Performance Evaluation of Staged Bosch Process for CO_2 Reduction to Produce Life Support Consumables

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Utilizing carbon dioxide to produce water and hence oxygen is critical for sustained manned missions in space, and to support both NASA's cabin Atmosphere Revitalization System (ARS) and In-Situ Resource Utilization (ISRU) concepts. For long term missions beyond low Earth orbit, where resupply is significantly more difficult and costly, open loop ARS, like Sabatier, consume inputs such as hydrogen. The Bosch process, on the other hand, has the potential to achieve complete loop closure and is hence a preferred choice. However, current single stage Bosch reactor designs suffer from a large recycle penalty due to slow reaction rates and the inherent limitation in approaching thermodynamic equilibrium. Developmental efforts are seeking to improve upon the efficiency (hence reducing the recycle penalty) of current single stage Bosch reactors which employ traditional steel wool catalysts. Precision Combustion, Inc. (PCI), with support from NASA, has investigated the potential for utilizing catalysts supported over short-contact time Microlith substrates for the Bosch reaction to achieve faster reaction rates, higher conversions, and a reduced recycle flows. Proof-of-concept testing was accomplished for a staged Bosch process by splitting the chemistry in two separate reactors, first being the reverse water-gas-shift (RWGS) and the second being the carbon formation reactor (CFR) via hydrogenation and/or Boudouard. This paper presents the results from this feasibility study at various operating conditions. Additionally, results from two 70 hour durability tests for the RWGS reactor are discussed.

Nomenclature

°C	=	degree Celsius
cm	=	centimeter
d	=	diameter
ft	=	foot
g-cat	=	gram of metal catalyst
GSA	=	geometric surface area
hr	=	hour
in	=	inch
kJ	=	kilojoules
L	=	liter
m	=	meter
ml	=	milliliter

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mol	=	mole
psia	=	pound per square inch absolute
slpm	=	standard liter per minute (21°C, 14.7 psia)
WHSV	=	weight hourly space velocity

I. Introduction

The CO_2 Reduction Assembly (CRA) along with the CO_2 Removal Assembly (CDRA) and Oxygen Generator Assembly (OGA) have long been an integral part of the closed-loop cabin Atmosphere Revitalization System (ARS) for future long-duration human space exploration to the Moon and Mars.[1,2] In the current International Space Station (ISS) and other low orbit missions, the metabolically generated CO_2 is removed from the cabin air and is vented into space, resulting in a net loss of O_2. This requires a continuous re-supply of O_2 via water electrolysis, and thus highlights the need for large water storage.[3] Efficient production of life support needs such as water and oxygen from in-situ resources can significantly reduce launch weight, size, and cost and is crucial for deep exploration of space where re-supply option is nonexistent. Thus atmosphere resource management and recycle becomes crucial. To achieve a complete closure of O_2 and H_2O, the CO_2 produced by metabolic processes is removed from the cabin air by CDRA and is then reacted with H_2 from OGA to generate water. This water can be collected via centrifugation, condensation, or an adsorption method and can be directly used for life support or utilized in OGA where it is electrolyzed to produce oxygen for crew members. A highly efficient closed-loop ARS will result in a near complete closure of O_2, which would significantly reduce the amount of re-supply water required. A CO_2 reduction reactor is additionally of interest to NASA as an integral part of In-Situ Resource Utilization (ISRU) application for on-site production of life support consumables.

Sabatier and Bosch processes are the two primary technologies, among several others, for application in the Environmental Control and Life Support System (ECLSS). Both processes catalytically reduce CO_2 with H_2 and enable recovery of metabolic oxygen. The Sabatier reaction stoichiometrically requires 4 moles of H_2 per mole of CO_2, which is in excess of the more practically available H_2 to CO_2 ratio of ~3.5 in spacecraft and ISS applications. The Bosch process on the other hand only requires half as much H_2. Factors favoring Bosch process are production of solid carbon and no need for additional H_2, versus Sabatier's need to vent CH_4 with some loss of O_2 and H_2.[4] However, the launch mass/volume for current single-stage Bosch reactors is significantly higher than the competing Sabatier technology.[4]

Major shortcomings of the single-stage Bosch process are slow reaction rates, fouling of catalyst by surface carbon, and somewhat less favorable thermodynamics as compared to the Sabatier process. Earlier work (1960's and 1970's) on Bosch process was restricted to iron catalysts,[5] operating at high temperatures (~700°C). Solid carbon with low packing density (~0.5 g/cm^3) was deposited on the catalyst with no regeneration capability, causing large storage problems and dependence on expendables. Other associated problems were migration of formed carbon from the reaction zone or formation outside the reaction zone.[6] For a Bosch reactor utilizing steel wool, a single-pass efficiency was significantly poor at ~10%, resulting in appreciably less water than that predicted by thermodynamics and a high recycle ratio, defined as the ratio of the amount of product gas recyled to the reactor inlet divided by the supplemental ("fresh") H_2 and CO_2 fed to the reactor. Work done by Manning and Reid[7] and Sacco and Reid[8] established that the formation of iron oxide concurrent with the hydrogenation process inhibited the formation of water. Simultaneous metal oxide formation was later shown to be thermodynamically unfavorable on Ni and Co systems and was expected to lead to a more efficient reactor.[9] In spite of all the advances over the years, relatively low single-pass efficiency (with high recycle penalty) remains to hound the practical application of the Bosch process.

The single-stage Bosch reaction (Eq. (1)) represents a complex multiple reaction system consisting at minimum of endothermic reverse water gas shift (RWGS) (Eq. (2)) and exothermic hydrogenation/Boudouard reactions (Eq. (3) and Eq. (4)).

Overall Bosch:	$CO_2 + 2H_2 \rightarrow C_{(s)} + 2H_2O$	$\Delta H^0 = -90$ kJ/mol	(1)
RWGS:	$CO_2 + H_2 \rightarrow CO + H_2O$	$\Delta H^0 = 41$ kJ/mole	(2)
Hydrogenation:	$CO + H_2 \rightarrow C_{(s)} + H_2O$	$\Delta H^0 = -131$ kJ/mole	(3)
Boudouard:	$2CO \rightarrow C_{(s)} + CO_2$	$\Delta H^0 = -172$ kJ/mole	(4)

The conflicting demands of temperature and space velocity for these reactions make single-stage Bosch reactor optimization highly complicated and less favorable as was suggested by Otsuji et al.,[10] and Abney et al.,[11,12] among others. Thus, a potential improvement to the process is to split the Bosch chemistry into a series reactor

configuration. The first reactor would be dedicated to CO formation via RWGS while the second reactor would be dedicated to carbon formation via hydrogenation and/or Boudouard reactions. The majority of the water production in the series configuration would be associated with the RWGS stage. Such a configuration will allow effective optimization of each reactor to maximize efficiency of each stage, minimize the overall reactor volume (combined volume of the two reactors in series vs. single-stage Bosch reactor volume) and improve water and carbon production rates. Another potential benefit is the reduction in size of the carbon containing cartridge as compared to the single-stage Bosch reactor. Both stages are, however, plagued by CH_4 formation at low temperatures due Sabatier side-reactions (Eq. (5) and Eq. (6)) which consume necessary reactants.

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \tag{5}$$
$$CO + 3H_2 \rightarrow CH_4 + H_2O \tag{6}$$

Thus, a primary design requirement for the RWGS reactor is to demonstrate high CO_2 conversions (close to equilibrium) at high space velocity, with minimal to no CH_4 formation. The unconverted CO_2 and water has to be removed before feeding it to the downstream carbon formation reactor (CFR). One option is to utilize a sorbent bed (e.g., Molecular Sieve 5A) to simultaneously remove CO_2 and water. The other option is to utilize a condensing heat exchanger to remove water followed by membrane based separation unit to recycle the unconverted CO_2 back to the RWGS reactor.

Previous work on CFRs has shown that Boudouard reaction with only pure CO as feed is very limited and thereby requires some H_2 to be present in the feed.[11] However, in addition to the hydrogenation and the Boudouard reactions, the presence of H_2 in the feed increases the proclivity for CH_4 formation via the Sabatier reaction, which is undesirable. CH_4 could also potentially be formed via reverse pyrolysis (Eq. (7)) representing a net loss of H_2 in the system:

$$C + 2H_2 \rightarrow CH_4 \tag{7}$$

Thus, the operating conditions and catalytic activity in the CFR need to be tailored to maintain low selectivity toward methanation. The CO_2 generated in the CFR via Boudouard would be separated in the CO_2 separation unit (e.g. membrane-based) and recycled back to the RWGS while the unconverted CO is recycled back to the CFR. Once the CFR has reached its capacity for carbon and its pressure drop has exceeded a safe threshold, the catalytic cartridge could be replaced. For safety reasons, the Bosch reactor for space applications needs to be operated at slightly less than ambient pressure in order to prevent leakage of combustible gasses to the atmosphere surrounding the unit.

In this paper, we describe the results from the feasibility study for a staged Bosch process utilizing our patented Microlith® technology as a step forward to dramatically reduce the overall reactor volume and further increase system CO_2 conversion at space velocities higher than those previously reported. Moreover, the metal mesh structure of the Microlith substrate is expected to keep the carbon formed locked in place, thus eliminating any downstream migration. The RWGS reactor was demonstrated to achieve equilibrium-limited conversions (~62% at 750°C) at high throughputs (WHSV ~315 L/(hr g-cat)). The ability to operate the Microlith-based reactor at high space velocities results in a compact and lightweight reactor that will reduce size and launch costs. Based on the test results, an approximately 20 ml Microlith RWGS reactor and ~54 ml CFR reactor (excluding the heat exchanger for both reactors) would be required for a single pass system for a 4-crew unit. Performance results at various operating conditions are reported to identify the optimum operating window for each stage. Further optimization and size estimation with recycle feed was beyond the scope of this study.

II. Microlith® Catalytic Technology

The catalyst and reactor described here are based on PCI's patented Microlith technology (trademarked by PCI).[13] 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 carbon formation

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. With increased carbon deposition over time, the CO_2 reduction reaction rate could be limited by gas-solid diffusion. High mass transfer coefficient of Microlith substrate should allow reasonably high reaction rates and maintain so whilst carbon is building on the catalyst surface. The Microlith substrate also provides about three times higher geometric surface area over conventional monolith reactors with equivalent volume and open frontal area (i.e., low pressure drop). The open structure of Microlith-supported catalyst substrate should result in lower pressure drop as compared to steel wool or foam-supported catalysts. This should enable the Microlith reactor to operate for relatively longer duration with reduced pressure build-up rate, enhancing the longevity of the reactor

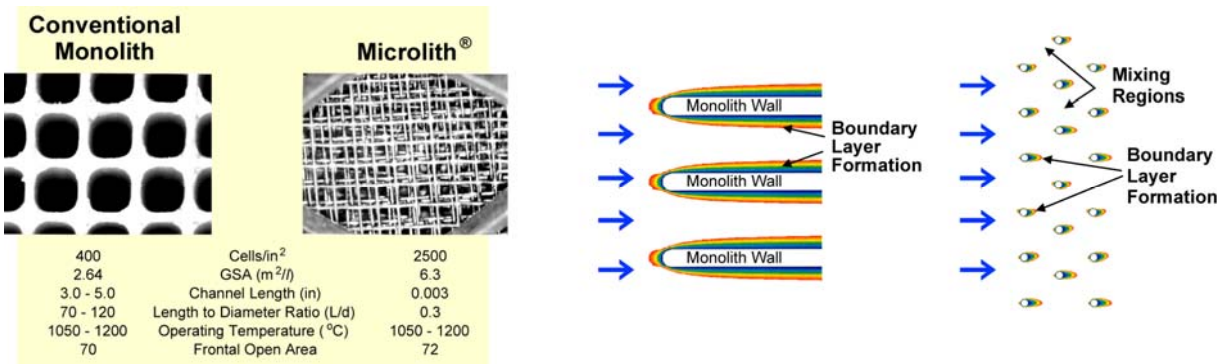

Figure 1. Physical characteristics of conventional, long honeycomb monolith and Microlith substrates, and CFD analysis of boundary layer formation for a conventional monolith and three Microlith screens.

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 monolith and Microlith screens. Finally, PCI's proprietary catalyst coating formulations and application methods, with high surface area washcoats, allow for very low catalyst usage with rigorously demonstrated long-term mechanical, thermal, and performance durability.

Another advantage of using a Microlith substrate is that it requires neither a completely premixed, completely vaporized, nor completely uniform mixture for stable operation. The high mass transfer rate of the Microlith substrate provides sufficient mixing to remove small-scale inhomogeneities in the reactor feed, but large scale variations still need to be removed upstream of the reactor. Therefore, a simple reactant mixture preparation strategy, using a standard static or quartz mixer, can be employed without risk of damaging the catalytic Microlith substrates. PCI has had considerable experience in providing a highly uniform mixture to the reactor and has identified simple premixing techniques with the design elements necessary for good reactor stability.

The use of catalyst substrates with high heat and mass transfer rates, high surface area, and low pressure drop has a significant impact on reactor performance and size. Current catalytic reactors are generally based on substrates such as pellets, monoliths, foams or microchannels. Work on short contact time substrates has been reported by groups at National Labs, universities, and commercial organizations. Notable among them is Professor Lanny Schmidt at the University of Minnesota.[14,15] However, PCI's Microlith short contact time substrate has shown several benefits over other such substrates on the basis of recent results and developments. 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,[16] trace contaminant control,[17,18] catalytic combustion,[19] partial oxidation of methane,[20,21] liquid fuel reforming,[22,23] CO preferential oxidation, and water gas shift reactors.[24] A scanning electron microscopy (SEM) micrograph of the coated Microlith substrate is shown in Fig. 2. SEM analysis indicates uniform catalyst coatings on the substrate with complete coverage.

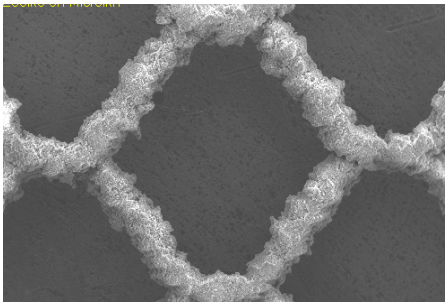

Figure 2. Surface-scan SEM micrograph of the coated Microlith catalytic substrate.

III. Results and Discussion

A. Apparatus

All testing was performed in a 3 ft long, 2 in diameter quartz tube (Fig. 3). Catalyst coated Microlith substrates were supported inside this quartz reactor and sandwiched between two alumina foam blocks. The alumina foam blocks were 2.5 in long and acted as supports for the Microlith substrates and provided additional heat transfer area to preheat the reactants. The volume of the catalyst bed was varied to achieve the desired space velocity for each test. The reactants flowed axially through the linear stack of Microlith screens.

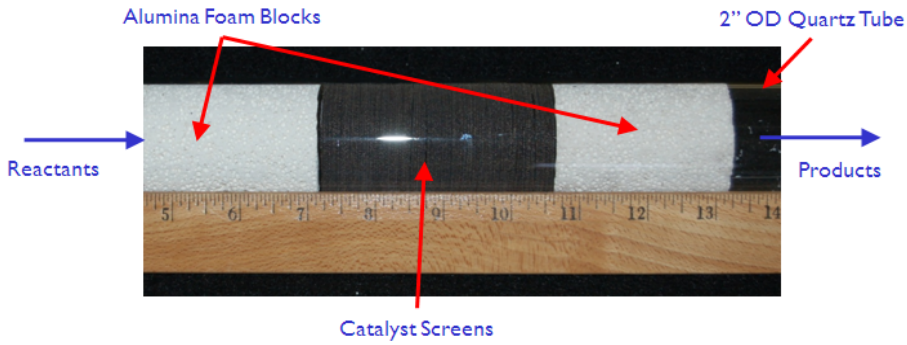

Figure 3. External view of the Bosch reactor for bench-scale testing.

The quartz tube was placed into a tube furnace which was used to preheat the reactants and maintain the catalyst at the desired reaction temperature. The reactor was instrumented with two thermocouples located at the center of each of the alumina blocks to monitor the inlet and outlet gas temperatures. The inlet feed and outlet product compositions were monitored using a micro-Gas Chromatograph (Agilent Technologies). The inlet sample port was located upstream of the furnace (after mixing, but prior to preheating) and the outlet sample port was located at the center of the exit alumina block. A small amount of nitrogen was introduced to the inlet feed, upstream of the catalyst bed, as an internal standard gas for the mass balance calculation to determine reactant conversion and product selectivity.

B. Bosch Reactor Performance Testing

In this study, the Bosch reactor testing was performed using Microlith coated Rh-, Ni- and Co-catalysts. Performance maps for these catalysts were developed as a function of H_2 to CO_2 ratio, operating temperature, and weight hourly space velocity (WHSV) according to the test matrix in Table 1. Note that the WHSV is defined as the standard liter flow (at 21°C, 14.7 psia) per hour per gram of the metal catalyst. Each catalyst was first reduced under the optimum reduction conditions prior to performance testing. Conversion and selectivity for the species of interest in each reaction were calculated by measuring the product gas composition at these operating conditions. The performance of the three metal catalysts were then compared with each other and with current state-of-the-art catalysts. From these tests, the potential benefits of the Microlith substrate, including short contact time kinetics, high heat transfer, and high surface area of catalyst active sites, were validated to achieve a highly efficient, compact, and durable Bosch reactor.

Table 1. Test matrix for developing the performance maps for Rh-coated, Ni-coated, and Co-coated Microlith substrates for the Bosch reaction.

Parameters	Values
RWGS Testing	
Reactor temperature	300°C - 750°C
H_2 to CO_2 ratio	1.0 – 2.0
WHSV	60 - 315 L/(hr g-cat)
Hydrogenation/Boudouard Testing	
Reactor temperature	300°C - 650°C
H_2 to CO ratio	0.5 – 1.0
WHSV	60 L/(hr g-cat)

(i) *RWGS Testing*

The performance of Rh-, Ni-, and Co-coated Microlith catalytic substrates was examined by evaluating the CO_2 conversion and CO and CH_4 selectivity at WHSVs from 60 – 315 L/[hr g-cat], H_2 to CO_2 ratios from 1.0 to 2.0, and temperatures from 300 to 750°C.

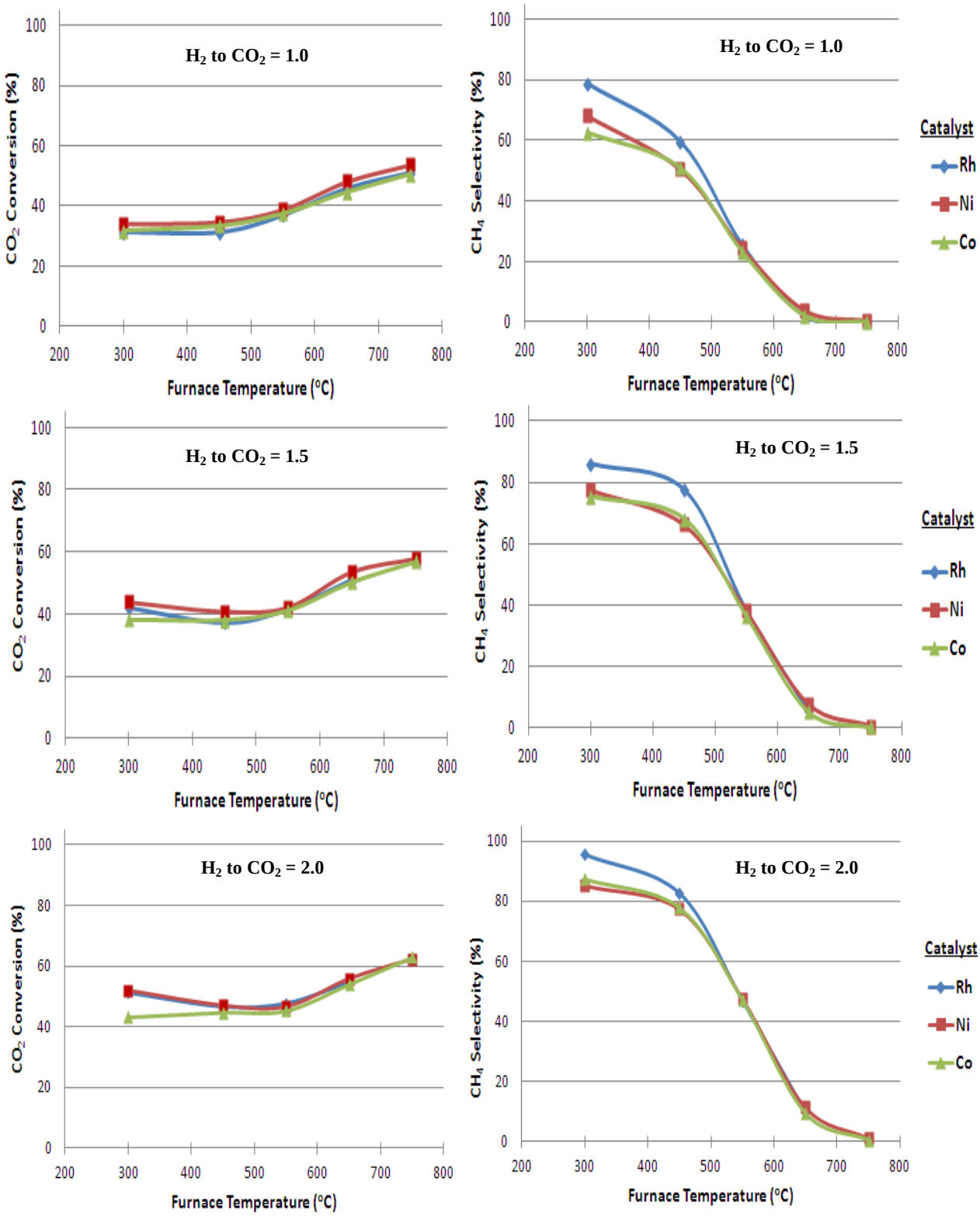

Figure 4. Comparison of CO_2 conversion and CH_4 selectivity in RWGS reactor for Microlith supported Rh, Ni and Co catalysts at WHSV of 60 L/[hr g-cat].

For all the tests, the feed to the RWGS reactor comprised of only CO_2 and H_2. 10 mole% N_2 was added as an internal standard to allow mass balance calculations for estimating CO_2 conversion as well as catalyst selectivity toward CO and CH_4.

Fig. 4 compares the performance of the Microlith supported Rh, Ni and Co catalysts in single-pass RWGS testing at WHSV of 60 L/[hr g-cat] as a function of temperature and H_2 to CO_2 ratio. As observed, all three catalysts showed near identical performance, except for Co at 300°C and a H_2 to CO_2 ratio of 2.0. As governed by equilibrium for an endothermic reaction, the CO_2 conversion increased with the operating temperature. Moreover, the CO_2 conversion increased at a given temperature as the H_2 to CO_2 ratio was increased. The data also shows that as the H_2 to CO_2 ratio increased, the CO_2 conversion profile showed more of a U-shaped trend which is likely due to a balance between the exothermic (higher conversion at lower temperature) Sabatier reaction and the endothermic (higher conversion at higher temperature) RWGS reaction. The CO_2 conversion via Sabatier is favored at low temperature especially at higher H_2 to CO_2 ratio. This hypothesis garners further support from the selectivity data shown in Fig. 4. As expected, the experimental test data showed high CH_4 selectivity at low temperatures due to the Sabatier reaction. This high CH_4 selectivity at low temperatures translated into a low CO selectivity and vice versa at higher temperatures. Moreover, the CH_4 selectivity increased as the feed H_2 to CO_2 ratio was increased. Rh which is a known Sabatier catalyst showed higher CH_4 selectivity at temperatures lower than 550°C in comparison to Ni and Co. However, at temperatures above 550°C, the catalyst selectivity of Rh/Microlith was similar to that of Ni/Microlith and Co/Microlith. Based on the experimental data, the optimum temperature for RWGS reactor for the catalysts studied in this effort was 650-750°C to maximize the CO_2 conversion and minimize the CH_4 formation. Ni and Co were selected for further testing, primarily due to lower cost in comparison to Rh catalyst to study the effect of space velocity on RWGS activity.

Table 2. Effect of space velocity on CO_2 conversion over Ni/Microlith as a function of temperature and H_2 to CO_2 ratio for the RWGS reactor. The WHSV was varied from 60 to 315 L/[hr g-cat].

Temp (°C)	H_2 to CO_2 Ratio	Weight Hourly Space Velocity (L/[hr g-cat])			
		60	**120**	**180**	**315**
		CO_2 conversion			
300	1.0	34.0	34.9	31.4	33.3
	1.5	43.9	41.3	41.4	40.2
	2.0	52.0	48.9	47.8	46.9
450	1.0	34.6	34.8	35.1	33.7
	1.5	40.9	41.4	40.8	40.8
	2.0	47.2	45.8	46.7	45.4
550	1.0	38.8	39.8	38.5	38.2
	1.5	42.3	44.4	45.5	43.4
	2.0	46.8	49.8	49.7	48.6
650	1.0	48.1	49.9	47.9	45.4
	1.5	53.6	52.7	52.8	51.3
	2.0	55.9	56.3	57.6	54.9
750	1.0	53.8	51.9	51.8	50.6
	1.5	57.8	57.2	59.4	56.8
	2.0	62.2	62.7	64.0	62.5

To study the effect of space velocity, the amount of catalyst was varied to target the desired WHSV for a given feed flow rate. In these tests, the WHSV for the RWGS reaction was varied from 60 to 315 L/[hr g-cat]. Table 2 shows the CO_2 conversion obtained in these tests over Microlith supported Ni catalyst in temperature range of 300-650°C for H_2 to CO_2 ratios of 1.0-2.0. The test results show that CO_2 conversion was nearly independent of space velocity over the studied range. A slight drop in the CO_2 conversion was observed at 300°C for higher H_2 to CO_2 ratios, e.g., the conversion of CO_2 dropped from 52% to ~47% at H_2 to CO_2 ratio of 2.0 as the space velocity was increased from 60 to 315 L/[hr g-cat]. These results indicate that the reaction is kinetically limited at this lower temperature. The observed CH_4 and CO selectivity trends were similar to that shown previously in Fig. 4. High temperature operation (650-750°C) showed low CH_4 selectivity, high CO selectivity, and high CO_2 conversion which were the design objectives for the RWGS reactor. Moreover, the selectivities were nearly constant over the range of WHSV studied, especially at high temperatures, in this testing.

Similar RWGS testing was also completed for Co catalyst supported on Microlith substrate to evaluate the effect of temperature, H_2 to CO_2 ratio and space velocity. In general, no change in the catalyst activity for Co/Microlith was observed as the space velocity was increased from 60 to 315 L/[hr g-cat] at a given temperature and H_2 to CO_2 ratio. CH_4 selectivity was higher at low temperatures while CO selectivity was higher at higher temperatures. Figure 5 compares the CO_2 conversion and CH_4 selectivity observed over Ni/Microlith and Co/Microlith at a H_2 to CO_2 ratio of 2.0. Figure 6 compares the water production rates across the two catalysts.

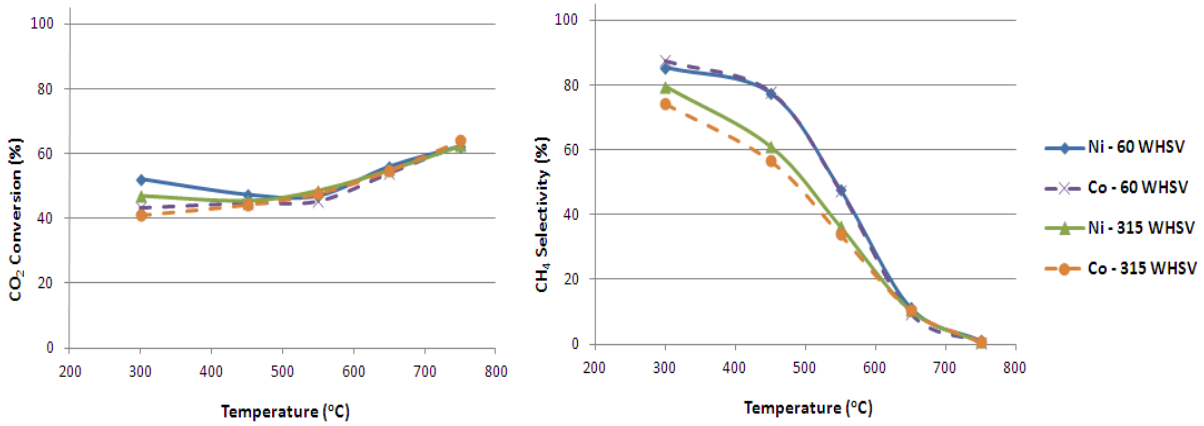

Figure 5. CO_2 conversion and CH_4 selectivity achieved over Ni/Microlith vs. Co/Microlith in a RWGS reactor at H_2 to CO_2 ratio of 2.0

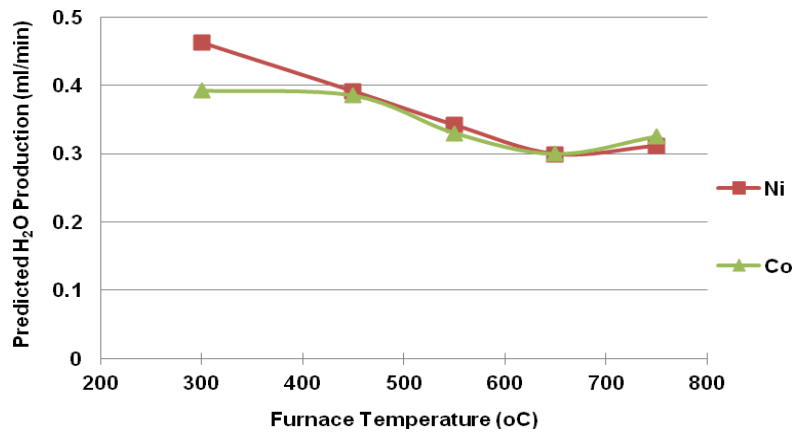

Figure 6. Predicted water production rate for Ni/Microlith and Co/Microlith at H_2 to CO_2 ratio of 2.0 at WHSV of 60 L/[hr g-cat]. The total feed flow rate was 2 SLPM (including 10 mole% N_2).

The data shows that for temperatures <450°C, higher CO_2 conversion was achieved on Ni/Microlith in comparison to Co/Microlith. This could be indicative of higher methanation on Ni catalysts at lower temperatures as compared to Co, i.e., higher CH_4 in the reactor outlet. The drop in the CO_2 conversion for Ni with increase in temperature from 300°C to 450°C also indicates that the increased CO_2 conversion is due to the exothermic activity of the Sabatier reaction at lower temperatures. However at higher temperatures, both catalysts showed near identical performance (i.e, CO_2 conversion and selectivity). Figure 5 shows that CH_4 selectivity at low temperature (<550°C) dropped as the space velocity was increased for both catalysts. Thus operating at even higher space velocities could further decrease the CH_4 formation.

Similar water production rates were also observed over Ni/Microlith and Co/Microlith (except at 300°C) as indicated on Fig. 6. It should be noted that the water production rates were predicted based on mass balance calculations since water was not condensed and collected at the exit of the RWGS reactor. Finally, similar trends (in CO_2 conversion, water production, as well as CO and CH_4 selectivity) were observed for Ni/Microlith vs. Co/Microlith at H_2 to CO_2 ratios of 1.0 and 1.5.

After completing the performance mapping for both Ni and Co catalysts supported on Microlith substrates, durability testing was performed for 70+ hours with multiple start/shutdown cycles to study the long term performance of the said catalysts. The durability testing was carried out at 650°C, a H_2 to CO_2 ratio of 1.0, and a WHSV of 210 L/[hr g-cat]. After every shutdown the catalyst was cooled down to room temperature and ramped up again during start up to the desired operating temperature. Figure 7 shows the results from this durability testing. It can be seen that no degradation in the catalytic activity toward RWGS was observed with multiple thermal cycles. No change in the CO and CH_4 selectivities were observed along with stable CO_2 conversion over the 70+ hour testing.

At temperatures above ~550°C, the experimentally observed CO_2 conversion was in close agreement with those thermodynamically predicted using ASPEN Engineering Suite™ for RWGS reaction. One such example is provided in Table 3 which shows the experimentally observed product distribution and CO_2 conversion over Ni/Microlith and Co/Microlith catalysts at 750°C and a H_2 to CO_2 ratio of 2.0. At temperatures below 550°C, the measured outlet compositions were closer to those predicted for a reactor operating with a mix of RWGS and Sabatier reactions.

In summary, the experimental data obtained for these tests, thus suggests that the RWGS catalysts (both Ni can Co) are capable of achieving equilibrium limited CO_2 conversion with minimum CH_4 formation at high temperatures (650-750°C). Moreover, no loss of performance with increased space velocity indicates the potential for a significantly smaller catalyst bed volume with higher throughput and increased water production. The 70+ hour durability testing showed no performance degradation and is indicative of the longevity of the RWGS catalysts. This test data suggests a reactor volume of ~20 ml (excluding the heat exchanger) is required for a single-pass RWGS operating at a H_2 to CO_2 ratio of 1.0 for a 4-crew unit. Current estimate of the Microlith catalytic substrate for single-pass RWGS required is ~3.6 grams per crew. This, however, is only preliminary single-pass sizing for RWGS reactor since the reactor performance is dependent on the downstream units in the two-staged Bosch system configuration, namely the CO_2 separation unit as well as the CFR. It should also be noted that this study was limited to a space velocity of ~315 L/[hr g-cat] due to rig limitations and that it may be possible to operate at even higher space velocities, further reducing the size/volume of the Microlith-based RWGS reactor whilst achieving close to equilibrium conversion and selectivity. In comparison, testing at NASA facility for RWGS reactor with alternate catalysts (e.g., Co-shavings, Ni-shavings, Ni-foam, shredded steel wool etc.) were operated at a maximum space velocity of ~1-2 L/[hr g-cat] to achieve equilibrium.[12] Thus, the Microlith-based RWGS reactor shows significant size/volume benefits with potential for further improvements.

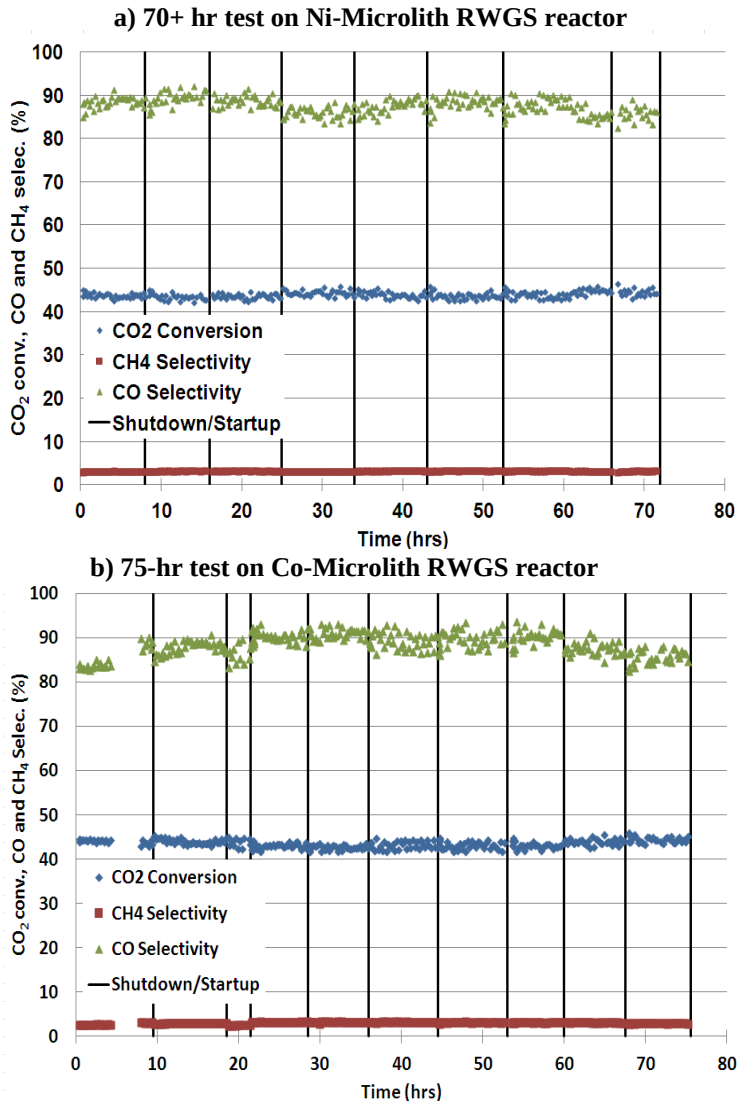

Figure 7. Durability testing for RWGS at a WHSV of 210 L/[hr g-cat] at 650°C and H_2 to CO_2 ratio of 1.0 on (a) Ni/Microlith and (b) Co/Microlith.

Table 3. Comparison of production distribution and CO_2 conversion for RWGS at 750°C at H_2 to CO_2 ratio of 2 predicted by thermodynamic calculations vs. experimentally observed CO_2 conversion and product distribution (mole%, N_2-free wet basis) over Ni/Microlith and Co/Microlith at WHSV of 315 L/[hr g-cat].

	Equilibrium	Ni/Microlith	Co/Microlith
CO_2 conv. (%)	62.4	62.5	64
H_2	45.46	43.94	43.92
H_2O	21.08	22.22	23.12
CO	20.69	21.04	20.64
CO_2	12.58	12.66	12.18
CH_4	0.19	0.14	0.15

(ii) Hydrogenation & Boudouard Testing

The second reactor in the two-stage approach would be the CFR in which the hydrogenation and Boudouard reactions (Eq. 3 and 4, respectively) convert the CO produced in the RWGS reactor to solid carbon. Both of these reactions are exothermic and therefore require heat removal to operate isothermally and achieve greater CO conversion and CO_2 selectivity. The reactor will also need provisions to recycle all of the gaseous products back to the water condenser and CO_2 and/or H_2 separator units. The test rig used in this study did not have any of these provisions and instead was operated adiabatically. Performance may improve beyond the results presented here when the reactor is operated isothermally. This reactor was also only examined under single-pass operation without a recycle. Performance of this reactor was evaluated based on CO conversion, CH_4 and CO_2 selectivity, water production, and carbon formation. All of the testing on this system was performed at a WHSV of 60 L/[hr g-cat] and at H_2 to CO ratios of 0.5, 0.75, and 1.0.

Figure 8 shows a comparison between each of the three catalysts studied at 60 L/[hr g-cat] and at a H_2 to CO ratio of 0.5. Except for the Co/Microlith at 300°C, CO conversion was observed to monotonically decrease as the reactor temperature increased. This behavior was expected due to the exothermic nature of the three reactions occurring within the reactor (hydrogenation, Boudouard, and Sabatier). This trend for CO conversion emphasizes the need for good temperature control so that the reactor can be maintained at lower temperatures to maximize CO conversion. Co/Microlith was found to be severely kinetically limited at 300°C resulting in minimal CO conversion and carbon production and therefore must be operated at slightly higher temperatures limiting its maximum achievable CO conversion. Rh- and Ni-catalysts could also show similar behavior, but at lower temperatures than that of the Co. Further investigation will be required to identify the temperature at which the activity of the Co/Microlith quenches and to determine its maximum achievable conversion. At temperatures of 450°C and above the Ni- and Co/Microlith produced nearly identical CO conversion with no foreseeable advantage based on this performance metric. The Rh/Microlith, on the other hand, was found to produce CO conversions that were at least 10% lower than the other two catalysts at lower temperatures. This difference in conversion increased to ~20% at a H_2 to CO ratio of 0.75 and ~30-40% at a H_2 to CO ratio of 0.5. At 650°C, the CO conversion on the Rh/Microlith approached the values for the Ni- and Co/Microlith, but was still lower by at least 5%. These results indicate that Rh/Microlith is not an optimum catalyst for the second stage of the two-stage Bosch process.

Even though Ni/Microlith and Co/Microlith showed similar CO conversions, the selectivity toward CH_4 and CO_2 was found to vary (Fig. 8(b-c)). Due to the complex nature and multiple reactions occurring in this system, the selectivity data reflects the proportion of the CO converted to either CH_4 or CO_2. Based on Fig. 8(b), it appears that all three catalysts produced about the same proportion of CO_2 from the converted CO. The production rate of CO_2, however, decreased at higher temperatures, as predicted by equilibrium due to decreased overall CO conversion. The constant CO_2 selectivity implies that the extent of CO conversion to CO_2 via Boudouard reaction was independent in the temperature range studied. The Co/Microlith showed poor selectivity at 300°C, however, at higher temperatures the selectivity was nearly identically to the other two catalysts. The extent of the Sabatier reaction for a given catalyst also appeared to be relatively temperature independent as shown in Fig. 8(c). However, the data indicated that the CH_4 selectivity was different for each catalyst. The Sabatier reaction seems to consume at least 20% more of the converted CO on the Rh/Microlith. This is further reflected in Fig. 8(d) where the carbon production rate on Rh/Microlith was significantly lower than the rate on the Ni/Microlith and Co/Microlith. Thus on Rh/Microlith, the CO is being converted to CH_4 via Sabatier rather than to carbon via hydrogenation. Minimizing CH_4 production is critical to avoid net loss of H_2. Any CH_4 produced within the reactor must be recycled through the system and therefore each component of the system must be sized to account for this additional volume. This negatively affects the size and weight of the system and will also require larger, more power intensive compressors and separation units. Co/Microlith, on the other hand, showed minimum CH_4 selectivity in comparison to Ni or Rh catalysts. Thus, Co/Microlith was demonstrated to be optimal choice from a CH_4 selectivity standpoint.

Although water production is not as important in this second stage since majority of the water will be produced by the RWGS reactor, it was another performance metric that was examined. As predicted by equilibrium the water production rates dropped as the temperature was increased suggesting that the forward reactions were occurring to a lesser extent. The Co/Microlith showed highest production rates while Ni/Microlith and Rh/Microlith substrates produced respectively lower amounts. The low water production rates on Rh could be associated to the lower overall CO conversion achieved on Rh/Microlith catalyst in comparison with Co/Microlith and Ni/Microlith. Ni and Co had similar CO conversions and hence the difference in their water production rate was possibly due to the reverse pyrolysis reaction shown in Eq. 7. This not only explains the decreased water production, but it also elucidates the decreased carbon production rate observed on Ni. Therefore the CH_4 present in the outlet for Ni/Microlith is most likely due, at least in part, to the reverse pyrolysis reaction and not just an increase in the Sabatier reaction.

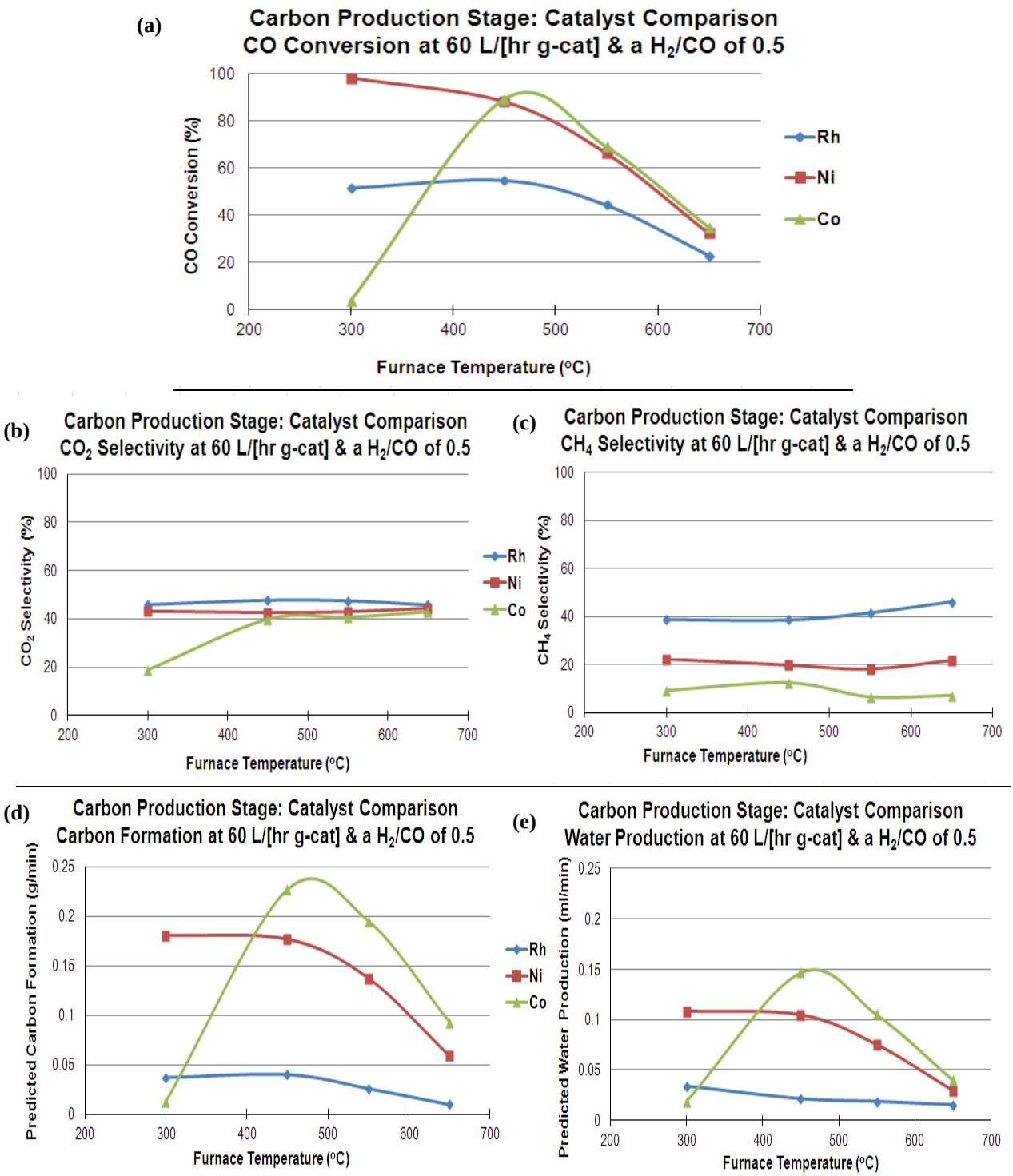

Figure 8. Catalyst comparison in the second, carbon production stage of the two-stage Bosch approach. Performed at a WHSV of 60 L/[hr g-cat] and a H_2/CO of 0.5.

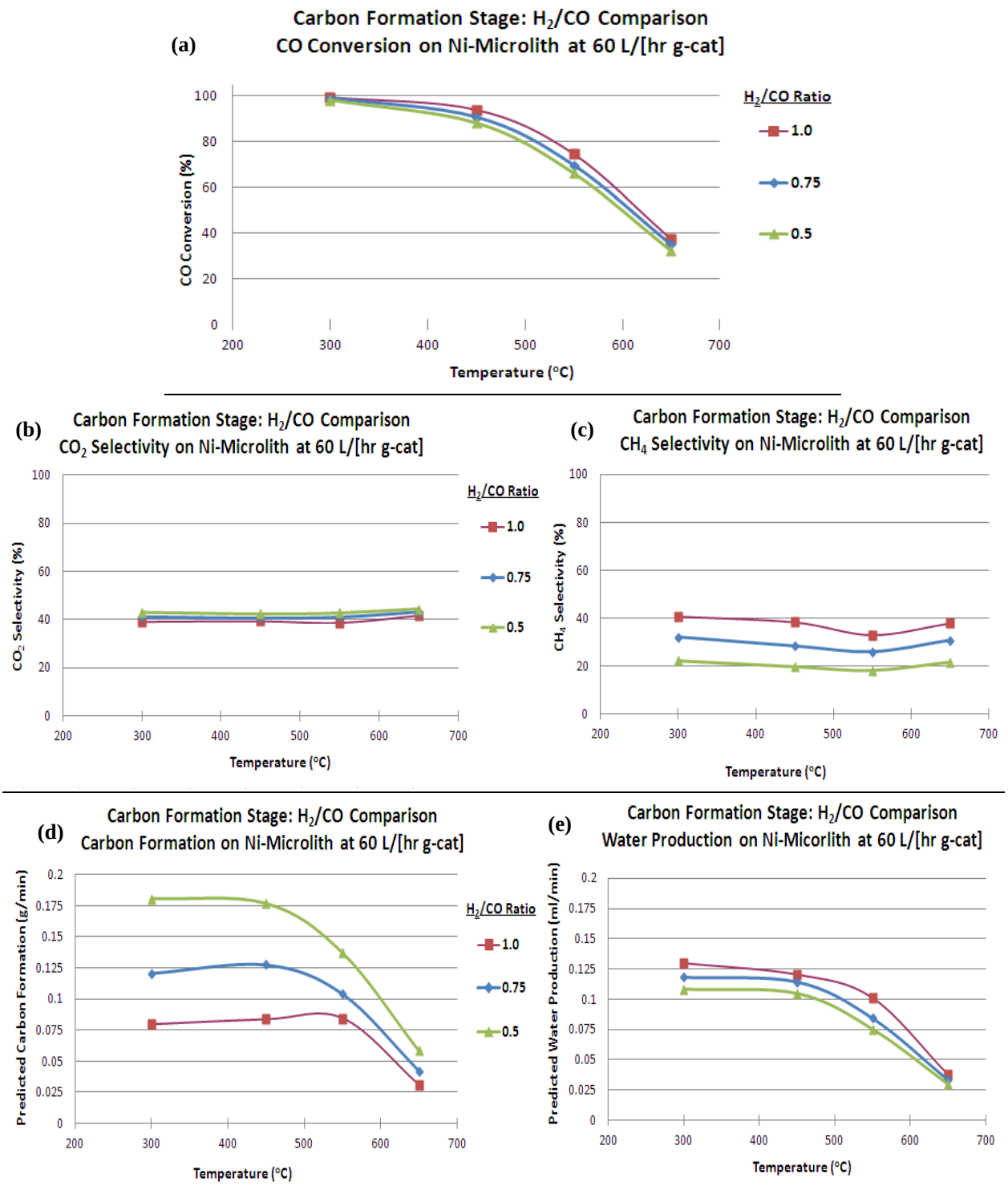

Figure 9. H_2/CO ratio study for Ni/Microlith at a WHSV of 60 L/[hr g-cat]. Rh- and Co/Microlith showed similar trends.

It is, thus, possible that more H_2 was consumed over Ni/Microlith associated with formation of CH_4 via reverse pyrolysis, reducing the carbon formation and water production rate.

In addition to the catalyst study performed on the CFR, the effect of varying the H_2 to CO ratio was also examined. The stoichiometric ratio for the hydrogenation reaction is 1.0, but prior work done by NASA[12] suggested

that operation at lower H_2 to CO ratios is optimal for carbon formation. Thus ratios of 0.5 and 0.75 were also investigated. Data for Ni/Microlith at all three ratios is shown in Fig. 9. Rh- and Co/Microlith showed similar trends.

CO conversion was found to marginally decrease as the H_2 to CO ratio was lowered due to the presence of less H_2 in the feed. This trend was more pronounced for the Rh/Microlith where the CO conversion dropped from ~98% to 51% at 300°C and 32% to 23% at 650°C. Operating at higher H_2 to CO ratios would increase the CO conversion, but at the expense of more CH_4 production because the Sabatier and reverse pyrolysis reactions would be favored. CO_2 selectivity and therefore the extent of the Boudouard reaction was found to be relatively independent of H_2 to CO ratio. CH_4 selectivity as expected increased at higher H_2 to CO ratios as higher the partial pressure of H_2 in the feed higher would be the proclivity toward Sabatier and reverse pyrolysis reactions.

Predicted carbon and water formation rates are shown in Fig.s 9(d-e). As the H_2 to CO ratio was decreased, carbon formation increased despite the relatively constant CO_2 selectivity and slightly decreasing CO conversion. These two observation provide support to the hypothesis that the carbon formation reactions are competing with the reverse pyrolysis reaction. The rate of reverse pyrolysis can thus be hindered by limiting the amount of H_2 in the feed in turn favoring the carbon formation rate. This is concurrent with NASA's findings that operating the carbon formation reactor in H_2 lean environment is favorable for carbon formation.[12] The slight decrease in water production shown in Fig. 9(e) is most likely due to the decrease in the hydrogenation and Sabatier reactions due to the decreased partial pressure of H_2 in the feed. This is not much of a concern for the two-stage system because the second stage is designed and optimized for carbon production while the first stage is optimized for water production.

In comparison to the traditional steel wool catalyst which has been reported to achieve 46% CO conversion at 500°C,[12] the optimum catalyst identified in this study, namely the Co/Microlith was able to achieve CO conversions of 87.0% and 75.4% at 550°C and 450°C, respectively at a H_2 to CO ratio of 1.0. Even though the Co/Microlith showed improved CO conversion, the CH_4 selectivity was poor in comparison to the steel wool catalyst. The CH_4 selectivity for Co/Microlith at H_2 to CO ratio of 1.0 and operating temperature of 550°C and 450°C was 20.9% and 15.9%, respectively, while that for steel wool was as low as 12% at 500°C.[12] Further testing for the Co/Microlith would be needed to ascertain improvements, if any, toward CH_4 selectivity. It should, however be noted that the catalysts tested in this study were able to achieve higher space velocity than that has been reported with the traditional steel wool catalysts.[12] Moreover, potential exists for operating the CFR at space velocity higher than those reported in this study, subject to experimental validation, to provide further size/weight and volume benefits over traditional carbon formation catalysts and reduce the size/volume of the expendable cartridges.

IV. Conclusion

This paper demonstrates the benefit of the Microlith catalytic substrates for an efficient Bosch reactor system. The properties of short contact time kinetics, high heat transfer, and high surface area of catalyst active sites enable significant size/volume/weight benefits as compared to the current systems. This proof-of-concept study also demonstrates potential benefits of a staged Bosch process over the conventional single-stage Bosch reactor design. A single stage Bosch reactor is typically operated as WHSV of 1-30 L/(hr g-cat) with low single-pass conversion (10-15%) and high recycle ratio (~14-18).[11] Splitting the reaction chemistry in two stages provides significant improvement over a conventional single stage Bosch reactor. This allows effective optimization (for temperature, size and selectivity) of each process allowing maximum system efficiency, maximum carbon and water production as well as dramatic reduction in overall reactor.

Microlith-based RWGS has demonstrated potential to be highly compact, durable, efficient and lightweight for converting CO_2 to CO in stage one of the two-stage Bosch process. Moreover, no loss of performance at increased space velocities (up to WHSV of 315 L/(hr g-cat)) indicates the potential for a significantly smaller catalyst bed volume with higher throughput and increased water production. Subject to further testing, the RWGS is projected to be ultra-compact, capable of being operated at even higher space velocities and being close to equilibrium. The 70+ hour durability testing showed no performance degradation and is indicative of the longevity of the RWGS catalysts. The RWGS reactor was demonstrated to achieve equilibrium limited conversions (~62% at 750°C) at high throughputs. Based on these test results, an approximately 20 ml reactor (excluding the heat exchanger) would be required for a single-pass RWGS for a 4-crew unit. This paper also investigated the CFR based on Microlith catalysts. Co/Microlith was identified as the optimum candidate owing to high CO conversion, relatively low methane selectivity, and high water and carbon production rates. The test results suggest that a single-pass CFR would be approximately ~54 ml reactor (excluding the heat exchanger), sized for the amount of CO generated in stage one. These are, however, preliminary single-pass estimations. When operated under recycle conditions the reactor volume for both the reactors could increase. Further reactor size/volume optimization is subject to testing the two stages under recycle mode.

This paper has laid a compelling technical foundation for a two-stage, Microlith-based Bosch reactor system Future work includes developing a 4-crew scale RWGS and CFR with an optimized design including efficient heat management. Catalyst formulations for the RWGS and CFR reactor will be further optimized for even higher space velocity operation.

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