

Report on the Construction and Operation of a Mars In-Situ Propellant Production Unit

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Introduction

The following is a report on a project to build and operate a chemical synthesis unit representing the core of a machine capable of manufacturing rocket propellant primarily out of indigenous materials freely available on the surface of the planet Mars. The project, which was carried out at Martin Marietta astronautics in Denver, Colorado between October 1993 and January 1994, was funded by the New Initiatives Office of NASA's Johnson Space Center in Houston, Texas. David Kaplan was the JSC program manager, and Steve Price was the project manager at Martin Marietta.

Prior to the project reported on here, a study, also funded by the New initiatives Office of JSC, had been undertaken at Martin Marietta, to examine the benefits and feasibility of accomplishing a Mars Sample Return (MSR) mission using locally produced propellant to fuel the rocket vehicle that would return the sample to Earth. That study¹, found

that a large mission enhancement could be achieved by such means, and recommended that the propellant production process employed be one termed the "Sabatier/Electrolysis" or "SE" cycle. Using such a system, the study found that an SE unit producing 1 kg of propellant per day could be used to support an MSR mission that would return several kilograms of soil and rock sample from Mars to Earth. A single Delta 7925 launch vehicle was indicated as sufficient to support the mission, which consisted of a single spacecraft being sent directly from Earth to the Martian surface, refueling there during a year and a half surface stay, and then returning directly from the Martian surface to Earth, without any intervening Mars orbit rendezvous maneuver, or the employment of an orbiter in the mission at all. The elimination of the orbiter offers the potential to significantly reduce both the cost and risk of the sample return mission, since only one spacecraft need be developed, and only one spacecraft must operate successfully in order for the sample to be retrieved.

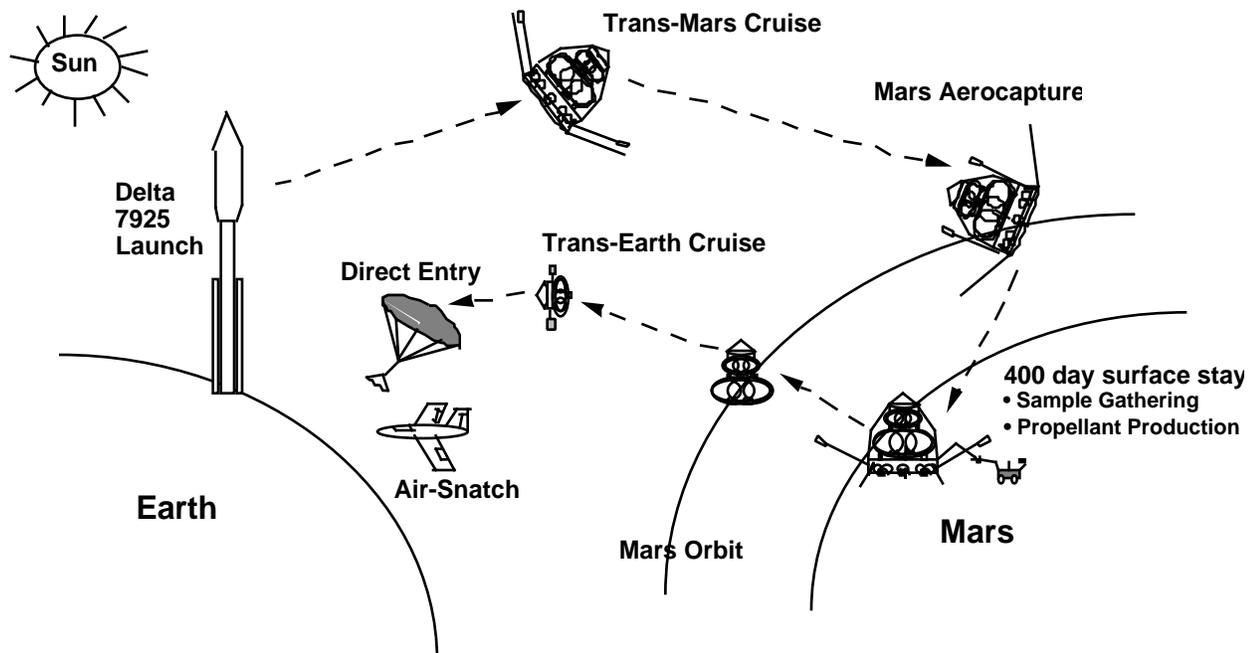


Fig. 1 The Mars sample return mission can be accomplished with a single Delta launch if the return propellant is made on the Martian surface. No orbiter is required.

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The SE cycle propellant plant employed in the mission works as follows: Hydrogen is transported from Earth to Mars where it is combined with CO₂ acquired from the Martian atmosphere in a Sabatier reactor to produce methane and water in a 1:2 molar ratio. The methane produced by this process is drawn off and liquefied, while the water is condensed and sent to an electrolysis unit to be split into hydrogen and oxygen. The oxygen produced by the electrolysis unit is liquefied, and the hydrogen is fed back into the Sabatier reactor.

It may be noted that under nominal conditions, 50% of the hydrogen needed by the Sabatier reactor is recycled from the products of water electrolysis, while the other 50% is provided by an external source.

The technology required to accomplish this cycle is well understood, and in fact has been in use on Earth for over a century. This high degree of heritage of the required component technology was the basis for the selection of the SE cycle for the MSR mission. However, despite the fact that each of the component technologies has long been used, to the best of our knowledge putting all of them in a cycle to make a complete system of the type described has never been done. The purpose of the laboratory demonstration reported on here then, was to do just that, and by so doing, demonstrate fundamental feasibility for the in-situ production propellant (ISPP) based MSR mission. In conformity with this objective, it was decided to build the ISPP unit near full scale, with a sufficient rate of propellant production to accomplish the mission described in the study report.

Design of the Demonstration System

The design of the system was done in October-November 1993, concurrent with the MSR mission design study effort. A schematic of the system is shown in fig. 2.

Hydrogen and CO₂ stored in compressed gas bottles are fed through flow meters to a set of needle valves. Using these valves to control the flow manually, the CO₂ and H₂ from these two reservoirs are then fed into the Sabatier reactor, which operates at about 0.8 bar (Denver ambient) pressure and 250 Centigrade, to form CH₄ and H₂O vapor. A small excess of H₂ is used in the input stream to assure that CO₂ is absent from the product. The Sabatier unit is brought initially to high temperature by a set of nichrome heaters driven by a manually controlled external power supply. Once the Sabatier unit is in full operation, its exothermic chemical reaction allow the heater power to be reduced or eliminated.

The CH₄ and H₂O vapor is then brought through a heat exchanger to lower its temperature, and the H₂O is then condensed out as liquid by bubbling the Sabatier exhaust gas up through the condenser bottle. The CH₄, remaining gaseous, is bled off to be vented outside the lab. A tap on the CH₄ exhaust line allows the fuel product to be grab sampled for chemical analysis. The water level in the condenser bottle can be read out by examining a transparent level gauge located on the side of the condenser bottle.

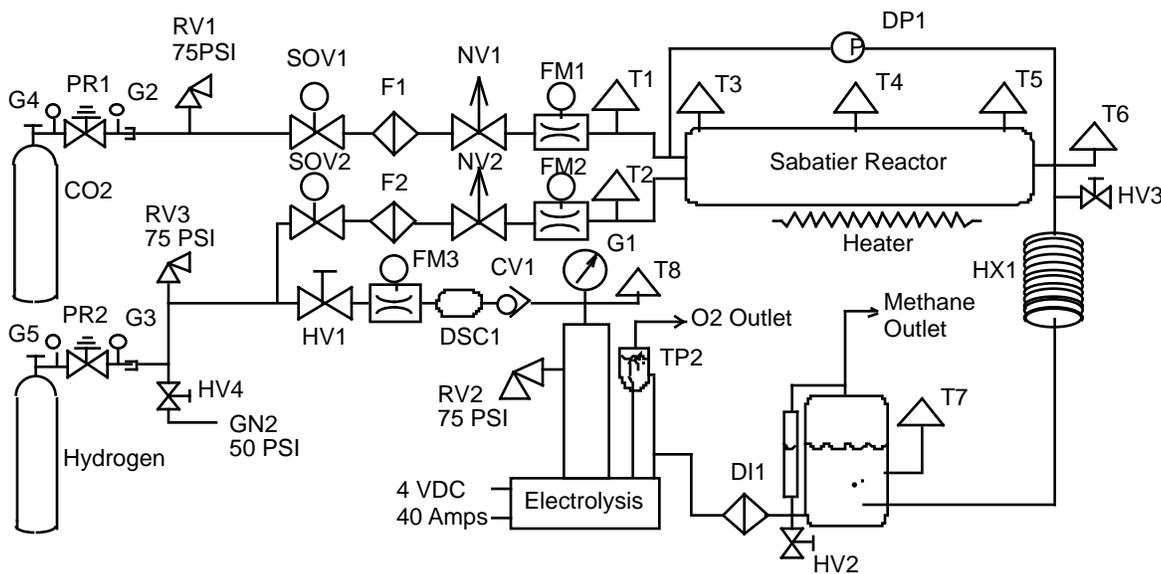


Fig. 2 Schematic diagram of Sabatier/electrolysis demonstration unit.

The Sabatier product water is flowed through a de-ionizing filter into an electrolysis unit where it is split into H₂ and O₂ gases. The electrolyser requires about 160 W, in the form of 4 V, 40 A DC power. The O₂ product is bled off to be vented, while the H₂ product is channeled back into the H₂ gas feedline for use in the Sabatier unit. A flow meter on the H₂ gas line from the electrolyser is used to measure the electrolysis unit hydrogen gas output directly. Power to the electrolyser is supplied by a rectifying power supply plugged into an AC wall socket. The amount of power supplied to the electrolyser is controlled manually.

Temperature sensors are positioned at numerous locations throughout the system, and a differential pressure sensor is located to provide pressure drop readings across the Sabatier reactor. The data from all these sensors is interfaced to a Macintosh computer located in the lab, which uses Labview software and hardware to record, graph, and otherwise display all relevant data.

Procurement of Components

At the commencement of the project, the group at Martin Marietta had in its possession a supply of commercial grade nickel Sabatier catalyst, produced by the United Catalyst Co. of Louisville, Kentucky. This material might have proved satisfactory, however a number of its characteristics raised

significant concerns. In the first place, the catalyst was such that it would not produce satisfactory reaction rates at temperatures below 350 C. Also, if the temperature of the catalyst bed were allowed to fall below 300 C, this catalyst was likely to produce highly toxic nickel carbonyl products when in contact with CO₂. This raised safety issues, as our plan was to vent the gaseous portion of the Sabatier exhaust to the environment. In discussions with vendors, it was found however, that superior ruthenium-on-alumina catalysts could be obtained. These catalysts are not generally used in the chemical industry because of their expense. However for small scale application, such as that intended in this project, ruthenium had many advantages. In the first place, its reaction rate is much faster than that of the nickel catalyst, allowing it to be used at temperatures as low as 150 C. Operating at low temperatures make possible a superior Sabatier reactor, as the equilibrium constant relating the partial pressures of product to feed gases increases by 6 orders of magnitude as temperatures are reduced from 350 to 150 C (see Fig 3), and the ratio of CH₄ to H₂ partial pressures in the exhaust increased by a factor of 30 (Fig. 4). Furthermore, the ruthenium catalyst does not form toxic carbonyl products, and thus was much better from a safety standpoint. For all these reasons, it was decided to obtain ruthenium. United Catalysts offered to obtain for us a suitable pelletized ruthenium-on-alumina catalyst from an allied company in Germany, and an order for 2 kg was placed during October 1993.

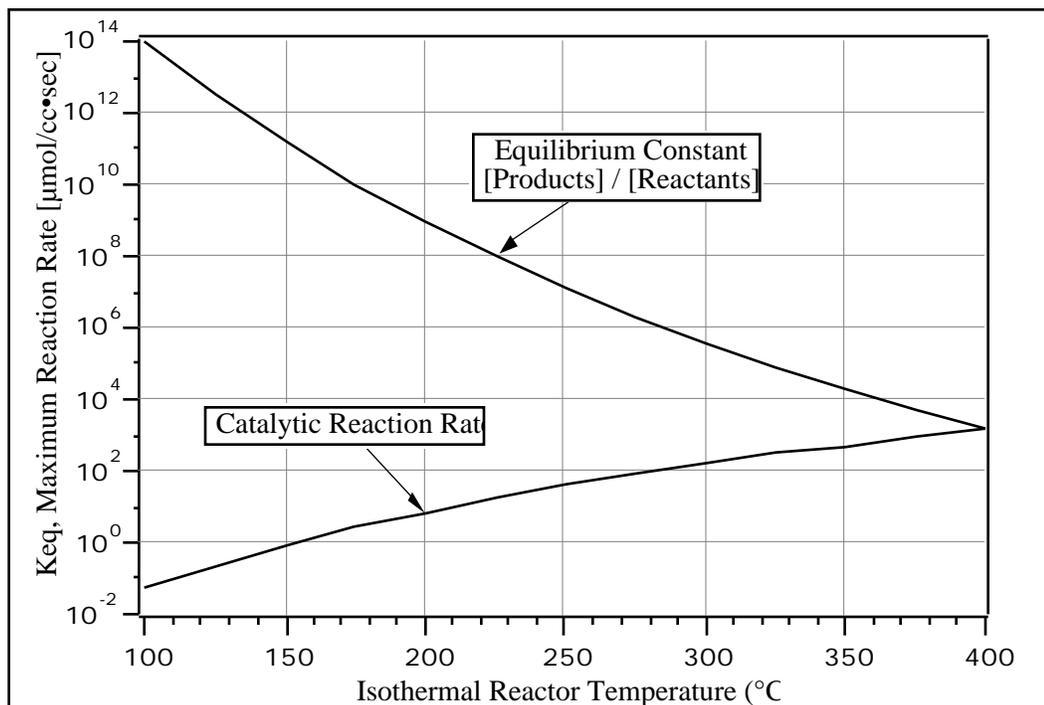


Fig. 3 Equilibrium constant and reaction rate of Sabatier reaction

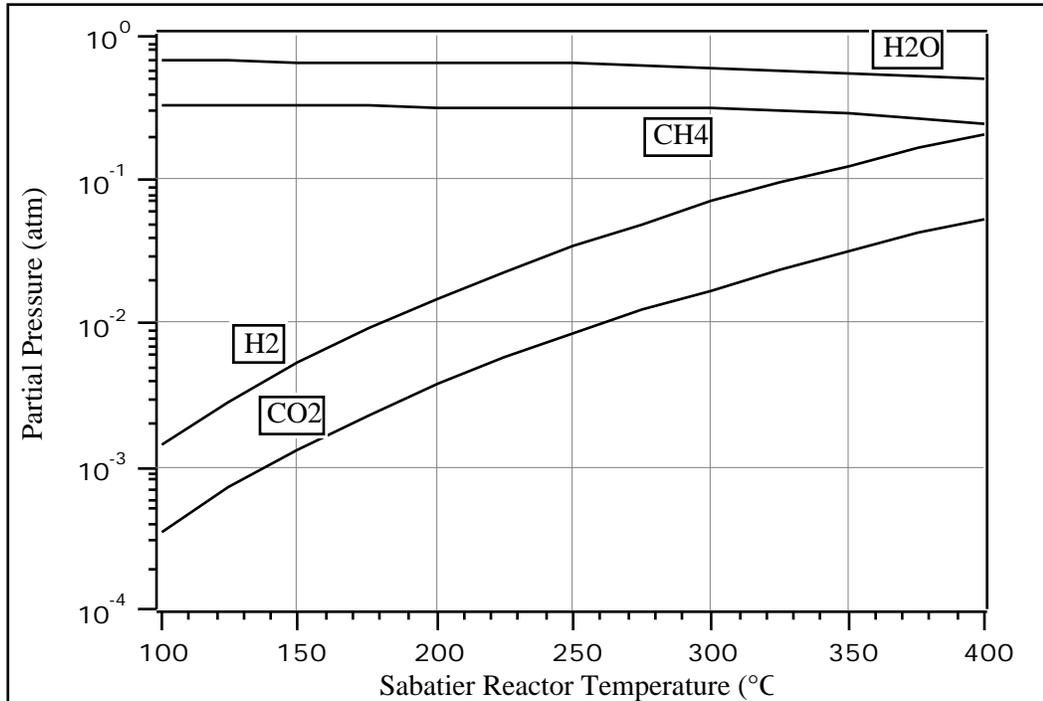


Fig. 4 Partial pressures of exhaust gases in a 1 bar Sabatier reactor

The first economical water electrolysis unit examined for use was an alkaline system manufactured by the Electrolyser Co. of Toronto, Ontario for use in producing hydrogen for weather balloons. This unit weighed about 30 kg, required a 2 V, 300 A power supply, and had a production rate capacity about 3 times that needed for our mission. An alternative solid polymer electrolyser (SPE) with a rated capacity about 70% of our nominal requirement was available as a complete turn-key system that could run off of an AC wall socket from Packard Instrument in Chicago, Illinois. This unit, used to produce high purity hydrogen for laboratory purposes, weighed about 20 kg. However, Packard informed us that the actual electrolysis device within their machine only weighed about 3 kg, and that they would be willing to sell it as a stand alone (i.e. no controls, power supply, meters, bells or whistles) for a price comparable to the Electrolyser Co. system. They also said that while rated at a hydrogen production rate of 500 cc/min (about 70% of the rate required to support the production of 1 kg of CH₄/O₂ per day), the unit probably could have its production rate run up to 700 cc/min (which would correspond to our full mission requirement). Without its externals, the Packard system would require a DC power supply of 4 V and 40 A, which was much less formidable than the power requirements of the alkaline Electrolyser system. The Packard unit was also quite compact, being basically a cylinder 2 inches in diameter and 10 inches tall. Since the light weight and small size of the Packard SPE system offered much better

correspondence to the needs of an actual MSR mission, the decision was made to order a Packard electrolyser, and the order was placed in Nov. 1993.

Three gas flow meters, rated to be accurate within 2%, were obtained from Sierra Instruments. Many other components, including the condenser, the Sabatier reactor vessel, steel piping, structural support for the assembly, solenoid valves, needle vales, pressure gauges, temperature sensors, nichrome heaters, the power supply, gas filters, water filters, gas supplies, sampling equipment, instrument control computer, and Labview software and hardware were loaned to the program from Martin Marietta's capital equipment supply.

Construction of the System

By the end of November, all necessary components were in hand and construction began. Construction took place at the Engineering Propulsion Lab at Martin Marietta, Denver, and was overseen by Larry Clark, with Steve Deden, a Martin Marietta technician, doing much of the fabrication work.

The central element which dictated the overall physical form of the system was the Sabatier reactor. Because of the limited time and money available for the project and the uncertainty of the performance, it was felt that the wisest course would be to overdesign the Sabatier reactor. An analytical model of the Sabatier reaction kinetics was

generated based upon published data for ruthenium on alumina catalyst. The reactor was therefore made three times as long as model calculations indicated would be necessary to assure complete reaction of the feedstock gasses (Fig. 5). Also complete input

gas mixing was desired. Calculations (Fig 6) indicated that a 5 cm length would be sufficient to assure such mixing using gas diffusion alone; a 15 cm mixing zone was therefore provided.

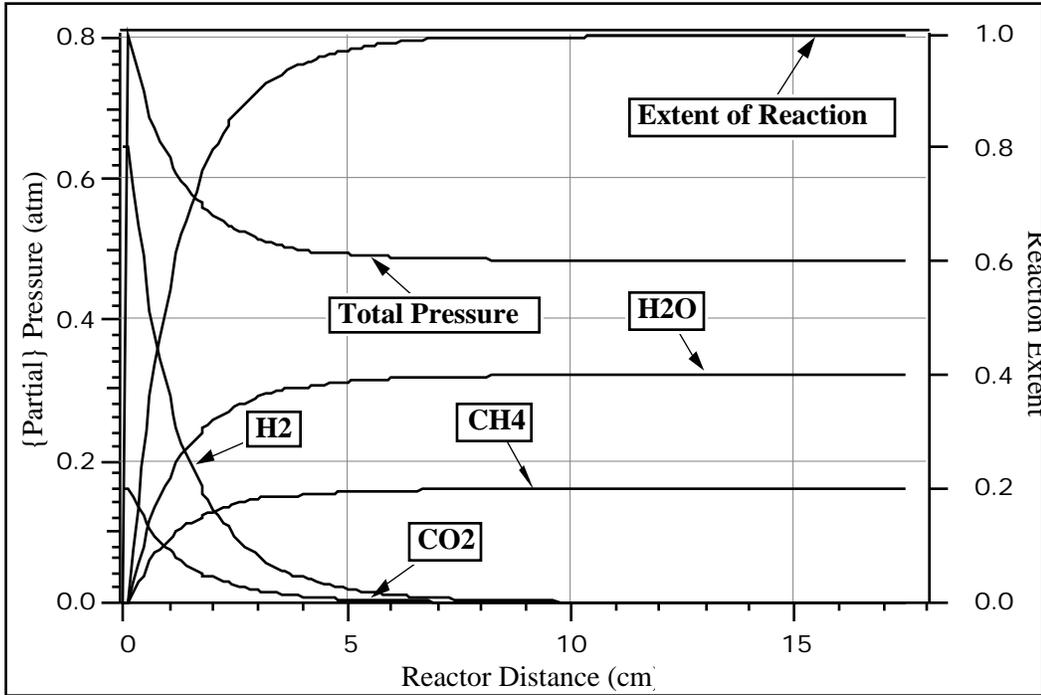


Fig. 5 Calculations of reaction rates indicated that a 5 cm length bed would be sufficient for complete reaction. A 15 cm bed was therefore chosen.

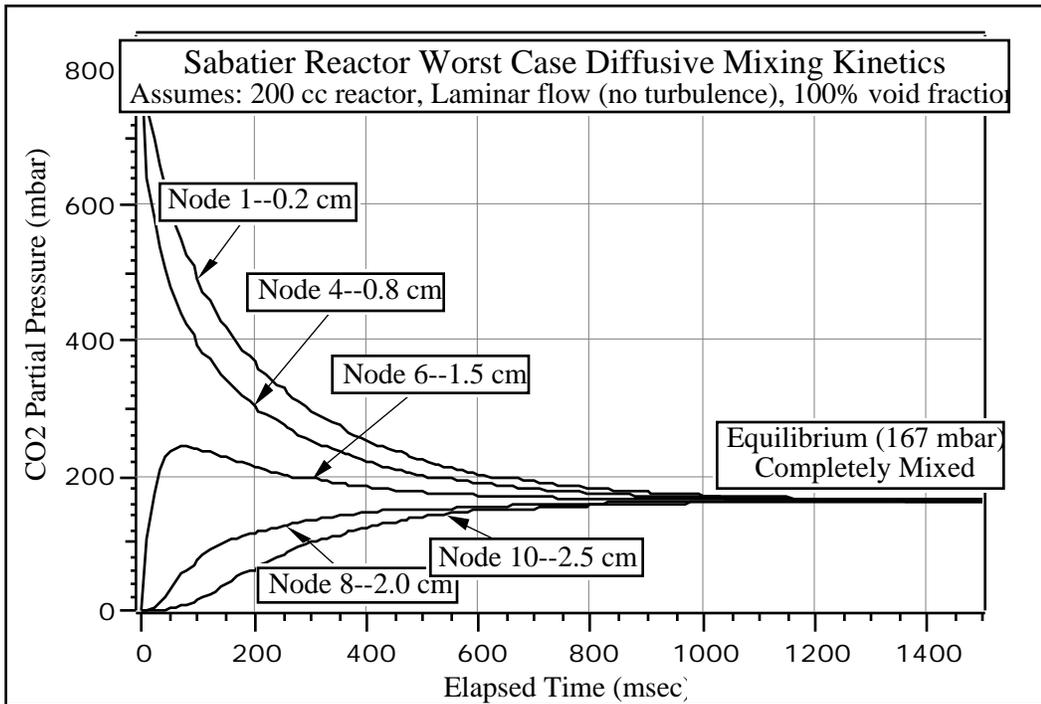


Fig. 6. Calculations of diffusion rates indicated that a 5 cm length space would be sufficient for complete mixing. A 15 cm empty mixing region was therefore chosen.

The net result was that the Sabatier unit was made a full 36 cm long

It was also decided that it would be necessary to orient the Sabatier reactor vertically, with the input gases entering from the top and the output stream leaving from the bottom, so that any water which condensed within the reactor would be drained out by gravity. For the same reason the heat exchanger was placed below the Sabatier reactor, and the condenser bottle placed below it. The electrolyser needed to be placed below the condenser to provide a small pressure head to ensure flow. The net result was a total system height of about 1 meter. The completed system is shown in Fig 7.

Initial System Operations: December 1993

On December 15, 1993, at about 2:00 pm, the machine was turned on for the first time. In this initial run, which lasted until about 4 pm, only the Sabatier reactor was operated. The electrolysis system was not turned on. Instead, Sabatier output water was allowed to accumulate in the condenser bottle.

The first indication that the machine was operating came around 2:30, when it was observed that the water level in the condenser bottle had risen about 0.2 cm, which corresponded roughly to a water accumulation of about 4 grams. By the end of the

x

x
x

x

Fig. 7. The complete Sabatier/Electrolysis Martian propellant manufacturing unit in the process of initial checkout. The long pipe attached to the panel in its upper right hand quadrant is the Sabatier unit, about which are clamped 5 nichrome heaters used for system startup. CO₂ and H₂ gas both enter the Sabatier from the top, the CO₂ traveling through the flow meter to the reactor's upper right and the hydrogen coming in from the meter on the reactor's upper left. Below the Sabatier unit is the condenser coil and water collection bottle. Methane gas produced by the reactor is bubbled through the bottle and then exits the system via the small tube leading to the right; water produced by the reactor is collected in the bottle and then travels to the electrolysis unit which is located near the lower left hand corner of the panel. Oxygen produced by the electrolyser is vented out through the tube leading off to the left; the H₂ product travels back up the panel to be recycled into the Sabatier reactor.

two hour run, the water level had risen by a full centimeter, indicating that roughly 20 grams of water had been produced. This was a rough measurement, because of the possibility of some of the water output accumulating in the reactor and other parts of the system, but if taken at face value would indicate that water was being produced at a rate that would support the production of about 320 grams of propellant a day, or about half of the machine's rated capacity.

At 3:47 PM a grab sample (Sample #1) was taken from the machine's methane vent, and brought to the Chemistry Lab for analysis in a gas chromatograph. The analysis was performed using a Varian Vista 6000 GC equipped with a molecular sieve packing, and used argon gas for the mobile phase. Calibration of the GC was performed using gas standards traceable to the NIST. Analysis showed that the sample consisted of 32% hydrogen, 37% nitrogen, 10% oxygen, and 17% methane by volume. Subsequent analysis on another GC machine at the Planetary Science Lab using a different GC system (Haynes DB porous polymer with helium carrier gas) indicated that the CO₂ content in the sample was less than 1%.

The results of analysis of Sample#1 were puzzling and initially dismaying. The fact that there was more hydrogen by volume than methane seemed to indicate very low conversion rates, and the large amount of air suggested that the apparatus might be leaky to an extent that could not be explained. It was pointed out, however, that each methane molecule contains 4 hydrogen atom, whereas each hydrogen molecule contains only two, and that for every methane molecule produced in the Sabatier reactor, two water molecules were also being produced, adding another 4 hydrogen atoms to the reacted total. In other words, each methane molecule in the output represents the equivalent amount of hydrogen fixed by the Sabatier reactor as is contained in 4 unreacted molecules of diatomic hydrogen. The 32% to 17% by volume ratio of hydrogen to methane gas in the exhaust thus actually indicates that 68% of all hydrogen that entered the machine during the Sample#1 run was being converted into methane and water, in rough agreement with the approximate 50% yield projected on the basis of condenser bottle water level rise.

After checking the apparatus for air leaks it was found that there were none, so an alternative explanation had to be found for the 47% air content of Sample#1. Initially it was thought that a large amount of air leaked into the sampling bottle during the sampling process. However, when despite great care in avoiding this during the taking of Sample#3,

Sample#3 still showed a large air content, this explanation was dropped. It was finally determined that the source of the large air content in Samples #1 and #3 was air entering the sample container by traveling up the 3 m long methane exhaust tube which vents to the environment in back of the laboratory shed. Despite its length, the entire interior volume of this 1/4 diameter vent tube is less than 100 cc. The sample bottle contained about 500 cc, and the ideal rate of production of methane gas from the Sabatier reactor was about 250 cc/min. Since the evacuated sample bottle filled itself in less than a minute, it needed more flow than is provided from the reactor, so much so that it sucked out the entire Sabatier exhaust content of the vent line plus additional air from the outside environment beyond. In order to prevent this effect, the large sample bottles were replaced with small capacity syringes, starting with Sample#4. Even with this adjustment, it took continued effort to improve sampling technique to the point where air contamination was less than 5% of the sample volume.

During the afternoon of December 15, temperatures in the Sabatier reactor were maintained by the use of nichrome heaters supplying about 40 W of power. Whenever the heaters were turned off, reactor temperatures would fall, presumably shutting down the reactor. This was considered undesirable, as in an optimal configuration the exothermic Sabatier heat output should be sufficient to maintain reactor temperature without any external power input. In order to attempt to achieve such self-sustained operation, a layer of fiber-glass insulation about 8 cm thick was placed around the reactor. On December 16, the reactor was run again with this modification, and it was found that only about 10 W of heater power was now needed to sustain reactor temperature. However during the run of December 16, the flow through the reactor mysteriously stopped, causing temperatures to drop as chemical energy release ceased. Upon investigation, it was found that the cause of the flow stoppage was an accumulation of ice within the long methane exhaust tube which traveled for several meters distance along the very cold environment in back of the shed. Apparently the exhaust methane, which is saturated with water vapor, had carried enough water out with it to clog the narrow gauge (0.25 inch diameter) exhaust vent. On an actual Mars apparatus, this problem could be solved by having a wide diameter cold trap remove the water from the methane effluent. We solved it on the experiment simply by cutting off all exhaust tubing immediately after the tube's exit from the shed. A sample (Sample#2) of the reactor's contents were taken while this forced shutdown was underway, but as the temperature of the reactor had fallen below the level needed for the

Sabatier reaction, no analysis of this sample was done.

On Friday, December 17, the reactor was started up again, with half of its hydrogen input (500 cc/min out of a total of 1000 cc/min) being supplied by the electrolyser, which was now activated for the first time in the program. The feedstock for the electrolyser, however, was not the reactor product but pure water from a bottle. This run proceeded well for several hours, and a sample (Sample#3) of the methane effluent was taken at 1:56 pm. Upon subsequent analysis in the Chemistry Lab it was found that this sample was similar to Sample#1, with 67% conversion of hydrogen from H₂ gas into methane and water, while analysis at the Planetary Science Lab showed that the CO₂ content was less than 1%.

The insulation was kept on the reactor (it remained on for all runs for the remainder of the program) and once again it was found that about 10 W of auxiliary power was required to maintain reaction temperatures. The water electrolyser was operated at its full rated output, and was found to consume 148 W of electricity (37 A, 4 V), somewhat less than the 160 W projected by the manufacturer. All was

going well, when about 2:30 PM the electrolyser suddenly failed, shooting water out of its oxygen exhaust port. This ended our operations for the week.

The next week we investigated the cause of the electrolyser failure, and found that it was probably caused by damage inflicted upon the unit when a technician attempted to test it in an incorrectly plumbed mode earlier in the program. On December 21, we contacted the manufacturer, Packard Instrument, and they very graciously agreed to send us a second unit, immediately, free of charge. Unfortunately, Packard management's desire to see the program succeed was not adequately conveyed to their shipping department, which elected to send the unit via ordinary UPS, not Federal Express. As a result, the unit did not arrive until January 4, 1994.

Lacking an operational electrolyser, we nevertheless resolved to continue experiments to attempt to improve the yields of the reactor. On December 22, we operated again, taking samples at 9:38 AM (Sample#4) and 3:03 PM (Sample#5). In both cases we operated with a maximum reactor temperature somewhat higher than previous runs, in an effort to improve reaction kinetics. Also on December 22, the

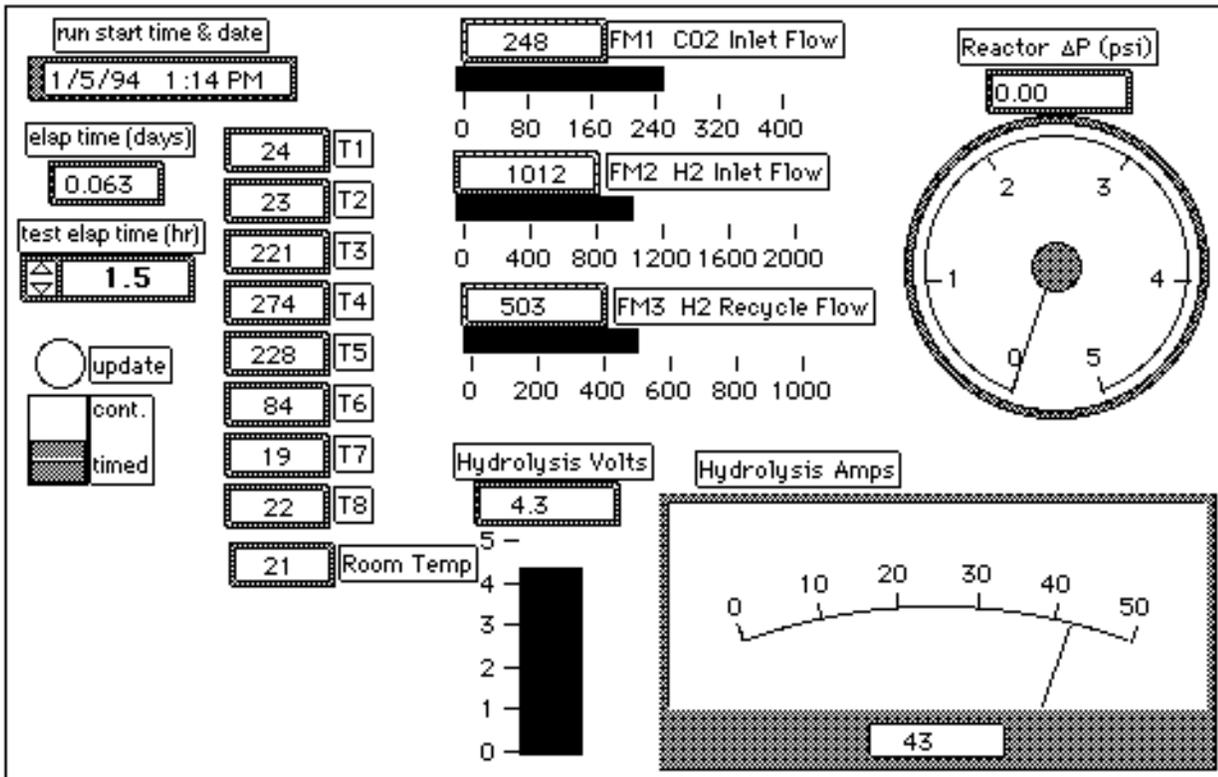


Fig 8 Labview software provided centralized and recorded data readouts of all continually monitored system variables, including power consumption, gas flow rates, and temperature and pressure at key locations throughout the apparatus.

Chemistry Lab brought on line a capability for analyzing CO₂ with its own equipment and personnel. This was important, because very low levels of CO₂ had been found in tests on Samples #1 and #3 by Planetary Science Lab personnel, but as that result was inconsistent with the modest hydrogen conversions found at the Chemistry Lab, it had been ascribed to relative lack of experience with GC analysis on the part of the PSL personnel. However, when Sample#4 was analyzed at the Chemistry Lab, it was found to contain 30% air, 31.2% hydrogen, 36.7% methane, and less than 1% CO₂, confirming the earlier PSL findings.

The other finding from Sample#4 was that the system was benefited by higher temperatures, with hydrogen conversion increased to 82% at a maximum reactor temperature of 298 C, compared to 67% at a maximum temperature of 259 C on Sample#3.

It was now apparent that the machine was being run hydrogen rich. To test this, during the run for Sample#5, the CO₂ flow was increased by 10% over the nominal (supposedly stoichiometric) values. When this was done, conversion yields rose to 85%, and for the first time, a measurable amount (2.4%) of CO₂ appeared in the methane exhaust. This was still much less than 32% H₂ gas in Sample#5, so it was apparent that the machine was still being operated hydrogen rich.

The first order of business was now to understand the reason for the hydrogen-rich operation of the machine. There were two explanations: either the flow meters for regulating gas input into the reactor were miscalibrated, or CO₂ hungry side reactions, such as the reverse gas shift reaction, ($\text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O}$) were occurring in the reactor. The manufacturer of the flow meters, Sierra Instruments, had provided calibration factors for adjusting the meters for use with either diatomic gases, such as hydrogen or oxygen, and triatomic gases such as CO₂, and guaranteed the accuracy of the result within 2%. For this reason, laboratory personnel were reluctant to believe that meter error could be the cause of the large hydrogen excess. It was proposed that the exhaust samples be tested for carbon-monoxide, a reaction product of the reverse gas shift. However it became apparent that such a measurement would be difficult to make accurately with the equipment at hand because nitrogen contamination of the samples could effectively mask out CO readings within the GC analysis. It was decided, therefore, to manually recalibrate all the flow meters used in the machine. On December 23, therefore, the relevant gases for each meter piped

through to be bubbled under water into an inverted graduated cylinder, allowing volumetric flow to be measured directly as a function of time. It was found that flow meters FM2 and FM3, measuring hydrogen flow, were accurate, but that the vendor supplied calibration factor for FM1 measuring the flow of CO₂ was inaccurate, overstating CO₂ flow by about 20%. This adequately explained the reason for the hydrogen excess, and suitable modifications were made to the machine's control system to compensate for the error.

Full System Operations: January 1994

Martin Marietta was shut down between December 25, 1993 and January 2, 1994. When work resumed on January 3, the replacement electrolyser still had not made its appearance, and it was decided to delay operations until the electrolyser was available, so as to be able to use the labor hours remaining in the contract to demonstrate full system operation. The electrolyser showed up on January 4, and was reintegrated into the system. Also on the 4th, modifications were made to the reactor, adding a heater near the T3 sensor (the empty upper part of the reactor tube), bending the gas inflow pipes down around the exterior of the reactor to pre-heat the gases with the reactor's waste heat, and installing a twisted vane inside the reactor so as to assure that gases entering the reactor would come in contact with the hot reactor wall before entering the catalyst bed. All of these modifications were made with the purpose of improving yields, as it was felt that yields were being limited by cold gas tunneling effects.

On January 5, 1994 at about 8:30 AM the machine was turned on again with just the Sabatier reactor running. Steady state operation was achieved by about 9 am, and a sample of product gas was taken at 9:35 AM (Sample 5A). This run, which was done with a small excess of input hydrogen (5% over stoichiometric) by design, showed improved yields over the 1993 results, with 90.9% conversion of hydrogen and 94.7% conversion of CO₂. Around 10 AM the new electrolyser was turned on, drawing from a reserve of de-ionized bottled water, and used at full nominal output to produce its required recycle stream of 50% of the input hydrogen for the reactor. With the system in this mode, and stoichiometric inputs, a gas sample was taken at 11:02 AM (Sample #6). Chemistry lab analysis of this sample showed both hydrogen and CO₂ conversion rates of 92.5%.

During the morning of January 5, output water was allowed to accumulate in the condenser bottle. The quality of this water was an issue, because the

specifications for the electrolyser requires input water with a conductivity lower than 20 micro-mho-cm. Water output from Run#1 (corresponding to Sample#1) had been measured to have a conductivity of 50 micro-mho-cm, and output from Run#3 had been measured at 35 micro-mho-cm. A de-ionizing filter had therefore been developed, which was found to reduce the conductivity of Run#1 water to 7 micro-mho-cm, and installed in the machine between the condenser bottle and the electrolyser. Measurement of water quality from Run#6, however, indicated that the output water, before deionization, was now 8 micro-mho-cm. In other words, the improvement in water quality observed between Runs#1 and #3 had apparently continued with machine operation to the point where the de-ionizing filter was no longer necessary. It was decided, nevertheless, to keep the filter in place. The improvement in water quality of output over time is believed to occur due to steam cleaning of particulates off the catalyst bed in the course of extended operation.

The other key issue of water quality had to do with the certainty that methane gas would be dissolved in the condenser bottle water to the point of saturation, about 30 cc of methane at STP in every liter of water. The effect of this dissolved methane on electrolyser operation was unknown. In addition to the possibility of damage to the electrolyser, there was concern that all or part of the dissolved methane would come out of the electrolyser in the oxygen flow. If this were to occur, then over time in the course of an actual sample return mission, enough methane could potentially be delivered to the oxygen tank to cause a combustion threat. On the other hand, if the dissolved methane came out with the hydrogen, there would be no problem, as in that case it would simply be fed back into the reactor. Methane gas could be removed from the condenser water by heating prior to delivering the water to the electrolyser, but we had no provision for such a purification step in our machine. Therefore if we were to achieve full system operation, with reactor product water feeding the electrolyser, we had no alternative but to take a necessary calculated risk.

It was decided to proceed with the closed loop tests. After lunch on January 5, the electrolyser was disconnected from its purified bottled water source and connected to the condenser bottle containing reactor output. At 1:15 PM the machine was turned on, with the electrolyser supplying about 10% of the input hydrogen. As things appeared to be working well, at 1:20 PM the electrolyser power was increased to allow it to supply 25% of the input hydrogen. This was increased again, bringing the electrolyser up to supply 35% of the hydrogen at

1:27 PM and finally reaching the design value of 50% at 1:50 pm. The machine was now operating as a completely integrated system at full rated capacity of 30 grams of propellant output per hour (720 grams/day). Stable, steady state operation was observed, with the electrolyser requiring 150 W of power to produce the required 500 cc/min of hydrogen and 250 cc/min of oxygen, and the heaters requiring 10 W to maintain temperature.

A sample of the Sabatier exhaust was taken at 2:20 PM (Sample#7), as well as a sample of the oxygen exhaust of the electrolyser. Upon analysis of Sample #7 at the Chemistry Lab it was found that CO₂ was being converted at a rate of 93.2%, and hydrogen was being converted at a rate of 92.2%. Analysis of the electrolyser product gas showed it to be essentially pure, consisting of 96.7% oxygen, 3.0% water vapor, and 0.3% nitrogen. That is, there was no methane, hydrogen, or CO₂ in the oxygen exhaust product; the only significant impurity, water vapor could be easily removed with a cold trap. With the success of Run#7, the concern over dissolved methane dissolved; the machine's oxygen output was propellant grade.

The machine continued to operate well as a completely integrated system during the afternoon of January 5. Around 2:30 PM it was decided to turn the heaters off to see if the reactor could sustain itself without auxiliary power and to test whether by operating at lower temperatures the better equilibrium constant could result in a higher reactor conversion efficiency. Both of these hopes proved negative. With the heaters off, the reactor temperature went into a slow decline, with the T4 reading reaching 235 C at 3:11 PM when Sample#8 was taken (T4 was 300 C when Sample#7 was taken). Far from resulting in improved performance, the drop in temperature caused reactor yields to drop to hydrogen conversions of 26%. The oxygen exhaust was also sampled, however, and was found to be as pure as Run#7.

We now had funding remaining for one full day of operation, and decided to use it to support a single long duration run, during which reactor temperature would be varied to try to optimize output. As Run#8 had shown a decrease in yield with lower temperatures, it was decided to go for improved reactor kinetics by driving the system temperature up. The final run of January 6th was therefore initiated about 8:30 am, with the machine operating as a completely integrated system and data being taken by 8:55 am.

Data outputs for this all day run are shown in Figs 9, and 10 The machine operated well until about

10:30, when a gas bubble got caught in a bent vent

Fig 9. Labview records showing system temperatures during the all day run of January 6.

Fig 10. Labview records showing the variation of gas flows during the all day run of January 6.

tube coming out of the electrolyser. This caused the electrolyser to be shut down for about 10 minutes, during which time the Sabatier reactor continued to operate. The full system was then brought up and running again about 10:40 am, and continued to run at full capacity without incident for the remainder of the day. Samples #9, 10, and 11 were taken at 12:23 pm, 2:08 pm, and 3:05 pm, with T4 readings of 281 C, 339 C, and 372 C, respectively. Hydrogen conversion yields of these samples respectively were 85.8, 93.4, and 93.9%, with similar efficiencies holding for CO₂ conversion. The temperature excursion of the Sabatier reactor was accomplished by increasing the external heater power from its usual 10 W to about 30 W. At around 3:30 PM the machine was shut down, completing the 7 hour run and concluding the experimental operations of the project.

Summary of Achieved System Performance

The following table summarizes the results of all sampled runs on the Mars propellant prototype machine. An additional run (#2) was done on Dec 16, but the results were not analyzed. Runs #1, 4, 5 and 5A were done with just the Sabatier reactor, Runs #3 and 6 were done with the Sabatier fed with hydrogen produced by an electrolyser using a bottled source, and Runs #7, 8, 9, 10, and 11 were done using the fully integrated Sabatier/Electrolysis system.

Figure 11 shows the hydrogen conversion efficiency of the Sabatier reactor as a function of its maximum temperature reading. Data shown is for Runs #5A through 11, in which hydrogen and CO₂ were mixed in a ratio close to the stoichiometric 4.0 proportion.

Table 1 Summary of Test Results

Run	#1	#3	#4	#5	#5A	#6	#7	#8	#9	#10	#11
Date	12/15	12/17	12/22	12/22	1/5	1/5	1/5	1/5	1/6	1/6	1/6
Time	3:47	1:56	9:38	3:03	9:35	11:02	2:20	3:11	12:23	2:08	3:05
T3 (C)	125	195	215	232	227	222	228	198	218	261	287
T4 (C)	227	259	298	320	294	295	300	235	281	339	372
T5 (C)	192	172	191	260	238	241	246	206	243	270	298
T6(C)	66	68	71	94	86	84	80	82	95	100	105
<u>Input (cc/min)</u>											
H2	995	1004	991	988	1012	1007	1020	1014	1016	1014	1026
CO2	203	205	203	230	241	252	253	253	256	254	254
H2/CO2	4.89	4.90	4.87	4.30	4.20	4.00	4.03	4.01	3.97	3.99	4.04
<u>Effluent Sample (% by vol)</u>											
H2	32.0	20.3	31.2	32.4	26.8	21.9	22.7	53.6	34.6	19.3	17.6
CO2	<1	<1	<1	2.4	3.7	5.5	4.9	17.4	8.8	5.5	4.5
N2	37.0	49.7	24.1	15.9	1.1	3.7	2.4	13.2	3.2	2.7	5.1
O2	10.0	14.0	6.5	4.3	0.3	1.0	0.7	3.7	0.9	0.7	1.4
CH4	17.0	10.3	36.7	46.1	66.7	67.6	66.8	4.8	52.1	68.8	68.2
<u>Reactor Output (cc/min)</u>											
H2	380	402	172	154	92	75	80	637	145	66	61
CO2	<1	<1	<1	11	13	19	17	196	37	19	16
CH4	202	204	202	219	228	233	236	57	219	235	238
<u>Reactor Gas Conversion Efficiency (%)</u>											
H2	68	67	82	85	90.9	92.5	92.2	26.4	85.8	93.4	93.9
CO2	>99	>99	>99	95.0	94.7	92.5	93.2	21.6	85.6	92.6	93.8

Efficiency of Sabatier Reactor

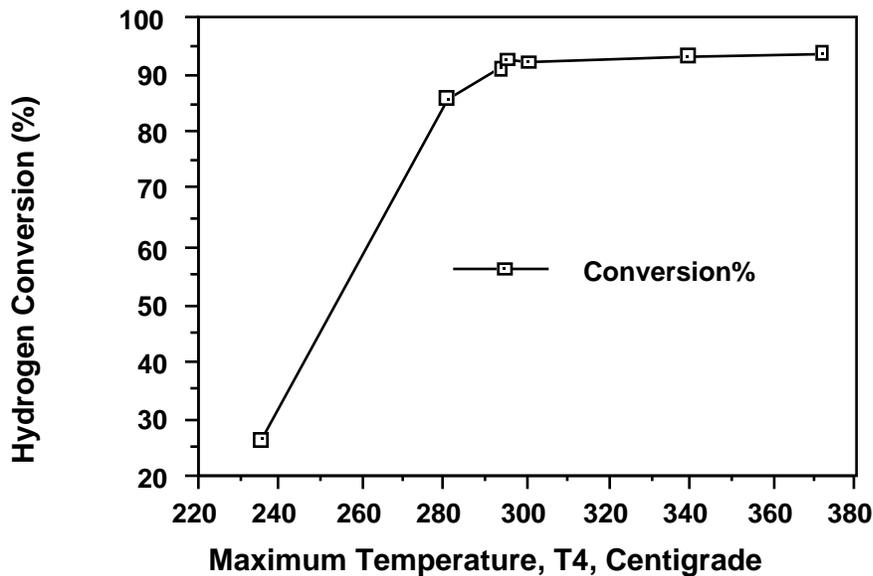


Fig. 11 Efficiency of the Sabatier Reactor as a function of maximum temperature.

Recommended Follow On Activities

The following activities are recommended to follow up the project reported on in this paper.

1. Further system optimization. In the limited time available for testing on the present system, conversion yields were increased from 68% to 94%. It is the belief of those involved in the project that with further adjustments, yields can be increased to better than 98%. In particular, increasing the amount of catalyst within the reactor vessel, inserting baffles within the vessel to reduce tunneling, modifying the heater system to give greater control over the temperature profile within the reactor, and increasing the reactor's operating pressure, all hold promise for increasing conversion yields. Installing an on-line system for real-time chemical analysis of the reactor output is possible, as the necessary equipment is available at Martin Marietta. Having such a capability would greatly accelerate the rate of system improvements.

2. Further system simplification, thermal optimization, and miniaturization. It is the belief of those involved in the project that significant simplifications and reductions in component masses and system size can be achieved with a moderate amount of additional work. The pressure differential gauge and the condenser coil can both be removed. If the pressure is increased, then the Sabatier reactor can be shrunk, possibly by as much as a factor of 10 in volume. The smaller Sabatier reactor would be a more intense heat source, allowing all

supplemental reactor heating power during operation to be eliminated and possibly allowing the elimination of the insulating cover as well. Much smaller flow meters than those employed during this demonstration are also available. If all of these modifications are implemented, we believe that a miniaturized core Sabatier/Electrolysis unit could be built that would be fit inside a bread-box and have a mass of approximately 10 kg.

3. A long duration test needs to be done. Whether with the present or an improved unit, a long duration run needs to be done demonstrating continuous operation over a substantial period, perhaps more than 30 days. This is essential if the practicality of in-situ propellant production for a Mars Sample Return mission is to be demonstrated.

4. A propellant acquisition system needs to be added. The next step is to add a pump or other device capable of acquiring CO₂ from a Mars like 8 mbar environment and pump it up to pressures suitable for input into the Sabatier reactor. The pump can then be placed in a Mars simulation chamber, used to acquire CO₂ for a combined test with the SE system. Ultimately, such a combined pump/SE system should be subjected to a long duration test.

5. A propellant refrigeration system needs to be added. As a final step in completing an end to end pilot demonstration of a propellant production system capable of supporting an MSR mission, a refrigerator needs to be added to the combined

pump/SE system demonstrated in programmatic step 4, above. The purpose of the refrigerator would be to liquefy the CH₄ and O₂ SE product gases, with all water, CO₂, and other impurities removed prior to propellant liquefaction. Ultimately such a combined pump/SE/refrigerator system should be subjected to a long duration test.

6. Complete system optimization. The combined pump/SE/refrigerator system demonstrated in programmatic step 5 will need to be optimized and miniaturized to produce prototype flight hardware.

Overall Project Conclusions

The overall conclusion to be drawn from the current project is that production of CH₄/O₂ propellant on Mars using a Sabatier/Electrolysis system is likely to be practical, and the necessary development will probably represent a very small portion of the total cost of a Mars Sample Return mission.

In the course of just three months, with a total budget of \$47,000, a full scale working system was built and made to operate with a conversion efficiency of 94%. The combined mass of all operating components of the prototype S/E system was less than 20 kg, with potential improvements that would cut that mass roughly in half clearly in sight. The output of the current prototype system, 720 grams of propellant a day, would allow it to produce close to 20 times its own weight in propellant in the course of a typical 500 day conjunction class Mars surface stay. The current system required a power of 160 Watts, which could be provided on Mars by either solar energy or a small state of the art RTG. The quality of the oxygen produced by the device was pure, propellant grade. The small percentage of CO₂ and water vapor impurities in the methane product could easily be removed by a cold trap device.

Much work remains to be done before the complete practicality of in-situ propellant production to support Mars missions is demonstrated end to end. Yet the relative ease with which so much was accomplished in so short a time on the present project can only be viewed as extremely encouraging. Taken together with the enormous benefits in-situ propellant production provides to both automated and piloted Mars exploration, the success of the current demonstration speaks forcefully for the wisdom of further development efforts.

References

1. R. Zubrin, L. Mason, and S. Price, "Mars Sample Return with In-Situ Resource Utilization; Phase I Final Report." Presented to NASA JSC Nov. 30, 1993.