

## Mars Atmospheric In Situ Resource Utilization Projects at the Kennedy Space Center

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### ABSTRACT

The atmosphere of Mars, which is ~95% carbon dioxide (CO<sub>2</sub>), is a rich resource for the human exploration of the red planet, primarily by the production of rocket propellants for Mars ascent vehicles and oxygen for life support. Three recent projects led by NASA's Kennedy Space Center (KSC) have been investigating the processing of CO<sub>2</sub>. The first project successfully demonstrated the Mars Atmospheric Processing Module (APM), which freezes CO<sub>2</sub> with cryocoolers and combines sublimated CO<sub>2</sub> with hydrogen to make methane and water. The second project absorbs CO<sub>2</sub> with ionic liquids and electrolyzes it with water to make methane and oxygen, but with limited success so far. The goal of the third project is to recover up to

100% of the oxygen in spacecraft respiratory CO<sub>2</sub>. A combination of the reverse water gas shift reaction and the Boudouard reaction eventually fill the reactor up with carbon, stopping the process. A system to continuously remove and collect carbon is showing promise.

## INTRODUCTION

The multi-NASA center Mars Atmosphere and Regolith Collector/Processor for Lander Operations (MARCO POLO) project was initiated by the Johnson Space Center (JSC) in 2011 to build and demonstrate a methane (CH<sub>4</sub>) and oxygen (O<sub>2</sub>) propellant production system in a Mars analog environment. Work at the Kennedy Space Center (KSC) has focused on the Atmospheric Processing Module (APM), which freezes CO<sub>2</sub> from a simulated Mars atmosphere at Mars pressures (~1 kPa) by using two alternating cryocoolers. The resulting pressurized CO<sub>2</sub> is combined with hydrogen (H<sub>2</sub>) in a Sabatier reactor to make CH<sub>4</sub> and water (H<sub>2</sub>O) vapor. The H<sub>2</sub> is obtained via electrolysis of purified water acquired by heating regolith in the Soil Processing Module (SPM, at JSC). The CH<sub>4</sub> is dried and sent to a Liquefaction Module. The H<sub>2</sub>O vapor is condensed and is sent to the Water Cleanup Module (WCM, from KSC) followed by the Water Processing Module (WPM, built by JSC), where it is electrolyzed. The resulting O<sub>2</sub> is liquefied and stored and the H<sub>2</sub> is sent back to the Sabatier subsystem to make more CH<sub>4</sub>. We previously reported the progress on the APM at Earth & Space 2014 in Muscatello *et al.* (2015). The MARCO POLO project was described in detail by Interbartolo *et al.* (2012).

Also, in 2014, KSC initiated a project entitled “Mars Propellant Production with Ionic Liquids”. The purpose of the project was to investigate and demonstrate the simultaneous production of CH<sub>4</sub> and O<sub>2</sub> via the electrolysis of CO<sub>2</sub> and H<sub>2</sub>O in one or more ionic liquids (ILs). The motivation for the project is to investigate the feasibility of this process, which is expected to greatly simplify the collection and processing of CO<sub>2</sub> on Mars and reduce mass and power requirements. Ionic Liquids are salts with large, bulky organic cations and/or anions that melt at or near room temperatures.

In addition, oxygen recovery from respiratory CO<sub>2</sub> is an essential aspect of human spaceflight and Mars exploration. Methods exist to capture the CO<sub>2</sub>, but production of O<sub>2</sub> needs further development. The current ISS Carbon Dioxide Reduction System (CRS) uses the Sabatier reaction to produce H<sub>2</sub>O which is electrolyzed to make O<sub>2</sub> for breathing air. O<sub>2</sub> recovery is limited to 50% because half of the H<sub>2</sub> used is lost as CH<sub>4</sub>, which is vented overboard, and supplemental H<sub>2</sub> availability is limited. The Bosch reaction (CO<sub>2</sub> + H<sub>2</sub> → C + H<sub>2</sub>O) is a promising alternative to the Sabatier reaction that does not consume H<sub>2</sub>. The Bosch reaction can be considered to be the combination of the Reverse Water Gas Shift (RWGS) reaction (CO<sub>2</sub> + H<sub>2</sub> → CO + H<sub>2</sub>O) and the Boudouard reaction (2 CO → CO<sub>2</sub> + C). However, during the Boudouard reaction step the resulting carbon buildup eventually fouls the nickel or iron catalyst, reducing reactor life and increasing the use of consumables. Abney *et al.* (2014) at MSFC have demonstrated full conversion of CO<sub>2</sub> into O<sub>2</sub> and carbon using the Bosch reaction with a steel wool Boudouard catalyst using only 0.0019 g of catalyst/g O<sub>2</sub> recovered. Nevertheless, the catalyst bed is eventually clogged with carbon and the catalyst is not recoverable.

To minimize this fouling, find a use for this waste product, and increase efficiency, starting in 2015, we have designed various self-cleaning catalysts and selected a few which we deem the most reliable for conversion and lack of fouling. Criteria that we considered include the estimated mechanical reliability of the cleaning method and its ability to maintain high conversion efficiency. The above chemical reactions are well understood, but reusable self-cleaning Boudouard catalysts have not been investigated before.

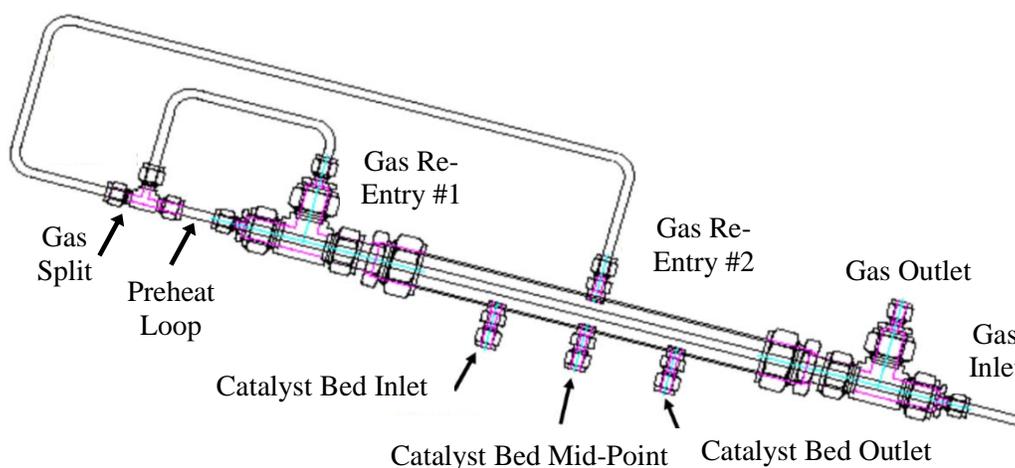
## MARS ATMOSPHERIC PROCESSING MODULE

Recently, the operation of the two CO<sub>2</sub> freezers of the APM has been verified to exceed its required 88 g CO<sub>2</sub>/h collection/supply rate. Tests of a new Sabatier reactor with CO<sub>2</sub> from the freezers show that it meets the 32 g/h CH<sub>4</sub> production rate design goal. The H<sub>2</sub>O produced by the Sabatier reactor is at 93% of its design requirement of 72 g/h. The JSC SPM is designed to extract an additional 72 g of H<sub>2</sub>O/h from simulated Mars regolith. The SPM H<sub>2</sub>O and the Sabatier H<sub>2</sub>O would be purified by the WCM and electrolyzed by the WPM to make a total of 128 g O<sub>2</sub>/h. The H<sub>2</sub> from the H<sub>2</sub>O extracted from regolith is the ultimate source of H<sub>2</sub> used to make CH<sub>4</sub>. These hourly rates of CH<sub>4</sub> and O<sub>2</sub> production are suitable for fueling a Mars Ascent Vehicle (MAV) for a small Mars Sample Return mission and are >1/10<sup>th</sup> scale of a human Mars mission ISRU unit.

The major tasks that preceded the verification of these production rates were to complete setup and testing of the Sabatier subsystem including a new Sabatier reactor, verify the operation of the CO<sub>2</sub> pump and the associated storage tanks, and operate them with the CO<sub>2</sub> freezers to ready the APM for a potential analog demonstration with the other components of MARCO POLO, i.e. regolith mining, H<sub>2</sub>O recovery from regolith, H<sub>2</sub>O purification, and H<sub>2</sub>O electrolysis, e.g. the proposed MASTER (Mars Atmosphere & Soil Testbed for Extraction of Resources) project at JSC and KSC. The APM can also be used to test alternative CO<sub>2</sub> collection and CO<sub>2</sub> conversion technologies as they become available by replacing the freezers or Sabatier reactor. Further details of our recent work follow below.

### Sabatier Subsystem

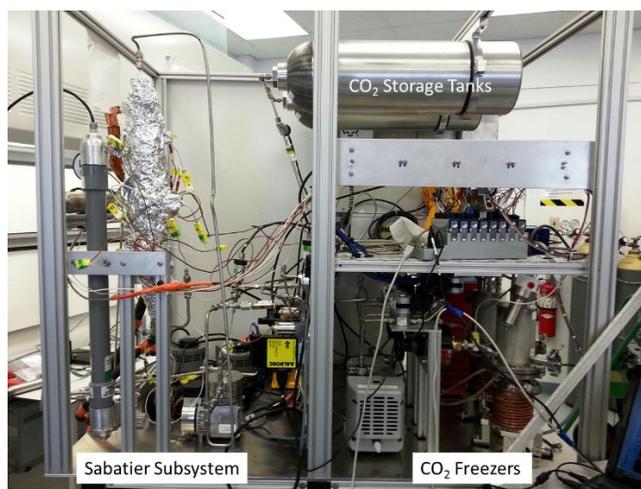
As mentioned in our 2014 report, we designed and built a new Sabatier reactor because of the overheating we encountered with a previous reactor design. The new reactor design was based on one developed at Pioneer Astronautics, as reported by Berggren *et al.* (2014), which has a novel heat exchanger designed to control the exothermic Sabatier reaction. Figure 1 shows the initial design for the new Sabatier reactor, which consists of a stainless steel tube that is 30 cm long with an O.D. of 2.54 cm and a wall thickness of 0.21 cm.



**Figure 1. Design of KSC Sabatier Reactor.**

The reactor was designed to contain the same amount of ruthenium on alumina catalyst as that in the previous design, but with the ability to shed controllable amounts of heat to the

environment from the gases heated by passing through the center of the catalyst bed instead of a shell surrounding the bed. During testing of the new reactor, we determined that the large outer heat exchanger (“Gas Re-Entry #2”) was not needed at our operating conditions due to heat loss from the long, narrow reactor, so it was removed to simplify operations. Figure 2 is a photo of the current setup with the Sabatier Subsystem on the left after installation of the recycling system and a heat exchanger/H<sub>2</sub>O condenser from Exergy (Model 00540-03) that is cooled to 3°C using a standard recirculating chiller bath. The H<sub>2</sub>O from the condenser is collected in a 300 cm<sup>3</sup> stainless steel vessel from Swagelok that is drained periodically during operations to measure the volume of H<sub>2</sub>O produced. The vessel is currently below and to the left of the aluminum floor plate and is not visible in Figure 2. The two CO<sub>2</sub> Freezers are on the lower right side of Figure 2 while the two CO<sub>2</sub> Storage Tanks are at the top right.



**Figure 2. Mars Atmospheric Processing Module.**

Testing of the Sabatier reactor with pure H<sub>2</sub> and CO<sub>2</sub> from compressed gas bottles at a 4.5:1 mole ratio showed >90% conversion of 88 g CO<sub>2</sub>/h to CH<sub>4</sub> in a single pass with no overheating issues (i.e. <600 °C) as determined by gas chromatography, confirming that we had a functional reactor. The original JSC design for the Sabatier subsystem used an electrochemical H<sub>2</sub>/CH<sub>4</sub> separator which was not available to us. Instead, we installed a membrane module-based separation system (see Muscatello *et al.* (2014) for details). The combination of the recycling system and the Sabatier reactor was successful, with pure CH<sub>4</sub> and H<sub>2</sub>O products being produced with near 100% conversion of the CO<sub>2</sub> feed as long as the pressure differential between the membrane retentate (CH<sub>4</sub>) and the permeate (H<sub>2</sub>/CH<sub>4</sub>/CO<sub>2</sub>) is ~200 kPa.

### CO<sub>2</sub> Freezer Subsystem

With the Sabatier Subsystem operating properly, we turned our attention to the CO<sub>2</sub> Freezer Subsystem to ensure it could supply CO<sub>2</sub> for methanation. Prior testing had shown that the cryocoolers freeze an average of 99 g CO<sub>2</sub>/h from simulated Mars atmosphere (95.4 % CO<sub>2</sub>, 3% nitrogen (N<sub>2</sub>), and 1.6% argon (Ar)) at Mars pressures and supply an average of 94 g CO<sub>2</sub>/h during 1.4-hour cycle times. The system has a compromised design that requires a pump to compress the CO<sub>2</sub> into two 10-liter storage tanks at up to 700 kPa to avoid pressurizing the cryocooler cold fingers, the connecting flange, and the freezing tanks. As noted in our prior work, the cryocooler and its flange are designed only for vacuum systems, not for the ~5.5 MPa

that would result from sublimating and liquefying the CO<sub>2</sub> product. The initial project budget did not support stamped and certified ASME code tanks required by NASA safety. The large copper cold head needed to freeze CO<sub>2</sub> for the anticipated 14-h daily operating time was not meeting requirements, so a 1.4-h cycle time and a smaller copper cold head was chosen. A KNF NPK 09 DC swing piston pump was selected to compress the CO<sub>2</sub>. Unfortunately, the piston pump leaks and contaminates the CO<sub>2</sub> with air if the inlet pressure is below ambient room conditions. A solenoid pump was procured and tested as a replacement, but, in addition to being rather loud, it failed after only a short time. The solenoid pump was repaired by the vendor, but failed quickly again during testing.

An alternate method was implemented that uses a 25-liter Tedlar<sup>®</sup> gas sampling bag to provide a volume into which the sublimating CO<sub>2</sub> can expand while not pressurizing the freezing chamber. Periodically, the CO<sub>2</sub> is pumped into the storage tanks by the swing piston pump, taking care not to completely evacuate the Tedlar<sup>®</sup> bag. This process results in pure CO<sub>2</sub> being stored at up to 700 kPa in the CO<sub>2</sub> tanks to provide sufficient feed to the Sabatier reactor for 1.4 h while a new batch of dry ice is collected for the next 1.4 h interval. The process could be automated by installing flow meters at the outlet of the freezer tanks and at the inlet of the piston pump. By knowing how much CO<sub>2</sub> has been sent to the bag and how much has been sent to the storage tanks, the amount left in the bag can be calculated and the pump can be stopped before the bag is empty. Testing of the CO<sub>2</sub> freezers using the bag as interim storage shows they collect CO<sub>2</sub> at the expected rate and that alternating them produces adequate CO<sub>2</sub> to run the Sabatier subsystem at the desired CH<sub>4</sub> production rate. Additional funding is being sought to upgrade the cryocoolers and the freezing tanks to make the subsystem more flight-like.

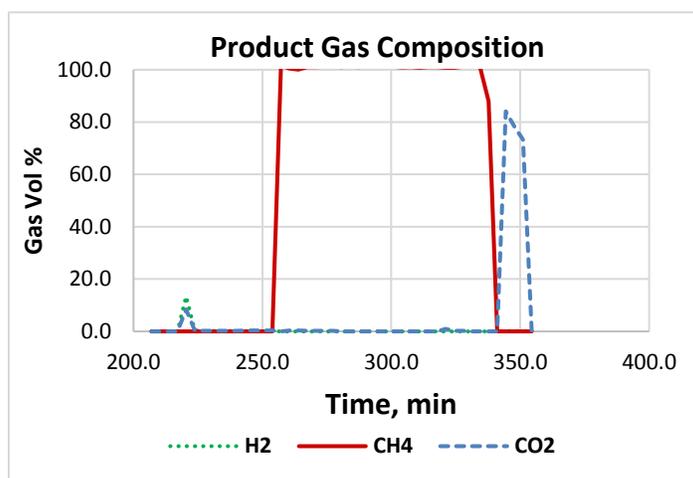


Figure 3. Integrated Atmospheric Processing Module CH<sub>4</sub> Purity.

### Integrated Testing

Next, we used the CO<sub>2</sub> Freezer Subsystem to supply the Sabatier Subsystem during a ~1.5 h test. Figure 3 shows the product gas composition for that test, as measured with a gas chromatograph. The Sabatier Subsystem was operated starting at 250 minutes and turned off at 340 minutes, producing pure CH<sub>4</sub> in the membrane module retentate. The CO<sub>2</sub> concentration increased after 340 minutes as the H<sub>2</sub> flow to the Sabatier reactor was stopped. An integrating flow meter showed that the CH<sub>4</sub> production rate was 32 g/h and 67 g H<sub>2</sub>O/h were collected by the condenser. All the other components operated as planned so we were ready to pursue our

goal of running the integrated module for three days with 7 h of pure CH<sub>4</sub> production each day at the desired rate of 32 g/h. The 7-h duration is based on 5 cycles of operation of the CO<sub>2</sub> Freezers while also fitting into a normal work day.

We were successful in operating the APM for the three non-consecutive days with the desired CH<sub>4</sub> production rates for 7 h each day as planned. Table 1 summarizes the results of the three long-duration runs plus a more recent run.

**Table 1. Results of the Long-Duration APM Tests.**

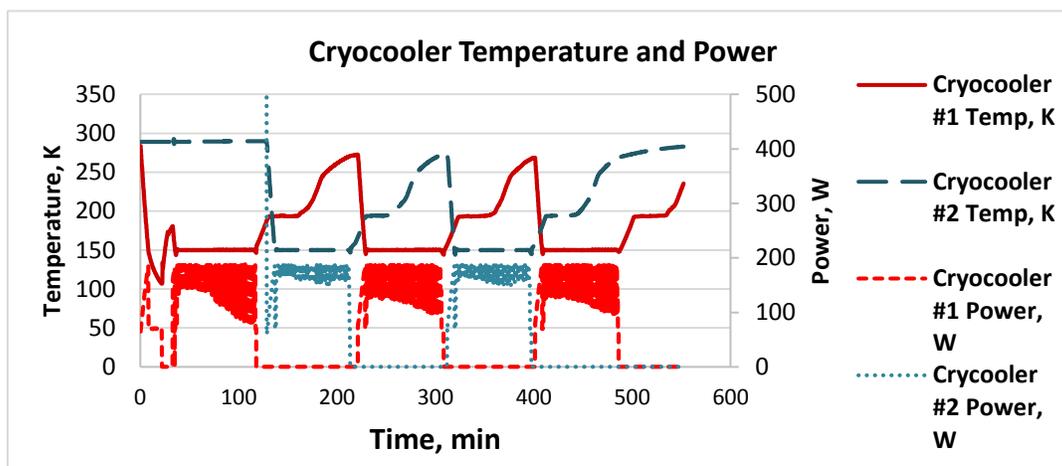
<i>Run No.</i>	<i>1</i>	<i>2</i>	<i>3</i>	<i>4</i>
Sabatier Run Duration	7.0 h	7.0 h	7.0 h	7.0 h
Gas Composition	CO <sub>2</sub>	CO <sub>2</sub>	Mars Gas	Mars Gas
Average CO <sub>2</sub> Freezing Rate	102 g/h	100 g/h	102 g/h	99 g/h
Average Fraction of CO <sub>2</sub> Frozen	79%	76%	72%	73%
Average Cryocooler Power	139 W	150 W	158 W	138 W
Average Power Needed to Freeze CO <sub>2</sub>	0.19 W/g/h	0.21 W/g/h	0.22 W/g/h	0.20 W/g/h
Average CO <sub>2</sub> Supply Rate to Freezers	128 g/h	142 g/h	146 g CO <sub>2</sub> /h	135 g/h
Average CH <sub>4</sub> Production Rate	32 g/h	32 g/h	32 g/h	32 g/h
Average CH <sub>4</sub> Purity	~99.9%	~99.9%	96.0%	~99.9%
Average H <sub>2</sub> O Produced	67 g/h	69 g/h	64 g/h	70 g/h

The Sabatier subsystem performed as desired with no overheating. The CH<sub>4</sub> production rate and gas chromatography indicate ~100% conversion of the 88 g CO<sub>2</sub>/h fed by the CO<sub>2</sub> Freezers and the storage tanks. During the first run, there was a minor issue with the loss of some CO<sub>2</sub> through a malfunctioning magnetic latch solenoid valve, which was replaced before the next run. The lost CO<sub>2</sub> was replaced with a Tedlar<sup>®</sup> bag filled from a gas supply bottle. Otherwise, the first run was nominal. The second run was fully nominal, with no interruptions or failures. The third run was nominal except that some gas escaped while manually draining water from the condenser, leading to a loss of efficiency in the membrane module, resulting in some H<sub>2</sub> in the CH<sub>4</sub> at times. This situation was corrected in the fourth run. Pure CO<sub>2</sub> was fed to the freezers during the first and second runs while the third and fourth runs were fed simulated Mars atmosphere. The freezers were slightly less efficient (72% and 73% CO<sub>2</sub> capture vs. 79% and 76% for the first and second runs) when using simulated Mars gas during the third and fourth runs because of the presence of N<sub>2</sub> and Ar. Prior to the start of the third and fourth runs, two additional freeze cycles using Mars gas were performed to prefill the CO<sub>2</sub> storage tanks for the runs. The results from these two freeze cycles were included in the data reported in Table 1.

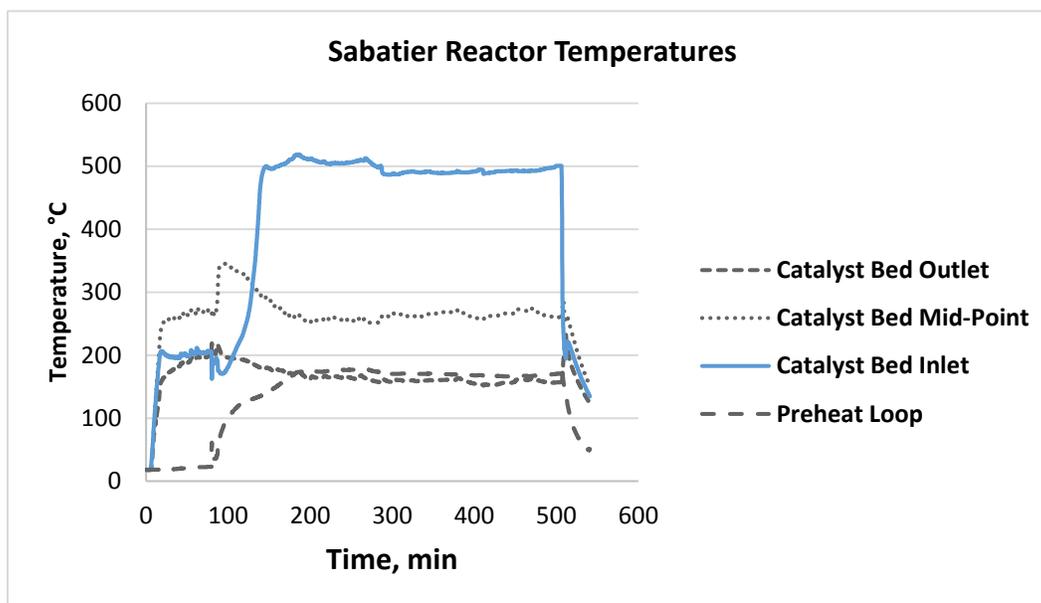
The average H<sub>2</sub>O collected was 67.5 g/h or 4.5 g/h less than the expected 72 g/h. More recent tests showed a dew point of about -23°C in the CH<sub>4</sub> product at 1 atm or 0.1 vol%. Thus, H<sub>2</sub>O loss to product would be only 0.03 g/h. Other causes of H<sub>2</sub>O loss will be investigated, such as adsorption by the separation membrane.

To illustrate the results of the four runs in more detail, Figure 4 shows the CO<sub>2</sub> Freezer cold head temperatures and cryocooler power consumption during the third run while Figure 5 shows

the temperatures of the Sabatier reactor during the second run.



**Figure 4. CO<sub>2</sub> Freezer Cold Head Temperatures and Cryocooler Power Consumption during the Third Run of the 7-h Integrated Test Series.**



**Figure 5. Sabatier Reactor Temperatures During the Second Run of the 7- Hour Integrated Test Series. (See Figure 1 for Locations.)**

The cryocooler power values are particularly important for future, large-scale CO<sub>2</sub> freezer designs. For example, one can estimate the mass, power, hardware, and thermal output for a freezer capable of supplying 3.1 kg of CO<sub>2</sub>/h to a Solid Oxide Electrolyzer producing 1.0 kg O<sub>2</sub>/h, which can be combined with duplicate modules to produce sufficient O<sub>2</sub> for a Mars Ascent Vehicle for a human Mars mission. The theoretical value to freeze 102 g CO<sub>2</sub>/h in the laboratory starting at 293 K is 20.6 W or 0.202 W/g CO<sub>2</sub>/h, including chilling unfrozen CO<sub>2</sub>, N<sub>2</sub>, and Ar, but not including heat leaks or chilling the copper cold head. The actual power consumed while freezing 102 g CO<sub>2</sub>/h averages 158 W out of a total capacity of 240 W for the Cryotel GT cryocooler. The GT model has a maximum cooling power (“lift”) of 34 W at 150 K so the actual lift used is 22.4 W, leading to a lift requirement of 0.219 W/g CO<sub>2</sub>/h, which is only 8.4% more

than the theoretical value. The measured value can then be used to estimate that the lift needed for the large-scale system is 680 W, which is 18% higher than the theoretical power of 576 W needed to chill the Mars atmosphere from 210 K and freeze 3.1 kg CO<sub>2</sub>/h.

The higher than theoretical value is caused by a higher starting temperature for the gases (293 K vs. 210 K), chilling the cold head, and by heat leakage from the environment, which should be less on Mars than in our lab. A Qdrive 2S241K-FAR cryocooler has a lift of 750 W at 150 K, which would be sufficient for freezing 3.1 kg CO<sub>2</sub>/h. This cryocooler requires an electrical input power of 4,500 W to provide 750 W of lift so the calculated electrical power for the large-scale system would be ~4,100 W. Our previous electrical power estimates had used the full Cryotel GT lift of 34 W since we had no measurement of the heat leak from the lab environment, which turns out to be small, greatly reducing the predicted power requirement on Mars.

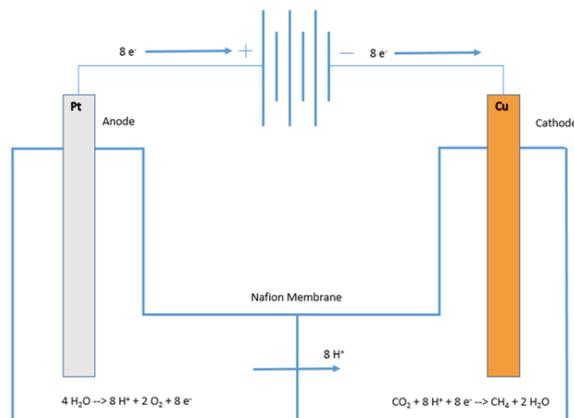
More recent work has automated the LabVIEW data acquisition/operating system to simplify testing. We plan to “virtually” integrate and operate the APM with other MARCO POLO hardware at KSC, which includes the RASSOR 2.0 (Regolith Advanced Surface Systems Operations Robot) excavator, the dust tolerant umbilical connector, the regolith feed system, the KSC WCM and the lander mockup along with the JSC SPM, the JSC WPM, and JSC propellant liquefaction. Virtual integration means simultaneous operation of hardware at the two centers while sharing data to control interdependent rates such as soil loading, water production, and H<sub>2</sub>/CH<sub>4</sub> production rates. Such testing will allow valuable experience to be gained while minimizing travel and shipping costs until sufficient funding becomes available. Overall, we are very pleased with our progress on this project.

## **MARS PROPELLANT PRODUCTION WITH IONIC LIQUIDS**

The Mars Propellant Production with Ionic Liquids project included the following tasks: 1) evaluation of process development; 2) process selection; 3) development of system requirements and experimental techniques; 4) system design, fabrication; applied research; and 5) preparation of documentation. As part of this project, KSC partnered with NASA Marshall Space Flight Center (MSFC) and Mercer University. MSFC was tasked to develop novel task-specific ionic liquids (TSILs) with high CO<sub>2</sub> solubility through a contract with AZ Technology. Mercer University was assigned the evaluation of the properties of the developed ILs, including measurement of their electrochemical windows and conductivity as well as CO<sub>2</sub> solubility as a function of temperature. The major accomplishments of the project are as follows: (1) CH<sub>4</sub> production was observed during the electrolysis of CO<sub>2</sub> dissolved in an IL. Carbon monoxide (CO) and possible CH<sub>4</sub> production was observed during electrolysis of CO<sub>2</sub> in AZ Technology-synthesized TSILs in a one-compartment electrochemical cell. (2) Five commercial and three MSFC synthesized ionic liquids were screened for feasibility by measuring CO<sub>2</sub> uptake, electrochemical window, conductivity, and compatibility with the electrode material. The AZ Technology-synthesized ILs were demonstrated to be capable of absorbing 70 - 90 mol% CO<sub>2</sub>. (3) Electrolysis experiments were performed on ILs that met feasibility requirements during screening. (4) Four different electrolysis cells and multiple electrode configurations were investigated in an attempt to produce CH<sub>4</sub>.

A detailed literature review of research literature and the internet was conducted regarding the use of ILs for conversion of CO<sub>2</sub> and H<sub>2</sub>O to CH<sub>4</sub> and O<sub>2</sub>. A great deal of literature exists describing the use of ILs in the electrochemical reduction of CO<sub>2</sub>. Based on the literature review, initial research was focused on using the commercially available [EMIM] and [BMIM] ionic

liquids with either tetrafluoroborate [BF<sub>4</sub>] or hexafluorophosphate [PF<sub>6</sub>] anions. Also, based on the literature review, a copper cathode and a platinum anode were chosen for the initial electrochemical cell design. Figure 6 shows a schematic of the electrochemical cell design and the desired reactions needed to make CH<sub>4</sub> and O<sub>2</sub>.



**Figure 6. Schematic of an Electrochemical System for Conversion of CO<sub>2</sub> to CH<sub>4</sub>. (Water is in the left cell and an IL is in the right cell.)**

During this project, eight ILs were evaluated for use in the electrochemical production of CH<sub>4</sub> from CO<sub>2</sub> and H<sub>2</sub>O. CO<sub>2</sub> capture capability was evaluated for all eight ILs, as well as determination of their electrochemical properties both with and without the presence of CO<sub>2</sub>. Additionally, the compatibility of the ILs with copper was evaluated to ensure that the ILs could be used with the chosen electrochemical cell design. The ILs that performed best overall in these evaluations were tested first in the electrolysis experiments.

Measurements of the electrical conductivity of TSILs were performed at Mercer University. The conductivity of the AZ Technology-synthesized ILs show a strong temperature dependence with and without the presence of CO<sub>2</sub>. Typical results show an order of magnitude increase in conductivity between room temperature and 80 °C. CO<sub>2</sub> reduces the conductivity of the IL's while the presence of H<sub>2</sub>O, at the level of a few percent, partially offsets the reduction.

Multiple electrolysis experiments were conducted in an effort to prove the feasibility of the simultaneous production of CH<sub>4</sub> and O<sub>2</sub> from the electrolysis of CO<sub>2</sub> and H<sub>2</sub>O. Initial CH<sub>4</sub> production experiments utilized polycarbonate electrochemical cells equipped with copper mesh working electrodes (cathode) and platinum mesh counter electrodes (anode). All cells used at KSC had two chambers, separated by a proton-exchange membrane. The first test cells were fabricated from polycarbonate, and initial experiments were carried out with a cell holding 10 ml of each electrolyte with a membrane area of 11 cm<sup>2</sup>. Test results obtained from electrolysis experiments performed using this cell were unexpected; the copper working electrode was poisoned and the presence of calcium and carbonate were detected on the surface of the electrode. Further investigation led to the conclusion that the source of the calcium and carbonate was the polycarbonate used for cell fabrication. To eliminate the presence of calcium and carbonate, an exact replica of the 10 ml cell was fabricated from high density polyethylene (HDPE).

Carbon monoxide, H<sub>2</sub>, and formate ion were produced with the HDPE cell, but no CH<sub>4</sub> was identified. Therefore, we used a different cell design from Pine Research Instrumentation which is a commercially available, two-chamber glass electrochemical cell. The Pine electrochemical

cell holds a total volume of approximately 25 – 30 ml of each electrolyte and is designed to allow a 5 cm<sup>2</sup> proton-exchange membrane to be used to separate the two halves of the cell. Small quantities of CH<sub>4</sub> were produced during electrolysis using this cell, but in all experiments, CO and H<sub>2</sub> were also produced. In total, six electrochemical cell designs were evaluated during this project.

Various ILs were utilized in the electrochemical experiments. Half of the ionic liquids initially selected were found to be incompatible with copper and were not subjected to further testing. Overall, the results of these experiments were somewhat inconclusive. Gas bubble generation was routinely observed on both the anode and cathode. However, the amount of gas produced was very near the detection limit of the gas chromatograph used for analysis and could therefore not be quantified. Although CH<sub>4</sub> was identified in multiple experiments, it was always produced with CO and H<sub>2</sub> indicating the electrochemical system was not very selective towards CH<sub>4</sub>. In addition, formate ion was identified in the cathode electrolyte. Experiments conducted using glass electrochemical cells were more successful, with the Pine Research Instrumentation glass cell having the best results. The results for experiments conducted using the 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM] [TfB]) IL were the most promising; the production of CH<sub>4</sub> was observed, but the production rate was determined to be very low. A darkening of the copper cathode was also observed in these experiments. Various tests were performed using a cathode with increased surface area (5x) to try to improve the CH<sub>4</sub> production rate. To date, however, increasing the surface area of the cathode has not resulted in increased CH<sub>4</sub> production rates.

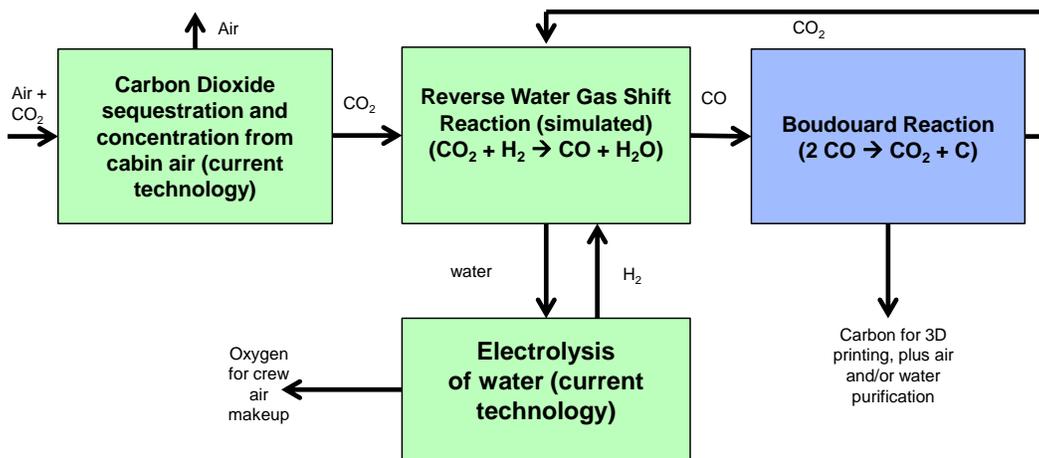
Experiments were also performed at Mercer University using a single compartment cell. This cell consisted of a titanium dioxide working electrode and a platinum counter electrode. The TSIL was saturated with CO<sub>2</sub> and 2% (by volume) H<sub>2</sub>O was added. Preliminary results show that small quantities of CH<sub>4</sub> and CO were produced.

There were a number of challenges identified during the project that remain unsolved: (1) CH<sub>4</sub> production occurred with very low faradaic efficiency, and always with the co-production of the unwanted byproducts, H<sub>2</sub> and CO, even though the literature suggested that the chosen electrode material and cell design should have high efficiency and minimize byproducts. (2) Even when initial screening indicated that the copper electrode was compatible with the IL, the electrode was always altered during electrolysis experiments. This indicates that electrode stability is an extremely complex issue that needs to be addressed. (3) The nature of the electrode material is important. The literature review indicated that copper electrodes were most successful in producing CH<sub>4</sub>. However, copper can have different crystalline forms and this was often not reported in the literature. In experiments performed at KSC, a sputtered copper electrode performed better than a copper mesh electrode. It is currently unknown why this difference exists. Future evaluations of this process should pay close attention to the electrode material, whether it is copper or something else. We plan to propose further activities in this area in the future after careful consideration of the issues encountered and we develop approaches to resolve them.

## **SELF-CLEANING BOUDOUARD REACTOR**

As noted in the Introduction, the current ISS O<sub>2</sub> recovery method utilizes the Sabatier process which is only 50% efficient due to limits on H<sub>2</sub> availability. This means that for a full crew over 3 kg of H<sub>2</sub>O/day are used in making O<sub>2</sub> that is not recovered from CO<sub>2</sub>. At cargo launch prices of \$10,000-\$40,000/kg, this costs \$30,000-\$120,000/day, depending on the supplier. For deep space

exploration missions, in-space resupply is virtually impossible so nearly 100% recovery is essential to reduce launch mass. The carbon product from the Boudouard reaction (box on the right side of Figure 7) could be used as air or H<sub>2</sub>O purification filters, which we will test, as a filler for 3D printing, as a dry lubricant suitable for low-pressure applications, or as a reactant in other processes, such as carbothermal reduction or as consumable electrodes for metal production. By producing a self-cleaning Boudouard reactor the single greatest challenge of the Bosch process is resolved and full O<sub>2</sub> recovery can be realized. The decrease in consumable requirements would be significant for the ISS and enabling for deep space exploration missions. In addition, O<sub>2</sub> production is a limiting factor in ISS population and a system such as this can help improve that situation.



**Figure 7. Schematic Representation of the Bosch Reaction by a Combination of the RWGS Reaction and the Boudouard Reaction Followed by Electrolysis of Water to Recover Oxygen from Carbon Dioxide.**

Using our experience with similar chemical reactions in ISRU and the Boudouard reaction expertise of team member Pioneer Astronautics, e.g. Berggren *et al.* (2009), we built two Boudouard reactors with two different cleaning methods for testing on a MSFC test stand that converts CO<sub>2</sub> to CO using a RWGS reactor. Calculations based on work at MSFC indicate the surface area of our reusable catalyst is comparable to that of their steel wool catalyst, but with the potential for removal of the carbon deposits as they form. During screening tests at KSC, the CO stream, which contains H<sub>2</sub> to enhance the reaction, was fed to the Boudouard reactors, which converts it to CO<sub>2</sub> and carbon fines. The gases were analyzed with gas chromatography and mass flow meters. Conversion of CO in the best design peaked at 72% in 37 h while 25% of the carbon was collected in a filter bag before the reactor clogged, showing the concept is viable. The goal is to arrive at a reactor and catalyst design which reduces or eliminates consumables with this reaction by 80% or greater. We are testing a modified cleaning mechanism before shipment to MSFC for testing in their system. Exact designs will remain proprietary until determinations are made on their patentability.

## CONCLUSIONS

At KSC, we have made excellent progress in developing the Atmospheric Processing Module, demonstrating integrated operations of the CO<sub>2</sub> Freezers and the Sabatier Subsystem to make methane and water from simulated Mars resources as part of a larger system that also

would produce oxygen to make a bipropellant suitable for use on Mars. Development of an alternate method to produce methane/oxygen bipropellant using electrolysis of CO<sub>2</sub> and water in Ionic Liquids has proven to be challenging, with unexpected issues with electrode and IL stability that need further work. We have also investigated a method to recover oxygen from spacecraft CO<sub>2</sub> using a self-cleaning carbon formation reactor. Our initial results have shown some success, but further work is needed to refine the process. In general, we are encouraged by our progress and look forward to continuing to develop the technologies needed to explore Mars.

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