16-20 July 2017, Charleston, South Carolina

Evolving Maturation of the Series-Bosch System

Christine Stanley[1]
Qualis Corporation, Jacobs ESSSA Group, Huntsville, AL 35806

Morgan B Abney[2] and Bill Barnett[3]
NASA Marshall Space Flight Center, Huntsville, AL 35812

Human exploration missions to Mars and other destinations beyond low Earth orbit require highly robust, reliable, and maintainable life support systems that maximize recycling of water and oxygen. In order to meet this requirement, NASA has continued the development of a Series-Bosch System, a two stage reactor process that reduces carbon dioxide (CO_2) with hydrogen (H_2) to produce water and solid carbon. Theoretically, the Bosch process can recover 100% of the oxygen (O_2) from CO_2 in the form of water, making it an attractive option for long duration missions. The Series Bosch system includes a reverse water gas shift (RWGS) reactor, a carbon formation reactor (CFR), an H_2 extraction membrane, and a CO_2 extraction membrane. In 2016, the results of integrated testing of the Series Bosch system showed great promise and resulted in design modifications to the CFR to further improve performance. This year, integrated testing was conducted with the modified reactor to evaluate its performance and compare it with the performance of the previous configuration. Additionally, a CFR with the capability to load new catalyst and remove spent catalyst in-situ was built. Flow demonstrations were performed to evaluate both the catalyst loading and removal process and the hardware performance. The results of the integrated testing with the modified CFR as well as the flow demonstrations are discussed in this paper.

Nomenclature

C/A	=	Center pipe/Annular distributing channel
CH_4	=	Methane
CF	=	Centrifugal
CFR	=	Carbon Formation Reactor
CM	=	Crew Member
CO	=	Carbon Monoxide
CORTS	=	CO_2 Reduction Test Stand
CO_2	=	Carbon Dioxide
CP	=	Centripetal
Δp	=	Differential Pressure
GC	=	Gas Chromatograph
O_2	=	Oxygen
OGA	=	Oxygen Generation Assembly
RWGS	=	Reverse Water-Gas Shift
S-Bosch	=	Series Bosch

I. Introduction and Background

For human exploration missions to Mars and other destinations beyond low Earth orbit, recovery and recycling of water and oxygen (O_2) are necessary to eliminate the considerable mass and logistics issues that accompany open-

[1] ECLSS Design Engineer, ECLSS Development Branch, Bldg. 5755, Room 405-3, MSFC, AL 35812.
[2] Assistant Branch Chief, ES62 ECLS Development Branch, Bldg. 4755, Room 407, MSFC, AL 35812
[3] Lead Test Engineer, ECLSS Development Branch, Bldg 4755, Room 403-4, MSFC, AL 35812.

loop systems where these resources are treated as consumables. State-of-the-art technology involves the Oxygen Generation Assembly (OGA) to produce O2 for the crew and Hydrogen (H2) via water electrolysis. The H2 is to the provided to the Sabatier reactor which converts metabolic carbon dioxide (CO2) to methane (CH4) and water as shown in Eqn. 1.

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

The water is directed to the Water Processing Assembly for purification and then recycled back to the OGA. A portion of the H2 is lost when it is vented to space as a waste product in the form of CH4. The net loss of H2 as a reactant for the Sabatier results in a maximum theoretical O2 recovery from metabolic CO2 of ~54%. Mars missions target >75% O2 recovery from CO2 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.2,3,4,5,6,7 A short overview of the process is presented here. The system involves two reactors, the Reverse Water Gas Shift reactor and the Carbon Formation reactor and two membranes, the Carbon Dioxide Extraction (CDEA) membrane (Polaris) and the Hydrogen Extraction (HEA) membrane (Proteus). Figure 1 shows an illustration of the integrated S-Bosch Process. Fresh CO2 enters the system as the sweep stream for the HEA and picks up H2 from the recycle stream while fresh H2 enters as the CDEA sweep stream picking up CO2. The membranes are operated at a pressure differential of ~5 psia to increase permeability. The sweep streams are combined prior to entering the RWGS where the reaction shown by Eqn. 2 occurs.

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 stream exiting the RWGS enters the compressor where it is mixed with the CFR effluent. The mixed stream becomes the process/recycle stream prior to entering the condensing heat exchanger. Water vapor is condensed while the remaining gases flow through the HEA and then the CDEA. The effluent of the CDEA enters the CFR where the CO Hydrogenation (Eqn. 3) and/or the Boudouard (Eqn. 4) reactions occur. The resulting net reaction is the Bosch process as shown in Eqn.5

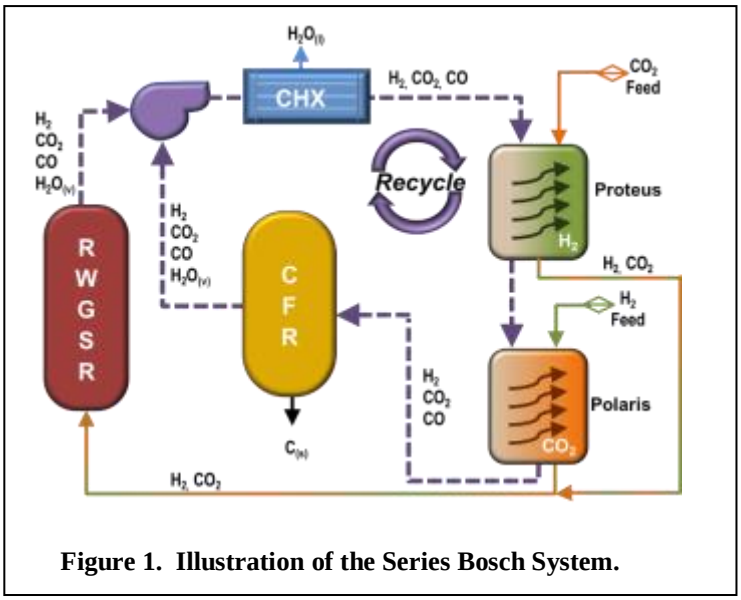


Figure 1. Illustration of the Series Bosch System.

Integrated closed-loop testing of the S-Bosch system was demonstrated in 2016 with the NASA developed Incofoam™ RWGS, the Polaris and Proteus membranes, and the CFR with the S-660 Amasteel bead catalyst. The system was successfully operated at the 0.25, 0.5, and 0.75 CM feed rates. Unfortunately, when running the system at the 1 CM feed rates, the overall system pressure did not reach steady state and continued increasing to well over ambient pressure. As a result, testing was halted. Upon opening the reactor and inspecting the catalyst, it was determined

that uneven flow distribution was occurring within the CFR. The CFR was retrofitted to address the uneven flow distribution and integrated testing was repeated to evaluate the performance. The success of this test could lead to more innovative modifications that will further advance the maturation of S-Bosch system.

In 2015, a continuous, moving bed CFR was designed with the capability to load new catalyst and remove spent catalyst in-situ. The CFR was built in 2016 and flow testing was performed in 2017. This system is ideally suited for surface missions where the regolith could be used as an abundant source of catalyst resupply.

Details of the hardware retrofit and test configurations for the integrated testing and flow test are discussed in the next section.

II. Hardware and Test Configuration

A. Fully Integrated Testing (RWGS + Membranes + Modified CFR)

The CFR was designed as a radial flow reactor. Radial flow reactors have many benefits compared to axial flow reactors, especially for space applications. Radial reactors allow for higher flow rates with a much lower pressure drop, are less susceptible to fouling, have a smaller footprint, and are linearly scaled-up. One design difficulty with radial flow reactors is insuring uniform flow through the catalyst. Research suggests that the cross-sectional area ratio of the center pipe to the annular distributing channel has a critical impact on attaining uniform flow.

There are two types of flow in a packed bed reactor, axial flow and radial flow. In an axial flow reactor, the feed enters one end and flows axially through the reactor and exits at the other end as show in Figure 2. Axial Flow Reactor. Radial reactors are classified by flow types, z-flow and π-flow, and radial flow direction, centripetal (CP) and centrifugal (CF). In the z-flow configuration, the flows in the annular distributing channel and the center pipe are in the same direction. The flows are counter-current in the π-flow configuration. In the CF configuration, the gas is fed to the center pipe and travels radial to distributing channel. In the CP configuration, the gas is fed to the distributing channel and travels radially to the center pipe. In all, there are four types of radial reactors, CP z-flow, CF z-flow, CP π-flow, and CF π-flow.[8] These are illustrated in Figure 3. The ratio of the center pipe to the annular distribution channel has a major impact on uniform flow distribution and the optimal varies depending on the reactor configuration.

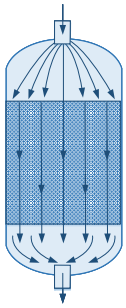


Figure 2. Axial Flow Reactor.

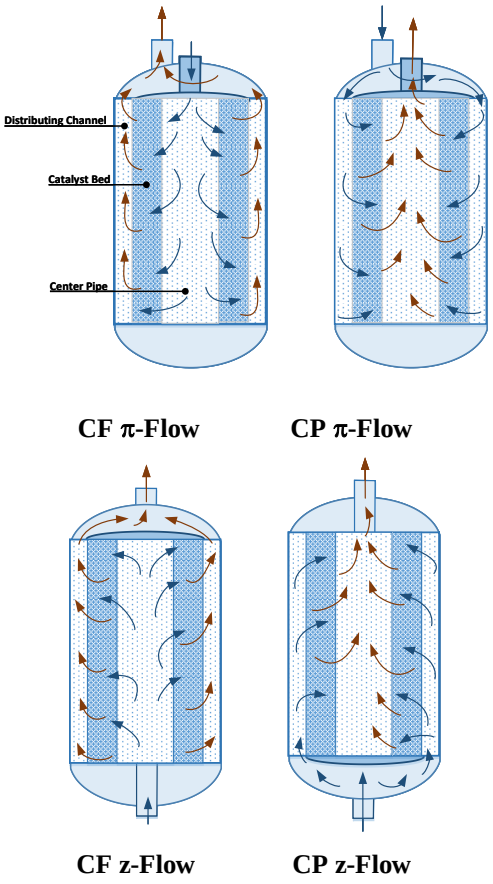
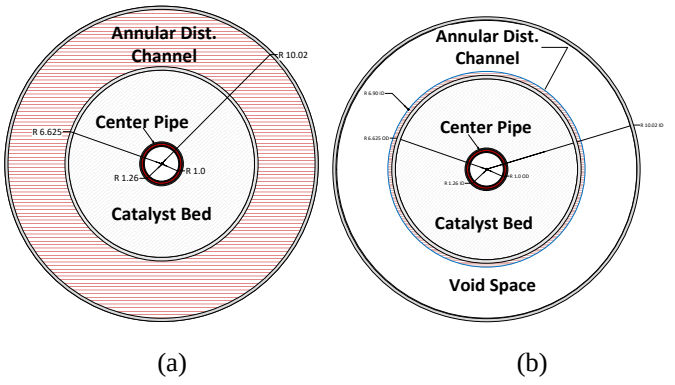


Figure 3. Four Radial Flow Reactor Configurations.

The CFR is designed in the CF π-flow configuration. Literature suggests that an optimum ratio for this configuration is between 0.21 and 1.0. Due to budget constraints, the CFR was fabricated from commercial off-the shelf materials and resulted in a reactor with a 0.01 C/A ratio. Test results reported previously[2] showed definitive evidence of flow maldistribution. The ratio for the CFR tested in 2016 was much too small to provide the needed back pressure to induce evenly distributed flow. To address the uneven flow distribution, the CFR was retrofitted with a 13 gauge, 6.90" diameter, 316 Stainless Steel tube with a wall thickness of 0.090". The tube was inserted between the catalyst bed and the outer vessel wall to reduce the cross-sectional area of the annular distributing channel. The ability to make a large increase in the ratio was limited due to the very small cross-sectional area of the existing center pipe resulting in a maximum ratio of 0.16. This is still below the optimum range, but is 16x greater that the original ratio. A comparison in the flow areas before and after the retrofit is illustrated Figure 4. As shown, a large reduction in the annular distributing channel was possible.



(a) (b)

Figure 4. Cross-sectional Area a) Before and b) After retrofit

The 2016 integrated testing using the Incofoam™ RWGS, the Polaris and Proteus membranes, and the CFR with the S-660 Amasteel bead catalyst was repeated for the 0.50 and 1 CM feeds. The modified CFR was re-installed into the CO2 Reduction Test Stand (CORTS). 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 psid as possible. This was accomplished using backpressure regulators and by maintaining the Incofoam™ RWGS reactor at ~5 psid below the CFR. Flow rates at CO2 feed equivalent to 0.5-CM and 1-CM were tested. The Incofoam™ RWGS reactor was set to 650°C with a 400°C inlet preheat and the CFR core heater was operated at 750°C. The CFR temperature setpoint during the 2016 testing was 700°C, but the mean CFR reator temperatures were nearly the same for both tests. This is due to the fact that larger copper beads were added to the center pipe than those used during the previous test and did not provide the same heat transfer capabilities. Initially, the system was run in the open-loop configuration until steady state was reached to avoid unnecessary build up of gases in the recycle loop. During the open-loop run, high levels of methane were produced which would increase the total system pressure once the system was in closed-loop. Raising the CFR temperature would mitigate the high methane levels, but the temperature in the CFR was at maximum capacity and could not be increased. Instead, the temperature in the RWGS was increased to 700°C and the methane levels decreased to acceptable levels. 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 2:1 H2:CO2 ratio and a CO2 feed rate equivalent to .05 CM. Once system steady state was achieved, system gas composition at the Incofoam™ RWGS reactor inlet and outlet, the inlets and outlets of the process streams and the outlet sweep streams of each membrane, the CFR inlet, and the CFR outlet was recorded and then repeated for the 1 CM feed. It should be noted that at startup during the 2016 testing, it was necessary to feed a 1:1 H2:CO2 feed ratio to limit the amount of H2 in the CFR recycle loop. This step was not required for this test. It should also be noted that periodic venting was not necessary for either CM feed rates. During the 1 CM feed rate run, the average system pressure was 14.9 psi. This is above ambient, but because the pressure was relatively stable, it was decided to forgo venting.

B. CFR Flow Test.

Carbon is a primary product of the S-Bosch system, specifically in the CFR. Over time the reactor will fill with carbon and the catalyst will become de-activated. Work performed in 2013 and 2014 explored to possibility of using in situ resources, such as, Martian regolith, as a source for CFR catalyst replenishment. Results of that research is promising, but more work is needed. To support this work, a design for a CFR with the capability to introduce fresh catalyst and unload spent catalyst was completed in 2015 and a prototype was built in 2016. The reactor is illustrated in Figure 5. Fresh catalyst is fed via the Loading Funnel at the top of the reactor, the Upper Valve, located between the funnel and the top of the reactor, is used to control the flow of fresh catalyst. The catalyst is distributed to the catalyst bed through the Catalyst Distributor located at the top of the reactor. The Bottom Funnel is attached to the bottom of the catalyst bed inside the reactor. Valve 2 is opened to release spent catalyst from the bottom of the reactor.

A simple flow test was performed using fresh catalyst to demonstrate the feasibility of the design concept. Prior to the flow test, the reactor was filled with fresh catalyst. The Lower Valve was opened to allow the catalyst to flow out and then was closed. Catalyst was introduced to the reactor when the Upper Valve was opened and then was closed. The objective of this testing was to determine if the catalyst would flow in and out as expected and whether or not the valves operate correctly.

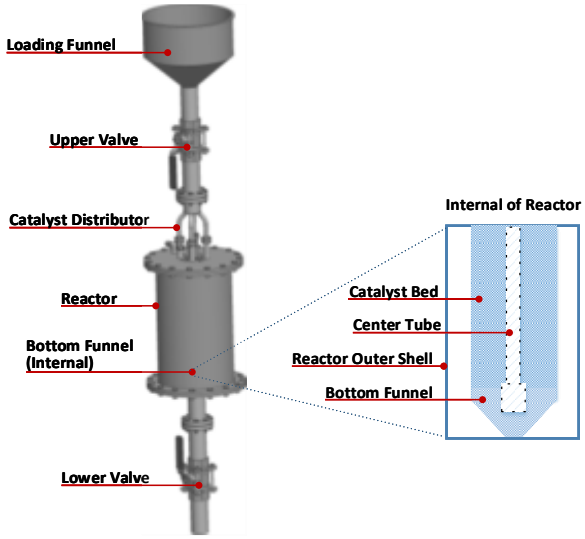


Figure 5. Prototype of a Continuous Moving Bed CFR. *The reactor is show in (a) and a blow-up of the catalyst bed and bottom funnel is shown in (b).*

III. Results and Discussion

Two tests were conducted, one to evaluate the modified CFR integrated in the S-Bosch system and two, a simple flow test to demonstrate the feasibility of a design concept for loading fresh and unloading spent catalyst.

A. Fully Integrated Testing (RWGS + Membranes + Modified CFR)

The closed-loop system was successfully tested at the 0.5 feed rates while maintaining sub-ambient pressure. Testing at the 1 CM feed rates was successful, but the system pressure averaged 14.92 psia, slightly higher than ambient. The pressure at this feed rate did stabilized, which was not the case during the 2016 testing where system pressure was above ambient from the start and continued to increase to the maximum allowable system pressure resulting in halting the test. A one-to-one comparison between this test and the previous test is not possible due to the difference in the RWGS reactor temperatures 650°C vs 700°C and differences in the CFR pressure. Table 1 lists the set-points for both the 2016 and the 2017 testing.

Table 1. Test Set-points and Average Recycle Flow Rate for the 2016 and 2017 Tests

Test Parameter	2016			2017	
	0.5 CM	0.5 CM	0.75 CM	0.5 CM	1 CM
RWGS Temperature (°C)	650	650	650	700	700
RWGS Pressure (psia)	8	8	8	8	8
CFR Temperature (°C)	700	700	700	750	750
CFR Pressure (psia)	13.5	10	10	12	12

Heat transfer from the heater through the catalyst was not as efficient in the recent testing. Copper beads were used in the center pipe to enhance heat transfer thoughout the reactor. The beads used in this test were larger in diameter than those used in the 2016 testing. A temperature profile is shown in Figure 6. Temperatures are displayed for both tests. Even with increasing the heater set-point to the maximum 750°C, the reactor temperatures were slightly lower with an overall average reactor temperature of 523.9°C compared to 547.7°C indicating the possibility that the bead size has an impact on heat transfer. The biggest temperature difference was observed at the bottom of the reactor, while the middle and upper sections had a smaller gap and in some cases were essentially the same.

The CFR pressure set-points were different for both tests. During the 2016 testing, CFR pressure needed to be lowered in order to maintain subambient pressure. This allowed for the test to run, but reduced the pressure differential between the membrane sweep and process streams below the minimum operating Δp. Throughout the 2017 testing, the required Δp was maintained although, the system pressure during the 1 CM run was slightly above ambient. This pressure

remained stable and for this reason, the test was not halted. Pertinent test results are shown in Table 2. Similar CO conversion was observed for all of the 0.5 CM test runs. The 1 CM run had a lower recycle rate as well as a much higher CO conversion rate compared to the 0.75 CM run from 2016. This suggests that at the lower flow rates, the CFR modification had little to no impact. At the higher flow rates, the modification greatly improved the performance, especially since it ran successfully at the 1 CM flow rate which was not possible in the earlier test.

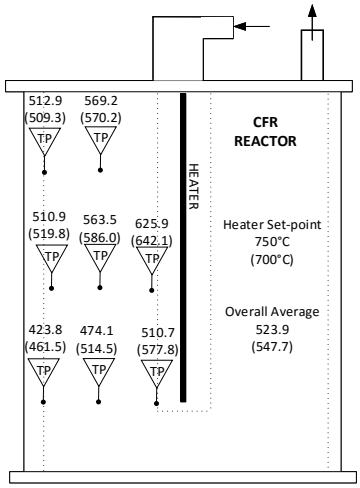


Figure 6. Temperature profile inside CFR. *Average temperatures at each thermocouple, heater set points and overall average reactor temperatures are shown.. Temperatures from the 2016 testing are indicated by parentheses.*

Table 2. Pertinent Test Results for the Integrated SBosch Test.

Measurement	2016			2017	
	0.5 CM	0.5 CM	0.75 CM	0.5 CM	1 CM
Ave. Recycle Rate (slpm)	1.3	1.22	3.1	1.37	2.69
Ave. System Pressure (psia)	14.25	10.99	13.70	13.05	14.92
CO Conversion CFR (%)	61.9%	67.3%	33.9%	65.6%	56.9%

B. Effect on Flow Distribution due to CFR Modifications.

After the integrated test was complete, the CFR was disassembled to evaluate the catalyst for flow patterns. Comparing the flow patterns between the two CFR configuration will help determine if the modification was effective in providing a more uniform radial flow distribution thoughout the reactor. Photographs of the inside, bottom of the CFR configurations are shown in Figure 7. The beads were removed via vacuum at ~2 inch increments and observations were photographed. It should be noted that the pre-modified CFR had a much longer run-time and therefore, will have a larger quantity of deposited carbon.

A photographic comparison of the flow patterns in the catalyst bed between the pre-modified and modified CFR are shown in Figure 8. Photos (a) through (d) are of the pre-modified CFR and were reported previously.[2] Photos (e) through (j) are of the modified CFR. The photos clearly show that flow through the catalyst bed was much improved after the CFR was modified. Carbon formation was much more disbursed though the catalyst and did not begin pushing towards the outer wall until ~20cm from the bottom of the center pipe. The equivalent distribution occurred much earlier, ~ 10cm in the pre-modified CFR. At ~25cm from the bottom of the center pipe, carbon formation was almost entirely occurring in the narrow rim along the outside wall of the pre-modified CFR. It wasn't until ~ 37cm that we saw the equivalent carbon formation pattern in the modified CFR. It should be noted that the copper surrounding the center pipe in the modified CFR is much cleaner, less carbon, than the center pipe of the pre-modified CFR. There are several possible explanations for this occurrence. It could be due to the shorter run time of the modified CFR, the higher heater temperature set point which could be less conducive to carbon formation, or that the improved flow distribution prevented carbon formation to be concentrated in that area. Additional testing would be needed to determine the reason for this difference.

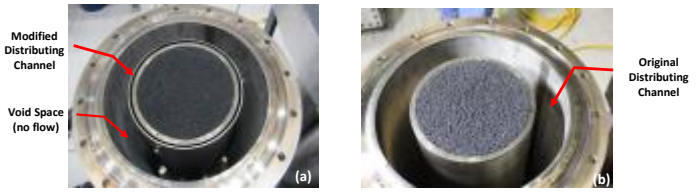


Figure 7. Disassembled Carbon formation reactors prior to catalyst removal, (a) with modification and (b) without.

C. . Continuous Moving Bed CFR Flow Test.

Test Results unavailable at this time. Anticipate results in the next few weeks.

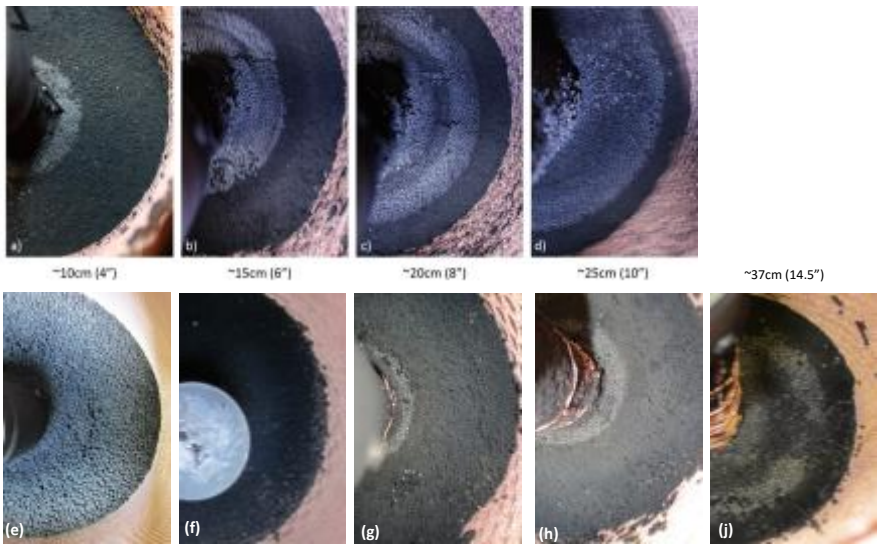


Figure 8. Photographic comparison of flow patterns in the catalyst bed between the pre-modified and modified CFRs.

IV. Conclusion

The results of the integrated test indicate that the increase in the cross-sectional area ratio between the center pipe and the distributing channel, while not within the optimal range, improved the flow distribution in the reactor significantly. In addition, the modification had a positive effect on performance as indicated by the successful run at the 1 CM feed rate with a 56.9% CO conversion rate. These results indicate that redesigning the internal CFR to optimize the radial flow uniformity could significantly improve the overall performance of the S-Bosch process. ADD FLOW TEST CONCLUSION.

V. Acknowledgments

The authors would like to acknowledge Heath Mullins and Tom Williams for key technical support in maintaining the CORTS and troubleshooting assistance. This work was funded by the Human Exploration and Operations Mission Directorate's Advanced Exploration Systems Program Life Support Systems Project for funding support.

VI. 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., et.al., "Demonstration of Robustness and Integrated Operation of a Series-Bosch System," 46th International Conference on Environmental Systems, AIAA 2016-262, Vienna, Austria, July 10-14, 2016.

[3] 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, Phoenix, AZ, July 2014.

[4] 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.

[5] 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.

[6] 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.

[7] 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.

[8] Kareeri, A.A., (2004*). Investigations of the flow and pinning phenomena in radial flow reactors* (Master's Thesis) Retrieved from Proquest Dissertations & Theses. (Publication number 1426735).