Acetylene Fuel from Atmospheric CO_2 on Mars

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Introduction and Background

UTILIZATION of resources available in situ is an enabling technology for permanent human presence in space. For high ΔV return missions such as manned Mars missions using chemical rockets, most of the initial mass in low Earth orbit (IMLEO) is rocket fuel. *In situ* propellant technologies where return propellant is produced on Mars reduce the required IMLEO significantly. Thus, production of rocket propellant from available resources is an extremely high-leverage approach to reducing mission mass.

The atmosphere of Mars consists of 95% carbon dioxide.[1] As a resource on Mars, atmospheric CO_2 is 1) abundant, 2) available at all points on the surface, 3) of known presence (requires no precursor mission to verify), 4) chemically simple (requires no precursor missions to verify composition or properties), and 5) obtainable by simple compression, with no requirements for mining or beneficiation.

The present discussion derives from the Mars mission scenario proposed by Baker and Zubrin.[2] Their proposal was for 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. The processing module processes the hydrogen along with atmospheric carbon dioxide into methane and oxygen by the exothermic reaction:

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

$$2\,H_2O \rightarrow (\text{electrolysis})\, 2\,H_2 + O_2 \tag{2}$$

Additional oxygen is produced by thermal decomposition of carbon dioxide[3,4]:

$$2\,CO_2 \rightarrow O_2 + 2\,CO \tag{3}$$

The purpose of this sequence 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. Another advantage is the ease of storage of methane compared to liquid hydrogen. The detailed mission scenario described by Baker and Zubrin includes safeguards to insure that the manned crew could reach a fueled return vehicle despite any credible worst-case scenario.

Mars-Derived Acetylene/Oxygen Rocket Fuel

The present proposal extends this sequence, with the intent to maximize the total impulse of fuel produced with a minimum mass of hydrogen from Earth. Of the hydrocarbon rocket fuels, the minimum hydrogen content fuel is acetylene, C_2H_2 (H-C$\equiv$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. Figure 1 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. Assumed chamber pressure here is 3000 psia ($2\cdot 10^7$ pa); for comparison, a curve at 200 psia ($1.4\cdot 10^6$ pa) is also shown for the AR = 10 case. This latter value is typical of a pressure-fed engine. For the highest performance case, at an expansion ratio of 500, peak I_{sp} is 425 s at a weight mixture ratio (oxygen:acetylene) of 2.25. As expected, the mixture ratio is slightly on the fuel-rich side of the stoichiometric ratio of 3.07. For the AR = 500 case, the specific impulse of acetylene used as a monopropellant, 349 s, is also shown. In some applications the simplicity of a monopropellant system may justify the lower I_{sp}.

The boiling point of acetylene is about $-82\,°C$ (assuming pressure of ≥ 1.2 atm to maintain the liquid phase), making it easier to store than methane (BP = $-165\,°C$). Density is 0.62 g/cm^3, compared to methane at 0.41.

Acetylene can be produced by thermal or electric arc pyrolysis of methane at above 1250°C (Ref. 5):

$$2\,CH_4 + 184{,}000\,\text{kJ} \rightarrow C_2H_2 + 3\,H_2 \tag{4}$$

A standard production sequence for acetylene is the partial oxidation of methane, where combustion of the methane with oxygen provides the energy required for pyrolysis[5,6]:

$$6\,CH_4 + O_2 \rightarrow 2\,C_2H_2 + 2\,CO + 10\,H_2 \tag{5}$$

This is an industrial reaction sequence, with production plants with capacity over 50,000 tons/yr in operation.[5] The hydrogen can be recycled to methane and reused in reaction (1). Recycling the hydrogen produces O_2 during the electrolysis step; enough O_2 is produced so that no additional production by reaction (3) is required. Use of acetylene instead of methane decreases the requirement for hydrogen by another factor of four at no reduction in specific impulse.

While acetylene is thermodynamically unstable, explosive decomposition is not likely to be a problem. Liquid acetylene stored at low temperature requires a considerable input energy

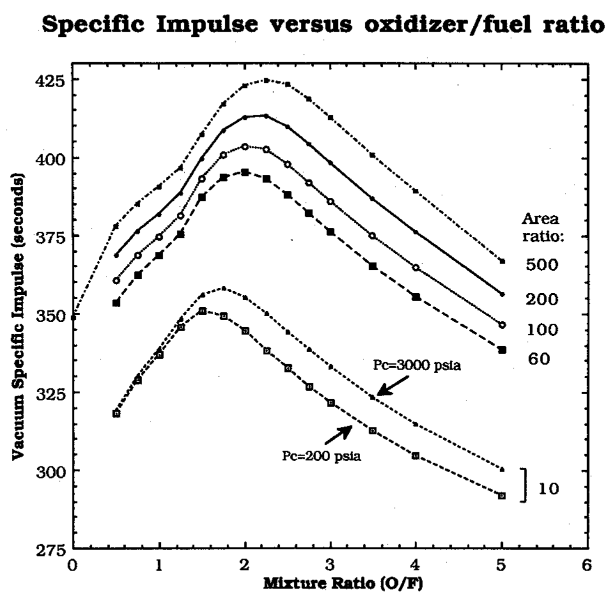

Fig. 1 Calculated vacuum specific impulse as a function of the oxygen:fuel mixture ratio for nozzle area ratios of 10, 60, 100, 200, and 500 at a chamber pressure of 3000 psia. Also shown for comparison is the area ratio 10 case with a chamber pressure of 200 psia.

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to detonate.[5] As the acetylene is heated, detonation will be inhibited by the presence of tube walls. Dilution of acetylene with carbon monoxide, discussed below, also stabilizes the material.

The high combustion temperature of the oxygen-acetylene flame will require development of rocket engine technology. An alternative possibility is to reduce the flame temperature 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. Burned with oxygen, CO produces a theoretical specific impulse of up to about 300 s, again depending somewhat on the assumed combustion.[3] Figure 2 shows the specific impulse (left, lower curve) and combustion temperature (right, upper curve) of mixtures of acetylene and carbon monoxide at $AR = 200$. An equal-mass mixture of acetylene and CO would produce a theoretical specific impulse of about 380 s. This represents a slight penalty in I_{sp} over the ~415 s of acetylene/oxygen alone, but the mixture has only half the requirement for hydrogen brought from Earth and a 200°C reduction in flame temperature, comparable to that of a methane/oxygen engine. Since optimum I_{sp} uses a fuel-rich mixture, it is still true that no additional oxygen manufacture is required. Less than 1% of the fuel mass is Earth-derived hydrogen.

Average ΔV from the surface of Mars to a Mars-Earth transfer orbit is about 5.7 km/s. At an I_{sp} of 415, a maximum of 24.5% of the rocket mass can be injected into the transfer orbit. For the CO/acetylene mixture I_{sp} of 380, this is reduced to 21.5%. (Engine and tank weight will reduce the actual payload to a fraction of these values). The reduction in mass fraction due to lower I_{sp} is more than compensated for by the decrease in requirement of Earth-derived hydrogen.

With such high leverage of hydrogen, it becomes possible to consider use of Mars sources of hydrogen. Water is believed to be present in the form of permafrost beneath the surface and in the form of water-ice in the polar caps.[7] Use of such a resource, however, would require both precursor missions to locate the resource and mining and refining equipment to dig out and purify the water. The Viking orbiter mapped the water vapor content of the Martian atmosphere,[1] and as a result we now know the atmosphere contains about 0.03% water vapor, varying considerably with location and season. This results in an amount of precipitable water between 1 and 100 μ.[7,8] Water can be precipitated out of the atmosphere by the relatively simple mechanical processes of adiabatic expansion[9] or isothermal compression.[10] Water could be produced from the atmosphere at a rate on the order of 1 kilogram per 10^6 m^3 of atmosphere processed and electrolyzed to produce the oxygen and hydrogen required.

Effect on Mission Mass

One figure of merit is the IMLEO. Clearly, mission mass 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.

A rough figure of merit can be calculated from the required orbital ΔV. Average ΔV needed to go from low Earth orbit to trans-Mars injection (Hohmann transfer) is 4.3 km/s (the actual value will depend on the mission year, since the orbit of Mars is significantly eccentric). The average return ΔV from the surface of Mars to trans-Earth injection is 5.67 km/s. The mass ratio (fueled vehicle mass over burnout mass), is exponential in the mission ΔV:

$$M_i/M_f = \exp(\Delta V/gI_{sp}) \tag{6}$$

Under the most optimistic assumptions, assuming aerobraking at Mars and Earth arrival at no cost in added mass, an I_{sp} of 450 s (LH_2/LOX), and no allowances for tank and engine mass, every kilogram injected from Mars to Earth requires 2.6 kilograms of fuel on Mars. Shipping this fuel to Mars would require an additional 4.3 kilograms 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., using lower values of I_{sp} (as would be required for space-storable propellants), or assuming propulsive braking rather than aerobraking will increase the advantage of Mars-manufactured propellant even further. It is quite clear that manufacturing fuel from in situ resources on Mars results in huge reductions in mission mass.

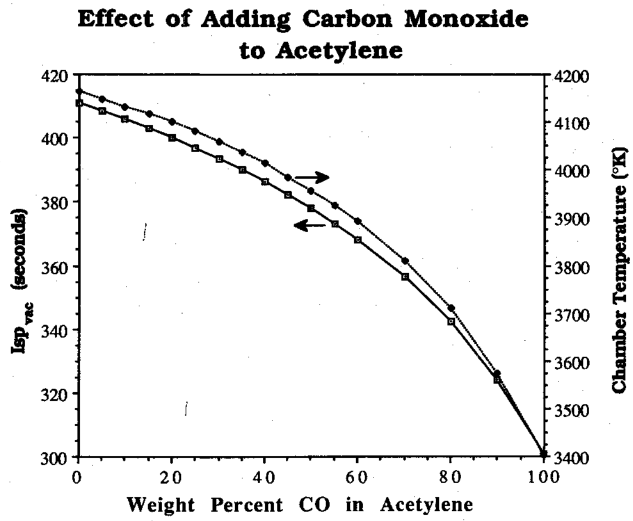

Fig. 2 Specific impulse (left; lower curve) and combustion temperature (right; upper curve) for mixtures of acetylene and carbon monoxide.

Conclusions

Relatively simple and well-understood chemical reactions can be used to produce acetylene/oxygen rocket fuel on Mars from hydrogen. Use of such a process allows an amount of fuel to be produced on Mars that 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 CO produced as a byproduct of acetylene production is also used as a fuel component. This reduces the amount of hydrogen required to be brought from Earth by roughly another factor of two.

Propellant brought from Earth can be eliminated entirely if a convenient source of hydrogen on Mars could be utilized. One possible source is atmospheric water precipitated by adiabatic expansion or by isothermal compression of the atmosphere and electrolyzed to produce usable hydrogen and oxygen.

If a single idea is to be emphasized, it is that the CO_2 atmosphere of Mars is a significant, abundant resource for manufacturing on Mars. There are many possible chemical sequences to utilize the CO_2; the processes discussed for making acetylene are only one possibility, and it may well turn out that other sequences are more useful. Even the simple processing sequence of manufacturing O_2 by thermal decomposition of CO_2 reduces propellant requirements on Mars by a factor of four even if the fuel is brought entirely from Earth.

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