

MARS *IN SITU* PROPELLANT PRODUCTION UTILIZING THE REVERSE WATER GAS SHIFT. R. Zubrin, B. Frankie, T. Kito, and T. Muscatello, Pioneer Astronautics, 445 Union Boulevard, Suite 125, Lakewood CO 80228 (Phone: 303-980-0890).

This report describes recent work accomplished on a Mars in situ propellant production project utilizing the reverse water gas shift (RWGS) reaction. This project began with a NASA Phase I SBIR in 1997 and has been continued as a Phase II program in 1998. John Connolly is the JSC program manager and Robert Zubrin is the principal investigator at Pioneer Astronautics.

During the project, Pioneer has successfully built and operated two chemical synthesis units representing the cores of machines capable of manufacturing oxidizer and a variety of fuels out of primarily indigenous Martian material. The units include a Reverse Water Gas Shift (RWGS) unit and a Methanol Synthesis (MEOH) or Fischer Tropsch (FT) unit.

The RWGS unit works in the following manner: Liquid hydrogen is transported from Earth to Mars, where it is combined with carbon dioxide acquired from the Martian atmosphere in a catalytic reactor to produce carbon monoxide and water. Water is condensed and separated from the gas phase. Unreacted feed components are compressed, recovered from the gas phase in a membrane unit separator, and recycled to the catalytic reactor. Effluent from the membrane unit ("retentate") is sent to the MEOH or FT units.

At H₂/CO₂ mixture ratios of 1:1 nearly all the hydrogen is reacted to make water, which can then be electrolyzed to produce oxygen and hydrogen, which can be recycled. Used in this way, the hydrogen brought to Mars can be recycled many times to produce an enormous amount of oxygen and CO. Alternatively, the feedstock to the RWGS can be run with an excess of hydrogen, in which case the effluent from the RWGS will contain both CO and H₂. Such a mixture is known as synthesis gas and is the ideal feedstock for making methanol, dimethyl ether, paraffins, olefins, or aromatics

The MEOH unit works in the following manner: Effluent from the RWGS unit, consisting primarily of carbon monoxide with some residual unreacted hydrogen, is combined with fresh hydrogen feed, if required, and sent to a catalytic methanol synthesis reactor. The synthesis reactor combines one carbon monoxide molecule with two hydrogen molecules to produce methanol. Production from the methanol synthesis reactor is condensed and separated from the gas phase. Unreacted feed components are separated in a second membrane separator and recycled to the RWGS reactor feed. The second membrane retentate, consisting primarily of excess carbon monoxide, is vented from the system.

The MEOH unit was designed in a generic fashion so that different varieties of catalytic reactors could be tested without changing the process configuration. In addition to the methanol synthesis reactor, Pioneer experimented with a hybrid methanol/DME reactor and a Fischer-Tropsch hydrocarbon synthesis reactor.

MARS *IN SITU* PROPELLANT PRODUCTION: R. Zubrin et al.Accomplishments to date:

Pioneer has recorded a number of significant accomplishments during the project. Highlights include:

- 1) Development, manufacture, and demonstration of a catalyst which is 100% selective for the RWGS reaction at a wide range of conditions.
- 2) Design, construction and operation of an ISPP machine including a RWGS unit and either a methanol synthesis unit or Fischer Tropsch unit.
- 3) Operation of the RWGS machine in oxygen production mode and attained mass leverages in excess of 1600.
- 4) Discovery that by altering the reactor temperature, pressure, and feed ratio, the RWGS unit could be run in combined Sabatier/RWGS mode with potential mass leverage of 20. Achieved an actual mass leverage during operation of 16.5, which compares to a 10.3 leverage for the S/E unit.
- 5) Operation of the machine in a mode to produce a combined 50/50 molar CH₄/CO ratio fuel with a stoichiometric oxygen ratio. In this mode, the system demonstrated a mass leverage of 31 with a 23 excess oxygen mass leverage.
- 6) Demonstration of production of synthesis gas (syngas) feed for methanol, dimethyl ether (DME, =CH₃OCH₃), Sabatier, or Fischer-Tropsch reactors. The quality of syngas produced was sufficient to allow a methanol/O₂ leverage of 16.3 or a Fischer-Tropsch/O₂ leverage of 22.4.
- 7) Demonstration of production of a 89% methanol/ 11% water fuel product with no other detectable contaminants.
- 8) Demonstration of conversion of 8% of the feed carbon dioxide to dimethyl ether (DME) in a one pass (no recycle) hybrid reactor.
- 9) Demonstration of conversion of at least 44% of the feed carbon dioxide to ethane or higher hydrocarbon species in a one pass Fischer-Tropsch reactor.
- 10) Demonstration of complete recovery of gaseous hydrogen in a two membrane loop system, with no gaseous hydrogen detected in the system vent.
- 11) Use of the RWGS system as a first stage of a Fischer Tropsch system incorporating a recycle loop and a combination Fe-K/ZSM5 catalyst to produce an olefin mixture predominantly composed of propylene (C₃H₈), with significant admixtures of methane, ethylene (C₂H₄), and C₄ and C₅ olefins, for an average H/C ratio of about 2.3.
- 12) Use of the RWGS system as a first stage of a Fischer Tropsch system incorporating a recycle loop and a combination Fe-K/ZSM5 catalyst to produce a liquid hydrocarbon fuel consisting predominantly of toluene (C₇H₈), with significant admixtures of benzene and xylenes, for an average H/C ratio of 1.2.

In conclusion, we find that based on the work done to date, that the RWGS offers a feasible and potentially attractive method of performing in-situ propellant production on Mars and should be researched further.