# Hydrogen Recovery by Methane Pyrolysis to Elemental Carbon

Stephen F. Yates[1], Amanda Childers[2], Nicholas Brom[3], Sean Skomurski[4]
*Honeywell Aerospace Advanced Technology, Des Plaines, IL, 60017*

Charles Lo[5]
*Honeywell Aerospace Mechanical Systems & Components, Phoenix, AZ 85034*

Morgan B. Abney[6]
*NASA Marshall Space Flight Center, Huntsville, AL, 35812*

**Use of a Sabatier reactor to recover the oxygen from the carbon dioxide exhaled by the crew on the International Space Station has been limited by the loss of the hydrogen contained in the methane it generates. Maximizing the oxygen recovered requires the hydrogen to be recovered from the methane product and recycled back to the Sabatier reactor. We describe the use of a tailored methane pyrolysis reactor to completely recover this hydrogen. The carbon-containing byproduct is elemental carbon, which is generated in the form of easily handled, non-sooty material that may have various uses. The process of creating this tailored carbon vapor deposition process involved exploration of the effects of temperature, pressure, substrate design and other variables to develop a high yield process that cleanly generates the desired products. Reaction kinetics and kinetics modelling were used to specify the temperature, pressure and reactor volume required to achieve the target conversion and to assure that the final average density was as high as possible. Reactor design included the selection of materials that will survive the high temperatures and environment in the pyrolysis reactor, and thermal modeling to achieve the required temperatures with minimum power consumption. The successful construction and demonstration of a brassboard prototype will allow the results of the chemical, thermal and mechanical models to be validated and should provide a useful alternative for a completely closed loop ECLS system. Integration of this technology with state-of-the-art (SOA) Sabatier hardware on ISS requires a complete understanding of the effects of impurities in the product hydrogen on the Sabatier catalyst. SOA Sabatier catalyst was evaluated over short and long-term exposure to anticipated contaminants to identify effects.**

## Nomenclature

| | | |
|---|---|---|
| CDRA | = | Carbon Dioxide Removal Assembly |
| CDRILS | = | Carbon Dioxide Removal by Ionic Liquid System |
| CDRS | = | Carbon Dioxide Removal Subassembly |
| $CO_2$ | = | Carbon dioxide |
| CRS | = | Carbon dioxide Reduction System |
| CVD | = | Chemical vapor deposition |
| ECLS | = | Environmental Control and Life Support |
| ECLSS | = | Environmental Control and Life Support System |
| $H_2O$ | = | Water |
| HOS | = | Hours on stream |

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[1] Research Fellow, Engines and Air Management, 50 E. Algonquin Road, Des Plaines, IL
[2] Senior Scientist, Engines and Air Management, 50 E. Algonquin Road, Des Plaines, IL
[3] Engineer III, Engines and Air Management, 50 E. Algonquin Road, Des Plaines, IL
[4] Scientist III, Engines and Air Management, 50 E. Algonquin Road, Des Plaines, IL
[5] Staff Engineer, Mechanical Systems and Components, 111 South 34th St., Phoenix, AZ
[6] Branch Chief, ECLS Development Branch, ES62, 4755 Tiros Road, MSFC, AL.

| OGA | = | Oxygen Generation Assembly |
| sccm | = | Standard cubic centimeters per minute |
| TCCS | = | Trace Contaminant Control System |
| UPA | = | Urine Processing Assembly |
| WMS | = | Waste Management System |
| WPA | = | Water Processing Assembly |

## I.  Introduction

CLOSING the loop for air and water management in the Environmental Control & Life Support System (ECLSS) for human spaceflight has long been an important goal for NASA.  Humans require oxygen, water, and food, and excrete carbon dioxide, urine and solid waste.  In order to avoid exorbitant requirements for lifting oxygen and water to space and storing them for prolonged missions, NASA has developed technologies to recycle air and water components.  However, completely closing the loop with respect to oxygen recovery has not yet been demonstrated. We report the development of a methane pyrolysis technology that, in combination with the current state of the art Sabatier process, can allow close to 100% of the oxygen in exhaled carbon dioxide to be recovered for reuse. Laboratory studies of the kinetics of this process allowed the process to be optimized, and a design scaled for supporting four crew has been created.  A brassboard prototype will be built in 2019.

## II.  Background

Figure 1 shows a simplified view of technologies that are either in use or under development for the ECLS system. Focusing on the air side of this system, carbon dioxide can be removed from air using the current Carbon Dioxide Removal Assembly (CDRA)[1] on ISS, or any number of proposed new $CO_2$ removal technologies such as a solid amine system[2], or the developmental Carbon Dioxide Removal with Ionic Liquids System (CDRILS)[3]. The concentrated carbon dioxide can be sent to a Sabatier reactor[4,5] in which it is reduced with hydrogen to generate methane and water. A condenser extracts the water, which is electrolyzed in the Oxygen Generation Assembly (OGA) to make oxygen and hydrogen. The oxygen is delivered to the cabin, and the hydrogen is used to supply the hydrogen needed for the Sabatier reactor. Since half the hydrogen used for this reaction was used to form methane, this hydrogen is lost if the methane is discarded, limiting the oxygen recovery for the overall process to ~50%.  The goal was to develop a methane pyrolysis assembly that would recover this hydrogen, and therefore increase the oxygen recovered from $CO_2$ to greater than 75%.
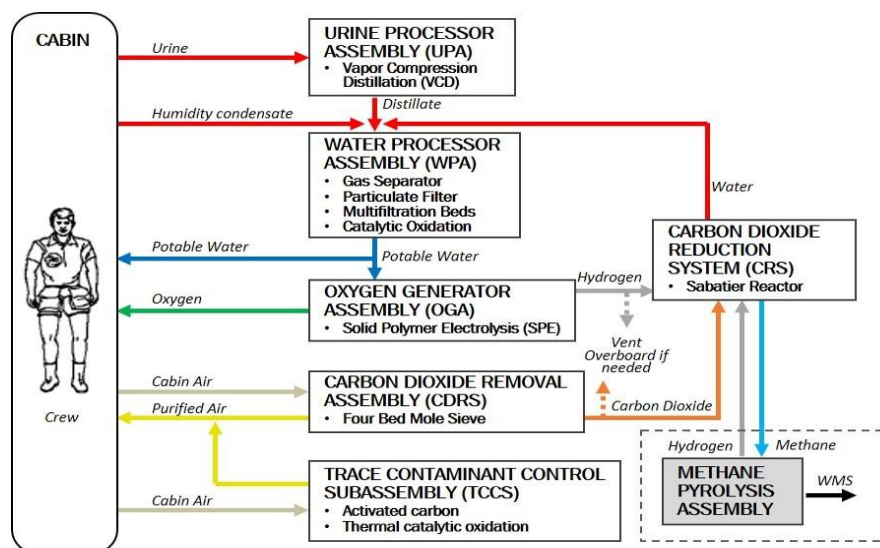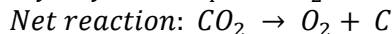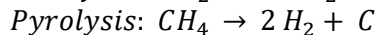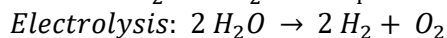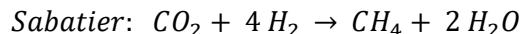


**Figure 1: Technologies for proposed ECLS system.**

The chemical equations for the required chemical reactions are shown below. The Sabatier reaction requires four moles of hydrogen to generate methane and water, and the electrolysis reaction consumes the water, generating two moles of hydrogen. Complete pyrolysis of the methane product from the Sabatier reaction produces hydrogen and solid carbon, closing the mass balance for hydrogen and enabling up to 100% of the oxygen to be recovered. As with any technology approach that achieves high oxygen recovery, solid carbon will be generated, which can present operational constraints in microgravity if it is in the form of soot or dust. Additionally, methane pyrolysis is a high temperature endothermic process. Thus, the goal was to develop a methane pyrolysis assembly that minimized weight, volume and power, and that generated carbon in a safe, easily handled solid form.

$$Sabatier: \ CO_2 + 4\,H_2 \rightarrow CH_4 + 2\,H_2O$$
$$Electrolysis: \ 2\,H_2O \rightarrow 2\,H_2 + O_2$$
$$Pyrolysis: \ CH_4 \rightarrow 2\,H_2 + C$$
$$Net\ reaction: \ CO_2 \rightarrow O_2 + C$$

## III.  Methane pyrolysis for hydrogen recovery

This approach to methane pyrolysis was based on using carbon chemical vapor deposition (CVD) onto a substrate. In order to fully balance the Sabatier and electrolysis reactions stoichiometrically, elemental carbon must be the final product of the pyrolysis reaction. Carbon-producing methane pyrolysis without a substrate is widely practiced industrially to make carbon black[6], but this is a sooty process with many gas phase byproducts. Instead, the carbon CVD process using a high surface area substrate is clean and generates carbon in the form of durable solid disks. This approach also has the advantage that solid carbon is retained in the reactor, eliminating the need for gas-phase separations to purify the hydrogen needed for the Sabatier reaction. It is also a well-established process that has been practiced industrially on a large scale for many years. Figure 2 shows a typical product from the process. The carbon product is easily handled without gloves, and may have reuse potential. CVD of carbon is a high-temperature, endothermic process that must be run at reduced pressure, but the power required can be reduced by use of appropriate technology. It also requires that a supply of substrates be available as a consumable. Later in this paper, the estimated volume required as a function of mission length will be reported.

**Figure 2: Typical carbon product from methane pyrolysis process.**

## IV.  Reaction kinetics and kinetic model

### A. Experimental CVD Studies

In order to develop a useful CVD process for hydrogen recovery, the kinetics of the process in a small scale reactor were investigated as a function of temperature, pressure, residence time and substrate design. A model for the process was developed based on the resulting data, which was then used to scale the process to larger and smaller mass flow requirements, and to conveniently measure any gas phase byproducts. This model predicted single pass conversion and aided in evaluating strategies for increasing the carbon loading for the substrates. Because the feed stream for the pyrolysis process comes from the Sabatier reactor, and the product hydrogen returns to the Sabatier reactor, a system model incorporating both reactors was also required to select the optimum single pass conversion to maximize oxygen recovery while minimizing reactor volume and power. This analysis also aided in efforts to understand and minimize the impact of this recycle on the operation of the Sabatier.
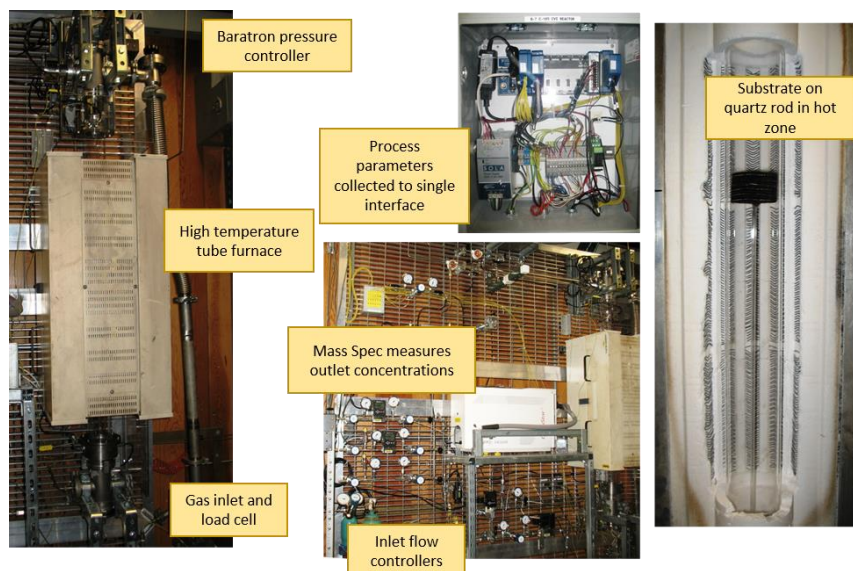
**Figure 3: Experimental test stand.**

Figure 3 shows the CVD system that was used for much of the studies in this paper. It comprised an inlet system with flow controllers, a reactor tube surrounded by a tube furnace, a pressure control system at the outlet, and a vacuum pump. Multiple substrates were positioned in the reactor and methane was introduced at a known flow rate. Temperatures, pressure, and flow rates were continually monitored, and an on-line mass spectrometer allowed continuous monitoring of the gas phase composition. Periodic samples were removed and analyzed by gas chromatography. Because the CVD reaction results in a change in the number of moles of gas, the outlet flow rate is a function of conversion and was measured periodically using a positive displacement meter. Upon completion of a run, the entire reactor was cooled and the weight of the product parts was compared with that of the initial substrates.

Conventionally, CVD is performed at a relatively low single pass conversion to optimize the properties of the carbon product. However, for the current application, a high single pass conversion is preferred. Figure 4 shows the effect of temperature and pressure on single pass methane conversion in the presence of a single carbon fiber substrate. As expected, increasing either temperature or pressure results in higher conversion. Based on these experiments, 100 torr was selected as the preferred operating pressure, and the temperature was adjusted to obtain the desired single pass conversion. Operating the system at pressures higher than 100 torr at certain temperatures resulted in visible byproduct generation.
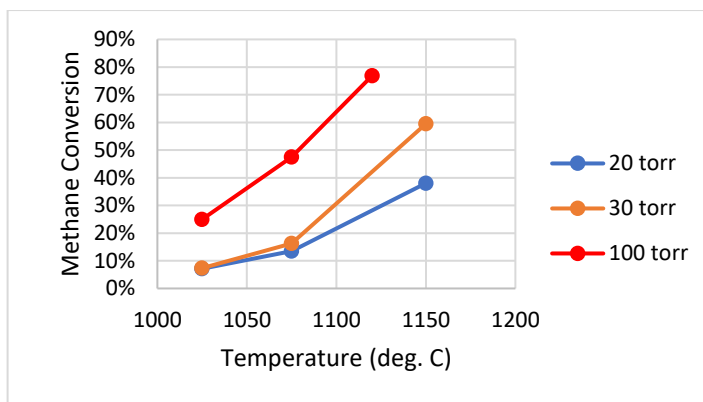


**Figure 4: Methane conversion as a function of temperature and pressure in the presence of a single carbon fiber substrate.**

The conversion of methane to carbon has been extensively studied[7] and proceeds through numerous molecular species and free radicals. The initial and rate determining step is generally considered to be the loss of hydrogen from methane, resulting in two-carbon species ethane, ethylene and acetylene. Of these, acetylene is generally considered to be a key intermediate because it is the lowest molecular weight intermediate with the potential of reacting directly with the growing carbon surface. Partitioning occurs from this intermediate between further gas phase reaction to make larger hydrocarbon species and deposition as solid carbon. The fraction of carbon deposited depends on the temperature, pressure, residence time, and the characteristics of the substrate. Each intermediate after acetylene also partitions between further gas phase reaction

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and deposition as solid carbon. Progressively larger hydrocarbons are made according to this mechanism, but the concentrations of these hydrocarbons will be extremely low under conditions favoring deposition. The ultimate gas phase reaction product is soot, which is reversibly formed if a gas stream containing high molecular weight species is allowed to cool[8]. Figure 5 shows a highly simplified methane pyrolysis mechanism with the basic steps.

   As the simplified mechanism shows, carbon and hydrogen are not the only possible reaction products from methane pyrolysis. Gas phase reaction products can also occur. Figure 6 shows that selectivity to carbon, as opposed to these gas phase reaction pathways, is increased by increasing the available surface area for deposition. In this set of experiments, all run at 1120°C and 100 torr pressure, the number of carbon fiber substrates was varied. Referring first to the left graph, the methane conversion and yield of hydrogen was essentially constant and in close agreement
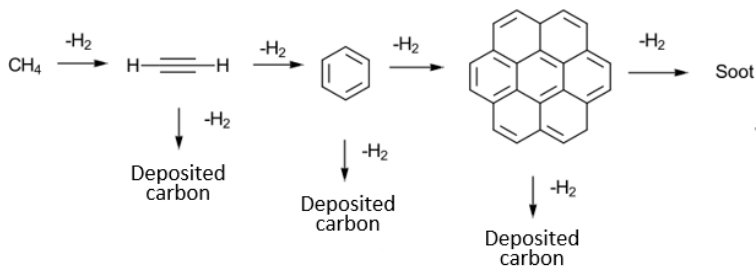


**Figure 5:  Simplified mechanism for carbon vapor deposition (CVD).**

as the number of substrates was increased.  Selectivity towards carbon as the reaction product increased as the number of substrates increased. The right plot shows the observed gas phase reaction products, including ethane, ethylene, acetylene and benzene. The concentrations of these byproducts decrease as the number of substrates (i.e. surface area) increases. This result clearly demonstrates the key role of the substrate in our pyrolysis process in preventing generation of significant quantities of these byproducts.
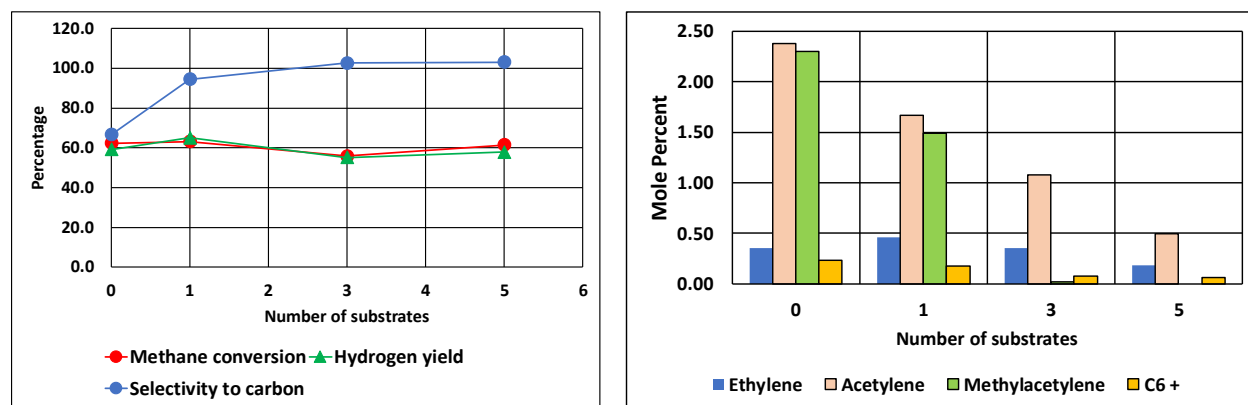


**Figure 6:   Effect of substrates on carbon vapor deposition (1120°C, 100 torr, 300 sccm methane).  Methane conversion, hydrogen yield and carbon selectivity (left) and gas phase product concentrations (right) vs. number of substrates..**

   The effect of residence time on methane conversion (and thus reactor design) was also studied while holding temperature, pressure, and substrate surface area constant. The residence time of methane in the reaction zone was varied by adjusting the inlet methane flow rate. Residence time in these experiments was calculated for the reaction zone in the furnace with a temperature higher than 950°C, and taking into account the change in flow rate down the reactor as a function of conversion. Several methane flow rates were studied in a single run at temperature, and the outlet flow rate and outlet gas concentrations of methane, hydrogen, and other gas phase hydrocarbons were measured. Because one mole of methane generates two moles of hydrogen at 100% conversion, the ratio of the inlet and outlet flow rates is a simple measure of reaction conversion. More accurate conversion values can be obtained using the outlet gas concentrations. Figure 7 shows a typical curve of the effect of residence time on methane conversion for this type of study. While prior investigations using reaction pressures between 12 and 20 torr have reported[9] first order

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kinetics for methane disappearance in CVD, this relationship did not hold for the conditions of study in these experiments, and the reaction order appeared to vary with reaction conditions. Figure 7 shows the general trend observed at the conditions of study: conversion of methane to >50% was observed to be extremely rapid, but became increasingly slower as conversion increased, and the methane concentration decreased and the hydrogen concentration increased. While hydrogen inhibition[10] was suggested as a possible explanation, deliberate introduction of hydrogen to the reaction feed in a separate study did not result in a rate change under the conditions of study. It is therefore proposed that the true reaction order is higher than one, but that the reaction kinetics are too complex to determine the exact reaction order. Instead, results



**Figure 7: Typical methane pyrolysis experiment at 1135°C and 100 torr as a function of residence time in the reactor.**

like those in Figure 7 were fit to equations selected to maximize the fit, and to use these empirical equations for reaction design. This approach has a low degree of risk because the laboratory test stand differs in scale from a 4-crew scale by only a factor of 15.
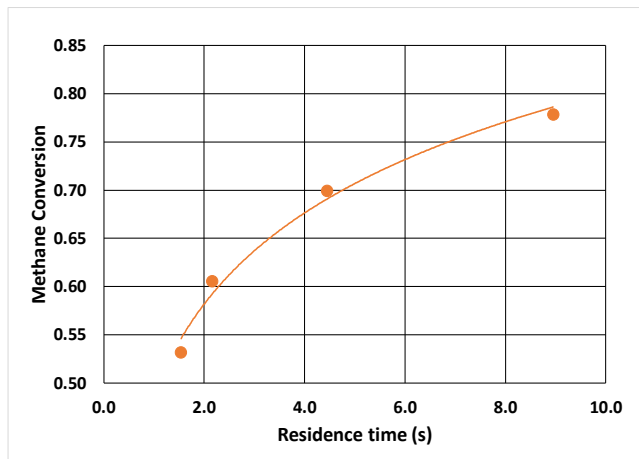
Finally, carbon loading of the substrate material must be optimized. A high final average density of the interior subtrates will increase the time per run before required periodic reloading, and decrease the overall amount of consumable substrates required per mission. Figure 8 shows the results of an experiment in which the "hot zone" was
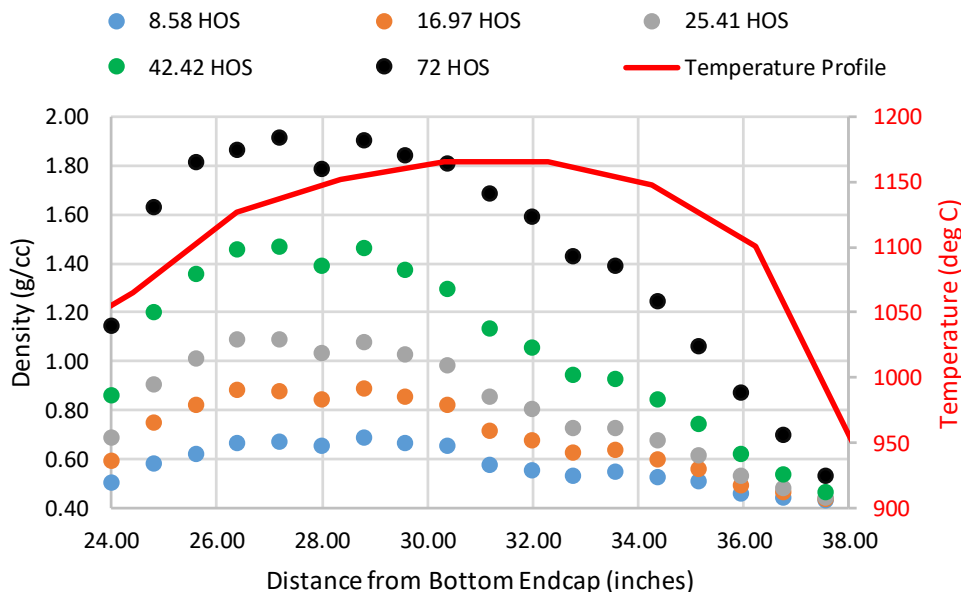


**Figure 8: Carbon accumulation during methane pyrolysis as a function of position in the reactor and hours on stream (HOS).**

filled with substrates of known weight, and a CVD run was initiated at a flow rate of 450 sccm and a pressure of 100 torr. A temperature scan down the reactor provides the temperature of each substrate (red line in Figure 8). The CVD run was interrupted periodically, and each substrate was weighed and then restored to the reactor in the same position. Note in Figure 8 that substrates near the inlet of the reactor tended to accumulate carbon most rapidly due to the high concentration of methane. Unbalanced loading of the substrates will lead to a premature end of the run because byproduct generation, including soot, increases as any significant portion of the substrates become too densified, resulting in decreased surface area for deposition.

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## B. Reactor Model

A differential reactor model was developed as a predictive tool to utilize the developed reaction kinetics for design of a proposed brassboard methane pyrolysis unit. As Figure 9 shows, the reactor was assumed to have methane flow at one end, and a substrate containing zone between two empty reaction zones. These three zones were divided into a series of differential reactor elements. Each element receives a feed flow from the element before it, and provides a product flow to the next element. Within each element, reaction occurs at a rate determined by the temperature, pressure and feed composition at that element. Carbon accumulation occurs within each element, and reduces the volume and therefore the residence time in that element. The empirical experimental fits were used.
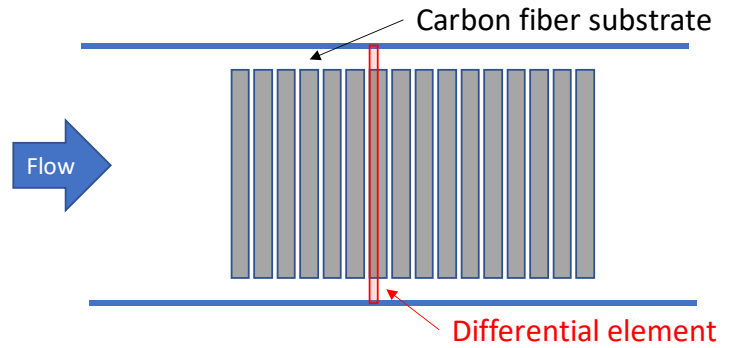


**Figure 9: Schematic for development of differential carbon deposition model.**

## C. System Model

While experimental studies focused on a stand-alone single pass methane pyrolysis system, the methane pyrolysis system will be integrated with the Sabatier unit and other ECLSS elements in a closed loop system. Therefore, if methane conversion is less than 100%, methane remains in the product stream and becomes part of the feed to the Sabatier reactor. Thus, the impact of true closed loop operation must be understood both for the methane pyrolysis unit, and for each of the other components of the system. The overall scale of the system is fixed by the input flow of carbon dioxide (for example, 4.18 kg/day for a crew of four), but flow rates to each component will be determined both by this input flow and the conversion for each component reactor.

In order to properly size the methane pyrolysis reactor and understand its impact on the ECLS system, a simple mass balance model was constructed for the operations shown in Figure 10. At the inlet and outlet of each component reactor, the mass flow of each chemical species was estimated subject to the governing assumptions. The only source of carbon in the system model was carbon dioxide, and carbon only leaves the system as solid carbon or via a vent stream. Similarly, hydrogen was assumed to be internal to the system and enters only if make up water is required, and leaves only via the vent. Conversion of the Sabatier and electrolysis reactions was assumed to be constant at 100%, and the molar ratio of hydrogen to carbon dioxide at the inlet to the Sabatier was held constant at 4.4. Recovery of water by the water condenser was assumed to be 95%.

One important goal of the model development was to understand the consequences of incomplete pyrolysis conversion on the scale of the reactor and other ECLS components. When pyrolysis conversion is incomplete, the residual methane contributes to the exit stream, increasing the overall volumetric flow. This methane, mixed with the hydrogen product, enters the Sabatier reactor and passes unchanged back to the pyrolysis reactor. Thus the immediate consequence of incomplete pyrolysis conversion is increased volumetric flow into both the pyrolysis and Sabatier reactors. Because methane conversion depends on residence time, increased volumetric flow results in increased reactor volume. Figure 11 shows the volumetric flow at the outlet of the pyrolysis reactor and the concentration of methane in this stream as a function of methane conversion. Experience with the Sabatier reactor[11] suggests that it is unwise to introduce methane at the inlet to the Sabatier at a concentration higher than 15 mole %. Taking into account the dilution of the hydrogen from the methane pyrolysis unit by hydrogen from electrolysis and the incoming flow of carbon dioxide, this corresponds to a limit for the methane concentration in the pyrolysis outlet stream of less than 25%, and therefore a methane conversion lower bound of 45%. In fact, conversion greater than 65% is preferred because of the effect on the reactor volume and weight.
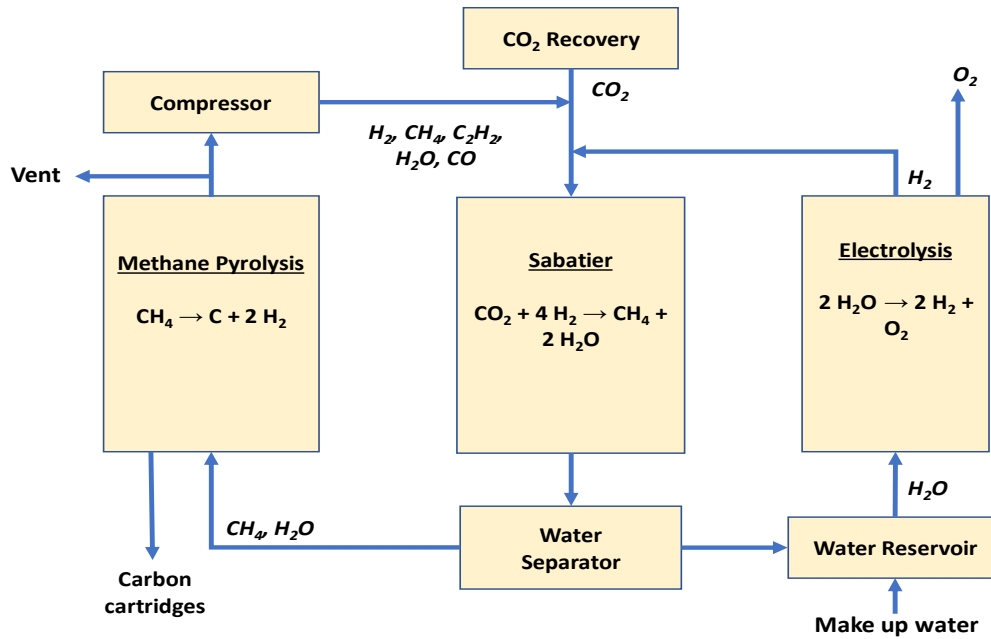
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**Figure 10:  Schematic of components in the ECLS system included in the system model.**
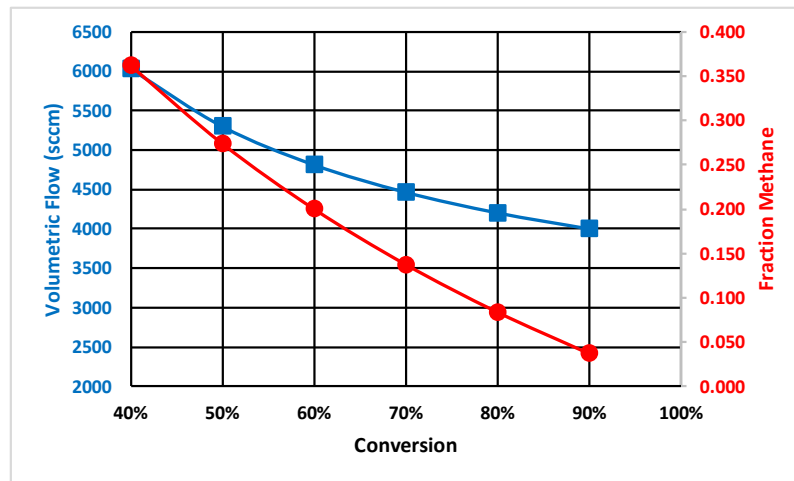


**Figure 11:  Volumetric flow and mole fraction methane at the pyrolysis outlet as a function of methane conversion.**

Another consequence of the closed system shown in Figure 10 is that oxygen recovery from carbon dioxide is very high. Oxygen leaves the model system only as molecular oxygen product or in the vent stream. The vent stream is present to avoid build up of inert components like nitrogen in the recirculating stream, since this would result in further increase in the volumetric flow. In the absence of nitrogen contamination of the feed carbon dioxide, the vent stream can be reduced to a low value. Oxygen recovery can be estimated within the system model by assuming that all the water generated by the Sabatier is consumed by the electrolysis reaction, and is the ratio of oxygen in the carbon dioxide fed to the Sabatier to the oxygen recovered in the form of water at the outlet of the Sabatier, and is >99%. Actual oxygen recovery will be less because only 92% of the oxygen inhaled by the crew is exhaled as carbon dioxide.

The same set of assumptions for system performance and the measured generation rates of byproducts can be used to predict the expected composition of the stream entering the Sabatier reactor. Table 1 shows predicted values for

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each component. Note that since water is present in the feed to the pyrolysis reactor, some conversion of water to carbon monoxide is expected. Also, trace amounts of acetylene and benzene are expected; other gas phase hydrocarbon concentrations are significantly lower than these.

**Table 1: Predicted composition of the inlet stream to the Sabatier integrated in an ECLS system vs. methane conversion. 4.4 moles hydrogen / mole carbon dioxide assumed.**

| $CH_4$ conversion | 65% | 75% | 80% |
|---|---|---|---|
| Hydrogen | 73.95% | 76.59% | 77.71% |
| Methane | 5.59% | 2.23% | 0.79% |
| Water | 3.10% | 3.21% | 3.26% |
| Nitrogen | 0.17% | 0.17% | 0.18% |
| Carbon monoxide | 0.34% | 0.36% | 0.36% |
| Acetylene | 0.01% | 0.01% | 0.01% |
| Benzene | 0.03% | 0.02% | 0.03% |
| Carbon dioxide | 16.81% | 17.41% | 17.66% |
| Flow rate (sccm) | 8915 | 8611 | 8489 |

## V.  Integration with Sabatier reactor

### A.     Motivation for Catalyst Challenge Testing

Realization of a closed loop oxygen recovery system based on the Sabatier reaction and a methane post-processor requires, not just technology development of the post-process, but also careful consideration for integration with the larger life support system. State-of-the-art Sabatier technology on the *International Space Station* (ISS) was designed, developed, manufactured, and integrated into the Oxygen Generation System (OGS) rack by Collins Aerospace (formerly Hamilton Sundstrand, Windsor Locks, CT). In an effort to advance Exploration life support technology, the ISS program office is facilitating flight experiments designed to compete and down-select Exploration technologies for use in future long-duration NASA missions. Assuming success of the development efforts of the CVD process, flight hardware would have the potential to be developed and integrated directly with the ISS Sabatier reactor. To this end, it is critical that integration risks be considered early in the program to ensure mitigations are designed into the technology and/or the architecture. A key integration risk identified early in the project was the potential for contaminants in the hydrogen recycle stream from the CVD process to foul the Sabatier reactor catalyst. CVD processing of methane in the presence of hydrogen and water vapor can result in a number of byproducts including, but not limited to, carbon monoxide, ethane, ethylene, acetylene, and benzene. Thermodynamic equilibrium calculations with these gas mixtures shows the potential for the production of solid carbon at the highest Sabatier operational temperatures. Deposition of this carbon on the Sabatier catalyst would ultimately result in fouling of the reactor and failure of the overall system.

To evaluate this risk, a study was undertaken to explore the effect of predicted recycle gas stream compositions on Collins Sabatier catalyst.

### B. Catalyst Challenge Testing Materials & Methods

*1. Materials*

To evaluate the effect of CVD post-processor recycle stream gases on the ISS Sabatier, both short- and long-duration challenge testing was conducted. Sabatier catalyst was purchased from Collins Aerospace (Windsor Locks, CT).  Challenge gas mixtures, as shown in Table 2, were purchased from SpecGas, Inc. (Northampton Township,

PA). Composition of the gases was based on predictions from chemical models developed in-house at Honeywell Aerospace. Challenge testing was conducted at NASA Marshall Space Flight Center using the Carbon Dioxide Reduction Catalyst Test Stand (COR-CaTS). The COR-CaTS is a facility capability that uses Alicat Scientific (Tuscon, AZ) mass flow controllers

**Table 2. Gas challenge mixtures based on predicted methane post-processor recycle composition.**

| Component | Challenge Gas (mol %) | | | |
|---|---|---|---|---|
| | Mix A | Mix B | Mix C | Mix D |
| Benzene | 0.20 | 0.01 | 0.02 | 0.02 |
| Methane | 9.98 | 25.10 | 5.68 | 17.90 |
| Carbon monoxide | 0.00 | 0.00 | 3.82 | 3.29 |
| Acetylene | 0.10 | 0.50 | 0.04 | 0.04 |
| Hydrogen | 89.72 | 74.39 | 90.44 | 78.75 |

and back pressure regulators to maintain flow and pressure in the reactor. Barnstead-Thermolyne F21135 (Ramsay, MN) tube furnaces are used to control temperature of the catalyst samples and an Agilent 3000A micro-gas chromatograph is used to measure dry gas composition at both the intlet and outlet of the reactor.

*2. Reactor and Catalyst Preparation*
Quartz tubes with 2.2cm inner diameter were purchased from National Scientific, Inc. (Quakertown, PA). Fiberfrax Durablanket S insulation was purchased from Unifrax (Tonawonda, NY) and used at the inlet and outlet of the reactor tube to provide both flow distribution and catalyst support for the vertically oriented reactor tube. A quantity of catalyst was measured and packed into the reactor tube and the tube was installed into the test stand. The height of the packed catalyst bed was targeted to fall entirely within the heated region of the furnace and was sufficiently short so as to prevent complete conversion of the $CO_2$ feed to the bed. This was done so that changes in catalyst performance could be readily observed and quantified.

*3. Baseline Tests*
Following introduction of fresh catalyst into the COR-CaTS, a baseline test (BT) was conducted to measure baseline performance at a 2-crew member (CM) equivalent carbon dioxide feed rate and a 4-CM equivalent feed rate. Gas flow rates were determined based on bulk velocities of the ISS Sabatier reactor at each crew member processing rate. Hydrogen was introduced with the $CO_2$ at a ratio of 4.5:1 for both the 2-CM and 4-CM feed rates. Additionally, an $H_2$:$CO_2$ ratio of 4.9 was tested at the 2-CM $CO_2$ feed rate. Pressure in the reactor was maintained at 86.2kPa (12.5psia) and the wall temperature of the reactor was maintained at ~200°C. No thermocouples were placed in the catalyst bed due to the test stand set-up; however, equilibrium calculations based on outlet composition indicate catalyst bed temperatures of between 380 and 390°C. In addition to the initial test of the catalyst material upon installation into the reactor, a BT was conducted at the beginning and end of each challenge run. The goal of the subsequent BTs was to compare the performance at any given time with the performance at the start of the test and with the goal of observing if and when fouling of the catalyst occurred.

*4. Challenge Tests*
Short duration challenge tests were conducted on the Sabatier catalyst with each of the four challenge gas mixtures (and balance of $CO_2$) until the test gas was exhausted. Due to differences in benzene and acetylene composition, there were varying quantities of challenge gas available in each standard bottle and resulting variation in total time for each short-duration test. A BT was conducted before and after each challenge run. For long-duration challenge testing, the Sabatier catalyst was challenged with each of the four challenge gas mixtures (and balance of $CO_2$) for a targeted duration of 100 hours each. During long-duration challenge testing, a BT was conducted at 10 hour intervals.

*5. Scanning Electron Microscopy/Energy Dispersive Spectroscopy (SEM/EDS) Catalyst Evaluation*
SEM/EDS was used to evaluate the Sabatier catalyst from the short-duration testing to determine if observable quantities of carbon formed during exposure to the challenge gas compositions. A Hitachi S-3700N SEM and an Oxford X-Max$^N$ 80 XDS were used to analyze the samples at 15kV and 60 Pa in variable pressure mode to reduce charging of the sample. Both a control (multiple pellets of unreacted Sabatier catalyst) and pellets of tested catalyst from the first 2mm of the reactor were placed in the SEM chamber at the same time so the vacuum could be maintained.

**C. Catalyst Challenge Results and Discussion**
Three considerations were made when determining whether the contaminants had an adverse affect on the Sabatier catalyst:

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1) Did the change in composition of the gases between inlet and outlet suggest carbon formation?
2) Did the performance of the catalyst change after exposure to contaminants as indicated by the BTs?
3) Was there a measurable quantity of carbon deposited on the Sabatier catalyst during exposure?

These questions were answered for both short-duration testing as described below.

*1. Short-Duration Testing*

A single quantity of Sabatier catalyst was loaded into the reactor for all of the short-duration tests. The bed was challenged with contaminated gas feeds for a total of 13 hours at a 2-CM rate and 3.3 hrs at a 4-CM rate. The exact duration of each test is shown in Table 3. Baseline tests were conducted between each challenge run and the combined exposure time is shown at 2-CM and 4-CM rates. The catalyst was not challenged at the 4-CM rate with Mix A due to extremely limited quantities of the gas.

To answer the first question above, the composition of the gases was measured during each challenge test at both the inlet and the outlet of the reactor. Because composition was evaluated using a micro-GC, all water was removed from the product gas stream before analysis. Total moles exiting the reactor would be expected to decrease both due to the Sabatier reaction and due to the removal of water product exiting the reactor. If we assume acetylene and benzene contaminants entering the system are not reacting, the relative molar percentage of the constituents would be expected to increase. Inlet and outlet compositions of acetylene and benzene are shown in Figure 2 and Figure 13, respectively. In all but one run, the acetylene at the outlet was below the detectable limit of the micro-GC. Run 13 was with Mix B (highest concentration of acetylene) at the 4-CM feed rate. While the acetylene was

**Table 3. Short-duration testing contamination exposure time.**

| Run | Rate | Feed | Exposure Time (hrs) |
|---|---|---|---|
| 1,3,5,7,9 | 2-CM | BT | 22.8 |
| 2 | 2-CM | Mix A | 2.9 |
| 4 | 2-CM | Mix B | 4.5 |
| 6 | 2-CM | Mix C | 3.2 |
| 8 | 2-CM | Mix D | 2.4 |
| 10,12,14,16,18 | 4-CM | BT | 4.7 |
| 11 | 4-CM | Mix A | 0.0 |
| 13 | 4-CM | Mix B | 1.3 |
| 15 | 4-CM | Mix C | 0.9 |
| 17 | 4-CM | Mix D | 1.1 |

measurable, the outlet percentage was significantly below that observed at the inlet. This demonstrates some reaction of acetylene in the Sabatier reactor. Similarly, benzene was observed to decrease in overall molar percentage from the inlet to the outlet of the reactor, with the exception of Mix B at 4-CM rate. However, if there was no reaction with benzene, the expected outlet dry composition for this run would have been 0.01 mol%. Thus providing further evidence of benzene reacting on the Sabatier catalyst.
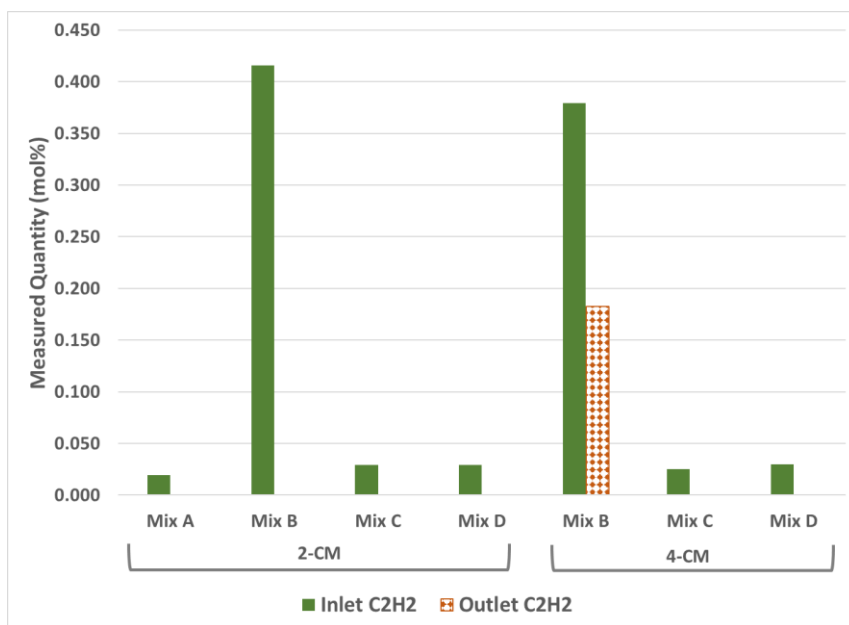
It is next important to consider what the acetylene and benzene could be reacting to form. The biggest concern is that acetylene could be directly disassociating to form solid carbon and benzene could be dissociating through a number of mechanisms to form other hydrocarbons and/or carbon and hydrogen. More favorably, acetylene could be hydrogenating, given the high concentration of hydrogen in the feed stream, to form ethylene, ethane, and methane. Due to the relatively small



**Figure 12. Observed differences in inlet and outlet acetylene composition during short-duration challenge testing.**

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quantities of these contaminants, a simple mass balance to determine if carbon was forming was not possible. However, no hydrocarbons other than those fed to the system were observed. This suggests that regardless of the the conversion of these hydrocarbons, the reaction is complete to the final products whether carbon, methane, carbon dioxide, or carbon monoxide. Further, the micro-GC data alone are insufficient to conclusively state whether or not solid carbon is forming on the Sabatier catalyst.

The second consideration in determining if carbon is forming on the catalyst was to observe performance of the catalyst over time. To this end, baseline tests were conducted before and after each challenge test and composition was measured at both the inlet and outlet of the reactor. Figure 14 shows the average $CO_2$ conversion of all baseline tests at 2-CM and 4-CM. Throughout the duration of the test, no significant decrease in performance was observed for any set of conditions, indicating that exposure to the contaminants over the short durations did not measurably affect the performance of the catalyst.

The third consideration in determining if carbon is forming on the catalyst was to evaluate the tested Sabatier catalyst versus virgin Sabatier catalyst using SEM/EDS. Due to the proprietary nature of the catalyst, no images will be shared. However, EDS mapping showed evidence of carbon across the surface of the tested catalyst that coincided with reactive sites on the catalyst particles. Further, analysis of the atomic map showed a statistically significant difference ($p \ll 0.05$) in surface carbon between the control catalyst and the test catalyst as seen in the box and whisker plot in Figure 15.

In discussions with catalyst experts, it was proposed that the observed carbon on the surface may be an effect of exposure to the $CO_2$ and CO in the gas stream, resulting in high quantities of residual surface adsorbed CO and $CO_2$. However, during operation of the tests, a strongly reducing environment was maintained (excess $H_2$ in all testing). When not undergoing testing, the catalyst was constantly purged with a nitrogen stream to prevent oxidation of the catalyst. Both the test catalyst and the control catalyst were exposed to air for the time required to load the samples into the SEM/EDS. Thus, it does not seem reasonable that significantly different quantities of carbonaceous gases could have adsorbed to the surfaces of the materials.

Short-duration testing was conducted with three considerations. In the first, no conclusive results could be drawn from the available data. However, data from SEM/EDS of the tested catalyst strongly suggests that carbon is forming in very small quantities when exposed to the tested dry gas compositions. A key point here is that the catalyst was
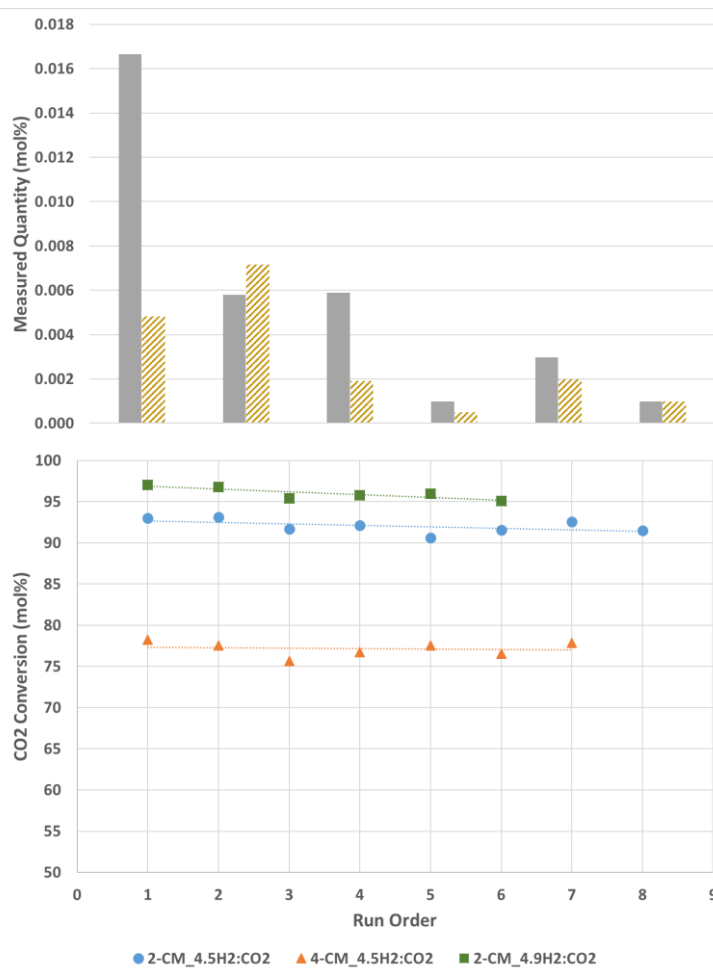


**Figure 14. Baseline test result for all control test conditions.** *Lines are drawn between points to help aid the eye and do not represent continuity of data.*
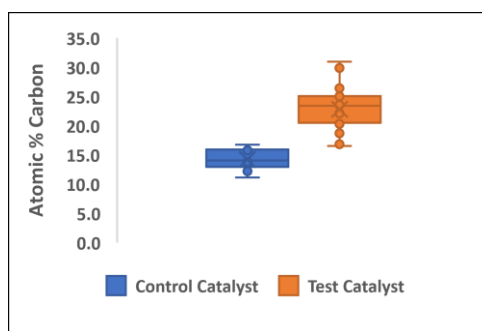


**Figure 15. Box and whisker plot of atomic % carbon data collected using SEM/EDS.**

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challenged with dry feed streams. Modeling of the CVD process suggests that water vapor fed from the Sabatier to the post-processor will likely pass unreacted (or minimally reacted) back to the Sabatier. The presence of water vapor in the challenge gas streams in sufficient quantities will push the reactions of acetylene and benzene toward more favorable carbon monoxide and carbon dioxide rather than solid carbon. Future testing will evaluate the effect of expected water vapor levels on both contaminant reactivity and overall Sabatier performance.

## VI.    Reactor and System Design

### A.    Reactor Design

Based on experimental results, a brassboard design for a methane pyrolysis reactor and system has been completed. A brassboard-level unit serves to prove the chemical approach and system integration at a 4-crew scale in a relevant ground environment, while providing a first pass assessment of a pathway towards flight with respect to system mass, volume, etc.  A practical design must minimize mass and volume. Since this process is inherently a batch process from which the carbon product must be periodically removed, increasing the length of time between these maintenance intervals is important. The process must be compatible with operation at zero gravity and be safe to operate. In particular, since carbon dust would easily become unmanageable in an occupied space at zero gravity, the design must ensure that the carbon product does not generate soot or dust and can be easily handled. Figure 16 shows the proposed reactor design.  It comprises a nickel alloy reactor shell with a removable lid, filled with carbon fiber disks in a cartridge format. Key dimensions and characteristics are shown in Table 4. Nickel alloy is used for compatibility with the high temperature and feed composition of the reaction.  In use, two such reactors would be required so that one reactor is continually online to convert methane to hydrogen and carbon. The offline reactor would be allowed to cool so that the lid can be removed and the cartridge of substrates can be replaced with a fresh cartridge.
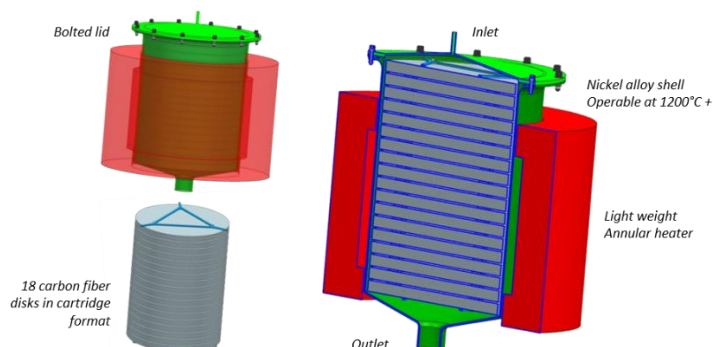


**Figure 16  Brassboard reactor design.**

**Table 4:  Dimensions and characteristics for brassboard reactor design.**

| Specification | Value |
|---|---|
| Internal volume | 10.9 L |
| Dimensions | 22.4 cm ID x 27.7 cm |
| Weight | 27 kg |
| Maintenance Interval | 7-11 days |
| Average Temperature | 1120°C |
| Pressure | 100 torr |
| Power requirement | 730 W |

Completing the reactor design required an iterative process of thermal and reaction modelling. Candidate reactor designs were assessed using the differential performance model outlined previously and a thermal resistance model (including appropriate insulation). Power is required to heat the reactor to temperature and hold it at that temperature against any losses through the insulation. In addition, power is required to heat the incoming methane feed to the reaction temperature (est. 79W) and to supply the endothermic heat of reaction (est. 81W). Using the maximum operating temperature of the metal shell as an upper limit, the power was minimized while still achieving the desired reactor performance. The internal volume of the reactor must meet two independent constraints. First, since the volumetric flow rate through the reactor is determined by the conversion for the pyrolysis reactor and other component reactors, as estimated by the system model, residence time in the reactor is determined by reactor volume. Second, regardless of the reaction kinetics, the maintenance interval between change-outs of the substrate cartridge is determined by how much carbon is held by the reactor. Four crew exhale 4.18 kg/day of carbon dioxide, on average, and this corresponds to 1.1 kg/day of carbon. The reactor volume required to hold this carbon is determined by the maintenance interval and the final average density of the substrates at the end of a run.

Figure 15 shows the predicted performance of the proposed brassboard design. The left chart shows the accumulation of carbon, as reflected by the density, at each element down the reactor from inlet to outlet.  The shape of this curve is determined by the conversion at each point, which is in turn determined by the temperature profile

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provided by the thermal model. As the number of hours on stream increases, the density of the substrates increases, and the location of maximum loading shifts down the reactor. The right chart of Figure 15 reflects the output of the reactor as a whole. Conversion over the length of the reactor begins at 73%, but gradually decreases as the reactor fills up with carbon and residence time decreases. As conversion decreases, more methane is left in the stream and the outlet volumetric flow increases. The maximum density down the bed increases with hours on stream, as does the average density of all the substrates. The run should be considered complete when either the risk of visible byproduct generation increases (experimentally observed to occur around the time maximum density exceeds 1.7 g/cc for the baseline substrate material used in these studies) or the outlet volumetric flow exceeds the capacity of the downstream Sabatier process.
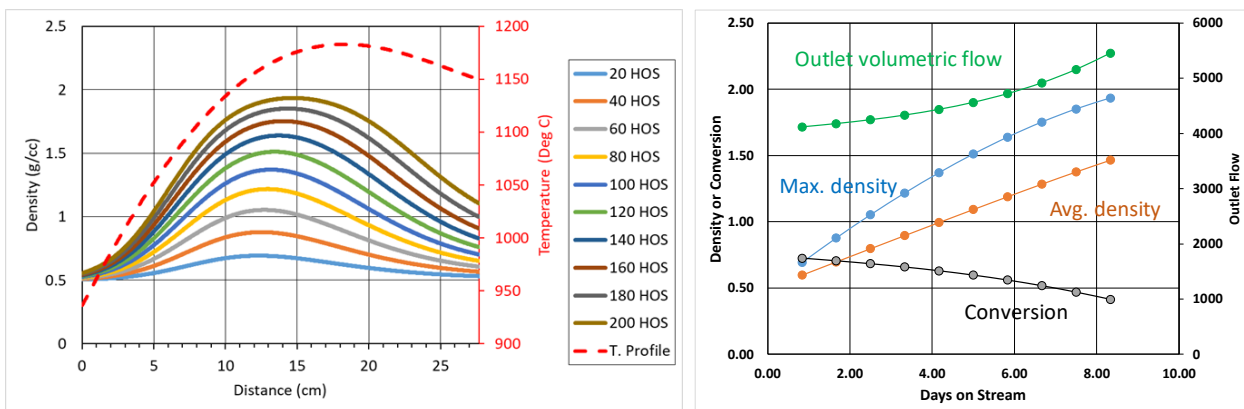


**Figure 15: Simulation of methane pyrolysis reactor via differential model. Left: substrate density vs. distance from the inlet vs. hours on stream, and temperature profile. Right: Reactor conversion, outlet volumetric flow (cc/min), maximum substrate density and average density.**

### B. System Design

Figure 16 shows a process flow scheme for the overall methane pyrolysis system. A dual reactor system allows constant treatment of the methane feed, allowing for alternating replenishment of substrate cartridges and faciliting a theoretical 100% $O_2$ recovery. Inlet flow is measured but is controlled by the Sabatier system. After a pressure regulator, the flow branches to the two reactors, and automated valves are provided to direct flow in the correct direction. Down stream of the reactors, a compressor brings the pressure back to that required for the Sabatier, preceeded, if necessary, by a pressure controller to modulate the pressure from the pump to the required reactor pressure. Measurement of the outlet flow is a convenient means of of monitoring

**Table 5: Substrate Requirements for 1000 day Mission.**

| Parameter | Baseline Substrate | Developmental Substrate |
|---|---|---|
| Capacity (g Carbon/g substrate | 0.8 | 1.3 |
| Maintenance interval (days) | 6.5 | 10.9 |
| Cartridges (1000 day mission) | 155 | 92 |
| 1000 day Storage Volume (m³) | 1.8 | 1.1 |
| 1000 day Storage Weight (kg) | 787 | 280 |

conversion. As noted previously, methane pyrolysis by CVD requires substrates that must be replaced periodically. This conveys many advantages to the process since carbon is generated in a hard, non-dusty, potentially reuseable format, but does require a supply of these substrates to be carried for any long duration mission for which this process would be used. Table 5 summarizes how many of these substrates would be needed, both with our current baseline substrate and with a developmental substrate now in initial testing. The quantities are significant, but the weight and volume are much smaller than the weight and volume of the oxygen, carried in the form of water, that would otherwise need to be carried.

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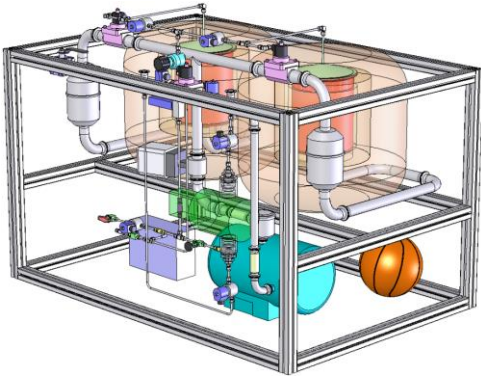
## VII.    Future Work



**Figure 17:  Spacefilling schematic of proposed brassboard skid.  (Basketball shown for scale).**

Further development of the methane pyrolysis system is underway. A ground prototype brassboard skid that will be sized to accept 1.5 kg/day of methane will be fabricated according to the designs above. A sketch of this unit is shown in Figure 17; it includes two insulated and heated reactors, a vacuum pump, the necessary valves and plumbing to alternate flow between the two reactors, a pressure regulation system and flow measurement. The system will be provided to NASA Marshall Space Flight Center, where a similarly sized Sabatier reactor already exists. This will allow the product methane stream from the Sabatier to be used as the feed for the pyrolysis reactor, and the product hydrogen stream from the pyrolysis reactor to be blended with the feedstream for the Sabatier. This experiment will capture the key synergies between the two reactors, identify integration requirements, and allow the effects of each reactor on the other to be quantified.

Further refinement of the methane pyrolysis technology is also necessary. Refinement of the substrates will lead to designs that have higher carbon capacity, reducing the inventory of substrates needed. Further reactor design will focus on improved reactor durability and simplified operation. As data becomes available for the composition of the streams entering and leaving the pyrolysis reactor after integration with the Sabatier, improvements in reaction conditions that amplify the advantages of the combined system can be explored. Integration of these two elements with an electrolysis system to generate oxygen and a carbon dioxide recovery



**Figure 16:  Schematic of methane pyrolysis brassboard design.**

system would complete an ECLS framework and allow all of the components to be integrated. An experimental flight unit would be the next logical step for the reactor itself. This would involve replacing many of the components in the brassboard unit with lightweight space-qualified components, and packing the system into a minimum volume configuration.
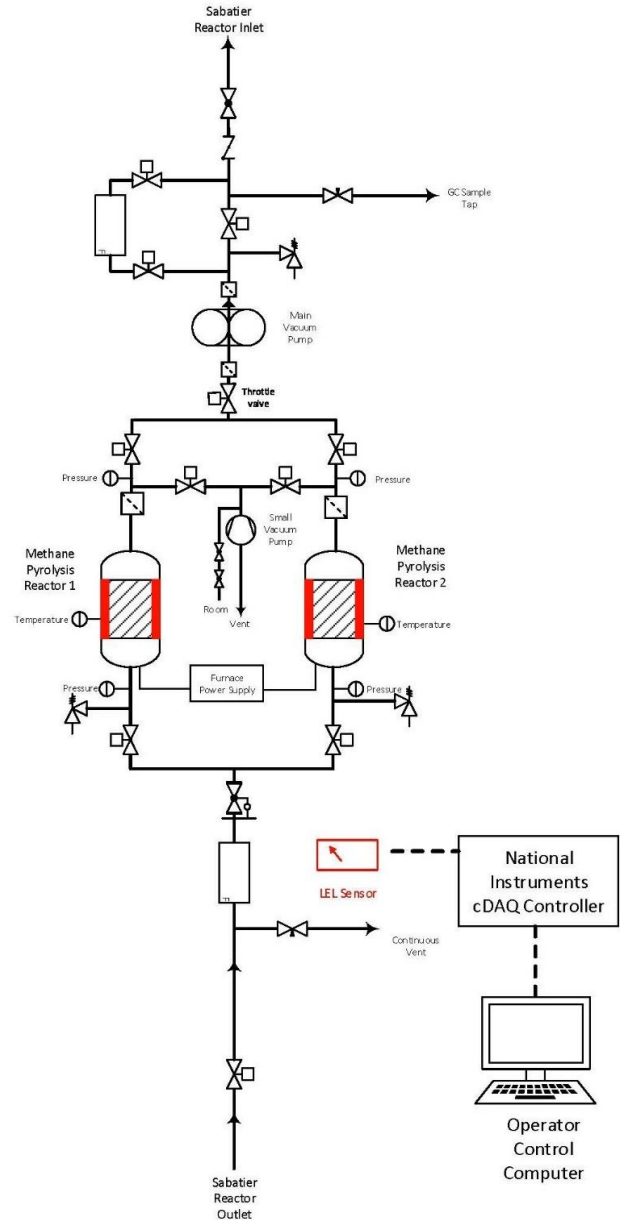
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# VIII. Conclusion

This work has demonstrated a practical methane pyrolysis system that enables >95% recovery of oxygen from carbon dioxide. Designed systematically from a thorough understanding of the kinetics of chemical vapor deposition of carbon under relevant conditions, it shows how methane from a Sabatier reactor can be converted to the hydrogen needed to complete the ECLS mass balance and durable non-sooty carbon. System modelling has been used to understand how this reactor should best be integrated with the other ECLS components. A reactor and a pyrolysis system brassboard design has been proposed, and ongoing work will validate our conclusion that this system will be compatible with an existing Sabatier reactor.

# Acknowledgments

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