Methane Post-Processor Development to Increase Oxygen Recovery beyond State-of-the-Art Carbon Dioxide Reduction Technology

Morgan B. Abney[1] and Zachary Greenwood[2]
NASA Marshall Space Flight Center, Huntsville, Alabama, 35812

Lee A. Miller[3]
ECLSS Technologies, LLC., Huntsville, Alabama, 35802

Giraldo Alvarez[4]
Florida State University, Tallahassee, Florida, 32306

Michelle Iannantuono[5]
NASA Academy Summer Intern 2012, Marshall Space Flight Center, AL, 35812

and

Kenny Jones[6]
Minorities in Science and Engineering Summer Internship Program,
Marshall Space Flight Center, Huntsville, AL 35812

State-of-the-art life support carbon dioxide (CO_2) reduction technology, based on the Sabatier reaction, is theoretically capable of 50% recovery of oxygen from metabolic CO_2. This recovery is constrained by the limited availability of reactant hydrogen. Post-processing of the methane byproduct from the Sabatier reactor results in hydrogen recycle and a subsequent increase in oxygen recovery. For this purpose, a Methane Post-Processor Assembly containing three sub-systems has been developed and tested. The assembly includes a Methane Purification Assembly (MePA) to remove residual CO_2 and water vapor from the Sabatier product stream, a Plasma Pyrolysis Assembly (PPA) to partially pyrolyze methane into hydrogen and acetylene, and an Acetylene Separation Assembly (ASepA) to purify the hydrogen product for recycle. The results of partially integrated testing of these sub-systems are reported.

Nomenclature

ASepA	=	Acetylene Separation Assembly
CDRA	=	Carbon Dioxide Removal Assembly

[1] Aerospace Engineer, ECLSS Development Branch, ES62, AIAA Member.
[2] Aerospace Engineer, ECLSS Development Branch, ES62, AIAA Member.
[3] Test Engineer, ECLSS Development Branch, ES62, AIAA Senior Member.
[4] NASA Undergraduate Student Research Program Intern, ECLSS Development Branch, Marshall Space Flight Center, Florida State University, AIAA Non-Member.
[5] NASA Academy Summer Intern, ECLSS Development Branch, Marshall Space Flight Center, College of Charleston, AIAA Non-Member.
[6] Minorities in Science and Engineering Summer Intern, ECLSS Development Branch, Marshall Space Flight Center, University of Huntsville-Alabama, AIAA Non-Member.

CM	=	Crew Member
CRA	=	Carbon Dioxide Reduction Assembly
ISS	=	*International Space Station*
MePA	=	Methane Purification Assembly
MSFC	=	Marshall Space Flight Center
OGA	=	Oxygen Generation Assembly
PPA	=	Plasma Pyrolysis Assembly
SDU	=	Sabatier Development Unit
SmLPM	=	Standard millLiters Per Minute
W	=	Watts

I. Introduction

HUMAN life support systems on the *International Space Station* (*ISS*) include a number of technologies to continuously provide breathable air to the crew. The Trace Contaminant Control System removes harmful volatile organic compounds and other trace contaminants from the circulating air. The Carbon Dioxide Removal Assembly (CDRA) removes metabolic carbon dioxide (CO_2) and returns humidified air to the cabin. The Oxygen Generation Assembly (OGA) electrolyzes water to produce oxygen for the crew and hydrogen (H_2) as a byproduct. The Carbon Dioxide Reduction Assembly (CRA), the most recently added technology, compresses and stores CO_2 from the CDRA until hydrogen is available from the OGA. The CO_2 and H_2 are then fed to a Sabatier reactor for reduction to form water and methane as shown in Equation 1.

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

The water product is condensed out of the product stream and recycled back to the Water Purification Assembly for crew use or to produce additional oxygen in the OGA. The methane is vented overboard as a waste product. For future long-duration missions or missions beyond low Earth orbit, the methane may prove to be valuable for a number of reasons. First, if purified from unreacted CO_2 and residual water vapor, methane may be stockpiled for use as a fuel or converted to other desirable chemicals. Second, the H_2 may be recovered from the methane and recycled back to the CRA to produce additional water product, thereby increasing total oxygen recovery.

Three technologies are presented here to address the potential need for purified methane and/or hydrogen recovery from Sabatier-produced methane. Additionally, architectural options are discussed in an effort to address increasing system complexity.

II. Background

To address the potential needs for a purified methane product as well as H_2 recovery from methane, an initial architecture was proposed. As shown in Figure 1, the integrated system includes a Methane Purification Assembly (MePA), a Plasma Pyrolysis Assembly (PPA), and an Acetylene Separation Assembly (ASepA).

Currently, the CRA on *ISS* is operated at a H_2:CO_2 ratio of 3.5. This results in almost complete conversion of the H_2, but only partial conversion of the CO_2. For this reason, the methane product leaving the CRA contains significant quantities of unreacted CO_2. Additionally, the condensing heat exchanger is air cooled and a downstream drum separator operates on the mid-temperature coolant loop. Thus, the methane product stream is also saturated with water vapor at approximately 15°C. The MePA is included in the initial architecture for the purpose of removing residual CO_2 and any uncondensed water vapor from the methane product stream. It should be noted that the MePA must be sized to accommodate all water vapor leaving the CRA. This will allow purified methane to be either stockpiled or fed to a down-stream post-processor.

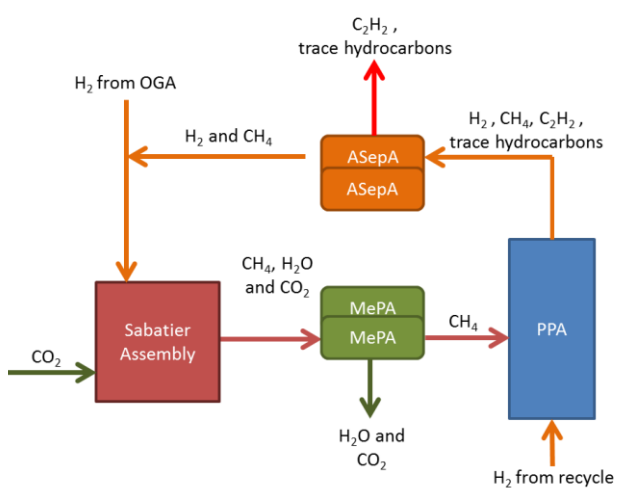

Figure 1. Methane post-processing initial architecture concept.

The Plasma Pyrolysis Assembly (PPA) is one potential methane post-processor for Sabatier-produced methane. Significant testing on a sub-scale system has been reported previously.[1-3] Briefly, this technology converts methane to H_2 and acetylene (C_2H_2) as shown in Equation 2.

$$2CH_4 \leftrightarrow 3H_2 + C_2H_2 \tag{2}$$

The system operates by generating a plasma using microwave power. Hydrogen is fed to the reactor in addition to CH_4 to promote conversion to acetylene rather than other products, particularly carbon. The gas effluent from the PPA generally consists of H_2, unreacted CH_4, and acetylene with trace quantities of ethylene and ethane. The first generation system was designed to process methane at a flow rate equivalent to ~1/2 crew member (CM). In 2012, a second generation system was designed and delivered to the Marshall Space Flight Center (MSFC) to process methane at a 1-CM rate.[4] Additionally, this system was designed for improved energy efficiency, better acetylene selectivity, greater methane conversion, and reduced carbon production.

Following recovery in the PPA, H_2 must be recycled back to both the CRA and the PPA for additional oxygen recovery. However, for this purpose, the H_2 product must be purified from gases that could adversely affect CRA performance during H_2 recycle. Previous testing of a CRA ground development unit, called the Sabatier Development Unit (SDU) showed no affect of CH_4 on Sabatier performance when introduced at up to 15 mol% of the H_2 feed stream.[4] Acetylene and the other hydrocarbons leaving the PPA have the potential to further decompose when recycled to the CRA. This would cause fouling of the Sabatier catalyst thereby dramatically reducing the anticipated lifetime of the CRA reactor. Traditional H_2 separation techniques such as membranes, metal hydrides, and cryogenic separations were dismissed early on. Membranes require very high pressure differentials for adequate separation. Acetylene will spontaneously decompose at pressures of just 2 atm, making membranes a poor option. Metal hydrides were eliminated as a potential option due to poisoning concerns. Finally, cryogenic separations were not considered due to the unavailability of cryogenic liquids for habitat use. This resulted in selection of a sorbent-based system that, rather than removing hydrogen, was intended to remove acetylene and other hydrocarbons. The added benefit of this approach is that unreacted methane is recycled back to the system for further reaction. Initial testing on two candidate sorbents for an ASepA system was reported in 2011.[5]

III. Hardware Description and Methods

Prior to this effort, no hardware existed for the MePA or ASepA beds. Below, the design considerations for the MePA and ASepA beds are discussed. Additionally, testing methods for the MePA bed are described. The PPA hardware used in this effort has been described previously and will not be discussed here. [4] However, testing methods for the 2nd Generation PPA are described below.

A. MePA Design and Testing

Design considerations for the 1st Generation MePA bed and testing methods are each discussed below.

1. MePA Design Requirements

Because of the operational parameters of the upstream CRA, the purpose of the MePA is to remove unreacted CO_2 and residual water vapor at a 4-crew member (CM) production rate. Additional requirements leveed on the MePA system design included:

1) Minimum cycle time of 4 hours
2) Power requirement of less than 200W
3) Desorption via vacuum and heat
4) Fabrication possible from inexpensive, easily obtainable, off-the-shelf components

The cycle time requirement was based upon experience with sorbent-based systems requiring regeneration when exposed to water. Because zeolites have a very high affinity for water molecules, considerable energy is required for desorption. Zeolites, particularly ones using clay binders, have very low thermal conductivity. Thus, based on the need to keep power to the MePA as low as possible, a fairly long cycle time is needed for the bed to reach desorption temperature and return to ambient before the subsequent adsorption cycle. The power requirement was based on an architecture-wide view of power usage. The PPA system uses considerable power, thus low power requirements on associated separation systems is desirable. The third requirement above was based on experience with the CDRA beds. CDRA uses heat and vacuum to remove CO_2 and heat and a dry air sweep stream to remove water. For the MePA, a sweep gas was considered impractical. There are two (mostly) dry streams that could

possibly be used for the purpose: the H_2 recycle stream leaving the ASepA or the CO_2 stream feeding the Sabatier. Because the bed will require heating regardless of the presence of a sweep stream, H_2 was determined to be undesirable due to safety concerns. Previous testing of a Sabatier reactor with water in the inlet stream showed decreased performance. If the CRA CO_2 feed stream was used to sweep the MePA, the performance of the CRA would likely be negatively affected. Thus, the CO_2 stream was eliminated from consideration. The only remaining option for MePA desorption is vaccum. This vaccum could be provided via space vacuum, but this would lead to the loss of O_2 in the forms of water and CO_2. Alternatively, a vacuum pump could be used and the desorbed water and CO_2 recycled back to the AR system. This would require considerably more mass, power, and infrastructure. A trade would be necessary to determine which option would best fit specific mission needs. The intention of the effort was to initially build a single-bed system with the assumption that a more refined dual-bed system would ultimately be designed and fabricated for fully integrated testing. The dual-bed system would have similar requirements, barring number 4 above.

2. 1st Generation MePA Testing

Once designed and fabricated, the MePA bed was integrated with a Sabatier Development Unit (SDU) located at MSFC. The SDU was operated at a 4-CM feed rate of CO_2 and a H_2:CO_2 ratio of 3.5. The SDU effluent was evaluated for dew point and CO_2 composition. Once steady state was reached, the SDU effluent was fed to the MePA to observe breakthrough curves. Following 90% breakthrough, the SDU was stopped and desorption of the MePA was conducted under vacuum (1 torr absolute) at a target temperature of 150°C at the bed wall. The test was repeated a total of three times.

B. 2nd Generation PPA Stand-Alone Testing

Following arrival of the 2nd Generation PPA at MSFC, stand-alone testing was desirable to evaluate the baseline performance and to ensure no damage had been done during transportation from UMPQUA Research Co. This testing was completed in three phases.

Phase I testing was conducted to map the performance over a range of pressures and microwave power. The system was operated at a methane feed rate of 350 SmLPM (or 1-CM) and 1400 SmLPM of hydrogen. Testing was conducted with pressures of 40 torr, 50 torr, and 60 torr and microwave power between 250 watts (W) and 600W in 50W increments.

Phase II testing was conducted to determine the effect of varied CH_4 mol% versus H_2 mol% in the feed gas. Testing was conducted at 50 torr and 450W microwave power. Methane feed composition points included 15, 17, 20, 23 and 25 mol% CH_4. Note that methane feed was maintained at 350 SmLPM and the H_2 modified to meet the required feed percentages.

Phase III testing was conducted to determine the carbon-accumulation effect of long-duration operation. The system was operated at 50 torr, 350 SmLPM CH_4, 1400 SmLPM H_2, and 450W microwave power.

C. ASepA Design

The purpose of the ASepA bed is to separate H_2 and CH_4 from hydrocarbons produced in the PPA including C_2H_2, ethylene, ethane, and others. Performance of the 1st Generation PPA system showed an outlet stream containing ~1 mol% CH_4, ~8 mol% C_2H_2, and <0.5 mol% of all other hydrocarbons. The ASepA requirements are shown below. Stringent safety controls were imposed on the ASepA due to acetylene handling. A thorough safety review and material analysis were completed prior to fabrication of the bed.

1) Minimum cycle time of 4 hours
2) Power requirement of less than 200W
3) Desorption via vacuum and heat
4) Fabrication possible from inexpensive, easily obtainable, off-the-shelf components (excluding safety-critical components)
5) Containing a sorbent capable of adsorbing >95% of hydrocarbons with the exception of methane
6) Operation at sub-ambient pressure

IV. Results and Discussion

Both a MePA and an ASepA bed were designed, fabricated and assembled in 2011. The MePA bed was tested while integrated with the SDU. Stand-alone testing of the 2nd Generation PPA was completed. These results are discussed below. Additionally, a discussion of the initial architecture and possible deviations from this architecture to minimize system complexity are discussed.

A. MePA Design and Testing Results

A MePA system was designed to meet the previously discussed requirements. Once fabricated, the bed was integrated at the exit of the SDU and tested. A discussion of the design and the results of initial testing are provided below.

1. *MePA Design*

The MePA subsystem was designed as a zeolite-based adsorbent bed. The bed was fabricated with metal fins along the length of the bed. An air cooling loop was designed to flow air across the fins to provide cooling during adsorption and following desorption. While the heat of adsorption without this cooling was not measured, isotherm data indicates that lower temperatures allow for greater capacity for CO_2 and H_2O. The cooling was implemented to take advantage of this fact. Four core heaters were designed to provide heat for desorption.

Figure 2. Base components of the MePA bed. *Outlet end cap with a small piece of steel mesh secured on (top left), interior of the steel bed tube (right), Inlet end cap with no heaters(bottom left).*

The sorbent bed was fabricated from 6061 aluminum. The base parts, including end caps, a tube body, and perforated plates, were fabricated in-house and are shown in Figure 2. A felt screen retainer, shown in Figure 3, started as a 1.27 cm thick aluminum ring. The ring was wrapped in Huyglas 1702HT fiber insulation (Filtration Specialties), with the woven side facing the metal. The fiber was secured by an interior snap ring, and excess fiber was removed with a razor. A perforated plate was attached to one side of the Huyglas felt-covered ring. On the opposite side, two layers of stainless steel mesh – a fine bottom layer and a course top layer – were attached to the retainer beneath a securing ring. These mesh circles were cut by hand and holes were made using a metal punch. The mesh side was positioned to face the zeolite. Four cartridge heater rods were installed into the five-hole inlet end cap. The seal on each endcap was provided by two high-temperature o-rings. On two of the heaters, thermocouples were imbedded halfway down the rod; on the remaining two heaters, thermocouples were imbedded at the endpoints.These thermocouples were intended to monitor the heater temperatures during desorption phases and the interior bed temperature during adsorption.

Figure 3. Felt screen retainer for the MePA bed. *Bottom view with coarse and fine steel mesh, along with a securing ring (left) and top view with the perforated*

The bed was packed first with 114.85g of glass beads, followed by 200.04g (≈5cm) of Sorbead water-safe silica gel sorbent, and a total of 1077.6g of Grace Davison 13X zeolite, and an additional layer of 96.36g of glass beads. The felt screen retainer, a wave spring, and the outlet end cap, were then installed, completing bed assembly. Once sealed, the bed was baked out overnight at 300°C. The purpose of the bake out was to eliminate any moisture adsorbed from the air during the packing process. A "wet mass" of 5107.45g was recorded pre-bake out. The bake out removed a total of 54.63g of moisture mass from the sorbent, as shown in Table 1.

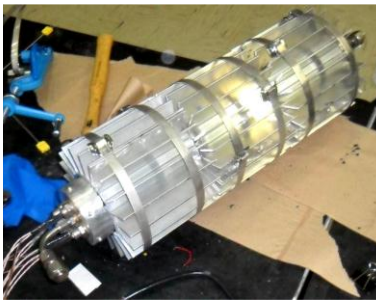

Figure 4. MePA sorbent bed with Qfin attached.

Table 1. MePA Mass Data. *Pre- and Post-Bake out.*

Glass Bead Mass (g)	211.27
Silica Bead Mass (g)	200.04
Zeolite Bead Mass (g)	1077.55
Total Wet Mass (g)	5107.45
Total Dry Mass (g)	5052.82
Mass Lost in Bake out (g)	54.63

Once the core sorbent bed was completed, the cooling system was fabricated and assembled. Six sections of Qmax Qfin extruded heat sinks were installed as shown in Figure 4. Each 360° pair of fins was placed at a 1/3 offset to the adjacent pair. The finned bed was installed into an aluminum duct 61cm long and 18cm in diameter. A system of solid state thermoelectric heat pumps, a fan, and ducting was used to flow cooling air around the bed assembly.

2. MePA Testing Results

As described previously, the MePA was integrated with the SDU and fed SDU effluent. Three adsorption runs were completed to breakthrough. The test was designed such that a constant H_2:CO_2 ratio of 3.5 should be maintained to the SDU. However, following testing, it was determined that the hydrogen flow controller was not maintaining accurate flow. As such, the feed ratios of the Runs 1, 2, and 3 were actually 3.80, 3.76, and 3.37, respectively. Additionally, in an ideal situation, the SDU separator would maintain a constant rate of water condensation. However, due to variations in the ambient conditions, dew points for the MePA feed were 78°F, 84°F and 86°F, respectively. The combination of these two variations to testing requirements led to vastly different feed compositions to the MePA. The actual feed rates to the MePA are shown in Table 2.

Table 2. Variation in MePA feed composition.

Feed to MePA (mmol/min)	Run 1	Run 2	Run 3
CO_2	4.84	5.18	11.00
H_2	6.65	5.78	3.98
CH_4	58.55	58.21	52.40
H_2O	3.25	4.00	4.11

An additional testing anomaly occurred during the desorption cycles of the test. During desorption following the first trial, one of the heaters failed, leaving only three for regeneration. In an attempt to compensate for this failure, the regeneration was continued until a steady temperature was observed at the wall of the sorbent bed. During desorption following the second trial, a second heater failed. Again, the bed was regenerated for a longer duration in an attempt to thoroughly heat the sorbent material. Due to the heater failures, the regeneration data was of little use for data comparison and cycle-time comparison purposes. When comparing breakthrough curves for each run, as seen in Figure 5, it appears that the loss of the heaters made a difference in the regeneration of the bed. This is observed by observing the curves of the breakthrough. Each subsequent breakthrough showed a much sharper curve, suggesting a cleaner breakthrough.

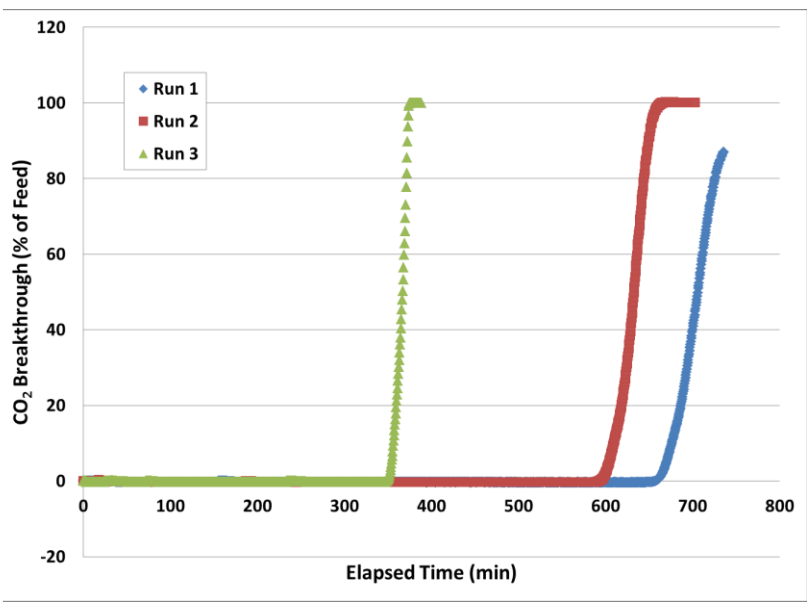

Figure 5. MePA breakthrough following subsequent regenerations.

A comparison of theoretical adsorption capacity versus observed adsorption capacity was also made. This effort was made more difficult due to variations in the adsorption temperature between runs and the varied composition of the MePA inlet stream. Both silica beads and zeolite 13X have an affinity for water and CO_2 that varies with temperature and pressure. On both materials, the water is preferentially adsorbed and displaces CO_2. Theoretical capacities of water and CO_2 on both sorbents are shown in Table 3 for each run (based on temperature). Percentage of theoretical capacity was calculated by first looking at water and assuming 100% adsorption on silica beads (to maximum capacity). This is not an entirely realistic assumption due to the fact that some water would invariable be expected to pass through the silica beads and adsorb on the 13X. However, this assumption was made for a simple comparison. Carbon dioxide adsorption was then evaluated based entirely on adsorption on 13X due to the relatively low affinity

Table 3. Theoretical capacities of water and CO2 on silica beads and zeolite 13X.

Silica Beads	Run 1	Run 2	Run 3
CO_2 (mol)	0.02	0.02	0.06
H_2O (mol)	3.20	3.20	3.20
13X Zeolite	**Run 1**	**Run 2**	**Run 3**
CO_2 (mol)	3.77	3.88	4.31
H_2O (mol)	15.09	15.09	15.09

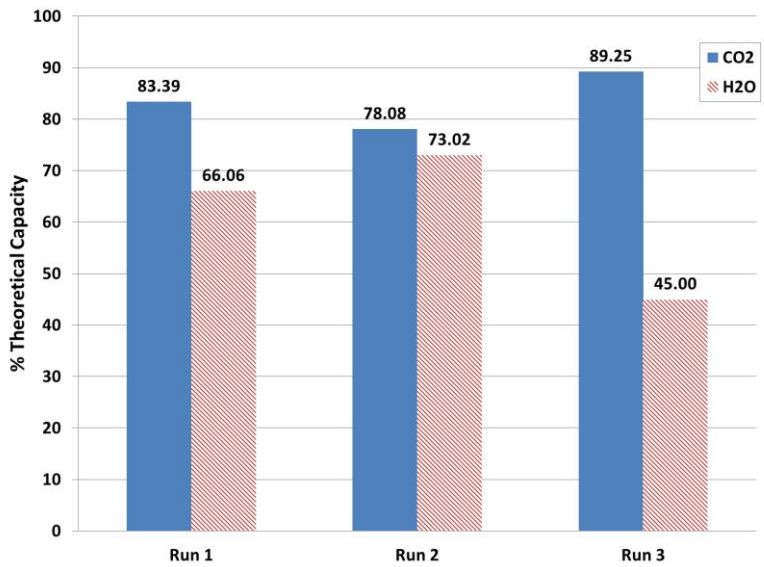

Figure 6. MePA bed performance compared to theoretical capacities.

of CO_2 on silica beads. As shown in Figure 6, there does not appear to be an obvious decrease in bed performance between runs. Because water was never observed to breakthrough, the variation in the water data is directly related to differences in quantities of water fed to the bed. Although it appears that water did not reach theoretical capacity, it was due to insufficient water rather than poor material performance. Carbon dioxide adsorption reached greater than 78% of the theoretical value for all runs. This corresponds to operation of over 8 hours before anticipated breakthrough based on the CO_2 expected to be unreacted by the CRA from a crew of four.

B. 2nd Generation PPA Testing Results

As mentioned previously, 2nd Generation PPA Testing was conducted in three phases. The results of each phase of testing are provided below.

1. *Phase I Testing Results*

The purpose of Phase I testing was to observe the effect of system pressure and microwave power on CH_4 conversion. Note that neither C_2H_2 selectivity nor carbon accumulation was considered for this comparison. The results of this test are shown in Figure 7. A number of observations were made based on this data. First, it appeared that there was a significant improvement in CH_4 conversion when increasing pressure from 40 torr to 50 torr. However, there was minimal improvement by further increasing the pressure to 60 torr. Second, the greatest influence on conversion was observed by an increase in microwave power between 250 and 450W. Beyond 450W, minimal additional improvement was observed suggesting increasing reflected energy and a more dramatic increase in system inefficiency.

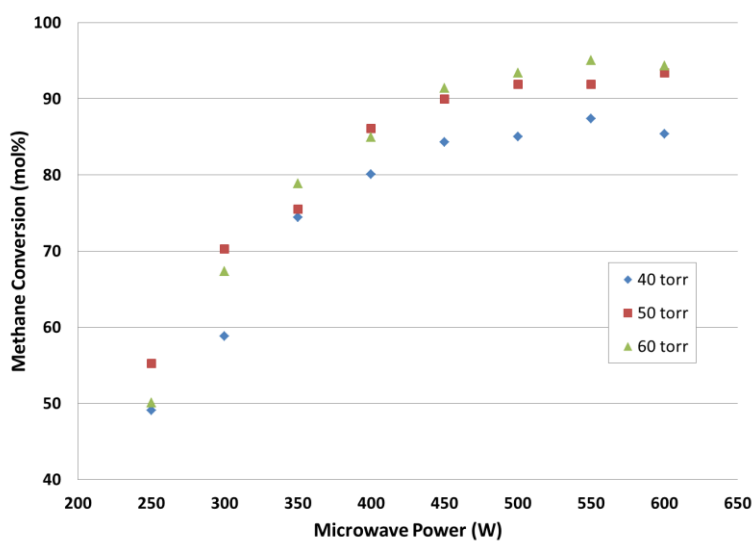

Figure 7. Results of Phase I 2nd Generation PPA testing.

2. Phase II Testing Results

The purpose of Phase II testing was to observe the effect of varied PPA feed composition on CH_4 conversion, C_2H_2 selectivity, and carbon formation. As mentioned previously, methane feed to the PPA was held constant at a 1-CM feed rate. Hydrogen feed was varied such that total CH_4 to the system varied from 15-25 mol%. Methane conversion data is shown in Figure 8. As seen in the graph, increasing the percentage of CH_4 in the feed stream ultimately resulted in increased CH_4 conversion and acetylene/hydrogen production. Additionally, undesirable conversion to ethylene also decreased at higher CH_4 levels. On first glance, it would appear that increasing the percentage of methane in the feed stream would ultimately produce better results. However, when the PPA reactor was examined at the end of each test, it was clear that additional carbon formation was also observed. Figure 9 shows the reactor interior following each run of 4 hour duration. From the images, it appears that there is a gradually increasing quantity of carbon, with the exception of the 17mol% run. This type of carbon formation is usually observed with either very high CH_4 composition in the feed stream or very high power at low pressures. When the data was reviewed, it was determined that for the 17mol% run, the PPA reactor was shut-down in an off-nominal procedure. Normally, the process for shutting down the PPA involves stopping the microwave power followed by dropping the pressure set-point to zero torr, and finally, stopping the gas flow. In the case of the 17mol% run, the pressure was dropped first. This resulted in a very low pressure with the full 450W of microwave power. Thus, the 17mol% image is not indicative of what would normally be observed for this set point. Finally, it should be noted that no decrease in performance was observed over the course of any run, despite the carbon formation.

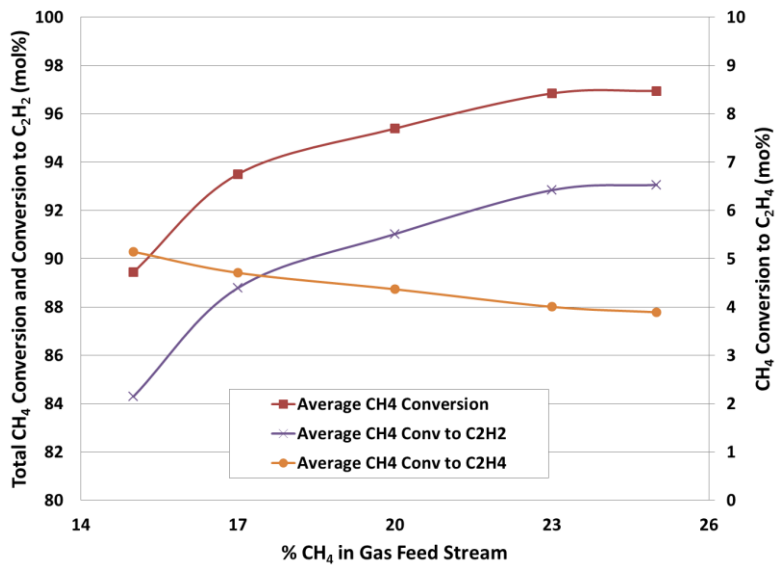

Figure 8. Methane conversion results for Phase II 2nd Generation PPA Testing.

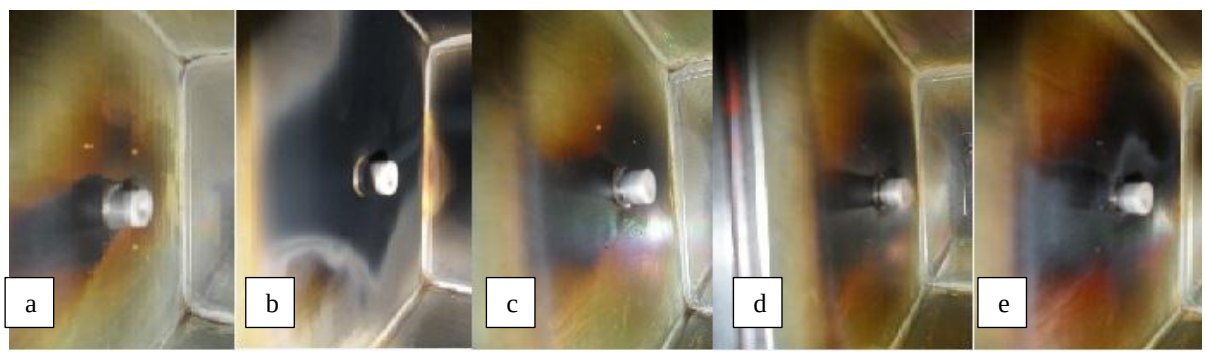

Figure 9. PPA Reactor carbonaceous material accumulation during Phase II 2nd Gen PPA Testing. *Images show build-up with methane feed composition of 15%(a), 17%(b), 20%(c), 23%(d), and 25%(e).*

Based on this data and PPA target performance parameters of >90% CH_4 conversion and minimal carbon production, a 20 mol% CH_4 feed stream was determined to be optimum for future testing. This type of operation will require a significant H_2 stream (1.4 SLPM for 1-CM, 5.6 SLPM for 4-CM) to be provided to the PPA. The fact that the architecture assumes H_2 recycle for the CRA enables recycle to the PPA for this type of operation. However, this capability will inevitably drive the mass/volume of the system up to accommodate the high volume of recycle gas.

3. Phase III Testing Results

The purpose of Phase III testing was to evaluate the performance of the PPA over long durations. During this test the PPA was run for a total of 117 hours. At 92 hours the pressure in the reactor began to increase. The test was stopped to determine the cause of the increasing pressure. When the reactor was disassembled, it was determined that the line leading from the reactor chamber to the primary filter assembly had significant quantites of carbon formation. The carbon build-up on the lines leading away from the reactor can be seen in Figure 10. The film coated the entire surface area of the inlet to the filter assembly and was determined to be 2mm thick. A cottom swab was used to clean the nearly-completely occluded tube. Carbon samples were taken for further analysis. Following cleaning of the outlet tube, the reactor was restarted and the pressures were easily maintained at the desired testing setpoints. It should be noted that these lines were on the original 1st Generation PPA and had never been cleaned by test personnel. Thus, this build-up of carbon was the accumulation of hundreds of hours of testing, not just Phase III testing.

Figure 10. Carbon build-up after 92 hours of testing. The carbon can be seen as an inner ring at the tip of the arrow inside the metal ring.

A second observation was carbon formation on the stub where the plasma reaction was centered. The carbon appeared at approximately 92 hours and became more pronounced over time as testing continued. Figure 11 shows this formation at the onset and then as the formation evolved after each run session. It is believed that this was an accumulation of the solid carbon as it cooled and precipitated on the surface of the stub. Due to PPA in-wall cooling, the outer edges of the stub are of much cooler temperature than the plasma itself, thus providing a cooler surface for carbon deposition.

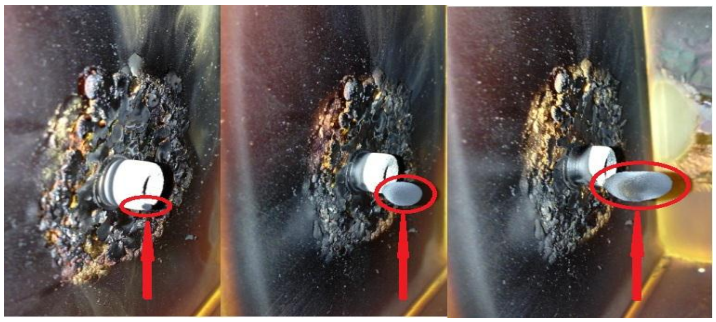

Figure 11. Carbon Build-Up on PPA Stub. The progressive build-up is shown in the red circles and were taken at 92 hours, 103 hours, and 111 hours of operation, respectively.

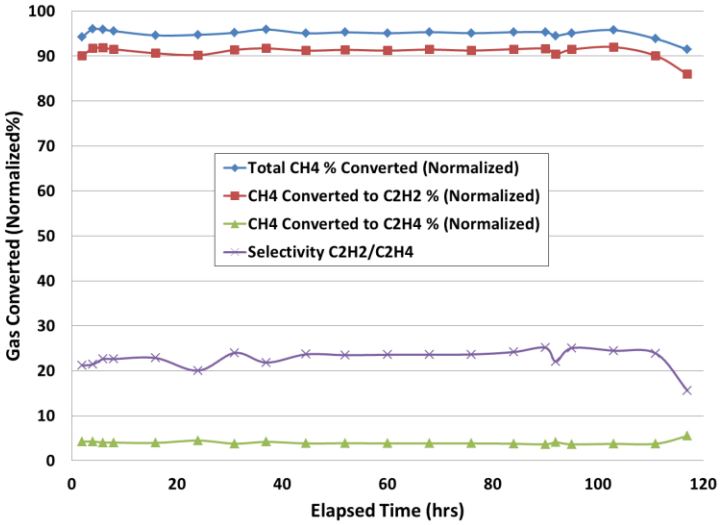

Figure 12. Long-duration performance of the PPA.

Prior to 92 hours of operation, the reaction was stable, as seen in Figure 12, and the product stream maintained a consistent acetylene to ethylene selectivity of about 25:1, where selectivity is defined as the ratio of the moles of acetylene produced to the moles of ethylene produced. As the PPA reactor approached the 111 hour mark, a decrease in selectivity and CH_4 conversion were observed. After the 111 hour mark the acetylene selectivity dropped below 20:1 and the desired product conversion started to decrease as gas remained unreacted. The test was continued to 117 hours to establish a baseline for the end of long-duration testing. Carbon samples from the reactor walls and all the filters were collected to be analyzed at a later date. These results suggest that the presence of the carbon build-up on the stub may have caused disruptions in the gas flow paths leading to the generation of two plasma spheres reacting side-by-side, rather than the single sphere as intended. Because neither of these spheres would be located in the ideal microwave and gas flow path, performance was negatively impacted.

This data shows that, while the system may be operated for several days without a decrease in performance, carbon formation from the process will

inevitably require a cleaning cycle to be implement for longer duration operation. A cleaning cycle was previously examined using a CO_2 plasma.[4] This type of chemical cleaning would likely be useful after several hours of operation. However, based on the images in Figure 11, a more intensive, possibly mechanical method would be required if several days were required between cleanings. A mechanical cleaning would likely require crew intervention, making this option undesirable. A chemical cleaning could be automated. However, no CH_4 could be processed during this time. This would require either CH_4 bypass to vent or some type of CH_4 storage. A bypass would result in loss of recoverable H_2 for the duration of the cleaning. Storing CH_4 would result in both additional mass for storage system as well as a larger PPA reactor to accommodate the combined CH_4 flow from the PPA and the CH_4 flow from the storage system. Specific mission scenarios will likely drive the path forward and be dependent on available mass/volume, crew time, and required resource recovery.

C. ASepA Design

The design of the ASepA bed and heating system was identical to that of the MePA bed. The design of the cooling system was identical with the exception of a second thermoelectric device located on the ASepA gas inlet to provide pre-cooling for the bed and the use of zeolite 4A as the packing material in the ASepA rather than the 13X zeolite and silica beads used in the MePA. This bed is expected to be tested in mid-2013.

D. Architecture Discussion

When an initial architecture for SDU post-processing was developed, it was believed that the MePA and ASepA systems would remain quite small, fairly simple systems due to the small quantities of gases to be. However, as development has progressed, the system has gradually begun to appear more complicated. First, both beds were originally planned to be desorbed with heat and vacuum only (no sweep gas). Initial modeling of the beds (not reported here) suggests that a sweep gas would be required for both systems to reach an adequate level of regeneration using the zeolite 4A. This presents both logistical and safety concerns. Second, imbedded tube heaters were believed to be a simple and effective method for heating the beds. Testing with MePA showed that these types of heaters are less reliable than originally believed. Additionally, because of the low thermal conductivity of clay-bound zeolite materials, the MePA bed was shown to require significantly more heat and longer times to reach adequate temperatures for desorption across the bed than originally planned. Third, thermoelectric devices were originally chosen as a method to cool ASepA inlet gases as well as circulation cooling air for both the ASepA and MePA. However, the devices as implemented in these systems have also been shown to be significantly less reliable than originally believed. Ultimately, all of these issues have added up to a larger, less robust system. Thus, it is of great interest to re-evaluate the architecture approach for a PPA-based CH_4 post-processing system.

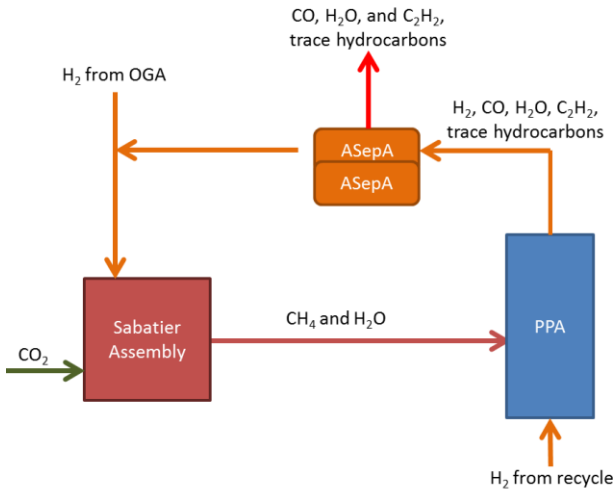

Figure 13. Methane post-processing alternate architecture with no SDU dryer.

There are currently two alternative architectures for consideration. Both options make a key assumption: that the CRA in future missions will be operated at an H_2:CO_2 feed ratio of 4.5. This will effectively eliminate all but trace quantities of CO_2 from the product stream. In contrast, H_2 will be the excess reactant. For a PPA-based architecture, this is actually desirable due to the quantities of H_2 needed for optimum PPA operation. The first architecture, as shown in Figure 13, assumes no water removal upstream of the PPA. Based on previous testing, this will mean water and carbon monoxide in the PPA effluent. Thus, what was previously the ASepA will now be a H_2/CH_4 purification bed that removes water, CO, and C_2H_2. This will make the system larger than the original ASepA, but with only a single system, the resulting architecture is still less complex than the initial architecture. This approach, like the original approach, assumes loss of all water vapor coming from the CRA. The CO produced in the PPA is due to a reaction between the solid carbon and the water vapor. No additional O_2 is lost compared to the original architecture approach.

The second architecture, as shown in Figure 14, assumes that the majority of the CRA effluent water is removed in a residual dryer, possibly based on Microwick technology developed by Pacific Northwest National Laboratories, or something similar. This is very similar to the initial architecture, but moves away from sorbent beds in the hopes of decreasing the size and complexity of the system.

Despite conceptualization of these architectures, no decision has yet been made as to the direction the CRA post-processor will go. However, the simplified assumption of a hydrogen-rich feed to the CRA allows for a much simplified system over previous efforts.

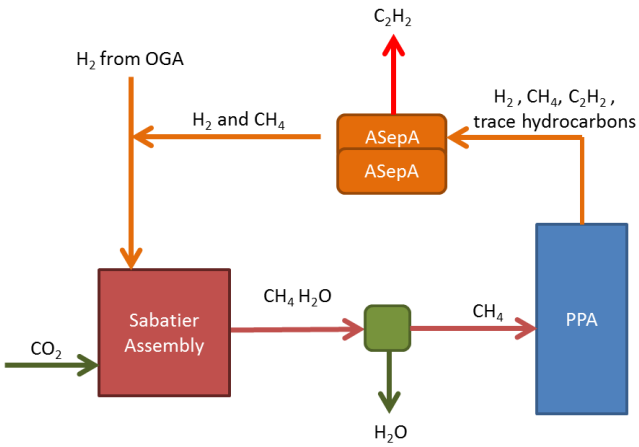

Figure 14. Methane post-processing alternative architecture with non-sorbent based dryer.

V. Future Work

Multiple trade studies and technology analyses are scheduled for 2013 and 2014. Once a thorough understanding of alternative architectures and technology is available, a decision will be made. Technology development on the most appropriate technologies will be pursued. During 2013, a secondary effort pursing a 4-CM PPA system will be concluded with hardware delivered to NASA. This hardware will be tested as a stand-alone unit and while integrated with an SDU in 2014.

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