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CO₂ Reduction Assembly Prototype using Microlith-based Sabatier Reactor for Ground Demonstration

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The utilization of CO₂ to produce life support consumables, such as O₂ and H₂O, via the Sabatier reaction is an important aspect of NASA's cabin Atmosphere Revitalization System (ARS) and In-Situ Resource Utilization (ISRU) architectures for both low-earth orbit and long-term manned space missions. Carbon dioxide can be reacted with H₂, obtained from the electrolysis of water, via Sabatier reaction to produce methane and H₂O. Methane can be stored and utilized as propellant while H₂O can be either stored or electrolyzed to produce oxygen and regain the hydrogen atoms. Depending on the application, O₂ can be used to replenish the atmosphere in human-crewed missions or as an oxidant for robotic and return missions. Precision Combustion, Inc. (PCI), with support from NASA, has previously developed an efficient and compact Sabatier reactor based on its Microlith[®] catalytic technology and demonstrated the capability to achieve high CO₂ conversion and CH₄ selectivity (i.e., ≥90% of the thermodynamic equilibrium values) at high space velocities and low operating temperatures. This was made possible through the use of high-heat-transfer and high-surface-area Microlith catalytic substrates. Using this Sabatier reactor, PCI designed, developed, and demonstrated a stand-alone CO₂ Reduction Assembly (CRA) test system for ground demonstration and performance validation. The Sabatier reactor was integrated with the necessary balance-of-plant components and controls system, allowing an automated, single "push-button" start-up and shutdown. Additionally, the versatility of the test system prototype was demonstrated by operating it under H₂-rich (H₂/CO₂ of >4), stoichiometric (ratio of 4), and CO₂-rich conditions (ratio of <4) without affecting its performance and meeting the equilibrium-predicted water recovery rates. In this paper, the development of the CRA test system for ground demonstration will be discussed. Additionally, the performance results from testing the system at various operating conditions and the results from durability testing will be presented.

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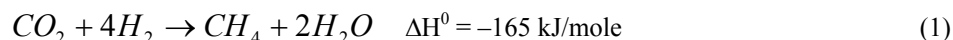
Nomenclature

<i>ARS</i>	= Atmosphere Revitalization System	<i>kJ</i>	= kilojoules
<i>BOP</i>	= balance of plant	<i>m</i>	= meter
$^{\circ}\text{C}$	= degree Celsius	<i>MFC</i>	= mass flow controller
<i>CDRA</i>	= CO ₂ Removal Assembly	<i>min</i>	= minute
<i>CRA</i>	= CO ₂ Reduction Assembly	<i>mL</i>	= milliliter
<i>ft</i>	= foot	<i>mm</i>	= millimeter
<i>g</i>	= gram	<i>OGA</i>	= Oxygen Generation Assembly
<i>GHSV</i>	= gas hourly space velocity	<i>PCI</i>	= Precision Combustion, Inc.
<i>gs</i>	= gravity (force)	<i>psia</i>	= pound per square inch absolute
<i>GSA</i>	= geometric surface area	<i>slpm</i>	= standard liter per minute (21°C, 14.7 psia)
ΔH^0	= enthalpy of reaction	<i>SDU</i>	= Sabatier Development Unit
<i>hr</i>	= hour	<i>TCCS</i>	= Trace Contaminant Control System
<i>Hz</i>	= hertz	<i>vol.%</i>	= percent by volume
<i>in</i>	= inch	<i>W</i>	= watts
<i>ISRU</i>	= In-situ Resource Utilization	<i>wt.%</i>	= percent by weight
<i>ISS</i>	= International Space Station		
<i>kg</i>	= kilogram		

I. Introduction

The proposed concept of closed-loop cabin Atmosphere Revitalization System (ARS) in the space shuttle, which includes the CO₂ Removal Assembly (CDRA), Oxygen Generator Assembly (OGA), and CO₂ Reduction Assembly (CRA), has become an integral part of NASA mission architectures for future long-duration human space exploration to the Moon and Mars.^{1,2} In International Space Station (ISS) and other low orbit missions, the metabolically generated CO₂ was removed from the cabin air via adsorption and vented into space, resulting in a net loss of O₂. This required a continuous resupply of O₂ via water electrolysis, and thus highlighted the need for large water storage.³ Recently, a Sabatier flight unit developed by Hamilton Sundstrand/UTC Aerospace Systems was integrated into the ARS system on the ISS to recover O₂ from the CO₂. To recapture and recycle O₂, the CO₂ produced by metabolic processes is removed from the cabin air by the CDRA and then reacted with H₂ in a Sabatier (CO₂ methanation) reactor (i.e., part of CRA) to produce methane and water.^{4,5} The necessary H₂ could be supplied from a combination of the OGA and a downstream CH₄ processing system (e.g., pyrolysis unit) to achieve a closed-loop ARS. A highly efficient ARS, with H₂ recapture and recycle concept, will result in at least 54% O₂ recovery, which would significantly reduce the required amount of water resupply, providing cost and logistics savings. Similarly, for generating oxygen and propellant fuel, CO₂ from the Martian atmosphere can be separated, compressed, and reacted with H₂ from OGA in a Sabatier reactor to produce water and methane.^{6,7,8}

In the Sabatier or CO₂ methanation process, CO₂ reacts with hydrogen in the presence of catalysts to produce methane and water, as shown in Eq. (1) below:



The water produced by the Sabatier process can then be collected via centrifugation, condensation, or an adsorption method and used as is or it can be further electrolyzed using photovoltaic solar energy to form O₂ and H₂. Hydrogen can be recycled back to the Sabatier reactor for carrying out more CO₂ reduction and to decrease the H₂ requirements. Depending on the application, methane can be stored and used as a rocket propellant (e.g., in a Martian ISRU application) or passed through a pyrolysis reactor to recover H₂ for recycle to the Sabatier reactor (e.g., in ISS application).

The Sabatier process is an exothermic reaction and is limited by thermodynamic equilibrium. Lower operating temperatures, typically around 250-400°C, are desirable for higher CO₂ conversion and higher CH₄ selectivity. To date PCI has developed a Sabatier reactor based on its patented Microlith[®] technology as an alternative to the traditional packed bed and Microchannel reactor designs. This reactor has been proven to produce high CO₂ conversion and near 100% CH₄ selectivity (i.e., $\geq 90\%$ of the thermodynamic equilibrium values) at high space velocities and low operating temperatures.^{9,10} The reactor was operated at GHSV's of 30,000 – 60,000 hr⁻¹. Additionally, the versatility of the Microlith-based reactor was demonstrated by operating it under H₂-rich (H₂/CO₂ ratio of >4), stoichiometric (ratio of 4), and CO₂-rich (ratio of <4) conditions without affecting its performance. This reactor has been examined for both ISS and Martian ISRU applications and its durability has been validated over

multiple 100 hour durability tests. Finally, preliminary integration studies between the Microlith-based Sabatier reactor and a Microlith based CO₂ Removal Assembly (Microlith-based adsorber) have been conducted to examine its feasibility and identify challenges which will need to be addressed.

In this paper, we will discuss the optimization of the 4-crewmember Microlith-based Sabatier reactor. Results from testing the optimized reactor will be presented along with the results of a 1000-hour performance durability test conducted on the same reactor. In addition, this paper will discuss the development of a standalone 4-crewmember CO₂ Reduction Assembly which incorporates the optimized Sabatier reactor with the necessary balance of plant components including mass flow controllers, water condenser and phase separator, and automated control system. Results from the performance validation and 100-hour durability tests of the system at various pressures (6 – 14 psia) and H₂/CO₂ ratios (3.5 – 4.5) will be discussed. The sizing and power requirements of the system will be presented to demonstrate the advantages of a Microlith-based system over the current state of the art pellet based system.

II. Microlith[®] Substrate and Catalytic Technology

The development efforts described here are based on PCI's patented Microlith technology (trademarked by PCI).¹¹ The Microlith substrate consists of a series of ultra-short-channel-length, catalytically coated metal meshes with very small channel diameters (Fig. 1). The mesh-like substrates provide high heat and mass transfer coefficients, low thermal mass, and extremely high reaction rates. The use of this kind of reactor, where the reacting stream is passed through the catalyst at extremely high space velocity, is generically termed a short contact time (SCT) approach. Whereas in a conventional honeycomb monolith, a fully developed boundary layer is present over a considerable length of the device, the ultra-short-channel-length Microlith substrate minimizes boundary layer buildup, resulting in remarkably high heat and mass transfer coefficients compared to other substrates (e.g., monoliths, foams, and pellets). In catalytic reactors involving exothermic reactions, such as the Sabatier process, enhanced heat transfer properties are necessary to eliminate local hot spots and temperature excursions at the catalyst surface, and to prevent catalyst deactivation due to metal sintering. The Microlith substrate also provides about three times higher geometric surface area over conventional monolith reactors with equivalent volume and open frontal area, resulting in a lower pressure drop.

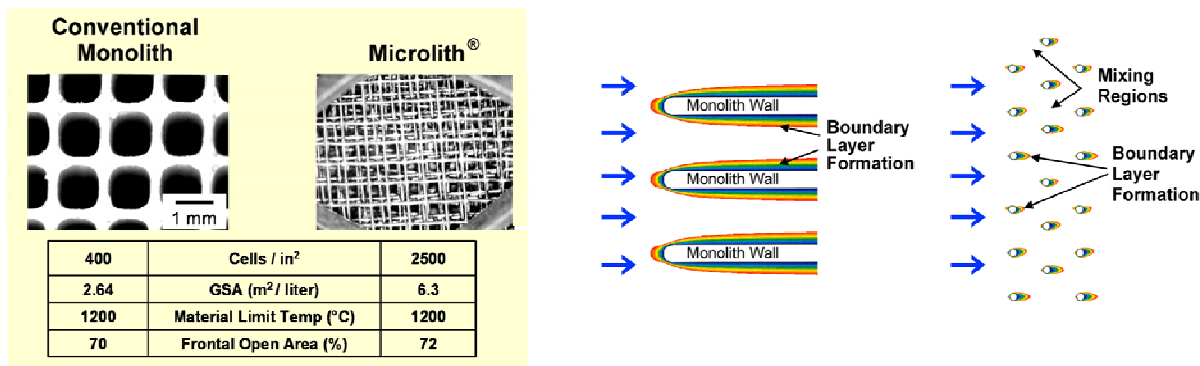


Figure 1. Physical characteristics of conventional, long honeycomb monolith and Microlith substrates, and CFD analysis of boundary layer formation for a conventional monolith and three Microlith screens.

The heat and mass transfer coefficients depend on the boundary layer thickness. For a conventional long channel honeycomb monolith, a fully developed boundary layer is present over a considerable length of the catalytic surface, thus limiting the rate of reactant transport to the surface of active sites. This is avoided when short channel length catalytic screens are used. A Computational Fluid Dynamics (CFD) analysis (Fig. 1) illustrates the difference in boundary layer formation between a long honeycomb monolith and Microlith screens. Finally, PCI's proprietary catalyst coating formulations and application methods, with high surface area washcoats, permit low sorbent and catalyst usage with rigorously demonstrated long-term mechanical, thermal, and performance durability.

The use of Microlith substrates with high heat and mass transfer rates, high surface area, and low pressure drop has a

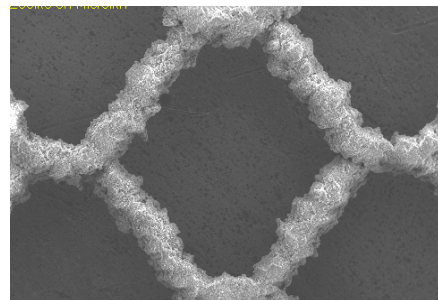


Figure 2. Surface-scan SEM micrograph of the coated Microlith substrate.

significant impact on reactor performance and size as compared to pellet or monolith based units. The effectiveness of the Microlith technology and long-term durability of PCI's proprietary catalyst coatings have been systematically demonstrated in different applications. These include exhaust aftertreatment,¹² trace contaminant control,^{13,14} catalytic combustion,¹⁵ partial oxidation of methane,^{16,17} liquid fuel reforming,^{18,19} CO preferential oxidation, and water gas shift reactors.²⁰ A scanning electron microscopy (SEM) micrograph of a coated Microlith substrate is shown in Fig. 2. SEM analysis indicates uniform coatings on the substrate with complete coverage.

III. Results and Discussion

A. Sabatier Reactor Design

We have previously reported on the development of a proof-of-concept Microlith-based Sabatier reactor capable of producing high CO₂ conversion and near 100% CH₄ selectivity (i.e., $\geq 90\%$ of the thermodynamic equilibrium values) at high space velocities and low operating temperatures.^{9,10} The reactor was operated at GHSV's of up to 30,000 hr⁻¹ (GHSV's were calculated based on the catalyst volume and the total inlet flow rate consisting of CO₂ and H₂). Additionally, the versatility of the proof-of-concept reactor was demonstrated by operating it under H₂-rich (H₂/CO₂ ratio of >4), stoichiometric (ratio of 4), and CO₂-rich (ratio of <4) conditions without affecting its performance. In recent years, a number of design features and modifications have been identified and implemented. The objective of these design changes was to not only improve the overall reactor performance, but also to increase the heat exchange efficiency (i.e., reduced weight and size) and controllability (e.g., self-sustainability) of the catalyst bed temperature. These reactor concept designs utilize the heat transfer benefit of the Microlith catalyst substrates to achieve better reactor performance and durability as well as faster start-up and transient response.

The first design modification was made to incorporate a reactor design with a robust thermal management approach that enables independent control of various temperatures within the catalyst bed to maintain optimal performance and to avoid catalyst deactivation. Prior to this modification, the reactor did not have any thermal management strategy, resulting in an inability to independently control the temperatures within the catalyst bed and a lack of self sustaining reactor operation.

In addition to optimizing the heat exchanger design, the overall reactor design was modified to improve thermal management and to achieve self sustained, steady state operation without additional, external heat input. Normally, the Sabatier reaction is self sustaining when at steady state conditions, but due to the high thermal conductivity of the Microlith substrates, the heat of reaction is rapidly conducted away from the catalyst and the reaction will quench without some level of preheat. Testing proved that the inlet feed must meet certain specifications in order to maintain the reaction in the catalyst bed. To accomplish this, a recuperation concept was incorporated into the reactor design to recover some of the heat removed from the catalyst bed and to use it to preheat the reactor feed stream. The advantage of achieving self sustained operation was that the reactor no longer required an upstream system of external heaters which reduced the weight and volume of the overall system and significantly reduced the system's parasitic power requirements during steady state operation.

To enable cold start-up of the Sabatier reactor, a resistive heater was integrated into the reactor design to initially heat the catalyst bed to the required light-off temperature. This was once again a smaller and more efficient method of achieving cold start-up as compared to the external heaters. Light-off could be achieved in 20 minutes or less with a power input of only 120 W. Once reaction light-off was achieved in the reactor, the reaction became self sustaining and the resistive heater (integrated into the reactor) was de-energized.

All of the modifications discussed above were incorporated into a single reactor component, as shown in Fig. 3, which underwent performance evaluation and characterization, durability studies, and integration into a standalone CO₂ Reduction Assembly for ground demonstration and validation. This optimized reactor was loaded with approx. 24 mL of PCI's Microlith-based catalyst optimized for the Sabatier reaction and was designed to operate at a gas hourly space velocity (GHSV) of at least 15,000 hr⁻¹ depending on the targeted H₂/CO₂ ratio. This reactor was designed to process up to 4 kg/day of CO₂ (1.3 slpm CO₂ when accounting for efficiency losses through the CO₂ removal assembly upstream of the Sabatier reactor at 100% duty cycle) metabolically produced by 4-crew members.

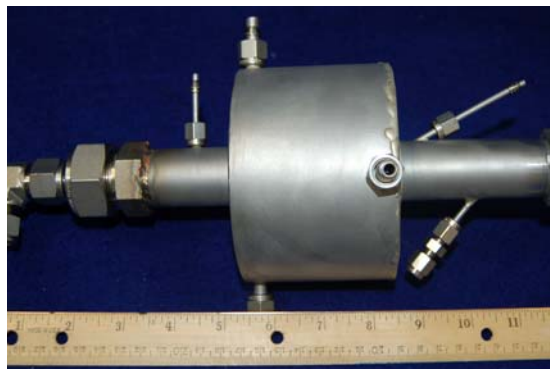


Figure 3. Photo of the modified, 4-crew, Microlith-based Sabatier reactor developed at PCI for ground demonstration.

The reactor optimally produces ~1.7 g/min of water when operating at a H₂/CO₂ ratio of 4.0 at atmospheric pressure. The final reactor weight and volume were 1.75 kg and 900 mL, which include the reactor housing components, resistive heater, heat recuperator, and heat exchanger.

B. Sabatier Reactor Performance Durability and Vibration Tests

After manufacturing and assembling the optimized Sabatier reactor discussed above, its performance was validated according to the test matrix shown in Table 1. The results of this testing at H₂/CO₂ ratios of 4 and 4.5 and at atmospheric pressure are shown in Fig. 4. The CO₂ conversion was calculated via the ratio of the quantity of CO₂ consumed in the reactor to the quantity of CO₂ fed to the reactor. These calculated values were then compared to the isothermal equilibrium values obtained from ASPEN Engineering Suite. CH₄ selectivity remained at ~100% for all conditions. The results of this testing were also used to determine the optimum operating conditions which would be used to conduct the 1000-hr performance durability test.

Table 1. Test matrix for evaluating the performance of the optimized Microlith-based Sabatier reactor.

Parameters	Values
Average temperature	250 – 400°C
H ₂ /CO ₂ ratio	Approx. 3.5 – 4.5
GHSV	15,000 – 20,000 hr ⁻¹
Pressure	6 – 14.7 psia
Catalyst vol. for 4-crew	Approx. 24 mL

After evaluating the performance of the Sabatier reactor with the new, optimized design, a 1000-hr (42-day) test was conducted to examine its performance durability toward continuous operation and thermal cycling. The 1000-hr durability test was performed at H₂/CO₂ ratios of 4.0 and 4.5 (alternating after every ~250 hours) while maintaining a total inlet flow rate of 6 slpm (i.e., GHSV of ~15,000 hr⁻¹) and a reactor pressure of 1 atm (14.7 psia). The inlet gas consisted of H₂, CO₂, and 10 vol.% N₂, resulting in a reactant partial pressure of 13.2 psia. A slip stream of product gas was analyzed using gas chromatography equipped with a thermal conductivity detector to determine the gas composition. The product gas consisted of CH₄, N₂, and unconverted H₂ and CO₂. Nitrogen was utilized as an internal standard gas to determine the CO₂ conversion and CH₄ selectivity from the mass balance calculation. Fig. 5 shows the CO₂ conversion observed throughout the 1000-hr durability test. The expected equilibrium CO₂ conversions (for an isothermal case) at the corresponding catalyst temperatures and at H₂/CO₂ ratios of 4.0 and 4.5 were also included for comparison. Ten shutdown-restart sequences were performed during the 1000-hr test to examine the catalyst durability over exposure to multiple thermal cycles. As shown in Fig. 5, the results from the durability testing of PCI's Microlith-based Sabatier catalyst *demonstrate extremely stable catalyst performance without any catalyst degradation*. Additionally, the CO₂ conversions at H₂/CO₂ ratios of 4.0 and 4.5 corresponded well to the equilibrium CO₂ conversions at the operating temperatures, with small variations which may be due to the difference between the actual catalyst temperatures and the monitored average values. Furthermore, 100% CH₄ selectivity was observed throughout the test.

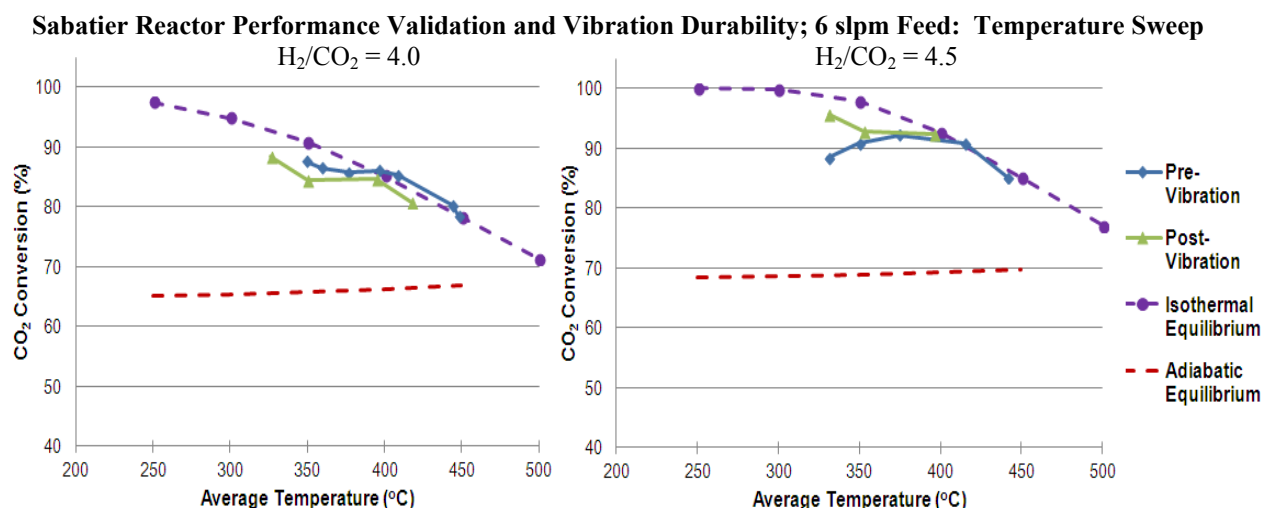


Figure 4. Performance validation of the optimized Sabatier reactor for the Sabatier Development Unit (SDU) prototype before and after the mechanical vibration testing. The reactor was exposed to 50 – 1250 Hz of vibration for 1 hour with a peak force as high as 7.0 gs.

At a H_2/CO_2 ratio of 4.0, the CO_2 conversion was observed to be ~88-90% (vs. equilibrium CO_2 conversion of 88% at 370°C). During the initial stage of the 1000-hr durability testing, the CO_2 conversion was slightly lower. We attributed this to an incomplete reduction treatment of the catalyst bed prior to testing. For the final Sabatier Development Unit (SDU) prototype system, the Sabatier reactor was operated for at least 100 hours prior to delivery to ensure that the catalyst bed is completely reduced. At a H_2/CO_2 ratio of 4.5, the CO_2 conversion was calculated to be 96-98% (vs. equilibrium CO_2 conversion of 95.2% at 370°C).

In summary, from the 1000-hr (42 day) testing of the Microlith-based Sabatier reactor prototype, we successfully demonstrated stable catalyst and reactor performance for efficient conversion of CO_2 and H_2 to CH_4 and H_2O at sustained high reactant conversions and CH_4 selectivity. On the other hand, the microchannel-based Sabatier reactor developed by Pacific Northwest National Lab (PNNL) showed significant catalyst deactivation during their 15-day testing, where the CO_2 conversion decreased from 70% to 48%.⁶ Additionally, the traditional pellet bed Sabatier reactor is typically oversized to account for the expected catalyst deactivation due to local hot spots which lead to catalyst sintering. The implementation of the Microlith-based catalyst substrate for the exothermic reactions, such as the Sabatier process, permits the reduction or elimination of local hot spots due to its high heat transfer property. This avoids catalyst sintering and prolongs catalyst lifetime utilizing a compact reactor package.

Post-durability catalyst evaluation was performed using Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS) to examine metal sintering and carbon deposition within the catalyst substrate that may have been developed during the 1000-hr test and multiple thermal cycles. SEM analysis showed that there were no indications of carbon deposition or metal sintering in the Microlith catalyst post 1000-hr test. The EDS analysis indicated overlapping spectra, corresponding to the preservation of the catalyst and its native components.

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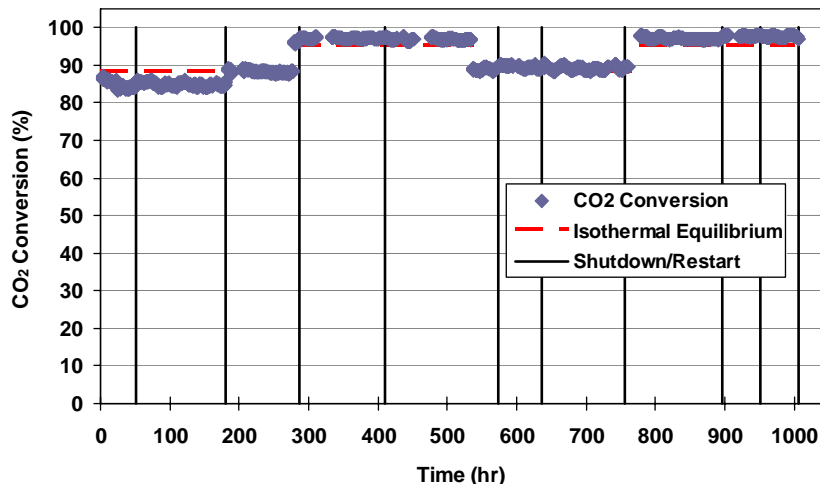


Figure 5. CO_2 conversion as a function of time obtained from the 1000-hr durability testing of the Sabatier reactor at H_2/CO_2 ratios of 4.0 (equilibrium CO_2 conversion = 88%) and 4.5 (equilibrium CO_2 conversion = 95%). Ten shutdown-startup sequences were performed during the durability test to examine the catalyst durability over multiple thermal cycles.

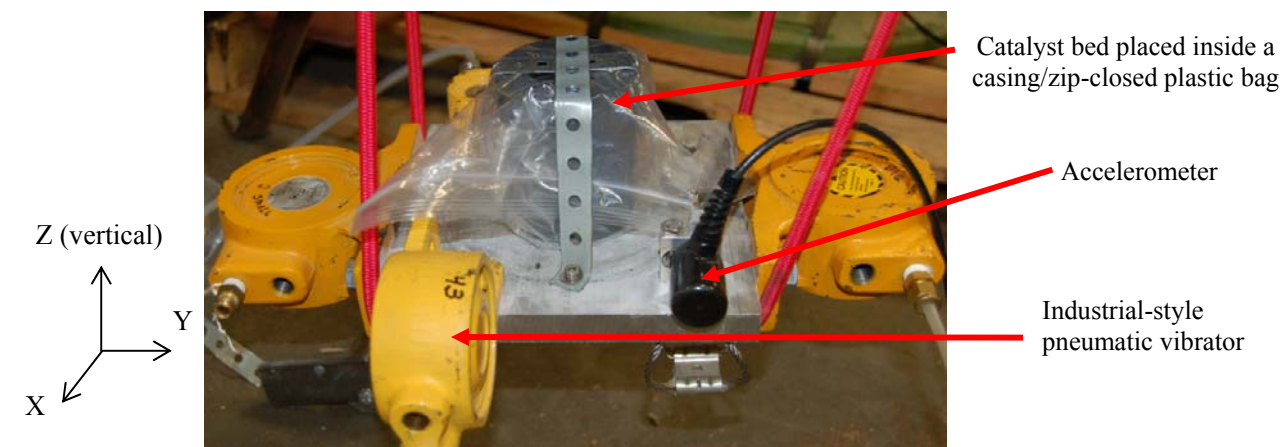


Figure 6. The vibration test setup used to examine catalyst and reactor mechanical durability to simulated launch loads.

Additionally, a mechanical vibration test rig was set up to examine the catalyst and reactor durability to simulated launch loads. The vibration rig consisted of a 12"×12" vibrating aluminum plate supported on vibration isolating mounts which was excited by industrial-style pneumatic vibrators (recirculating ball style) mounted to the center and sides of the plate. The setup is shown in Fig. 6. The frequency, g-force, and axis of vibration was controlled by either repositioning or removing the vibrators as needed. The figure shows the catalyst coated Microlith substrates loaded into a pre-weighed housing and secured to the aluminum plate. After undergoing vibration, the catalyst screens were removed and re-weighed while watching for any particulates/fines that were generated. After weighing, the screens were loaded back into the reactor and their performance was re-evaluated to ensure no degradation. The same setup (Fig. 6) was utilized for vibration testing of the whole Sabatier reactor, where the reactor consisting of the Microlith-based catalyst was strapped to the vibration plate.

A summary of the vibration test conditions used for the Sabatier reactor evaluation is provided in Table 2. The reactor was vibrated without insulation and therefore this study is expected to be a worst case scenario as insulation is expected to provide additional support and dampen the vibration of the ports and thermocouples attached to the reactor. The presence of the sample ports and thermocouples along with the non-symmetric shape of the reactor led to a noisy frequency spectrum as these elements vibrated at much different frequencies depending on their shape and mass. Only the frequency with the peak observed g-force is listed in Table 2; however, the total force column includes the force observed across the entire frequency spectrum.

Table 2. A summary of the test conditions used during the reactor vibration testing.

Test #	Duration (min)	Axis	Frequency (Hz)	Total Force (gs)
1	30	X	1250	5.0
		Y	1250	7.0
		Z	50	7.0
<hr/>				
2	30	X	70	5.5
		Y	80	7.0
		Z	80	4.0

After the vibration test was completed, the reactor was removed from the plate and examined for mechanical failures. The purpose of this study was to identify potential failure points and to begin developing alternative component designs as a path toward a flight-ready unit. A couple of mechanical failure points were identified resulting from metal fatigue of insufficiently supported components such as TCs and sample ports. These failure points were relatively minor and were easily repaired. Vibration tolerant thermocouples have already been identified in an effort to overcome this challenge. The sample tubes were only included in this design to characterize the performance at various points along the reactor and to gain a better understanding of how the reactor operates at different conditions. Therefore, these sample tubes will not be present in a flight-ready design.

After identifying and repairing the identified failures, the performance of the reactor was evaluated again to look for any performance degradation post-vibration. Fig. 4 above shows the observed CO₂ conversion before and after vibration at H₂/CO₂ ratios of 4.0 and 4.5. Minimal performance degradation was observed at these conditions and the reactor showed consistent start-up, functionality, and controllability. CH₄ selectivity remained at ~100% for all conditions both before and after mechanical vibration. This demonstrated the robustness and relatively vibration-resistance of the Sabatier reactor and its components for the SDU prototype, including the Microlith catalyst substrate, reactant pre-heater/recuperator, and heat exchanger.

C. CO₂ Reduction Assembly Prototype Design and Fabrication for Ground Demonstration

After optimizing the reactor design and examining its long term durability, the resulting Sabatier reactor was integrated into a standalone system as shown in Fig. 7. This system consisted of mass flow controllers, the Sabatier reactor, a condensing heat exchanger, and a phase separator along with the support equipment such as solenoid valves, power supplies, relays, and control hardware. The condenser consisted of an air cooled heat exchanger which uses forced convection to cool the product gasses exiting the reactor and condense out any water that was produced. This dual phase mixture then passed through a gravity based separator to separate the product water from the product methane and unreacted hydrogen and carbon dioxide. As the system is designed to operate at sub-ambient pressures (~6 psia) to simulate the actual operating conditions in the ISS, the separator was equipped with a peristaltic pump to draw the water out of the separator and into an atmospheric pressure collection tank. The water level in the separator was monitored via a differential pressure transducer. This transducer would send a signal to the solenoid water drain valve to prevent the separator from overflowing which would result in a reduced water yield or from emptying which would result in combustible gasses building up in the water collection tank. As this separator design is gravity based, it is only feasible for ground demonstration. Alternative phase separators, including a centrifugation-based unit, will be investigated when developing flight-ready hardware.



Figure 7. Photo of the integrated SDU prototype system with the downselected Sabatier reactor and all necessary BOP components.

In addition to the hardware system, the CO₂ Reduction Assembly was equipped with a fully-automated, Labview based control system. The user interface consisted of a laptop computer which allowed the user to gain full control over the feed flow rates and reactor optimum operating temperature. This control system had the capability to automatically start-up and shutdown the system with a single push button. When in steady state, the control system monitors the catalyst temperatures and adjusts the cooling air flow as required to maintain the target temperatures. The external dimensions of the enclosure were 21" × 17.5" × 10.75" resulting in a volume of 2.3 ft³, excluding the components mounted to the top of the enclosure (Sabatier reactor, condensing heat exchanger, and MFC's), the water collection tank, and the user interface (laptop computer). The final system weight was approx. 90 lbs, nearly half of which corresponded to the steel enclosure. A lighter duty enclosure will be investigated as the system is moved toward a flight ready unit demonstration.

D. CO₂ Reduction Assembly Prototype Performance Testing

After the shakedown testing to evaluate the component functionality was completed, the system prototype was characterized at a range of conditions (Table 1) to develop the operating window and to confirm the system performance metrics. The optimum performance results, including average reactor temperature, CO₂ conversion, and CH₄ selectivity, at different operating conditions are summarized in Table 3 (system operated at atmospheric pressure) and Table 4 (system operated under vacuum). Integrating the Sabatier reactor into the complete system was not found to affect its performance in any way. Increasing the CO₂ throughput from 1.3 slpm to 1.5 slpm was found to have a minimal effect on the achievable CO₂ conversion, suggesting the reactor has the potential to process even higher CO₂ throughputs. In all cases, the optimal average reactor operating temperature was found to be ~350°C. Also, as predicted by thermodynamics, the maximum achievable CO₂ conversion fell slightly at reduced pressures. However, the SDU prototype was still capable of meeting equilibrium conversion at the reduced pressures.

The efficiency of the water recovery sub-system, consisting of a condenser, phase separator, and peristaltic pump, was also examined by comparing the total amount of water collected over a fixed period of time with the theoretical amount of water that should have been produced based on the inlet and outlet gas composition and CO₂ conversion. For a CO₂ flow rate of 1.3 slpm and at a H₂/CO₂ ratio of 4.0, the efficiency of the water recovery sub-system was found to be ~96% at atmospheric pressure and ~85% at vacuum.

Table 3. Optimum CO₂ conversion and water production rate achieved by the SDU prototype at atmospheric pressure.

CO ₂ Flow Rate (slpm)	H ₂ /CO ₂ Ratio	Ave. Reactor Temp. (°C)	CO ₂ Conversion (%)	CH ₄ Selectivity (%)	H ₂ O Production (g/min)
1.3	3.5	350	78.6	100	1.55
	4.0	370	89.3	100	1.75
	4.5	360	96.2	100	1.84
1.5	3.5	360	79.9	100	1.76
	4.0	370	88.2	100	1.97
	4.5	400	94.0	100	2.10

Table 4. Optimum CO₂ conversion and water production rate achieved by the SDU prototype at vacuum.

CO ₂ Flow Rate (slpm)	H ₂ /CO ₂ Ratio	Ave. Reactor Temp. (°C)	Vacuum (psia)	CO ₂ Conversion (%)	CH ₄ Selectivity (%)	H ₂ O Production (g/min)
1.3	3.5	350	7.5	77.4	100	1.50
	4.0	360	7.5	84.7	100	1.67
	4.5	360	7.5	91.9	100	1.80
1.5	3.5	350	8	75.7	99.5*	1.64
	4.0	350	8	83.3	100	1.84
	4.5	360	8	90.5	100	2.00

*Reduced CH₄ selectivity was due to CO formation at this condition.

The maximum water collection rate of ~2.0 g/min (theoretical water production rate was 2.1 g/min) was achieved when operating the SDU prototype with 1.5 slpm CO₂ at H₂/CO₂ ratio of 4.5 and at atmospheric pressure (94% CO₂ conversion). At the nominal condition of the SDU prototype, operating with 1.3 slpm CO₂ at H₂/CO₂ ratio of 4.0 and at vacuum (84.7% CO₂ conversion), a water production rate of ~1.67 g/min was achieved and ~1.4 g/min was collected using the water recovery sub-system. Based on this experimental data and the weight and power consumption of the 4-crew scale SDU prototype, the performance metrics, including the specific mass and specific power consumption, were calculated and are listed in Table 5. Both the specific mass and specific power consumption (at steady state) for the delivered SDU prototype were much lower compared to the state-of-the-art values (i.e., specific mass of 1960 kg/[kg water produced per hour] and specific power of 2000 W/[kg water produced per hour]) suggesting the SDU prototype weighs less and requires less power to produce a given quantity of water.²¹ The steady state power requirements for the system are only ~90 W and the peak power consumption was ~120 W which is only encountered during the 20 minute start-up routine.

Table 5. Performance metrics of the 4-crew scale SDU prototype.

Performance metrics	Nominal Condition	Maximum Condition
Water collection rate	1.4 ml/min	2.0 ml/min
Water collection rate per volume of catalytic substrates (24 mL of catalytic substrates)	58 ml H ₂ O/min/L	83 ml H ₂ O/min/L
Specific mass (standalone SDU prototype system = 90 lbs)	486 kg/(kg/hr of H ₂ O collected)	340 kg/(kg/hr of H ₂ O collected)
Specific power consumption (at steady state, power = 90 Watts)	1071 W/(kg/hr of H ₂ O collected)	750 W/(kg/hr of H ₂ O collected)

One final test was conducted in which 5 wt.% of water was included as a contaminant in the feed stream (corresponding to ~5 wt.% of water in the CO₂ feed stream) to simulate the effect of water presence (potentially) in the CO₂ stream fed from the CO₂ Removal Assembly. The CO₂ Reduction Assembly was operated at atmospheric pressure with a 1.5 slpm CO₂ at a H₂/CO₂ ratio of 4.0 and the CO₂ conversion was only found to drop by ~0.5% (absolute). The water separation efficiency of the system remained unaffected at ~95%.

E. CO₂ Reduction Assembly Durability Testing

Finally, the CO₂ Reduction Assembly prototype was tested for 100 hours to examine its durability and to validate system integrity, including controls, heat exchangers, and phase separator, during prolonged operation. The 100-hr durability test was performed at a H₂/CO₂ ratio of 4.0 with a CO₂ flow rate of 1.3 slpm (i.e., GHSV of

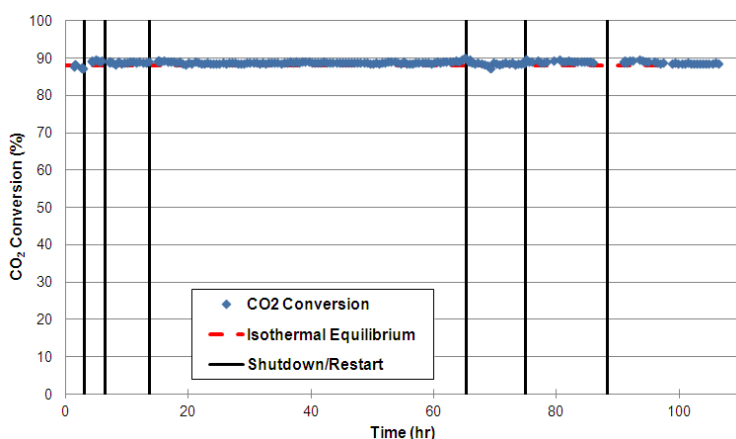


Figure 8. CO₂ conversion as a function of time obtained from the 100-hr durability testing of the SDU prototype with 1.3 slpm CO₂ at a H₂/CO₂ ratio 4.0 and atmospheric pressure. Six shutdown-startup sequences were performed to examine the catalyst durability over multiple thermal cycles.

conversion of 88% at 370°C). Furthermore, 100% CH₄ selectivity was observed throughout the test. Six shutdown-restart sequences were performed during the 100-hr test to examine the catalyst, reactor, and system durability over exposure to multiple thermal cycles.

To date, a second, identical CO₂ Reduction Assembly system has also been assembled and tested and it showed similar performance and durability over 100 hrs as the system discussed here. In addition to the 100-hr durability test with multiple start/stop sequences, this second system was operated continuously for an additional 170 hrs and once again no performance degradation was observed.

F. Potential Future Work: Integration with Other ARS System Components

The efforts discussed in this paper have resulted in a fully-functional, stand-alone CO₂ Reduction Assembly for ground operation and demonstration. As this is only one component of the ARS, it will be necessary to integrate the CO₂ Reduction Assembly with the rest of the system, including the CO₂ removal (CDRA), trace contaminant removal (TCCS), and O₂ generation assemblies (OGA). This effort will require collaboration with the other system manufacturers along with partners in the space industry. Many of the CO₂ Reduction Assembly's components, which were acceptable for stand-alone operation, will need to be replaced during integration. For example, the mass flow controllers require a minimum inlet pressure of 60 psia which cannot realistically be delivered by the OGA or CDRA, and thus have to be replaced with a set of sensors and/or metering devices. The control system will also need to be integrated with those of the other components to ensure they communicate properly and safely.

G. Potential Future Work: Preparation of a Flight Ready CO₂ Reduction Assembly

In parallel with the integration of the CO₂ Reduction Assembly with the rest of the ARS sub-systems, the existing CO₂ Reduction Assembly will need to be modified to meet the requirements for flight-ready hardware. The Sabatier reactor has already undergone preliminary vibration testing and a couple of design modifications have been proposed; however, many of the BOP components within the system are not rated for vibration or for operation in microgravity environments. Research will be required to identify candidate component replacements. Efforts will also need to be made to reduce the volume and weight of the various BOP components. Many of the components are

oversized for their intended use and it should be possible to identify more appropriately sized and custom-made components. As mentioned above, the system can also be repackaged to reduce its volume and the enclosure can be manufactured out of lighter materials. The fully-automated control system (currently consisting of a Labview compact RIO chassis) and many of the electronic components, such as relays and fuses, will be migrated into a single, compact control board to both reduce its size and increase its tolerance to vibration. Finally the water separation sub-system will need to be replaced with one that is suitable for microgravity environments, such as a centrifugation-based system.

IV. Conclusion

A stand-alone, bench top CO₂ Reduction Assembly prototype was developed, demonstrated, and characterized, which is capable of producing high CO₂ conversion and CH₄ selectivity (i.e., $\geq 90\%$ of the thermodynamic equilibrium values at its optimum conditions) at high space velocities and low operating temperatures. The prototype consists of a Microlith-based Sabatier reactor (sized for a 4-crew mission) that is much more compact and lightweight compared to the current state-of-the-art pellet-based Sabatier reactor. The volume and weight of the 4-crew Sabatier reactor unit were 0.9 liter and 1.75 kg. It included the Microlith catalytic substrates (24 mL), reactor housing components, reactant pre-heater/heat recuperator, heat exchanger, and start-up heater packaged in a compact, robust design.

The Sabatier reactor was successfully operated for 1000 hours at H₂/CO₂ ratios of 4.0 and 4.5 with multiple shutdown-startup sequences (i.e., thermal cycles) without detectable performance degradation. The reactor was also subjected to vibration test to simulate launch load. Post-vibration reactor testing and catalyst analysis were performed, showing minimal performance degradation and no observable catalyst dusting and particulates/fines formation. The Sabatier reactor was integrated with the necessary BOP components and control system to permit an automated single “push-button” for start-up and shutdown as well as an automated temperature control to maintain the reactor at its optimum operating condition. Finally, the versatility of the SDU prototype was demonstrated by operating it under H₂-rich (H₂/CO₂ of >4), stoichiometric (ratio of 4), and CO₂-rich conditions (ratio of <4) at ambient and sub-ambient pressures without affecting its performance and being able to meet the equilibrium-predicted water recovery rate at each operating condition. The integrated system has also showed stable performance for more than 250 hours of operation. In summary, by experimentally addressing the integration issues, examining system efficiency, and optimizing the catalyst and reactor configurations, we have developed multiple modular, compact, efficient, and durable CO₂ Reduction Assembly prototypes for ground demonstration.

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