

Demonstration of Robustness and Integrated Operation of a Series-Bosch System

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Manned missions beyond low Earth orbit will require highly robust, reliable, and maintainable life support systems that maximize recycling of water and oxygen. Bosch technology is one option to maximize oxygen recovery, in the form of water, from metabolically-produced carbon dioxide (CO_2). A two stage approach to Bosch, called Series-Bosch, reduces metabolic CO_2 with hydrogen (H_2) to produce water and solid carbon using two reactors: a Reverse Water-Gas Shift (RWGS) reactor and a carbon formation (CF) reactor. Previous development efforts demonstrated the stand-alone performance of a RWGS reactor containing Incofoam™ catalyst and designed for robustness against carbon formation, two membrane separators intended to maximize single pass conversion of reactants, and a batch CF reactor with both transit and surface catalysts. In the past year, Precision Combustion, Inc. (PCI) developed and delivered a RWGS reactor for testing at NASA. The reactor design was based on their patented Microlith® technology and was first evaluated under a Phase I Small Business Innovative Research (SBIR) effort in 2010. The Microlith® RWGS reactor was recently evaluated at NASA to compare its performance and operating conditions with the Incofoam™ RWGS reactor. Separately, in 2015, a fully integrated demonstration of an S-Bosch system was conducted. In an effort to mitigate risk, a second integrated test was conducted to evaluate the effect of membrane failure on a closed-loop Bosch system. Here, we report and discuss the performance and robustness to carbon formation of both RWGS reactors. We report the results of the integrated operation of a Series-Bosch system and we discuss the technology readiness level.

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Nomenclature

CH_4	=	Methane	*GC*	=	Gas Chromatograph
CF	=	Carbon Formation	*O_2*	=	Oxygen
CFR	=	Carbon Formation Reactor	*OGA*	=	Oxygen Generation Assembly
CM	=	Crew Member	*PCI*	=	Precision Combustion, Inc.
CO	=	Carbon Monoxide	*RWGS*	=	Reverse Water-Gas Shift
CORTS	=	CO_2 Reduction Test Stand	*S-Bosch*	=	Series-Bosch
CO_2	=	Carbon Dioxide			

I. Introduction and Background

FOR manned missions to Mars, recovery and recycling of life support water and oxygen (O_2) will provide considerable mass and logistics savings over an open-loop system where these resources are treated as consumables. State-of-the-art technology involves the Oxygen Generation Assembly (OGA) to produce O_2 for the crew via water electrolysis. Hydrogen (H_2) produced in the OGA is provided to the Sabatier reactor which converts metabolic carbon dioxide (CO_2) to methane (CH_4) and water as shown in Eq. 1.

Sabatier Reaction $$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \quad (1)$$

The water is recycled back to the OGA after purification in the Water Processing Assembly and the CH_4 is vented overboard as a waste product. This causes in a net loss of reactant H_2 for the Sabatier and results in a maximum theoretical O_2 recovery from metabolic CO_2 of ~54%. Mars missions target >75% O_2 recovery from CO_2 with a goal of >90%.[1] Series-Bosch (S-Bosch) technology has a theoretical maximum recovery of 100% and is one approach to achieve the goal of >90% recovery.

The development progress of an S-Bosch system for long-duration manned missions has been reported previously.[2,3,4,5,6] Briefly, the S-Bosch system involves two reactors and two membrane systems for gas recycling. The first reactor performs the Reverse Water-Gas Shift (RWGS) reaction, as shown in Eq. 2 to covert metabolic CO_2 and OGA H_2 into carbon monoxide (CO) and water. The second reactor performs two carbon formation reactions as shown in Eqs. 3 and 4. The net reaction, called the Bosch process, is shown in Eq 5.

RWGS	$CO_2 + H_2 \leftrightarrow H_2O + CO$	(2)
CO Hydrogenation	$CO + H_2 \leftrightarrow H_2O + C(s)$	(3)
Boudouard	$2CO \leftrightarrow CO_2 + C(s)$	(4)
Bosch Process	$CO_2 + 2H_2 \leftrightarrow 2H_2O + C(s)$	(5)

The membrane system provides a recycling mechanism for unreacted CO_2 (Polaris Membrane) and H_2 (Proteus Membrane) exiting the RWGS reactor. To maximize selective permeability of CO_2 and H_2 across the membranes, fresh inlet gases are used as sweep streams across the membranes and the membranes are operated at a pressure differential of ~5 psi. This increases thermodynamic favorability of carbon formation in the Carbon Formation Reactor (CFR) by concentrating CO and ultimately minimizes system gas recycle volume. A basic S-Bosch block diagram is shown in Figure 1.

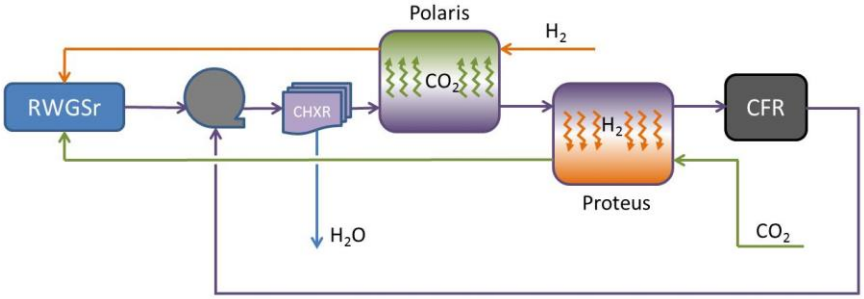

Figure 1. Series-Bosch block diagram.

Testing in 2014 with an S-Bosch system demonstrated the stand-alone performance of a RWGS reactor, the initial performance of a Polaris and a Proteus membrane, and the performance of a batch CFR containing both a transit catalyst and a surface catalyst. Efforts in 2015 sought to continue this work.

A RWGS reactor containing an Incofoam™ nickel foam catalyst was previously developed and tested at NASA Marshall Space Flight Center. Incofoam™ was specifically chosen based on subscale testing demonstrating its resistance to carbon fouling via Eqs. 3 and 4 above. Testing of the Incofoam™ reactor in 2014 for the RWGS reaction demonstrated performance near thermodynamic equilibrium. However, the Incofoam™ reactor was not tested at the full scale for carbon fouling resistance. As an alternative to the Incofoam™, a RWGS reactor based on Microlith® technology and developed by Precision Combustion, Inc. (PCI) as part of a Phase I Small Business Innovative Research contract was acquired for evaluation in 2015. The Microlith® reactor was known to have considerably smaller mass, volume, and power requirements than the Incofoam™ reactor. In 2015, PCI's Microlith® RWGS reactor was delivered to MSFC for performance evaluation and comparison with the Incofoam™ RWGS reactor with the intention of down-selecting between the two reactors for the S-Bosch system. Two tests were conducted. The first was to compare nominal performance of each reactor for the RWGS reaction under conditions expected in S-Bosch operation. The second test was to evaluate the relative resistance to carbon fouling of each catalyst and the long-term effects of that fouling.

In 2014, initial testing of the Proteus and Polaris membranes was attempted. Unfortunately, tears in the membrane material were identified during testing, resulting in only minimal useful data. In 2015, both membranes were returned to Membrane Technology Research, Inc., the developers of the membranes, for analysis and repair. It was determined that the tears were a result of disassembly of the membrane housings at MSFC and that leakage across the membranes was due to an incorrect alignment of the membranes during initial assembly. The membranes were repaired and returned to MSFC for additional testing.

In an effort to advance the overall technology readiness level of the S-Bosch system, two integrated tests were conducted in 2015. The first test was conducted to demonstrate fully integrated, closed-loop operation of an S-Bosch including an RWGS reactor, the two separation membranes, and a CFR. Due the previous membrane failure and a concern as to the robustness of the membranes for a long duration mission, the second test was conducted as risk mitigation to demonstrate the effect of membrane failure in an integrated S-Bosch system.

Considerable progress was made in 2015 toward further understanding and operating an S-Bosch system. Here we report the results of head-to-head testing of the Incofoam™ and Microlith® RWGS reactors, the results of the Proteus and Polaris membrane testing, the results of a closed-loop S-Bosch system demonstration, and the results of testing designed to evaluate the effects of membrane failure in a closed-loop S-Bosch system.

II. Hardware and Test Configuration

Two RWGS reactors, two separation membranes, and one CFR were evaluated as stand-alone units and/or as contributors to an integrated S-Bosch system. Each piece of hardware is described below as well as the test configuration for each test.

A. Reverse Water-Gas Shift Reactors

1. Microlith® RWGS Reactor

The Microlith® RWGS reactor, sized for 4-crew members (CM), was designed and fabricated by PCI. The primary objective was to develop a highly compact RWGS reactor operating optimally at very high space velocity and catalyst temperature of ~800°C to maximize CO_2 conversion. The reactor contains only 89.4 cm^3 Microlith® catalyst bed, including void space. The reactor is 3.81 cm (1.5 inch) diameter x 38.1 cm (15 inch) in length (including the heater section that is outside of the reactor housing). The RWGS reactor comprises an embedded electric heater rod (¾ inch diameter and a heated length of ~9 ¾ inch) placed at the center of the reactor, a preheating section (without catalyst) and a catalytic Microlith® section where the RWGS reaction will take place at very high space velocity. Cobalt (Co) supported on Microlith® was chosen as the catalyst of choice based on the demonstrated high activity toward RWGS reaction demonstrated in Phase I SBIR activity.[7] The reactor design was optimized to enhance the heat transfer from the cartridge heater to the preheating section and the catalytic section at high catalyst temperatures (~800°C).

2. IncoFoam™ RWGS Reactor

The Incofoam™ RWGS reactor was designed at NASA MSFC and sized for 4- CM. The catalyst was chosen based on sub-scale testing demonstrating high selectivity for CO and resistance to solid carbon formation at temperatures between 500°C and 750°C.[3] The details of the design of the reactor were provided previously.[5] Briefly, the reactor (without any preheating section) is 12.7 cm (5 inch) diameter x 27.6 cm (10.875 inch) in length with a total catalyst

volume (including void space) of 2,438 cm^3. The remainder of the reactor volume is packed with Fiberfrax Durablanket S insulation. The reactor is heated using three 3.81 cm width band heaters from Applied Thermal Systems (Brooklyn Park, MN) located on the outer diameter of the reactor.

B. Carbon Formation Reactor

The Batch CFR was described in detail previously.[6] For the described testing, the CFR was packed with S-660 Amasteel beads from Irvine Industries, Inc. (Ann Arbor, MI). Due to inadequate preheating of the inlet gas in previous testing, the inlet annulus was packed with 1 mm diameter copper beads to improve conduction of the heat from the reactor core heater to the inlet gas. This resulted in considerably better heating of the inlet gas and overall heating of the reactor. A preheater to the reactor was set to 400°C to mimic regenerative heating.

C. Membranes

One Proteus and one Polaris membrane were purchased from Membrane Technology Research (Newark, CA) and were described previously.[6] The Proteus membrane is designed to selectively separate H_2 from a bulk gas when operated at 130-145°C. The Polaris membrane is designed to selectively separate CO_2 from a bulk gas when operated at low temperatures. For all testing involving the membranes, a target temperature of 130°C was selected for the Proteus membrane and the Polaris membrane was operated at ambient temperature.

D. Test Configurations

Three tests were conducted to further develop and optimize the S-Bosch system. The CO_2 Reduction Test Stand (CORTS), described previously, was used to facilitate testing. The test configuration and methods of each test are provided below.

1. Stand-Alone Testing of RWGS Reactors

The purpose of the stand-alone testing was to generate the data necessary to down-select between the two reactor options. An optimum RWGS reactor would have high (near thermodynamic equilibrium) single-pass conversion of CO_2, high selectivity for the RWGS reaction over the competing Sabatier reaction, and be highly resistant to carbon fouling. The standard performance data including single-pass conversion and selectivity was experimentally taken for the Microlith® reactor to compare with data previously taken with the Incofoam™ reactor. The resistance to carbon formation for the two reactors cannot be currently compared, since PCI's RWGS Co catalyst and reactor design were not specifically downselected to impede carbon formation. For example, PCI's prior work has demonstrated that Rh has a lower carbon formation rate but comparable RWGS activity to Co at temperature of >550°C.[7] Reactor design modifications along with carbon resistant catalyst like Rh have the potential to achieve the desired performance (high RWGS activity and resistance to carbon formation) for the Microlith® reactor.

Table 2. RWGS Standard Performance Testing Variables.

Parameter	Values
Heater Set Points	600°C, 650°C, 700°C
CO_2 Feed Rates	1.41 SLPM, 2.82 SLPM
H_2:CO_2 Ratios	1:1, 2:1, 3:1
Inlet Pressures	20.7 kPa (3 psia), 34.5 kPa (5 psia), 55.1 kPa (8 psia)

Table 1. Fouling Testing Variables.

Parameter	Test Values
Heater Set Points	600°C, 650°C, 700°C
CO Feed Rates	0.04 SLPM – 0.57 SLPM
H_2:CO Ratios	100:1, 70:1, 50:1
Inlet Pressures	34.5 kPa (5 psia), 55.1 kPa (8 psia)

Standard performance data of each reactor was conducted at multiple temperatures, pressures, equivalent crew feed rates of CO_2, and feed ratios. Table 1 provides the values varied during testing. The reactor was fed with ultra-high purity (UHP) H_2 and CO_2. The effluent composition was evaluated on a dry basis using an Agilent 3000 micro-gas chromatograph (GC) and vented from the facility.

Fouling testing was conducted in two phases after standard performance testing for the Incofoam™ reactor. Phase I was conducted to determine the rate of carbon formation, as well as the concentrations of CO at which carbon production occurs, by testing under conditions that favor the Boudouard reaction. Table 2 provides the values varied during Phase I testing. Phase II testing was conducted to determine the effects of carbon fouling on net reaction rates and selectivity. In this case, higher concentrations of CO were used in order to intentionally foul the reactor. The performance before and after this treatment was used to determine alterations in activity levels due to carbon formation and surface deactivation. Testing of a reference point (a specified set of reactor operating conditions representing

midrange points of all variables) occurred after every step in this process. Gas flow rates were kept at a total of 3 SLPM with 0.15 SLPM (5%) of that being N_2. The reference point chosen was 600°C, 8 psia, and 2:1 H_2 to CO_2 in the feed mixture. Duration at each test point was carefully controlled with the intention to ensure that the reactors were exposed to identical conditions for carbon formation. Again, the effluent composition was evaluated on a dry basis using the Agilent GC and vented from the facility.

2. Fully Integrated Testing (RWGS + Membranes + CFR)

Fully Integrated Testing was conducted using the Incofoam™ RWGS reactor prior to fouling testing. Both membranes were integrated, as well as the batch CFR containing the Amasteel steel beads. The system was operated as shown in Figure 1. The CORTS provided gas feed and control, fluid vent and recycle, water condensation and separation, and gas analysis sub-assemblies. The pressure differential across the membranes was maintained as close to 5 psi as possible. This was accomplished using backpressure regulators and by maintaining the Incofoam™ RWGS reactor at ~5 psid below the CFR. Flow rates beginning at CO_2 feed equivalent to 1/4-CM and increasing up to 1-CM were tested. The Incofoam™ RWGS reactor was operated at 650°C with a 400°C inlet preheat and the CFR core heater was operated at 700°C. The coolant water for the condensing heat exchanger was maintained at 4°C. The Polaris membrane temperature was not controlled beyond ambient conditions and the Proteus membrane was maintained at 130°C. At system start-up, fresh feed was provided to the RWGS at a 1:1 H_2:CO_2 ratio and a CO_2 feed rate equivalent to 1/4-CM. Once total H_2 in the CFR recycle loop was ~13 mol%, the H_2 feed rate was increased to achieve a 2:1 H_2:CO_2 ratio. Once system steady state was achieved, system gas composition at the Incofoam™ RWGS reactor outlet, the inlets and outlets of both sides of each membrane, the CFR inlet, and the CFR outlet was recorded and the total flow to the system increased to the next data point, all while maintaining a 2:1 H_2:CO_2 feed ratio. This was repeated until the maximum feed rate was achieved without exceeding ambient pressure anywhere within in the system. It should be noted that 13 mol% of H_2 in the CFR loop was selected to minimize CH_4 in the recycle loop and to maximize Boudouard reaction rates. This effectively limited the total pressure in the system by minimizing the quantity of unreacting gas circulating in the system. Periodic venting was required to remove N_2 from the system.

3. Membrane Risk Mitigation Testing (RWGS + CFR)

Within the S-Bosch system, the RWGS reactor and the CFR are designed to be robust. The highest risk components then, are the membrane separators. To identify the operational performance of the system in the event of membrane failure, the Membrane Risk Mitigation Testing was conducted. During this testing, the system configuration omitted the membranes as shown in Figure 2. The fresh gas was fed directly to the Incofoam™ RWGS reactor and all unreacted gas leaving the CFR was recycled back through the condensing heat exchanger to the inlet of the CFR. The Incofoam™ RWGS reactor was operated at 650°C with a 400°C inlet preheat and the CFR core heater was operated at 700°C. The coolant water for the condensing heat exchanger was maintained at 4°C.

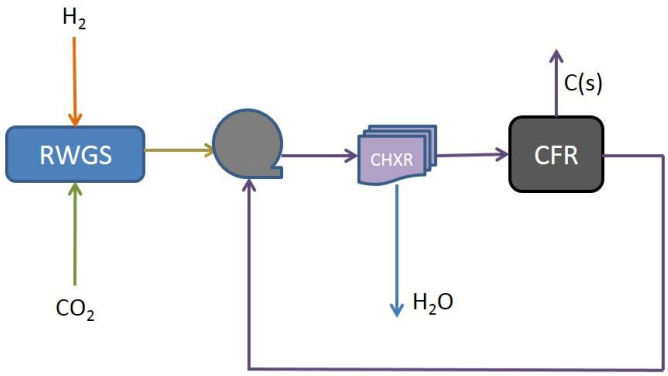

Figure 2. S-Bosch Membrane Risk Mitigation Testing Configuration.

At system start-up, fresh feed was provided to the RWGS at a 2:1 H_2:CO_2 ratio and a CO_2 feed rate equivalent to 1/4-CM. Once steady state was achieved, system gas composition at the Incofoam™ RWGS reactor outlet, the CFR inlet, and the CFR outlet was recorded and the total flow to the system increased to the next data point, all while maintaining a 2:1 H_2:CO_2 ratio. This was repeated until the maximum feed rate was achieved without exceeding ambient pressure anywhere within the system.

III. Results and Discussion

Three tests were conducted to evaluate the S-Bosch system and one risk mitigation scenario. The results of this testing and a discussion of the findings are provided below.

A. Microlith® vs IncoFoam™ RWGS Reactor

The ultimate goal of the RWGS reactor testing was to down-select either the Microlith® approach or the IncoFoam™ approach. Testing was conducted to compare the two reactors. The results of this testing is provided below.

1. *Stand-Alone Performance Comparison*

The Microlith® and IncoFoam™ reactors were tested under the same range of total reactant flow rates and temperatures for performance comparison. It should be noted that due to the lower volume of catalyst in the Microlith® reactor, this resulted in a higher space velocity for Microlith® RWGS reactor. Identical molar ratios were also targeted. However, a software error with the mass flow controllers, resulted in slight differences between the two tests. This did not affect the relative quality of the data and conclusions can still be drawn. Secondly, it was determined at the conclusion of testing, that the temperature of the Microlith® RWGS catalyst was inadvertantly controlled at the outlet of the reactor, rather than the average catalyst bed temperature. The current Microlith® reactor design resulted in a significant temperature gradient with a minimum catalyst temperature of ~550°C at the inlet and ~650°C at the outlet. The average catalyst bed temperature was ~606°C for the Microlith® reactor compared to ~650°C for the Incofoam™ reactor. Reactor design optimization can result in a more uniform catalyst bed temperature distribution for the Microlith® reactor which is ideally suited for RWGS reaction, but this was beyond the scope of the current effort. Thus, a direct comparison of performance between the Microlith® and Incofoam™ was not possible. Rather, a comparison of the observed performance to the thermodynamic equilibrium at the average catalyst operational temperature of each reactor was made.

Overall, the reactors performed similarly with respect to total CO_2 conversion relative to their respective theoretical equilibrium performance. Both reactors also demonstrated preferential conversion to CO over CH_4, as desired in this application. However, there was an observable difference between the two reactors when comparing each to their equilibrium selectivity. Selectivity was calculated as shown in Eq. 6.

$$S_{CO} = \frac{moles\ CO\ produced/min}{moles\ CH_4\ produced/min} \tag{6}$$

Single-pass conversion of both reactors and their respective equilibrium conversions are shown in Figure 3. Both reactors effectively achieved equilibrium at near a 1:1 ratio of H_2:CO_2. Conversion deviated further from equilibrium as the feed to the system was progressively more H_2 rich. A possible reason for this observation is the marginally lower catalyst bed temperature for each reactor with increase in total feed flow rate (due to increase in feed H_2 flow rate) compared to the temperature at which the equilibrium is predicted. Nevertheless, this data suggests that the two reactors would be expected to achieve nearly identical conversions under identical conditions. If the down-select were based solely on base performance, the Microlith® would be the clear choice given the significantly smaller size of the Microlith® RWGS reactor (a factor of 27).

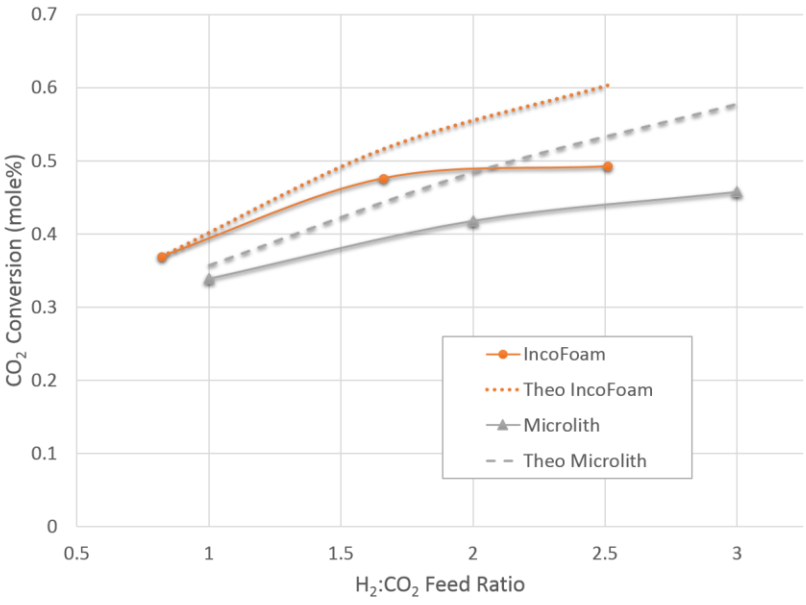

Figure 3. Comparative single-pass CO_2 conversion performance of Incofoam™ and Microlith™ RWGS reactors. *IncoFoam™ reactor at 650°C, Microlith® reactor at 606°C. Both reactors at 8 psia.*

However, selectivity of the catalyst for the RWGS reaction over the Sabatier reaction is also of considerable importance.

Selectivity of both reactors and the theoretical equilibrium selectivity for each reactor are shown in Figure 4. Selectivity higher than theoretical equilibrium indicates that the Sabatier reaction is kinetically limited compared to the RWGS reaction at the given conditions. Extremely high selectivity is most desireable in this application. Both reactors showed considerably higher selectivity for CO over CH_4. However, the Incofoam™ demonstrated selectivity an entire order of magnitude better than equilibrium selectivity predicts. The Microlith® selectivity was approximately twice the equilibrium selectivity. This is very important for closed-loop operation where the RWGS reactor will feed a closed loop carbon formation reactor. From this perspective, the IncoFoam® reactor significantly outperformed the Microlith® reactor and lends considerable weight for its selection over the Microlith® reactor. However, it is important to note that performance mapping of RWGS reactor conducted at PCI demonstrated that CO selectivity is highly dependent upon the space velocity, in addition to temperature. Lower space velocity leads to higher CO selectivity. Further, IncoFoam™ reactor employed an external preheat of ~400°C whereas the inlet to PCI's RWGS reactor was at ambient temperature. PCI's internal testing demonstrated significant ΔT across the catalyst inlet and outlet when operating the reactor at temperature lower than ~800°C. The ΔT (i.e., the temperature difference between inlet and outlet of the catalyst bed) at lower operating temperature leads to lower CO selectivity. The data shown in Figure 4 do not provide sufficient information to define a relationship between CO selectivity and space velocity. However, the generated data may be used to further optimize the Microlith® RWGS reactor such that an optimum space velocity and temperature profile is achieved to provide a balance between high CO selectivity, high CO_2 conversion, and significant reduction in reactor volume and mass (compared to the existing IncoFoam™ RWGS reactor).

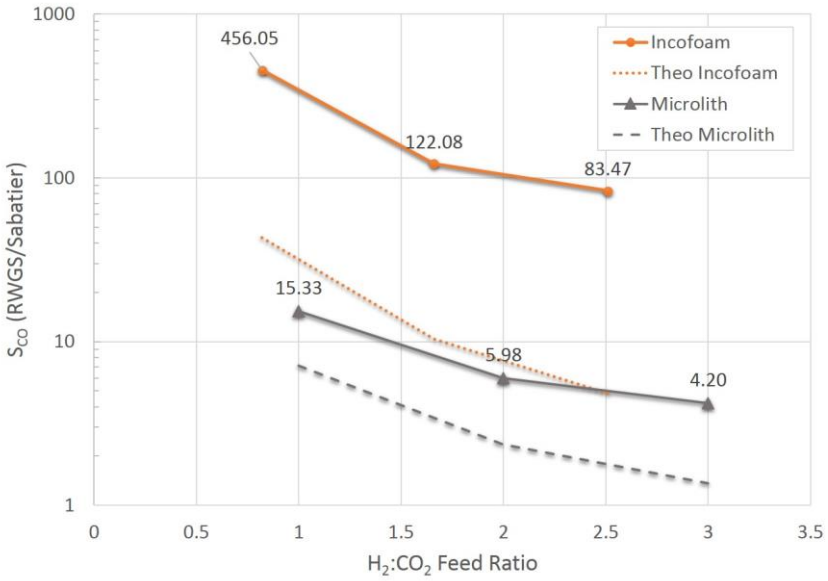

Figure 4. Selectivity of RWGS reactors for CO_2 conversion via RWGS reaction versus Sabatier reaction. *IncoFoam™ reactor at 650°C, Microlith® reactor at 606°C. Both reactors at 8 psia.*

2. Fouling Performance Comparison

Within the S-Bosch, the RWGS is not intended to be a replaceable unit. The catalyst within the reactor must be robust against carbon fouling for the duration of one or more Mars transit and surface missions. In a closed loop S-Bosch system, the RWGS reactor will inevitably be exposed to some quantities of CO resulting in possible carbon formation. The IncoFoam™ catalyst was specifically selected due to observed carbon formation resistance in previous testing. Fouling performance testing was conducted to verify the design resisted carbon formation under various feed conditions. The Microlith® reactor was designed purely for the purpose of catalyzing the RWGS reaction with minimal consideration given to carbon formation. Despite this, the Microlith® reactor was subjected to identical conditions as the IncoFoam™, not to directly compare the reactors, but to provide a baseline assessment of the Microlith® reactor and its catalyst under carbon formation conditions.

Figure 5 shows the performance of the IncoFoam™ and Microlith® reactors at multiple H_2:CO feed rates. As designed, the IncoFoam™ reactor exhibited very low levels of carbon formation at all conditions. In a worst case condition (assumed to be 20 mol% CO with a balance of H_2 at the inlet to the reactor), the IncoFoam™ reactor produced only ~3.5 mg C/min. This corresponds to <1% conversion of CO to solid carbon and matches previous results for the catalyst. The Microlith® reactor demonstrated increasing carbon formation rates as ratio of H_2:CO decreased (as more CO was available for reaction). At the worst case, the Microlith® reactor produced ~41 mgC/min. This corresponds to over 13% conversion of CO to solid carbon. This value represents a baseline performance for the Microlith® reactor whereby future iterations of the reactor can be compared for performance improvements. The lower catalyst temperature in addition to the choice of catalyst for Microlith® reactor (Co catalyst and ~560°C) compared to the IncoFoam™ reactor (Ni catalyst and ~600°C) could be attributed to the higher carbon formation rate.[7]

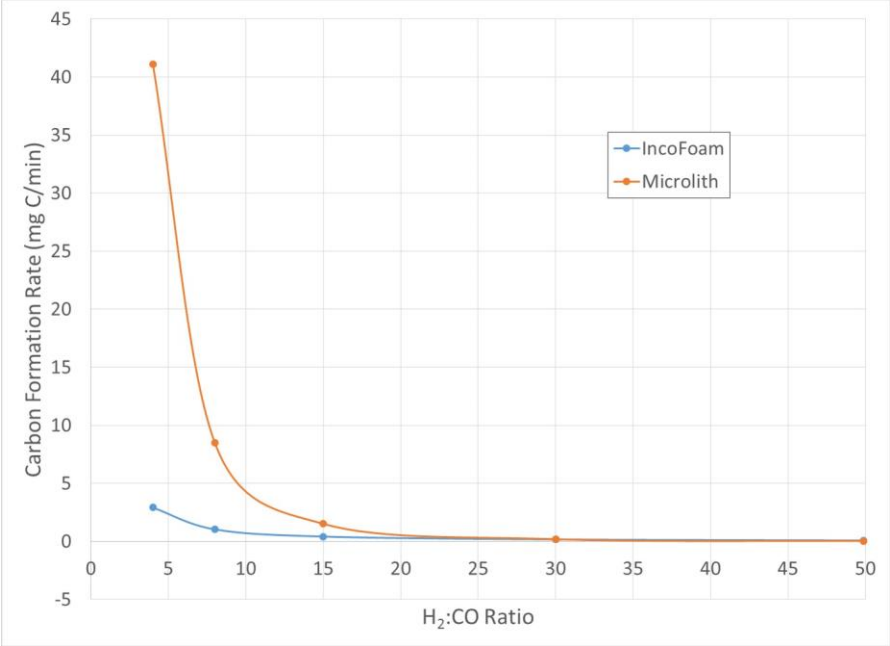

Figure 5. Carbon formation rate on RWGS reactors as a function of H_2:CO feed ratio. *IncoFoam™ catalyst at 600°C, Microlith® catalyst at an average of 560°C. Both reactors at 8 psia.*

The IncoFoam™ reactor demonstrated low carbon formation rates, as expected given previous testing of the IncoFoam™ catalyst. Comparison between the IncoFoam™ and the Microlith® RWGS reactor for resistance to carbon formation is currently not possible as the Microlith® RWGS reactor was not designed to impede carbon formation as explained earlier. Appropriate design modifications, improved temperature control, and a carbon resistant catalyst (such as Rh) could be implemented so that the Microlith® RWGS reactor could be tested to provide a representable comparative analysis.

B. Fully Integrated Testing

The goal of the Fully Integrated Testing was to demonstrate a closed-loop S-Bosch system including a RWGS reactor, the Polaris (CO_2 separation) membrane, the Proteus (H_2 separation) membrane, and the batch carbon formation reactor. The IncoFoam™ RWGS reactor was used in all fully integrated testing as the reactor could be exposed to CO and has been tested for resistance to fouling due to carbon formation. In initial testing, start-up was performed by feeding a 2:1 H_2:CO_2 ratio to the system. However, CH_4 built up quickly in the carbon formation loop despite recycle of CO_2 and H_2 from the membranes. To eliminate this issue, start-up was modified to include a feed of 1:1 H_2:CO_2 ratio until the effluent of the carbon formation reactor dropped to 13% H_2. It was at this point that CH_4 was observed to drop below 5 mol% in the CFR effluent. From that point on, a 2:1 ratio of H_2:CO_2 was fed to the system and CH_4 was effectively maintained at very low levels.

The closed-loop system was successfully operated at 1/4, 1/2, and 3/4-CM scales while maintaining sub-ambient pressure. There was no significant change in performance or steady state conditions for any of these data points. However, when attempting to increase system feed to a 1-CM equivalent, the pressure in the system exceeded ambient and was shutdown. The Incofoam™ reactor has been shown to perform at sub-ambient pressures for up to 4-CM. Total flow to the reactor including recycle from the membranes did not even approach this level. Additionally, no change in performance of the membranes was observed when increasing the total flow. Ultimately, it appears that the CFR limited total processing rate. The CFR was designed to process up to 4-CM of gas flow, including recycle. The observed performance was far less than that. Following testing, the CFR was disassembled to explore why this may have occurred. Those results are discussed in Section D, below.

The membranes both showed considerably better performance than in previous testing where a tear was identified in the material. The average permeation of each gas is shown in Figure 7 for the membranes. It should be noted that although the CH_4 permeation percentages are relatively high, the total gas permeating was very low given the low quantities in the circulating gas. The permeation of CO across both membranes, while not ideal, is still sufficiently low such that the feed composition to the CFR was still ~50% CO for all data points (~25% H_2 and ~25% CO_2).

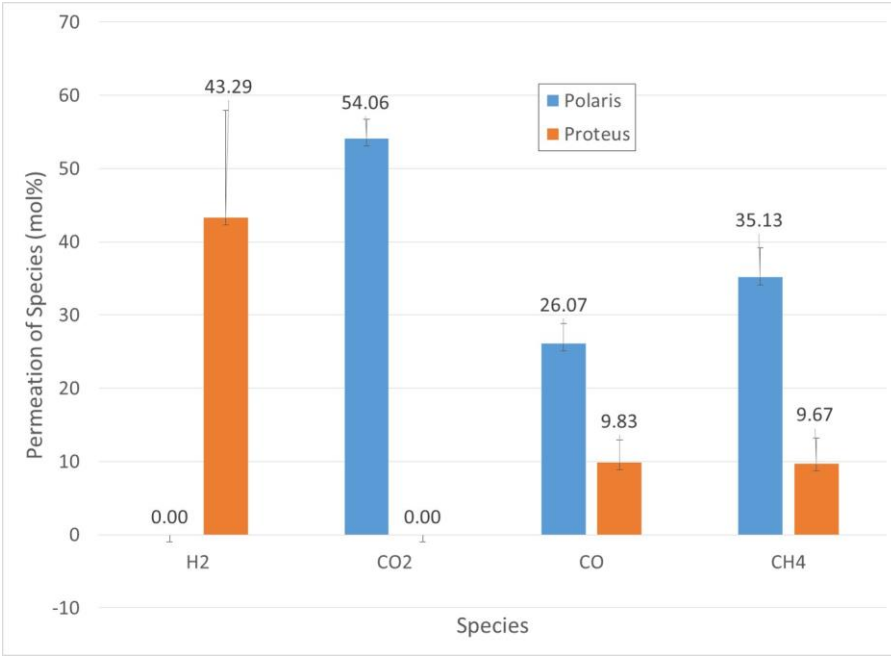

Figure 6. Steady-state permeation of gases across Proteus and Polaris membranes during closed-loop S-Bosch testing.

C. Membrane Risk Mitigation Testing

To evaluate the effects of the potential risk of losing the separation membranes during the mission, testing was conducted in a closed-loop system without the membranes. The system was successfully operated up to 1/2-CM flow rates without exceeding ambient pressure. However, the total recycle ratio in the system (ratio of recycled gas to fresh feed) was over 20:1, compared to values observed in testing with the membranes of between 3:1 and 7:1. This tells us that in the event of a loss of the membranes, the system could continue to be operated. However, it would be at a lower total processing rate to account for the loss of recycled gas, or the system would need to operate at higher pressures.

D. Batch Carbon Formation Reactor Performance

The BCFR was designed to form carbon at a rate of 1.09 kg carbon/day from CO, or the equivalent of the carbon in the CO_2 from a crew of 4. Observed performance of the reactor was considerably lower than this despite a superb thermal profile in the reactor. At the end of testing, the BCFR was disassembled to evaluate the catalyst. The reactor showed considerable carbon formation near the feed annulus outlet, as can be seen in Figure 8. In this image, the bottom cap of the feed annulus can be seen in the center. The catalyst beads, covered in carbon are seen surrounding the annulus. The outer wall is lined with copper, giving it a pinkish tint. Farther from the annulus outlet, a decrease in

carbon was observed, with significantly less at the center of the reactor. This carbon deposition path followed a linear trajectory, as shown in Figure 9, suggesting an unanticipated and undesirable flow distribution. A secondary carbon deposition path also emerged around 15cm (6 inch) from the annulus outlet and was located between the reactor core and the primary deposition path, as can be seen most clearly in b) and c) below. At the distance furthest from the annulus outlet, at the top of the reactor, high carbon quantity was again observed. This suggests that at least some of the gas flow was reaching the top of the reactor, although the pathway is not clear.

It is clear that even distribution of flow is not occurring in the reactor. Further research into the reactor design for these types of reactors suggests that the ratio of the outer annulus to the inner annulus in the current reactor is too large to provide sufficient backpressure for even flow distribution.[8] For optimum performance, a ratio of 0.21 to 1.0 is desirable. To do this, the BCFR will be retrofitted with a machined and fitted metal tube to simulate this gap. If this solves the flow distribution issue, future CFR designs will incorporate the smaller annulus ratio.

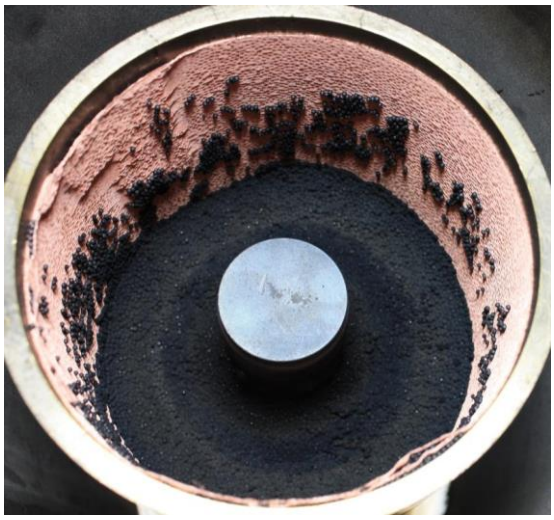

Figure 7. Carbon formation across entire radius of reactor, though concentrated near annulus outlet at center.

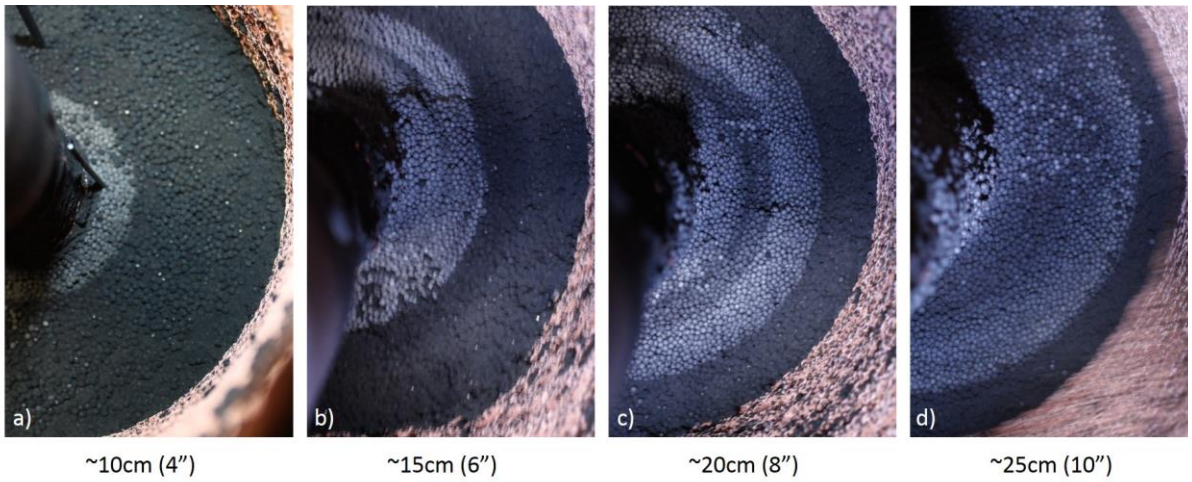

Figure 8. Carbon formation distribution in BCFR as a function of distance from the gas feed annulus. *Image a) was take ~10cm, b) ~15cm, c)~20cm, and d)~25cm from the annulus outlet.*

IV. Future Work

The results discussed here demonstrate the ongoing development of the S-Bosch system. Experimental data for IncoFoam™ and Microlith® reactors suggest similar CO_2 conversion performance. Selectivity for CO over CH_4 appears to be higher for the IncoFoam™ catalyst, but modifications to the Microlith® reactor including design changes to achieve uniform catalyst bed temperature distribution and marginal decrease in space velocitycould improve performance significantly. The IncoFoam™ reactor demonstrated expected robustness against carbon formation and a baseline evaluation of the Microlith® RWGS reactor design was completed. Future work will include a redesign with carbon resistant catalyst and improved thermal management followed by a comparative analysis before downselection. Both the Proteus and Polaris membranes performed adequately in the closed-loop test. Risk mitigation testing demonstrated the ability to continue to process CO_2, but at a lower capacity. Future testing will continue to include these membranes to maximize system performance. Finally, the Batch CFR was shown to produce considerable quantities of carbon, but at rates significantly lower than designed for. Disassembly of the reactor and an

evaluation of the catalyst suggests unfavorable flow distributions within the catalyst. This will be addressed with a reactor design modification and testing to confirm improved performance.

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References

[1] NASA Technology Roadmaps TA 6: Human Health, Life Support, and Habitation Systems Section 6.1.1.2 (2015).

[2] Abney, M.B., Mansell, J.M., "The Bosch Process - Performance of a Developmental Reactor and Experimental Evaluation of Alternative Catalysts," 40th Annual Conference on Environmental Systems, AIAA Technical Paper, AIAA-2010-6272, Barcelona, Spain, July 11-15, 2010.

[3] Abney, M.B., Mansell, J.M., "Evaluation of Bosch-Based Systems Using Non-Traditional Catalysts at Reduced Temperatures," AIAA International Conference on Environmental Systems, AIAA-2011-5059, Portland, OR, July 17-21, 2011.

[4] Abney, M. B., Evans, C., Mansell, M., and Swickrath, M., "Series Bosch System Development," AIAA International Conference on Environmental Systems, AIAA 2012-3554, AIAA, San Diego, CA, 2012.

[5] Abney, M. B., Mansell, J. M., Stanley, C., Edmunson, J., DuMez, S. J., Chen, K., "Ongoing Development of a Series Bosch Reactor System," AIAA International Conference on Environmental Systems, AIAA 2013-3512, AIAA, Vale, CO, 2013.

[6] Abney, M.B., Mansell, J.M, et al., "Series-Bosch Technology For Oxygen Recovery During Lunar or Martian Surface Missions," 44th Annual Conference on Environmental Systems, Pheonix, AZ, July 2014.

[7] Vilekar, S. A., Hawley, K., Junaedi, C., Walsh, D., Roychoushury, S., Abney, M. B., Mansell, J. M., "Performance Evaluation of Staged Bosch Process for CO_2 Reduction to Produce Life Support Consumables," AIAA International Conference on Environmental Systems, AIAA 2012-3555, AIAA, San Diego, CA, 2012.

[8] Kareeri, A.A., Zughbi, H.D., Al-Ali, H.H., "Simulation of Flow Distribution in Radial Flow Reactors," *Ind.Eng. Chem. Res.*, 2006, 45, 2862-2874.