (22)

The pyrolysis may be written:

$$NH_4NO_3 \rightarrow N_2O + 2H_2O \tag{23}$$

Class F, Peroxide Synthesis. Hydrogen peroxide may be synthesized indirectly from H₂ & O₂ using an anthroquinone method, or by electrolysis of sulfate solutions.²³ The latter appears more useful for Mars production since production of H₂ & O₂ for the former method will also generally require water electrolysis.

We may describe the persulfate electrolysis by the following equations: ^{24, 25}

$$2NH_4HSO_4^{Electrolysis} \rightarrow (NH_4)_2 S_2O_8 + H_2$$
 (24)

$$S_2O_8^- + 2H_2O \rightarrow H_2O_2 + 2HSO_4^-$$
 (25)

Propellant Properties

The physical and thermochemical properties of the propellant compounds are listed in Table VII. The maximum thermal range for liquid storage (under pressure) is between the melting and critical temperatures. Mars storable fluids may be taken as

fluids whose critical temperatures are above -25° C. Storage of compounds with higher melting points (e.g. HCN, HCOOH, N₂O₄, H₂O₂, etc.) as liquids may require supplemental heating in insulated tanks.

Some of the unsaturated storable fuels may be subject to gradual polymerization, but stabilization is usually possible.

Compounds with positive heats of formation provide high combustion energies as fuels but are inherently unstable and must be stored with suitable precautions.

Summary

The resources available at Mars and its moons appear to be sufficient to support a broad range of industrial chemical operations. Large scale operations requiring water will probably be confined to geographic locations where water is readily accessible. Limited water requirements at other locations will probably be met by water importation as for terrestrial desert sites.

A diversity of propellants and fuels will gradually evolve which will be optimized for a diverse range of applications.

Surface exploration (transportation) and base and outpost energy storage would favor widespread use of liquid carbon dioxide obtainable by atmospheric compression and removal of minor elements (Ar, N₂). Thus, CO₂ can be heated and expanded to obtain shaft power or reaction (rocket propulsion). Although the specific impulse is quite low, it can be used for suborbital trajectories to avoid surface vehicular problems from difficult terrain.

One can foresee a network of storable fuel stations to permit exploration vehicles to traverse large distances without carrying all of their energy supplies. Alternatively, systems of both exploration and energy service vehicles, the latter equipped with high rate power, compression and liquefaction equipment, could move from base to base to maintain necessary inventories to support the desired exploration programs.

TABLE I

COMPOSITION OF MARTIAN SURFACE MATERIALS

	CHRYSE FINES	CHRYSE DURICRUST	CHRYSE DURICRUST	UTOPIA FINES	ESTIMATED ABSOLUTE ERRORS
SIO ₂	44.7	44.5	43.9	42.8	5.3
Al_2O_3	5.7	n/a	5.5	n/a	1.7
Fe ₂ O ₃	18.2	18.0	18.7	20.3	2.9
MgO	8.3	n/a	8.6	n/a	4.1
CaO	5.6	5.3	5.6	5.0	1.1
K ₂ O	< 0.3	< 0.3	<0.3	< 0.3	
TiO ₂	0.9	0.9	0.9	1.0	0.3
SO ₃	7.7	9.5	9.5	6.5	1.2
Cl	0.7	0.8	0.9	0.6	0.3
SUM	91.8	n/a	93.6	n/a	

TABLE II

COMPOSITION OF ATMOSPHERE AT MARTIAN SURFACE

CONSTITUENT	VOLUME FRACTION		
Carbon dioxide	95.32%		
Nitrogen	2.7%		
Argon	1.6%		
Oxygen	0.13%		
Carbon monoxide	0.07%		
Water vapor	.03%		
Neon	2.5 ppm		
Krypton	0.3 ppm		
Xenon	0.08 ppm		
Ozone	0.03 ppm		

Table VI
PROPELLANT PRECURSOR COMPOUNDS

Compound	Source	Reference
Carbon Precursors		
CO	CDR 1,5	5,6
C	CDR 2,3	24
НСООН	CDR 5	6
CaC,	CP	11
Nitrogen Precursors		
CaCN ₂	CYP	See Text
HCN 2	HAS	See Text
NH,	FE or hydrol. CaCN,	See Text
NO,	FE or ER 3	See Text
Hydrogen/Oxygen Precursors		
H ₂ O	WR	
H_2 O_2	WR,ER 1	7
O_2^2	WR,ER 1	7
NaH	FE	19
Silicon Precursors	. 37:0	
SiX ₄	FAL	13
SiF ₂	FAL	13
Mg ₂ Si	FE	7-7
FeSi	FE or ER 2	
Aluminum Precursors		
AlX ₃	FAL	13

FE = From Elements, CP = Carbide Process, CYP = Cyanamide Process

TABLE III

INDUSTRIAL CHEMISTRY ON MARS (COMMON REAGENTS DERIVABLE FROM LOCAL SOURCES)

Ino	rganic					
	Acids	Bases	Oxidizers	Reductants	Solvents/Misc.	
					H ₂ O	
	H_2S	NH_3	O_2	H_2	SO_2	
	H_2SO_3	NH ₂ OH	O_3	N_2H_4	SOCl ₂	
	H ₂ SO ₄	N_2H_4	H_2O_2	SO_2	SOCl ₂	
	HNO_3	(NH4)2CO3	HOC1	H_2S	NH_3	
	HC1	CaO	HClO ₄		CO_2	
	HOCI		ClO ₂			
	HClO ₄		ClNH ₂			
	CO_2		NCl ₃			

 NO_2

NH₄ClO₄ NO₂ClO₄

Organic

H₃PO₄* HF**

HCOOH	R-NH ₂	R-NO ₂	CH ₂ O	C_nH_{2n+2}	Hydrocarbons
CH ₃ COOH	Pyridine	$C(NO_2)_4$	HCOOH	CH ₃ OH	Alcohols
HCN	Aniline			$(CH_3)_2O$	Ethers, Ketones
CCl₃COOH	etc.			CH ₂ Cl ₂	Chlorocarbons
C ₆ H ₅ SO ₃ H				CHCl ₃	Esters
$(COOH)_2$				CCl ₄	Sulfocompounds
				CS_2	
				(CH ₃) ₂ SO	*
				(CH3)2SO2	

Salts Ca, Mg, Al, Fe, NH₄, Na, K - Salts of above acids.

- * (Probably)
- ** (Possibly)

Table IV
CIS-MARS IN-SITU PROPELLANT OPTIONS

	Resource Class						
Propellant Combination	A	В	A + B	С	A + C	D	
	Atmosphere	Damp Soil/ Rock	Soil/ Dry Soil/ Rock (Mars)			Dry Soil/ Rock (Ph/D)	
Cryogenic							
1. H ₂ O ₂	TIF	X	X	TIF	TIF	TIF	
2. CH ₄ /O ₂	PIF	*	x	LIF.	PIF	PIF	
3. CO/O ₂	X	*	x		X	*	
4. Other	^		^		^		
H-Containing Storables							
5. HCN/NO _x	PIF		X		PIF		
6. SiH ₄ /H ₂ O ₂	TIF,PIO	X	X	PIF,PIO	PIF,PIO	PIF,PIO	
7. AIH ₃ /H ₂ O ₂	TIF,PIO	X	X	PIF,PIO	PIF,PIO	PIF,PIO	
8. SiH ₄ /CO ₂	TIF	*	X		PIF	100 C	
9. C ₃ H ₈ /H ₂ O ₂	PIF,PIO	*	X		PIF,PIO		
10.CH ₃ OH/H ₂ O ₂	PIF,PIO	*	X		PIF,PIO		
11.HCOOH/H2O2	PIF,PIO	*	X		PIF,PIO		
C,N,O Storables							
12. (CN) ₂ /NO _x	X		X		X		
13.C ₃ O ₂ /NO _x	X		X		X X		
14.CO(CN)2/NOx xzzZ	X		X		X		
15. Other							
Non-Combustion Storables							
16. CO ₂	X	*	X		X	*	
17. H ₂ O ₂	PI	X	X	PI	PI	PI	

PI,TI = partial, total import F,O = fuel, oxidizer * = available sole resource for carbonaceous soils

TABLE V

PROCESS CHEMISTRY MATRIX

	Resource Class							
Propellent Combinations	A. Atmosphere	B. Damp Soil/Rock	A + B	C. DrySoil/ Rock [Mars]	A+C	D. Dry Soil/ Rock [Ph/l		
1. H ₂ /O ₂	CDR(3,4)or(ImH)CDR(1)	WR,ER(1)	(B)	FAL,ER(2)	(A) or (C)	(C)		
2. CH ₄ /O ₂	+ ER(1) (ImH) CDR(1)+ER(1)	*WR,HCR,HR ER(1)						
3. CO/O ₂	CDR(4) or CDR(3)+CO or CDR(2)+CO+ER(4)	*WR,HCR,CO, ER(1)						
5. HCN/N ₂ O,N ₂ O ₄	(ImH)+ER(3),HAS, NS		WR,ER(1)+ ER(3),HAS, NS					
6.SiH ₄ /H ₂ O ₂	(ImSiH ₄),H)+CDR(1),PS	WR,ER(1),PS+ FAL,ER(2),SS	(B)	(ImH),FAL,ER (2),SS,+WG,PS	(C)	(C)		
7.AIH ₃ /H ₂ O ₂	(ImAIH ₃ /H ₂)+CDR(1),PS	WR,ER(1),PS+ FAL,AHS	(B)	(ImH)FAL,AHS, +WG,PS	(C)	(C)		
8. SiH ₄ /CO ₂	(ImSiH ₄),AC	*WR,ER(1), FAL/ER(2),SSH CR,CO	WR,ER(1)+ FAL/ER (2),SS,AC		(ImH)FAL/ER (2)SS,AC			
9. C ₃ H ₈ /H ₂ O ₂	(ImC ₃ H ₈ ,H ₂)+CDR(1),PS	*WR,ER(1),PS+ HCR,HR	(2),00,110		(ImH)CDR(1), ER(1),HR+ WG,PS			
10.CH ₃ OH/H ₂ O ₂	(ImH)CDR(1)or CDR(5)ER(1),PS	*WR,HCR,CO, ER(1)			(A)			
11.HCOOH/H ₂ O ₂	(ImH)CDR(5),ER(1)PS	*WR,HCR,CO, CDR(5)			(A)			
12. (CN) ₂ /N ₂ O,N ₂ O ₄	ER(3),CS,NS		(A)		(A)			
13. C ₃ O ₂ /N ₂ O ₁ N ₂ O ₄	ER(3),CSS,NS		(A)		(A)			
14CO(CN) ₂ /N ₂ O,N ₂ O ₄	ER(3),CCS,NS	Control of the Contro	(A)		(A)			
16. CO ₂	AC	*HCR,CO	(A)		(A)			
17.H ₂ O ₂	(ImH)+CDR(1),PS	WR,ER(1),PS	(B)	(ImH)FAL/ER (2),WG,PS	(A)	(C)		

Legend: AC = Atmospheric compression

AHS= Aluminum hydride synthesis

CCS = Carbonyl cyanide synthesis

CDR = Carbon dioxide reduction

CO = Combustion

CS = Cyanogen synthesis

CSS = Carbon suboxide synthesis

ER = Electrochemical redox

FAL = Fluoroacid leach

HAS = Hydrocyanic acid synthesis

HCR = Hydrocarbon recovery

HR = Hydrocarbon reforming

NS = Nitrogen oxide synthesis

PS = Peroxide synthesis

SS = Silane synthesis

WG = Water generation

WR = Water recovery

Im = Import

* = Martian moons only

Table VII

PHYSICAL AND THERMOCHEMICAL PROPERTIES

Compound	MP (TP)	BP	CP	Density (liq.)	ΔHf°
	°C	°C	°C	g/cm ³	KJ/mole
CH	-182	-164	-82.6	.466 (@ BP)	-74.8 (v)
co	-199	-191.5	-140	.793	-110.4 (v)
HCN	-13.3	25.7	183.5	.688	+108.9 (1)
SiH ₄	-185	-111.8	-3.5	.68	+32.6 (v)
AlH ₃	(polymeric)				-46 (s)
C ₃ H ₈	-189.7	-42.1	98.6	.585	-103.8 (v)
CH₃OH	-93.9	65.1	240	.791	-238.31 (v)
НСООН	8.4	100.7	d.	1.22	-424.7 (I)
(CN) ₂	-27.9	-21.2	127	.954 (@ BP)	+308.9 (v)
C ₃ O ₂	-107	6.8	d.	1.114	-117.3 (I)
CO(CN) ₂	-36	65.5		1.124	
CO ₂	-56.6	-78.6(Subl)	31	1.178	-393.5 (v)
N ₂ O	(-90.8)	-88.5	36.4	.913 (0°C)	+82.05 (v)
N ₂ O ₄	-9.3	21.1	158.2	1.447	-19.6 (I)
H ₂ O ₂	4	150.2	d.	1.443	-187.78 (I)
MP,TP,BP,CP	= melting,	triple,	boiling or	critical points	resp.
ΔH _f "	= heat of formation	(@ 25"C		•	

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