Atmosphere Processing Module Automation and Catalyst Durability Analysis for Mars ISRU Pathfinder

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Atmosphere Processing Module Automation and Catalyst Durability Analysis for Mars ISRU Pathfinder

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The Mars In-Situ Resource Utilization Pathfinder was designed to create fuel using components found in the planet's atmosphere and regolith for an ascension vehicle to return a potential sample return or crew return vehicle from Mars. The Atmosphere Processing Module (APM), a subunit of the pathfinder, uses cryocoolers to isolate and collect carbon dioxide from Mars simulant gas. The carbon dioxide is fed with hydrogen into a Sabatier reactor where methane is produced. The APM is currently undergoing the final stages of testing at Kennedy Space Center prior to process integration testing with the other subunits of the pathfinder. The automation software for the APM cryocoolers was tested and found to perform nominally. The catalyst used for the Sabatier reactor was investigated to determine the factors contributing to catalyst failure. The results from the catalyst testing require further analysis, but it appears that the rapid change in temperature during reactor start up or the elevated operating temperature is responsible for the changes observed in the catalyst.

Nomenclature

APM	=	Atmosphere Processing Module
CH_4	=	Methane
CO_2	=	Carbon Dioxide
CO	=	Carbon Monoxide
FESEM	=	Field Emission Scanning Electron Microscope
GC	=	Gas Chromatograph/Gas Chromatography
H_2	=	Hydrogen
H_2O	=	Water
ISRU	=	In-Situ Resource Utilization
ISS	=	International Space Station
MIP	=	Mars ISRU Pathfinder
PSI, PSIA	=	Pounds per Square Inch (Absolute)
SLPM	=	Standard Liter per Minute
SEM/EDS	=	Scanning Electron Microscope/Energy Dispersive X-ray
XPS	=	X-ray Photoelectron Spectroscope

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I. Introduction

A. Atmosphere Processing Module

In-Situ Resource Utilization (ISRU) technologies are currently being developed to convert resources available on extra-terrestrial bodies, as well as the waste generated during long duration, deep space missions into useable products. ISRU supports human spaceflight and allows for a broader range of missions by reducing supply payload weight, logistical volume, and launch costs.

One such project, the Mars ISRU Pathfinder (MIP), is currently under development to provide fuel for an ascent vehicle to return a crewed or sample return mission from Mars, eliminating the need to transport this fuel from Earth. Creating the fuel where it will be used greatly decreases the volume, weight and cost requirements of the mission. The MIP will be sent to Mars ahead of a crewed mission to convert carbon dioxide from the Martian atmosphere and water from its regolith into methane and oxygen. The methane and oxygen will be stored on the planet as cryogenic liquids until they are used as rocket propellant to launch spacecraft from the surface of Mars on the return trip to Earth.

The MIP consists of a 3x3 meter, octagonal lander which will house an atmosphere processing module, a fuel liquefaction module, a water processing module, a water cleanup module, and a soil processing module. Lab-scale demonstration MIP lander components have been developed and constructed as a NASA cross-center effort. The components are currently undergoing testing, and soon, integrated testing will begin.

At Kennedy Space Center, the Mars Atmosphere Processing Module (APM), a subunit of the Mars ISRU Pathfinder, has been constructed at $1/20^{th}$ scale of flight productivity. The APM converts atmospheric carbon dioxide (CO_2) to methane (CH_4) using cryogenic freezing to separate CO_2 from the atmosphere and collect it. The Martian atmosphere is composed of approximately 2.7% nitrogen, 1.6% argon, 95.7% CO_2 and trace levels of water vapor, oxygen, and carbon monoxide [1] at a pressure of 8 Torr [2]. Carbon dioxide freezes at a higher temperature than the other major components of the Mars atmosphere. The APM takes advantage of this fact by using a cryocooler to freeze the CO_2 from the atmosphere at 150K as a means to isolate and collect the carbon dioxide needed for the fuel reaction. The APM test set up was designed to freeze and collect 88 g/h CO_2 [2]. Once the CO_2 has been collected, the frozen CO_2 is sublimed by heaters, then the gaseous CO_2, along with hydrogen (H_2), are fed into a Sabatier reactor. The CO_2 and H_2 pass over a catalyst in a packed bed and react to form CH_4 and water vapor as seen in the equation below.

$$CO_2 + 4H_2 \rightarrow 2H_2O + CH_4 \qquad \text{[Eq. 1] [3]}$$

The hydrogen needed for this reaction is currently provided by bottled H_2, but another component of MIP is under development to produce H_2 by isolating and electrolyzing water found in the Martian regolith.
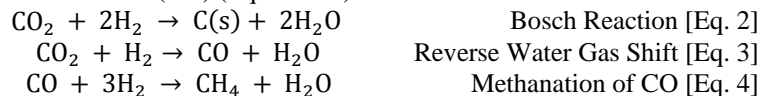
The APM has already proven to be effective, and previous laboratory tests have been successful at nominal conditions. The operating system is now being optimized for upper and lower performance limits. Along with the process optimization, further testing is needed to determine failure mode(s) of the catalyst, prove operating longevity of the apparatus, and to successfully automate all processes carried out by the APM, particularly the Sabatier reactor.

The purpose of the runs described in this paper was to test the automation system that was recently implemented to control the cryocooler subsystem of the APM. Completing this testing for APM will move ISRU closer toward integrated testing among the centers, connecting the operation of all the subunits that comprise the Mars ISRU Pathfinder, an important step in the flight readiness process.

B. Catalyst

The APM Sabatier reaction requires a catalyst for the reaction to proceed with reasonable conversion rates. Known effective catalysts include nickel, ruthenium, cobalt, and rhodium [4]. The chosen catalyst must be not only effective but also robust and able to withstand a wide range of conditions. It must also be able to perform for a long period of time without diminishing significantly in effectiveness. Ruthenium (Ru) was chosen for the APM. Ru is a more active catalyst than cobalt and rhodium, and it does not present as many operating issues and has a higher methane product selectivity compared to nickel [4], [5]. However, rhodium has shown to exhibit higher conversion than ruthenium in certain conditions [5].

The selectivity of the catalyst is especially important, because when carbon dioxide and hydrogen are combined in a heated, high h pressure environment, many other reaction can occur in addition to the desired reaction displayed in Equation 1. The three main side reactions of concern are: the Bosch reaction (Equation 2), the reverse water gas shift (Equation 3), and the methanation of carbon monoxide (CO) (Equation 4).

$$CO_2 + 2H_2 \rightarrow C(s) + 2H_2O \qquad \text{Bosch Reaction [Eq. 2]}$$
$$CO_2 + H_2 \rightarrow CO + H_2O \qquad \text{Reverse Water Gas Shift [Eq. 3]}$$
$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad \text{Methanation of CO [Eq. 4]}$$

While these reactions may be desirable in other processes, this system requires pure CH_4 product gas to ensure proper storage and function in a rocket engine.

A 0.5% ruthenium on alumina pellet was selected for the Sabatier reactor in the APM. The catalyst pellets were commercial off the shelf (COTS) and purchased from Aldrich. Testing has shown that the catalyst provides a high conversion rate in this setup (up to 90% in a single pass [6]), but the operational lifetime may be shorter than desired. The longevity of the catalyst appears to be affected by anticipated, off-nominal operating conditions.

The idea of using a Sabatier reactor to enable long-duration space missions is not new. A Sabatier reactor has been in used on the International Space Station (ISS) since October 2010 [7]. This reactor was designed and implemented in order to close the oxygen loop on the ISS by producing water from metabolic CO_2. The water is then electrolyzed to provide oxygen to the crew and H_2 for the Sabatier reaction. Currently, the methane is vented overboard as a waste byproduct. In order to accommodate a wide range of operating parameters, especially variability in the CO_2 load, Hamilton Sundstrand developed a proprietary catalyst for use in the Sabatier reactor that is described as a, *"highly dispersed, high mass loading of a noble metal catalyst deposited on a robust, high surface area alumina"* [7]. The reactor is expected to provide over 99% conversion rates for at least 10 years [7].

Figure 1. The spent catalyst (left) was removed from the Sabatier reactor after it no longer performed as expected. It is much lighter in appearance and has many broken pellets compared to unused catalyst (right).

Off-nominal conditions were tested to determine a range of suitable operation parameters for the reactor. During a test with flow rates higher than nominal, the Sabatier catalyst reached 586°C at feed gas flow rates of 3.2 SLPM for CO_2 and 4.0 SLPM for H_2. Following that test, the Sabatier reactor was unable to maintain a steady reaction resulting in temperature swings throughout the reactor. Gas Chromatograph (GC) analysis of the product gas revealed carbon monoxide production during this period. The catalyst was removed from the reactor in December 2015 and replaced with unused catalyst. Figure 1 shows that the appearance of the spent catalyst differs from the unused catalyst. The spent catalyst is much lighter in color than the black, unused catalyst, and the spent catalyst contains many broken pellets.

During nominal operation, the reactor undergoes a slow preheat up to 210°C, then the temperature inside the reactor rises to temperatures between 453°C and 467°C within approximately 7 minutes before stabilizing at approximately 450°C at the inlet. The temperature of the reactor typically decreases as the distance from the inlet region increases.

It is believed that this sudden change in temperature is heat shocking the catalyst and causing sintering and physical damage to the pellets. The pellets expand in the elevated temperatures but are restricted by the packed bed reactor which may also be causing physical damage to the catalyst.

Sintering can occur in ruthenium at temperatures greater than 500°C, irreversibly damaging the catalyst [8]. Sintering can cause a reduction in catalytic surface area due to crystal growth of catalytic phase, the support area may decrease due to support collapse and pore collapse, or it could cause a transformation of catalyst from a catalytic phase to a non-catalytic phase [8]. Okal and Kepinski showed that at temperatures of 600-700°C, the smallest ruthenium particles migrate and coalesce to form clusters, but a majority of the ruthenium particles remain on the surface similar to the as-prepared catalyst [9].

Ruthenium catalyst can be poisoned by oxygen, carbon monoxide, water, sulfur, and acetylene. Ruthenium oxide (RuO_4) can be formed in the presence of oxygen and will cause oxidation of hydrocarbons [8].

The goal of the catalyst testing it to determine the cause of catalyst failure that occurred after approximately one year of intermittent, successful Sabatier reactor operation.

II. Materials and Methods

A. Atmosphere Processing Module

Kennedy Space Center built and performs testing for the APM component of the MIP. The simplified equipment configuration diagram for the cryocooler section is shown in Figure 2. The carbon dioxide collection section of the APM contained two Cryotel GT cryocoolers operating at 150K. The cryocoolers functioned to isolate and capture CO_2 from Mars gas. The Mars gas simulant was delivered to the cryocoolers from a k-bottle with the composition of 3.0% nitrogen (N_2), 1.6% argon (Ar), and 95.4% carbon dioxide. During earlier tests, bottled CO_2 was used instead of

the Mars gas simulant as a cost-saving measure. The cryocoolers were covered by aluminum hoods that enabled the simulation of the Mars atmosphere with an air pressure of 8 Torr achieved by the use of a vacuum pump. The
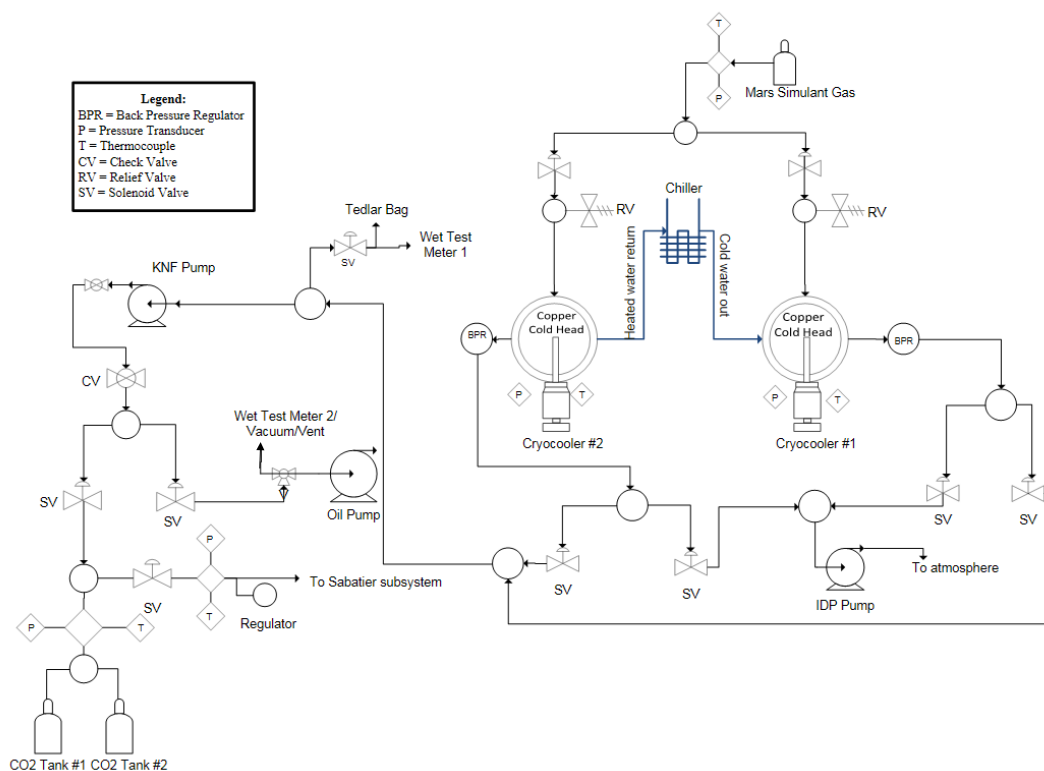

Figure 2. The cryocooler section of the APM. This section was responsible for isolating, collecting and storing CO_2.

cryocoolers froze carbon dioxide from the flow of Mars simulant gas at 150K for 75 minutes with target Mars gas simulant flow rate through the hoods of 1.2 SLPM. Following the freezing period, the heaters within the cryocooler hood turned on, forcing the frozen CO_2 to sublime. This sublimed CO_2 gas was collected in a Tedlar bag before being pumped into storage tanks that were maintained at a pressure of 60-100 psia. From the storage tanks, the CO_2 flowed into the Sabatier reactor at a stoichiometric, 4:1 ratio of H_2 and CO_2 respectively.

Before the reaction was initiated, the Sabatier reactor had to be preheated to 210°C. The Sabatier reaction section of the APM is shown in Figure 3. During preheating, a hydrogen blanket flowed through the reactor to purge the reactor, protect the catalyst by preventing oxidation, and cause the reactor to reach its operating pressure of 40 psia. The catalyst used throughout testing was 0.5% ruthenium on alumina, 3.2mm cylindrical pellets procured from Aldrich. Once the inlet of the reactor reached 210°C, a 4.5:1, H2:CO2 ratio was fed into the reactor at 3.375 SLPM and 0.75 SLPM respectively. When the reactor inlet temperature stabilized around 450°C, the H_2 flow was reduced to 3.0 SLPM to provide a 4:1 feed gas ratio.

The reactor exit gas stream contained water vapor, methane, and unreacted carbon dioxide and hydrogen. This stream passed through a chilled heat exchanger to condense and collect the water before entering an Air Products PA1020-N1-2A-00 membrane separator. The methane retentate exited the assembly through a flow meter and GC to monitor product quantity and purity. The carbon dioxide and hydrogen permeate were recycled into the reactor.

The flow controllers, cryocooler power, and the Sabatier reactor heating coils were operated by LabVIEW. Thermocouples, pressure transducers and flow meters provided data which was recorded by LabVIEW during testing. Watt meters measured the power requirements of the APM components throughout testing. These values were recorded by hand throughout testing.

The ideal testing run consisted of a two hour Sabatier reactor preheat followed by a seven hour continuous reactor operation. During this time, the cryocoolers ran approximately five cycles. Each cryocooler cycle consisted of periods of carbon dioxide freezing, sublimation, and storage of the collected CO_2. Cryocooler operation alternated between the two cryocoolers and the cycles were timed to maintain adequate flow of CO_2 to the reactor. The temperature in

the reactor and cryocoolers were monitored closely, the gas flow rates were recorded to assess any anomalies, and the pressure drop across the membrane separator was maintained at approximately 30 psi for optimal operation. The GC
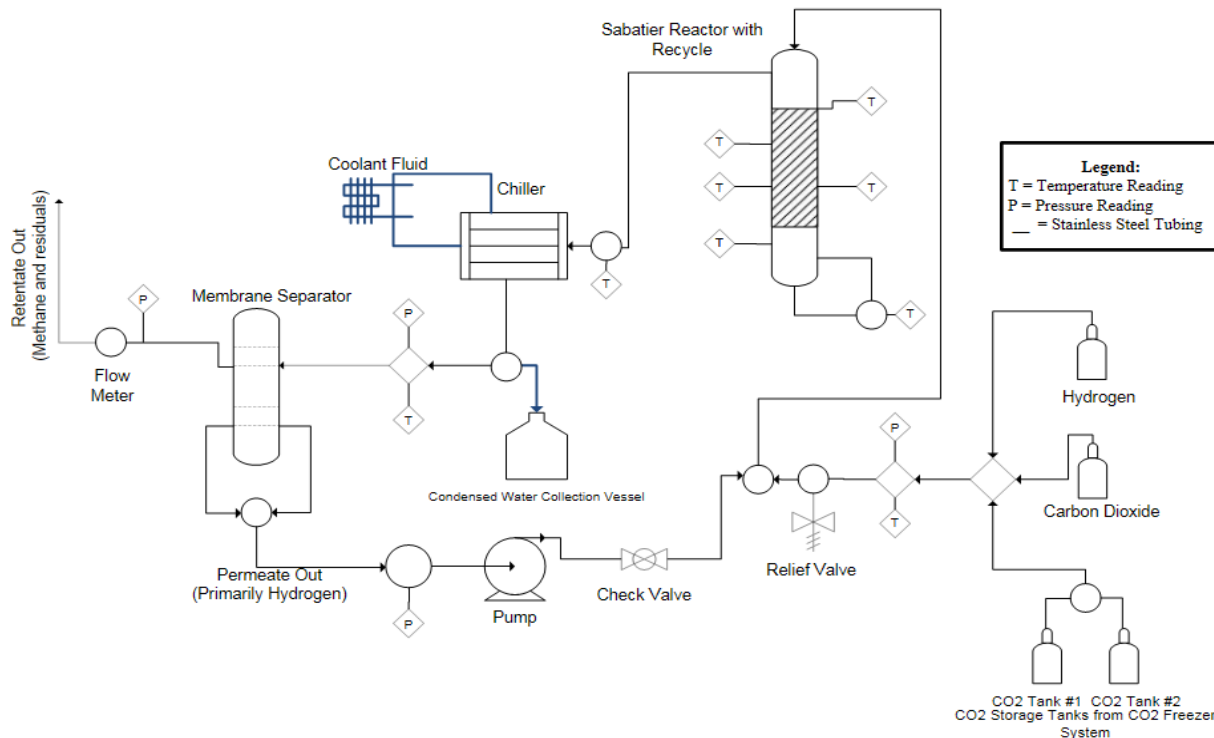

Figure 3. The Sabatier reactor section of the APM converts the CO_2 from the cryocooler section of the APM and hydrogen from a k-bottle into a methane product stream.

provided gas composition data for the product gas stream to ensure proper purity was achieved. The relative humidity of the product stream and the mass of the water collected in the condenser were measured to determine if the expected water production had occurred. Finally, the power data collected was used to establish the electrical needs of the current components, and these values will be taken into account in further design efforts.

B. Catalyst

The catalyst was tested in conditions similar to those that occur in the APM reactor chamber to determine the cause of the catalyst failure. To mimic the conditions in the reactor, the catalyst went through heat shock cycles packed in a small stainless steel tube. Unconstrained catalyst pellets in an open crucible were also exposed to the same heat shock cycles to act as a control. The diagram in Figure 4 shows the catalyst packing configuration for testing. The stainless steel tube had a 1/2" OD and was three inches long. The ends were packed with glass wool in the first five cycles, however, the high temperatures caused degradation of the glass wool. The wool was replaced with glass tape for the remaining five cycles. Each catalyst tube underwent a total of ten heat cycles.
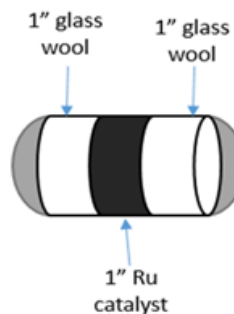

Figure 4. The catalyst was packed into a ½" OD, 3" long stainless steel tube in order to mimic the constricted conditions in the Sabatier reactor.

For the heat shock testing, a Whip Mix Pro 100 ceramic furnace was used, because it had the capability raising a platform into a preheated furnace providing a thermal shock to the catalyst placed on the platform. The furnace with the platform lowered can be seen in Figure 5.

The furnace used a vacuum and nitrogen gas line to provide an inert environment for the catalyst during testing. The catalyst arrived in an oxidized state, but to prevent further oxidation and to more closely match the conditions in the reactor, the inert environment was used during each run.

Figure 5. The Whip Mix Pro 100 ceramic furnace was used to heat shock the catalyst samples. The samples were placed on the platform which lifted them into the preheated
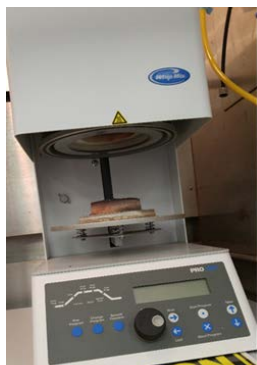
Two packed tubes like those shown in Figure 4 were initially made, one for each heat shock temperature. One tube was cycled at 450°C, the nominal operating temperature of the reactor, as a control. The other tube was cycled at 600°C, the maximum temperature reached before the catalyst in the reactor failed. Each heat cycle consisted of a furnace preheat to the desired temperature, the catalyst tube and free pellets, placed in a stainless steel crucible, were set on the furnace platform and mechanically lifted into the heated furnace. The catalyst remained at the elevated temperature for 20 minutes, then the furnace reduced temperature over approximately 2 hours until the platform lowered at 200°C. The tube and loose pellets were weighed before and after every cycle.

After the first five cycles, each tube was unpacked, and all the pellets were analyzed using a scanning electron microscope/energy dispersive X-ray (SEM/EDS) and optical microscope. The same catalyst was repacked in the tubes, and after five more cycles, they were analyzed using a field emission scanning electron microscope (FESEM), SEM/EDS and X-ray photoelectron spectroscopy (XPS). A third trial was conducted with fresh catalyst packed in a tube in the same manner as the first two tubes and run through ten heat shock cycles at 450°C. The pellets inside the third tube were analyzed visually.

III. Results

A. Atmosphere Processing Module

A snapshot of the results for all the runs performed this semester can be seen below in Table 1. Tests 8 and 9 were completed by pumping the sublimed CO_2 from the cryocoolers through a wet test meter to measure the volume instead of pumping the CO_2 into the storage tanks. The cryocooler CO_2 feed rate shows the value for only the CO_2 component of the mixed gas, and the cryocooler freezing effectiveness is a ratio of CO_2 frozen over the CO_2 component of the gas flow through the cryocoolers.

Table 1. The results for cryocooler cycle and Sabatier reactor cycles show relatively consistent results with high methane purity in the exit stream.)

Run	1	2	3	4	5	6	7	8	9
Date	2/4/2016	2/9/2016	2/18/2016	3/3/2016	3/8/2016	3/17/2016	3/23/2016	3/31/2016	4/5/2016
Sabatier Reactor Operation Time (h)	0	1.4	4.8	3.1	2.6	7.2	0	0	0
Number of Cryocooler Cycles	1	1	3	3	2	5	1	4	4
Cryocooler Feed Gas	CO2	CO2	CO2	CO2	CO2	Mars Gas	Mars Gas	Mars Gas	Mars Gas
Avg Cryocooler Power (W)	167	159	161	153	159	138	135	140	105
Cryocooler Freezing Efficiency (J/g CO2)	4938	4040	5240	5003	4880	5022	4833	4339	3730
Cryocooler CO2 Feed Rate (g/h)	164	166	145	152	154	138	135	136	113
Avg CO2 Freezing Rate (g/h)	121	142	110	110	117	99	101	116	103
Cryocooler CO2 Freezing Effectiveness (%)	78	86	80	76	80	74	74	78	78
Methane Production (g/h)	-	32	32	32	32	32	-	-	-
Methane Purity (%)	-	97.95	99.91	99.96	99.89	99.98	-	-	-
Water production (g/h)	-	86	69	73	68	70	-	-	-
Inlet Reactor Temp, T8 (°C)	-	430	431	422	434	440	-	-	-
Mid Internal Reactor Temp, T9 (°C)	-	258	283	257	286	293	-	-	-
Upper Internal Reactor Temp, T10 (°C)	-	161	171	159	179	183	-	-	-
Reactor Exit Temp, T11 (°C)	-	46	54	54	54	56	-	-	-
Condensed Water Temp, T12 (°C)	-	4	5	5	5	5	-	-	-

B. Catalyst

After the first five heat shock cycles, the catalyst pellets from the 600°C and 450°C test groups were compared to unused catalyst and the spent catalyst that had been removed from the reactor in December 2015. First, the pellets were photographed using an optical microscope at an apparent magnification of 55x (Figure 6) to examine the condition and color of the pellets. The catalyst that had been removed from the reactor in December was much lighter in color than the unused catalyst. The 600°C cycle pellets appear to be slightly lighter in color, and the 450°C cycle pellets are similar in hue to the unused pellet. The SEM/EDS analysis did not reveal any trends.

Figure 6. The catalyst pellets were photographed after five heat cycles using an optical microscope at an apparent magnification of 55x.

The pellets were analyzed again after 10 heat shock cycles. The image below, Figure 7, shows that the pellets were physically damaged. One pellet split in half at the lower heat shock temperature.
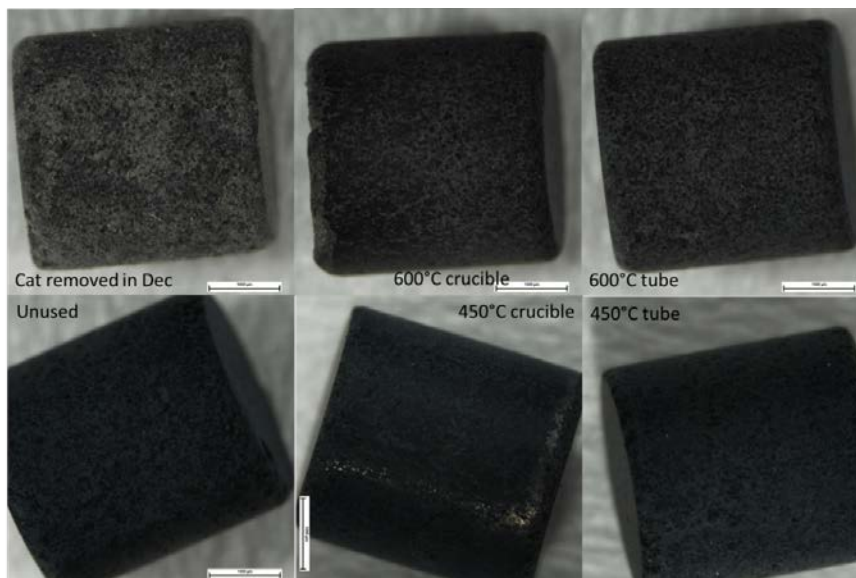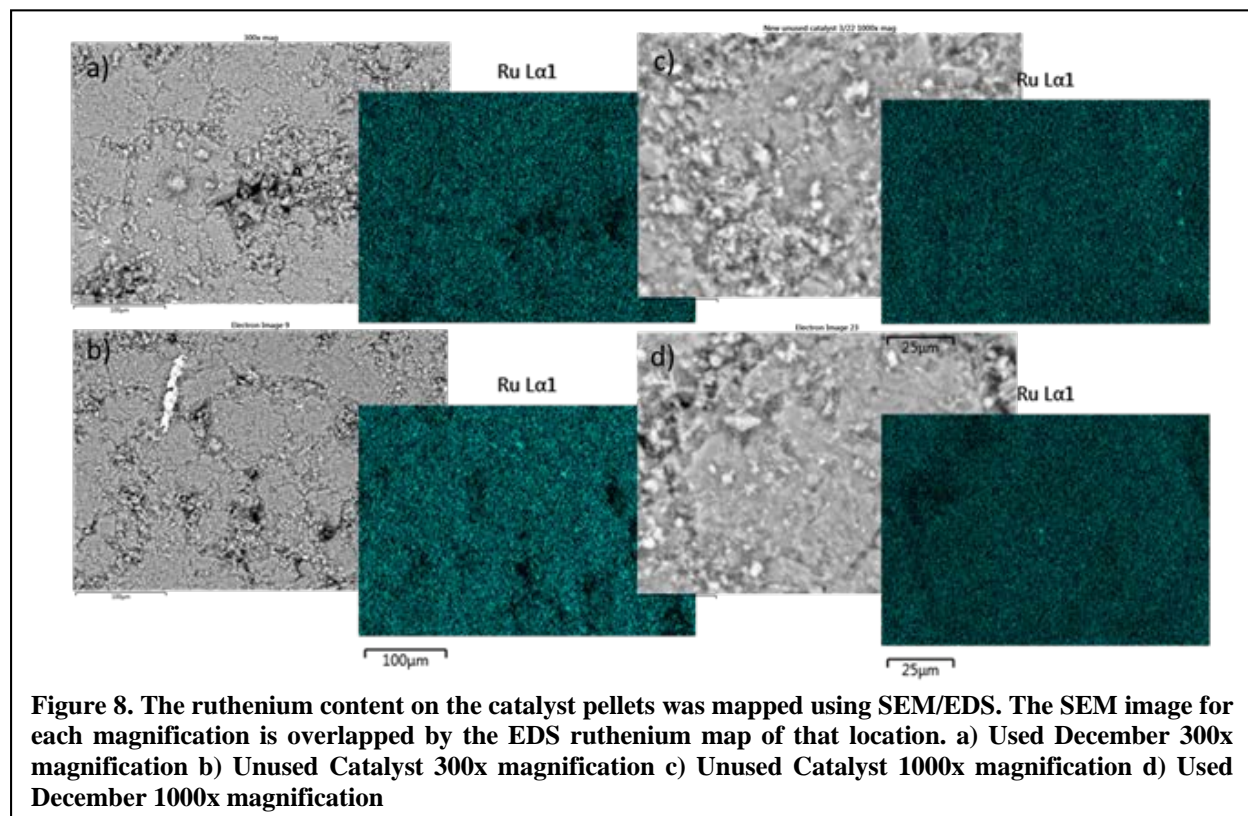

Figure 7. The catalyst pellets that were constricted in packed tubes show signs of physical damage after ten heat shock cycles. The arrows show the damaged pellets from the 450°C heat shock tube (left) and the 600°C heat shock tube (right).

The catalyst pellets were examined under SEM/EDS using the EDS mapping. The results can be seen below in Figure 8. Unused catalyst was compared to the catalyst removed from the reactor in December. The ruthenium element maps do not show a trend at 300x or 1000x magnification.

Figure 8. The ruthenium content on the catalyst pellets was mapped using SEM/EDS. The SEM image for each magnification is overlapped by the EDS ruthenium map of that location. a) Used December 300x magnification b) Unused Catalyst 300x magnification c) Unused Catalyst 1000x magnification d) Used December 1000x magnification

The catalyst pellets from the heat shock trials, unused catalyst and spent catalyst were imaged with the SEM/EDS at a very low magnification. The images in Figure 9 show that the condition of the edges of the catalyst pellets and the surface condition of the pellets do not exhibit a trend in physical appearance changes or damage related to pellet use conditions.
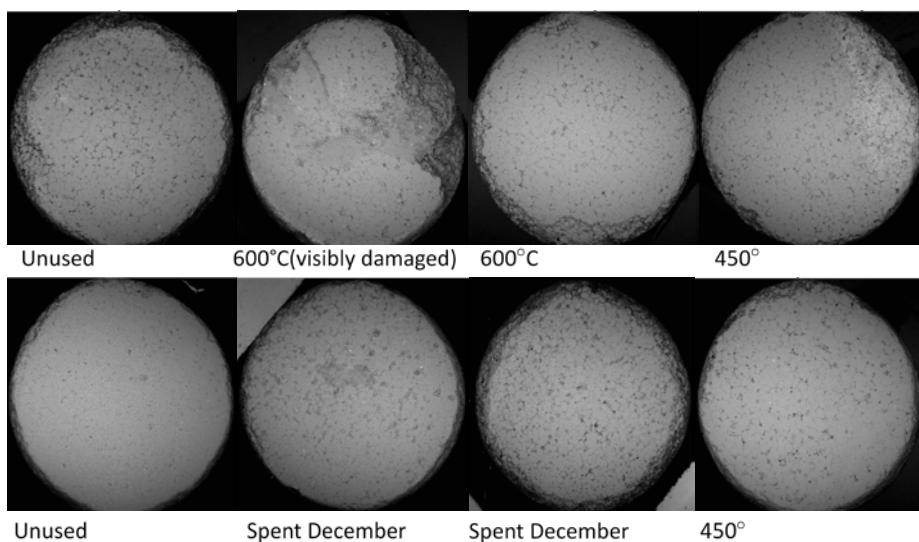

Figure 9. The catalyst pellets were imaged using the SEM/EDS on low magnification. There does not appear to be a trend in the amount of physical damage to the pellet compared to the use conditions of the pellet.

A FESEM was used to collect images of the pellet surfaces at 15,000x magnification of the unused pellets and spent reactor catalyst pellets. The images of spent reactor catalyst have disperse, white spots covering the surface. The unused catalyst images have fewer or no white specks. Representative images of this trend can be seen in Figure 10.
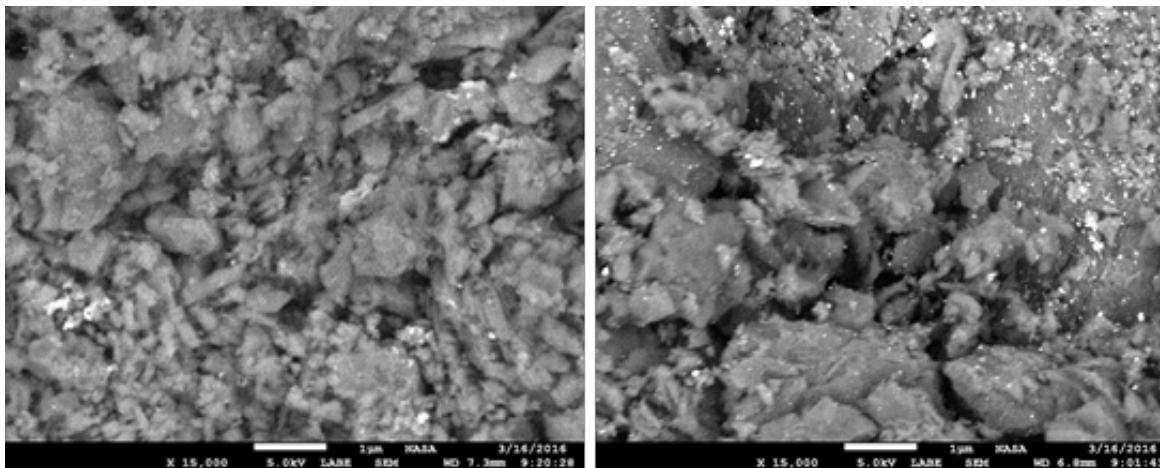

Figure 10. The unused catalyst (left) shows fewer bright specks than the spent catalyst (right) when imaged at 15,000x magnification on an FESEM.

The last test carried out on the ten-cycle pellets was XPS analysis. Sample pellets from each group (unused, spent catalyst from the reactor, 600°C heat shock tube, and 450°C heat shock tube) were analyzed. The results show that, in general, for the surface scans, the new catalyst has two peaks in the aluminum and one in the ruthenium binding energies, whereas the used catalyst show one peak in the aluminum and two or more peaks in the ruthenium binding energy. Representative images of the trends in bond energies of surface peaks are displayed in Table 1.

Table 2. The surface peaks from XPS analysis of pellets representing the trend of one peak in aluminum and two or more peaks in ruthenium for the heated pellets and two peaks in aluminum and one peak in the ruthenium for the unused catalyst.)

Type of ↓ Catalyst Peak→	Aluminum 2p	Ruthenium 3d
Unused Catalyst		
450°C Heat Shock		
Spent Catalyst Removed December 2015		

A third tube of catalyst was prepared and tested at 450°C for 10 heat shock cycles. This tube also exhibited pellet damage (Figure 11).

IV. Discussion

A. Atmosphere Processing Assembly

The automation software for the cryocoolers has operated successfully for approximately 20 cryocooler automation cycles. Adjustments had to be made to prevent valves in other parts of the system from closing when a cryocooler cycle started, and the software was altered to allow time for data transmission so that information such as the cryocooler temperature could be
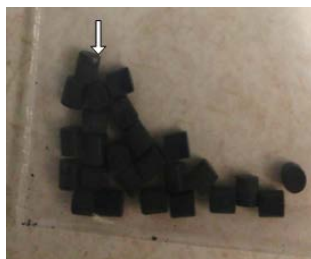

Figure 11. The 450°C heat shock experiment was repeated with fresh catalyst. The second experiment also resulted in physical damage to the pellets.

monitored and used for the automation software. Also, the cryocooler power supply and communication system was rewired and the software improved to prevent arbitrary cryocooler function.

For many runs, the amount of water that should be produced given the amount of methane production exceeds the amount of water collected during the run. This disparity can be off by more than 11%. It was thought that the membrane separator may have been collecting water, so the membrane separator apparatus was weighed before and after Runs 2 and 3. The mass of the apparatus did not change, indicating that water was not collecting there. Other possible explanations could be that the relative humidity of the product stream varied from approximately 3% to 16% over time, or the orientation of the water condenser heat exchanger could be trapping water.

During testing, the water collected from the condenser located downstream of the reactor had a pH of 5.5. Previously, the water collected tested at a pH of 7. An increase in the amount of CO_2 in the reactor effluent stream could be causing an increase in acidity in the condensed water. An increase in CO_2 in the reactor effluent stream indicates the reaction is not reaching the same conversion as it was previously. Soon, a water cleanup module will be connected to the water collection system. Water with non-neutral pH may cause this equipment to malfunction.

When the hood from cryocooler #2 was removed in February, a fine layer of brown dust was observed over all interior surfaces. Analyses by SEM and XPS was inconclusive, but the main component of the dust was determined to be copper. It is important to determine origin of this dust and its production rate, because if the copper cold caps degrade over time, the flight equipment will need to be more robust or thicker to accommodate for the observed wear.

The heater damage caused by the vacuum tubing could be prevented by shortening the vacuum tube. However, earlier tests showed that the vacuum tube must be placed very close to the cold finger to encourage gas flow across and through the freezing surfaces. The cryocooler equipment was not altered other than the new heater installation.

During Mars gas flow, the pressure inside the cryocooler hoods increased throughout the run, starting at 8 Torr and reaching just over 11 Torr. Large changes in pressure have minimal effects on freezing temperature, so the 3 Torr change in pressure will likely have a negligible effect on the freezing temperature of each Mars gas species.

At Mars gas flow rate as low as 1.0 SLPM (Run 9), the CO_2 freezing rate greatly exceeded the 88 g/h freezing rate required by the Sabatier reactor. This lower flow rate meets the system requirements and uses far less energy than the higher flow rates. However, during Sabatier operation at nominal cryocooler gas flow of 1.2 SLPM, the cryocoolers were unable to provide the carbon dioxide needed to maintain the storage tank pressure. The CO_2 freezing rate calculated for Run 6, which fed the cryocooler CO_2 to the storage tanks, and Run 8, which measured the amount of frozen CO_2 using a wet test meter, show that Run 8 had a much higher freezing rate of 116 g/h versus the 99 g/h for Run 6. Both values are well above the goal CO_2 capture rate of 88 g/h, yet the CO_2 tanks had to be supplemented with facility CO_2 during every lengthy Sabatier operation. The flow controllers providing gas to the cryocoolers and Sabatier reactor were calibrated multiple times throughout the testing period, so the reported flow rates should be relatively accurate.

Table 1 shows a great variation in performance among the runs. Each cryocooler performs with some variation between them and from cycle to cycle. One cause of variation could be ambient air temperature swings in the lab, which can vary more than 20 degrees Fahrenheit throughout the day, this temperature swing affects the temperature of the cryocooler housing and the feed gas. A great deal of variability in cryocooler performance has been observed on a cycle to cycle basis, but the average performance of the cryocoolers across multiple cycles is relatively consistent.

B. Catalyst

During the heat shock trials, the pellets packed in the stainless steel tube showed signs of physical damage, but the unconstricted pellets that were heated in the crucible did not show signs of physical damage. The packing procedure may have played a role in the pellet damage, but the majority of the observed physical damage is likely due to the constriction caused by the pellets expanding when heated and pressing into each other and the walls of the tube. Prior to the heat shock trials, it was believed that the damage to the catalyst pellets in the Sabatier reactor was caused by the 600°C temperature anomaly, however, cycling the pellets at 450°C, the nominal Sabatier reactor operating temperature, caused substantial physical damage.

The observed change in pellet color, turning from black to grey, occurred more rapidly in the catalyst cycled at 600°C. It is unknown if the grey color is indicative of catalyst degradation or failure, but the catalyst removed from the reactor were starkly lighter in hue than unused catalyst as seen in Figure 1.

The lower magnification SEM mapping does not show an apparent difference between the unused and spent catalyst, however the high magnification, FESEM images show a trend of an increase in the number of white specks in the spent catalyst. The white specks are believed to be ruthenium. The brightness of the spots indicates that it is an element much heavier than the oxygen and aluminum that make up the alumina support pellet. The brightness of these spots rules out silica from the glass wool packing material. Some EDS analysis and the test configuration indicate the specks are ruthenium and not copper from the cold heads. The visible white specks on the spent reactor catalyst could

be caused by ruthenium sintering and coalescing into clusters that are large enough for the FESEM to detect. Fewer visible ruthenium specks on the unused catalyst could indicate that the ruthenium is still very disperse across the surface of the pellet.

One of the potential sources of catalyst poisoning is the thermal paste used to mate the cryocooler cold finger with the copper cryocooler cap. The compound used, Céramique 2, is likely not a poison due to its chemical composition of: synthetic oil, aluminum oxide, boron nitride, and zinc oxide, which are not known to be ruthenium catalyst poisons. The thermal paste had to be reapplied when the heater was repaired in cryocooler #2 meaning that the previous application had dispersed from the cryocooler cold finger and passed through other components of the APM after it left the cryocooler. It was a small amount of product, but its effects on the other components are unknown.

The XPS results show that aluminum and ruthenium bond energy spectrums at the surface of the pellet are consistently different on the unused pellet compared to the pellets that had undergone heat shock. The spent pellets from the reactor and the 450°C and 600°C heat shock pellets showed very similar peak trends to each other. This indicates that the high temperatures experienced by the pellets or the rapid increase in temperature was the driving factor in the change and not other factors such as poisoning. Further analysis is underway.

V. Future Work and Recommendations

When the CO_2 tank pressure neared or fell slightly below 60 psia, the Sabatier system would not function properly due to the pressure drop required for proper flow controller operation. To avoid these disruptions in flow to the Sabatier reactor, the CO_2 tanks should be maintained at pressures between 65 psia and 100 psia.

The automation software currently opens the valves connecting the cryocooler hoods to the Tedlar bag two minutes after the end of CO_2 collection. At the end of two minutes, the pressure in the hood is still quite low, so when the valves open, the vacuum is filled with the contents of the Tedlar bag, and possibly air if the bag is empty. The possibility of air and water vapor leaking into the system during this step could be mitigated by altering the software to open the valves after the cryocooler reaches the temperature of CO_2 sublimation, approximately 190K. When the change is made, the sublimation period may take longer, because pulling in this CO_2 and air increases the temperature in the hood very quickly, aiding in the rate of sublimation.

Cryocooler #1 should be opened to see if the dust found in cryocooler #2 is present. Further analysis should be done to find the composition of the dust, and if the dust is determined to be from the cryocooler caps, the cause of the dusting and rate of loss should be determined. This will ensure that the cryocoolers can sustain a sufficient CO_2 freezing rate for long duration operation on Mars.

The results from the XPS analysis indicate a clear trend between the used and unused catalyst. Analysis is complicated by the fact that the carbon peak overlaps the ruthenium peaks [10]. Some literature is available on typical ruthenium on alumina binding energy peaks, but more work is needed to interpret the results.

If the alumina pellets that currently support the ruthenium catalyst in the packed bed cannot withstand the operating conditions, other options will need to be explored. A miniature reactor could be assembled for testing various catalysts at the upper and lower bounds of operating conditions. Various sized pellets and other support structures with heavier catalyst loads could be tested. A heavier catalyst load with a robust support structure has been successfully implemented by Hamilton Sundstrand for the Sabatier reactor currently in flight on the ISS. If the pellet damage and heat damage is caused by the heat shock experienced by the pellets, the gas flows rates to the reactor could be increased more slowly so that the temperature of the pellets ramps up more slowly and prevents the formation of hot spots.

The pH of the water collected from the water condenser should be measured again to confirm the previous finding of a pH of 5.5. If the water is more acidic than expected, the composition of the product stream should be checked to ensure that proper CO_2 conversion is occurring.

The next step in testing for the APM is a virtual integration test across a network connecting the MIP components to each other from the centers that house them. The components of the Mars ISRU Pathfinder need to interface with each other successfully and perform in a synchronized manner so that the components providing materials needed for another component are performing as needed and communicating effectively.

During my internship, I exercised and honed some skills I had previously developed, while learning many new ones. I spent approximately one day per week operating and troubleshooting the APM. During this time, I learned more about LabVIEW and about experimental procedures and typical lab equipment such as flow meters, pumps, etc. I collected and analyzed the APM data and recorded information about each run for future use, encouraging me to think critically about which data were important and practice proper documentation techniques. I also learned how to calibrate the GC and make calibration gas mixtures. For catalyst testing, I developed an experimental plan, carried out

testing, and analyzed the results to develop conclusions. In order to analyze the catalyst, I learned to operate an optical microscope, an SEM/EDS and an FESEM. I also received instruction on XPS operation and result analysis. By writing this paper, I further developed my technical and report-writing skills. All of these accomplishments and practices will be very useful in the future as I enter graduate school in the fall and continue to conduct research throughout my career. I also very much enjoyed my time at Kennedy performing such interesting work with a very supportive group of people.

VI. Conclusion

The cryocooler automation software functions well and is ready for Mars ISRU Pathfinder integration testing. The calculations and measurements of CO_2 freezing rates indicate they surpass the rate needed to maintain the Sabatier reaction, but during long-duration testing, the flow was insufficient and had to be supplemented with facility CO_2. More testing is needed to determine why the cryocooler cycles are not maintaining the flow needed for the Sabatier reactor. Other minor issues like the water collection disparity, the condensed water pH, and the copper cryocooler cap dusting will need to be considered as the Atmosphere Processing Module proceeds through the flight readiness levels.

The catalyst pellet damage appears to be caused by elevated temperatures or heat shock and not poisoning or interference by the alumina support structure. The stainless steel tubes and furnace could be used to test the effectiveness of ramping the temperature more slowly to the reaction temperature, and simple changes to the procedure could be made to insure the reactor temperature does not increase too rapidly. A miniature reactor could be constructed for testing other catalysts, catalyst loading weights, or catalyst supports if the current conditions will not meet flight requirements.

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