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The RMR technology has the potential to have a transformational reduction in cost and size of steam reforming natural gas for a wide variety of application from distributed energy production, to efficient H2 generation at home, the H2 fueling station and fuel for SOFCs. Also a significant reduction in flaring gas, the cost and size of GTL process on land and at sea will reduce CO2 emission and enable cost reductions in the generation of energy in many small market economies.

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Final Report

Power & Energy, Inc.

Reporting on

Contract N00014-11-C-0194

Technical Report BAA III, Period Ending, 2013.03.31

Principle Investigator: Peter R. Bossard, Ph.D.

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Summary

1) Supported Hydrogen Permeable Membrane

Currently there are no commercially available substrates that have a uniform porosity at the one micron level or that have low enough build-in stress levels. So, additional layers have to be deposited on the surface for a selective hydrogen permeable membrane that is stable when in operation. The lack of uniform porosity in the substrates at a scale of 1 micron results in a high percent of the membrane being blocked which significantly reduces the effective surface area of the deposited Pd alloy. Besides this, the addition of an adequate graded porous alumina layer as an after treatment resulted in a significant additional pressure drop that reduced the gas flow. We were unable to obtain porous substrates made from alloys that have the ability to grow whisker type Al_2O_3 that would both support and reduce the blockage effect between the porous substrate and the hydrogen permeable layer. We believe that the data taken over the course of this contract indicate strongly that there are no porous substrates commercially available that are suitable for depositing a stable thin and highly hydrogen permeable layer.

2) P&E's MFMR Integration with PCI Steam Reformer

The PCI Steam Reformer, operated at 11 Bar of reformate pressure, generated initially a reformate containing 33.2% hydrogen and achieved a carbon conversion efficiency of 72.7%, as measured from the reformate gas stream's carbon containing species composition. The total flow of such species was 14.1 SLPM. The rate hydrogen was recovered using the MFMR was measured to be 16 SLPM which is in agreement with the MFMR simulator. The final measurements on the use of the MFMR were made at the end of a 250 hour test of the Steam Reformer. The rate of hydrogen production at that time was measured at 16.8 SLPM which is 5% greater than the initial measurements and was due principally to a lowering of the outlet hydrogen pressure by 5 psi. The MRMR functioned as predicted in both tests. Near the end of the 250 hours of operation the measured carbon conversion efficiency was 68.4% as was determined from the reformate gas stream's carbon containing species composition. The total flow of these carbon species was 14.8 SLPM.

3) P&E's Radial Microchannel Reactor, (RMR) used in CH4 Steam Reforming

The RMR was operated over a of three week period. Over the range of flow rates tested, the CH4 conversion was consistently 90% with a hydrogen production of 73%. The power entered into the endothermic reaction of methane and steam is greater than 2MW per kg of catalyst.

The RMR was presented Oct 2012 at the AIChE conference in Pittsburg and March 2013 at NASCRE-3 in Houston and was well received. The AIChE presentation resulted in an invitation to contribute an article on process intensification in a DOE initiated dedicated issue of the journal 'Energy & Fuels'. This article represents work done under this contract and was jointly written by Dr Wilhite of TAMU and the staff at P&E. The paper scored good for originality in the peer-review process and is currently completed and accepted. A preprint will be available in the 2nd quarter of 2013.

This manuscript represents a first published report on the Radial Microchannel Reactor (RMR) architecture and reports the achieved breakthroughs in heat transfer and thermal efficiency in the catalytic steam reforming of methane into synthesis gas. Synthesis gas is used in the production of hydrogen, in GTL and other chemical processes.

Steam reforming in an RMR was studied separate from an external combustion by passing a precisely measurable electrical heat flow through a reactor wall maintained at a well determined temperature. The unique absence of thermal cross talk and scalability of the RMR design makes the results of such study immediately applicable to large parallel systems. The tube shape allows for precise measurement of the reaction dynamics as the process gas travels along the microchannel which is the space in the annulus between the tube in tube architecture. When these results are scaled up to the number of RMR channels that would be placed in an 8 inch diameter 2 ft long pipe, the hydrogen production would be about 1000 kg/day which is equal to 500 NM3/hr or 7800 SLPM. The reforming catalyst required for this system is approximately 0.2kg. The metal to metal sealing required is a small fraction of the metal to metal sealing required for any other type of steam reformer systems. The thermal stress is low and the pressure rating is high because only small diameter tubes see high pressure at operating temperatures of 750 °C or less.

Computational fluid dynamic (CFD) simulations being done by Dr. Wilhite at TMAU on the RMR design have shown the ability to predicting methane steam reformer performance of the RMR channel. Subsequently the dimensional analysis for rapidly optimizing the various physical parameters will be greatly enhanced and a focusing of experimental and production activity is expected.

This technology has the potential to have a transformational reduction in cost and size of steam reforming natural gas for a wide variety of application from distributed energy production, to efficient H_2 generation at home or the H_2 fueling station. Also a significant reduction in flaring gas, the cost and size of GTL process on land and at sea will reduce CO2 emission and enable cost reductions in the generation of energy in many small market economies.

4) Outlook for Supported Hydrogen Permeable Membrane

The appropriate substrate is the key to unlocking the benefits derived from a low cost, highly selective hydrogen permeable membrane that can operate over a wide variety of pressures and temperatures. We think that a uniformly porous substrate needs to be manufactured starting with a narrow size distribution of spherical 1 micron particles made of a AlFeCr type super alloy. From these particles a tube of approximately 2mm OD, 0.8mm ID needs to be extruded. A well designed extruding process is necessary to improve porosity, uniformity and stress reduction. A key property of this type of tubular alloy is that when properly heated in an oxidizing environment it will grow a whisker form of Al_2O_3 directly from the AlFeCr alloy. This substrate can be coated with a thin Pd alloy because the contact area with the long (50nm – 100nm), thin ceramic whiskers is small. Using such stable base with relativity low contact area would leave significant surface available for H-H recombination on the Pd alloy. The open space between the whiskers allows lateral diffusion of the hydrogen, enabling it to reach open pores efficiently.

Starting with a uniformly porous AlFeCr tubular substrate, as described above, would enable the rapid development of the desired low cost, highly selective hydrogen permeable membrane suitable for a wide variety of process applications.

5) **P&E MFMR Integration with PCI steam reformer**

Initial test the system with MFMR connected to the reformate output of the steam reformer was operated at 11 bar (in test 1 and 2) of reformate pressure and a UPH of 6.1 psig in test 1, resulting in 153.4psi across the hydrogen separation membrane and nominally operated at 380C. The partial pressure of the hydrogen in the reformate stream as it entered the Pd cell was 68.2psi and the pressure on the low pressure side of the Pd membrane was held at 6.1psig. This gives an initial differential pressure of 47.4psi between the partial pressure of hydrogen in the reformate stream and the pressure of hydrogen on the low pressure side of the Pd membrane.

Table 1

	Reformate composition (mole%, dry basis)	Reformate composition (mole%, wet basis)	Reformate flow rate (SLPM)	Raffinate composition (mole%, dry basis)
H_2	60.99	34	22	30.22
CH_4	10.64	5.93	3.84	20.33
CO	9.91	5.52	3.57	17.71
CO_2	18.46	10.29	6.66	31.74
H_2O	-	44.25	28.63	-

Table 1: PCI data on the run at the start of the test period.

PCI calculated hydrogen separation efficiency of 74% with 16 slpm UPH flow.
Calculating the Fuel Conversion Efficiency from the GC data gives 73%, using:

100*(1 – CH4%/(CH4% + CO% + CO2%))

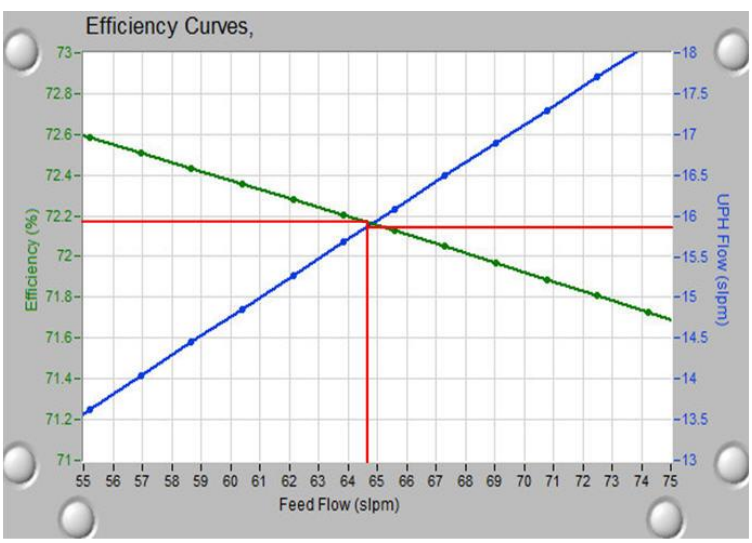

Figure 1: P&E expected UPH flow from the reformate composition, flow and operating pressure 15.9 slpm hydrogen.

After approximately 250 hours of operation the above experiment was repeated with the modification that the UPH pressure was reduce from 6.1psig to 1 psig.

Table 2

	Reformate composition (mole%, dry basis)	Reformate composition (mole%, wet basis)	Reformate flow rate (SLPM)	Raffinate composition (mole%, dry basis)	Raffinate flow rate (SLPM, dry basis)
H_2	56.18	32.5	21.57	22.06	4.82
CH_4	12.21	7.07	4.69	21.69	4.74
CO	8.06	4.66	3.09	15.57	3.4
CO_2	18.34	10.61	7.04	31.52	6.89
N_2	5.21	3.01	2.0	9.15	2.0
H_2O	-	42.15	27.97	-	-

Table 2: PCI data at the end of the test period (250 hrs).

The UPH flow calculated from Table 2, is 16.8slpm this is approximately the increase that would be expected by lowering the UPH pressure from 6.1psig to 1psig. The 2slpm of N_2 in Table 2 lowers the operating partial pressures of the reactive gases by 3% effectively.

Separation efficiency 100*(slpm H_2 ref – slpm H2 raf) / slpm H_2 ref or 77.6%

Fuel conversion efficiency 100*(1 – CH4%/(CH4% + CO% + CO2%)) equal to 68%

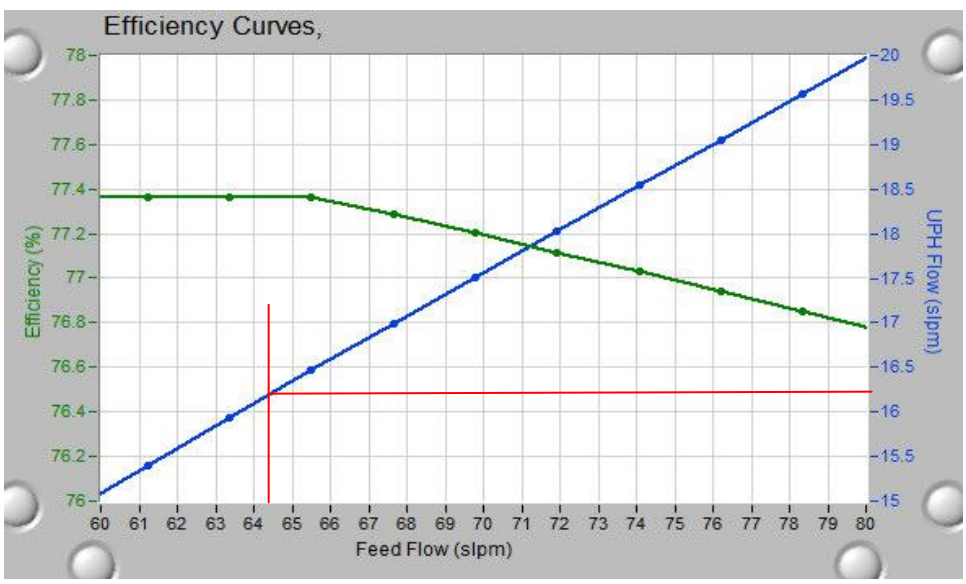

Figure 3: P&E simulated spec. final test point.

The P&E simulator calculates 16.2 slpm of separated hydrogen and a 77.4% separation efficiency for the given pressures and composition.

Results:

Measured/simulated	UPH [slpm]	Fuel conversion eff. %
Initial test	16/15.9	73
Final test	16.7/16.2	68

The measured PCI data and the simulated P&E data are in good agreement for both the initial run and the run near the end of the test period. The 6% decrease in carbon conversion efficiency during the test period needs further investigating.

6) P&E's Radial Microchannel Reactor (RMR), for Steam Reforming CH4

P&E constructed a test setup for more efficiently testing the RMR design. The previous test results were obtained using a 700 micron gap and the current tests are using a 300 micron gap in the annulus between the tubes in the RMR. Experiments were performed with Catacel catalyst that is a Ni based with an Al_2O_3 slurry, loaded with ~1% Rh.

The model simulation that was done by Dr Wilhite and reported on previously indicated that a narrow gap for the microchannel may improve mass transport because the 700 micron gap at space velocities exceeding 100,000/hr may start to introduce mass transport limiting effects.

A presentation of initial results was given October 30 2012 at the AICHE annual meeting which resulted in an invitation to write a paper to appear in a DOE NETL in a dedicated issue on the topic "Accelerating Fossil Energy Technology Development through Integrated Computation and Experimentation". This paper has been accepted for publication, with revisions for clarity. Preprints will be available in the 2nd Qt in 2013 and will be distributed to our contacts at ONR who was the main source of funding for this project. It describes the bulk of the results together with Comsol modeling done at TAMU during this contract.

The latest experimental results are presented in this report using a smaller 300 micron microchannel and achieve the higher performance anticipated by the Comsol modeling and simulations. Additionally, the new test setup measures the gas composition which will allow P&E to distinguish the reforming reaction from WGS contributions and to refine future simulation. Results show space velocities significantly greater than 100,000 /hr and reactions that are close to equilibrium. It indicates that a high efficiency small reactor could be built that uses a small amount of catalyst and has a small foot print. These traits indicate that compact and efficient reforming of biofuels to generate syngas could significantly enhance the performance and reduce cost of CHP systems based on SOFC.

The experiments, results and conclusion on the 300 micron gap Radial Microchannel Reactor, RMR, are discussed below.

Experiment Description

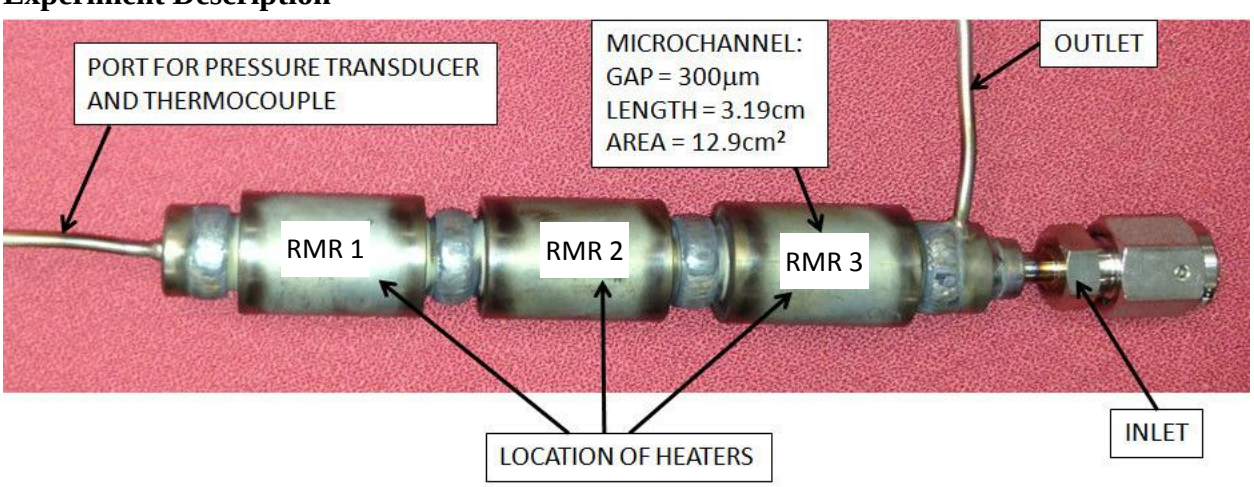

Figure 1: Three RMR channels in series and locations for independently controlled heaters.

The fluid and heat flows in the RMR 1 segment are shown in figure 2. The fuel and steam mixture passing through the center tube reverse direct as soon as it passes RMR 1 and now flows in the opposite direct in the annulus and in close contact with the catalyst represented by the blue line in figure 2. The length of the catalyst is 1.25 inches. Precision programmable DC power supplies are use to control each RMR segment and hold it at constant temperature while the reforming reaction is taking place on inner surface, blue line. The power required indicates the level the reforming reaction is occurring.

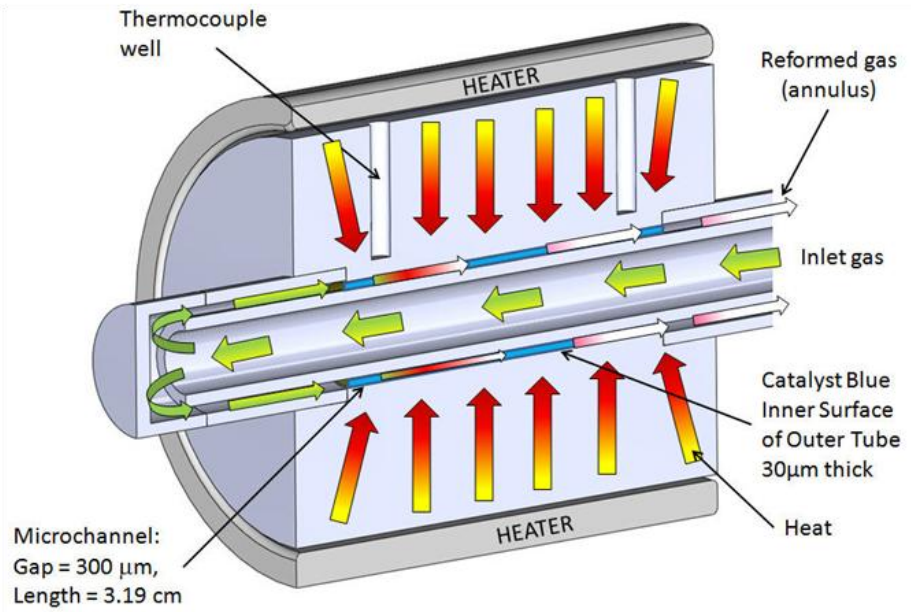

Figure 2: RMR Design shown fluid flow, electrical heater and TC locations

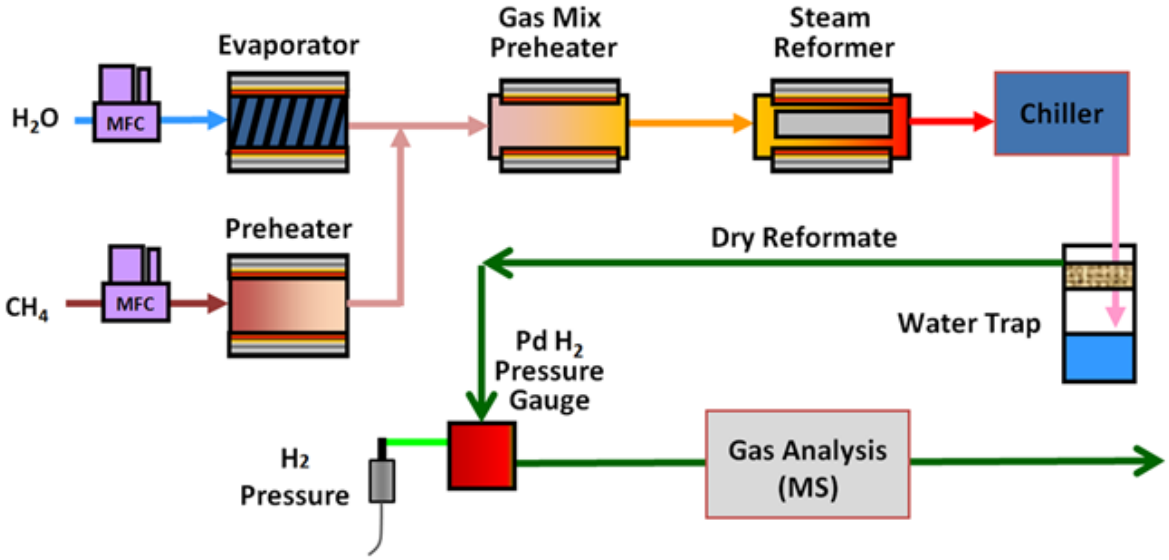

Figure 3: Experimental Test Bench

A schematic representation of the experimental setup and the analytical equipment is given in figure 3. Measuring the hydrogen partial pressure in the reformate stream is done with a Pd probe and does not require that hydrogen be removed from the reformate strea.

Measurement Results

Results are given for methane steam reforming for various flow rates at 750 °C and a 3.3:1 steam to carbon ratio. Heat transfer in terms of W/cm2 through the reactor wall are shown in figure 4 for the three reactor segments which shows that for the flow rates investigated the bulk of the heat transfer takes place in the first segment RMR 1.

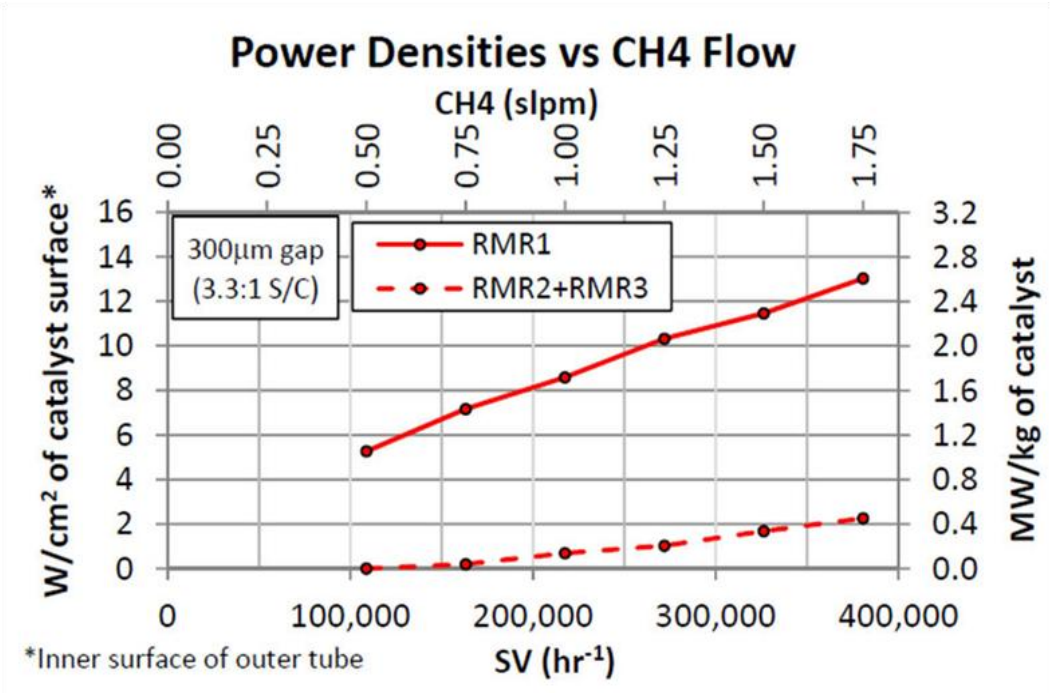

Figure 4: Power densities in the reactor segments

Limitations with the steam evaporator prevented the experiment from making steam flows larger than about 6 slpm. Figure 5 shows the obtained partial pressure of hydrogen in dry raffinate for various flow rates of methane representing a stable 73 percent of the composition.

In figure 4, it is seen that most of the reforming reaction occurs in RMR 1, up until the space velocity exceeds 200,000/hr. The space velocity is calculated using the sum of the lengths of the catalyst on the inner surface of the outer tube. If the experiment was setup without RMR channels 2 and 3 the space velocity for RMR channel 1 would start at over 200,000/hr and terminate at 1,140,000/hr.

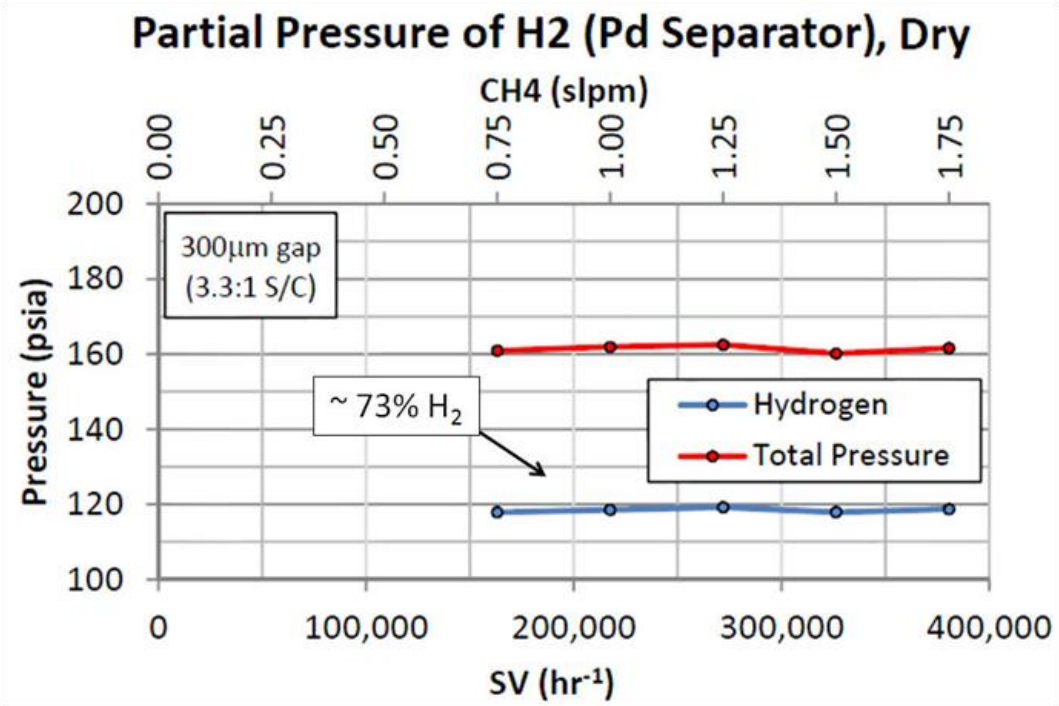

Figure 5: Partial pressure of hydrogen in the dry raffinate.

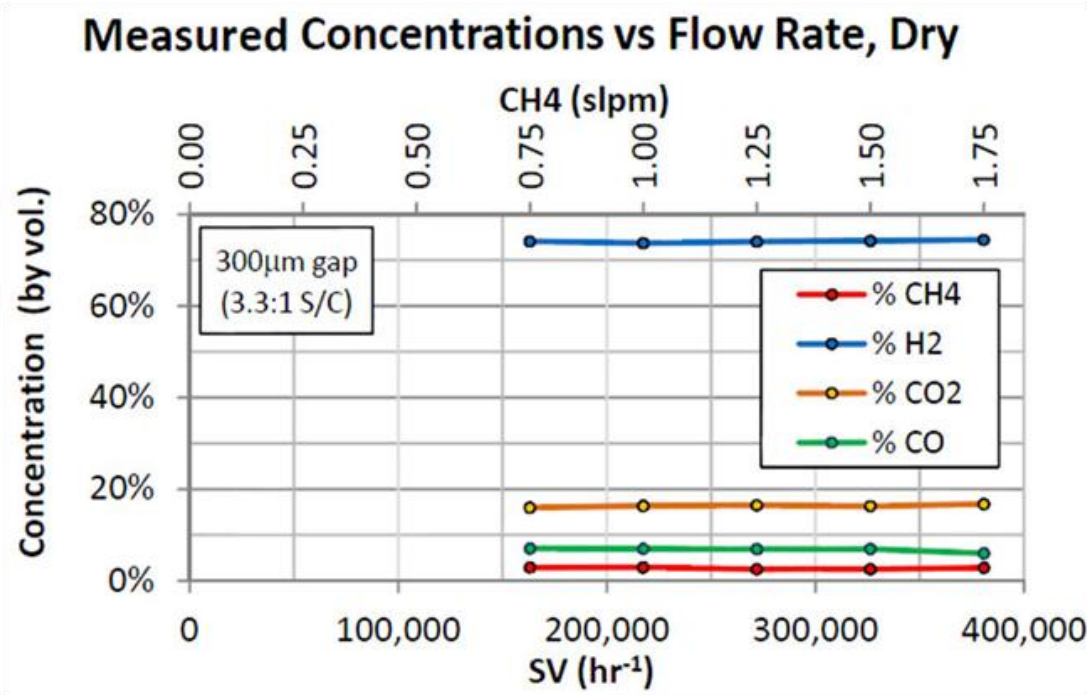

Figure 6: Composition of the dry raffinate.

The composition of the carbon containing molecules shown in figure 6, allows calculating the methane conversion in a standard manner as:

CH4 Conversion = 1 - CH4 / (CH4 + CO2 + CO)

Results are shown in figure 7 & 8 showing a constant 90% methane conversion and linearly increasing functions of the methane flowrate for the net power into the reactor and the rates of produced hydrogen & converted methane.

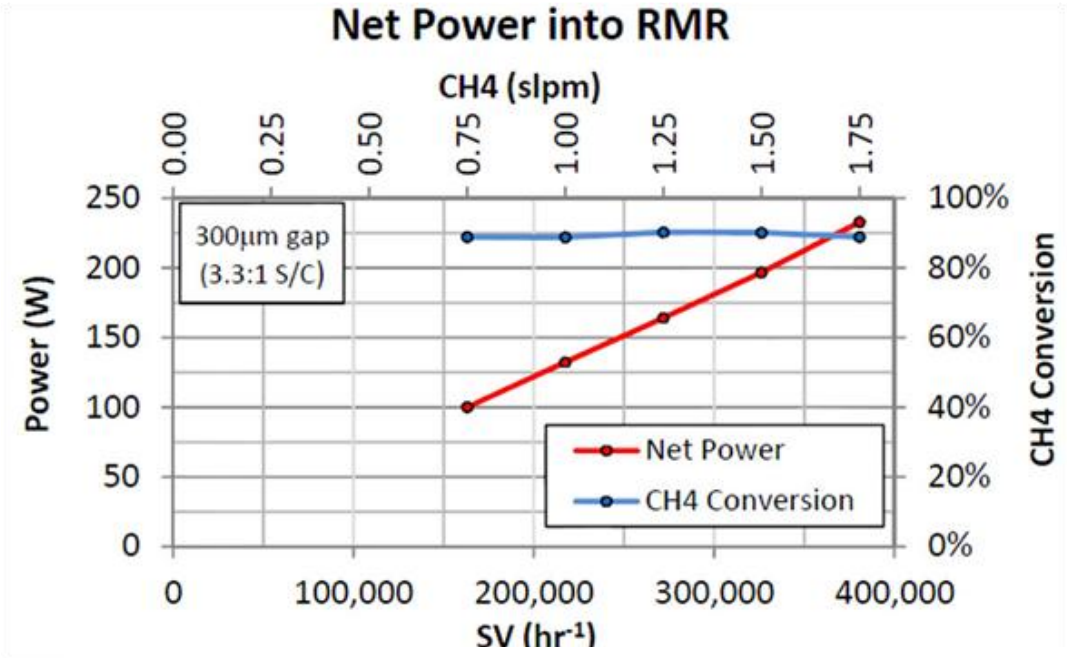

Figure 7, Converted methane percentage and net power into the RMR channels function of the methane flow rate.

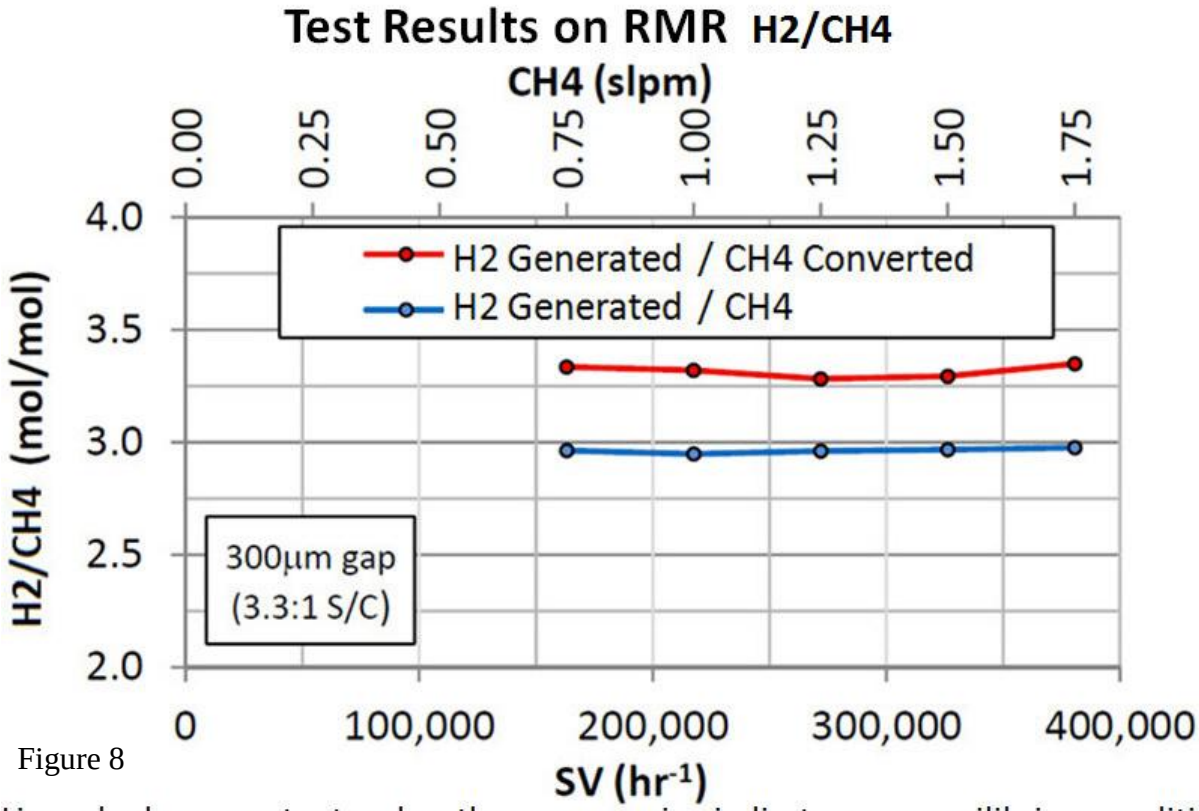

Figure 8

Linear hydrogen output and methane conversion indicates near equilibrium conditions

As a comparison with the previous 700 micron gap measurements at 3:1 S/C, the achieved power densities for the two gap distances are shown in figure 9. Noteworthy is that the 700 micron curve already starts to flatten at space velocities where the 300 micron still is linear.

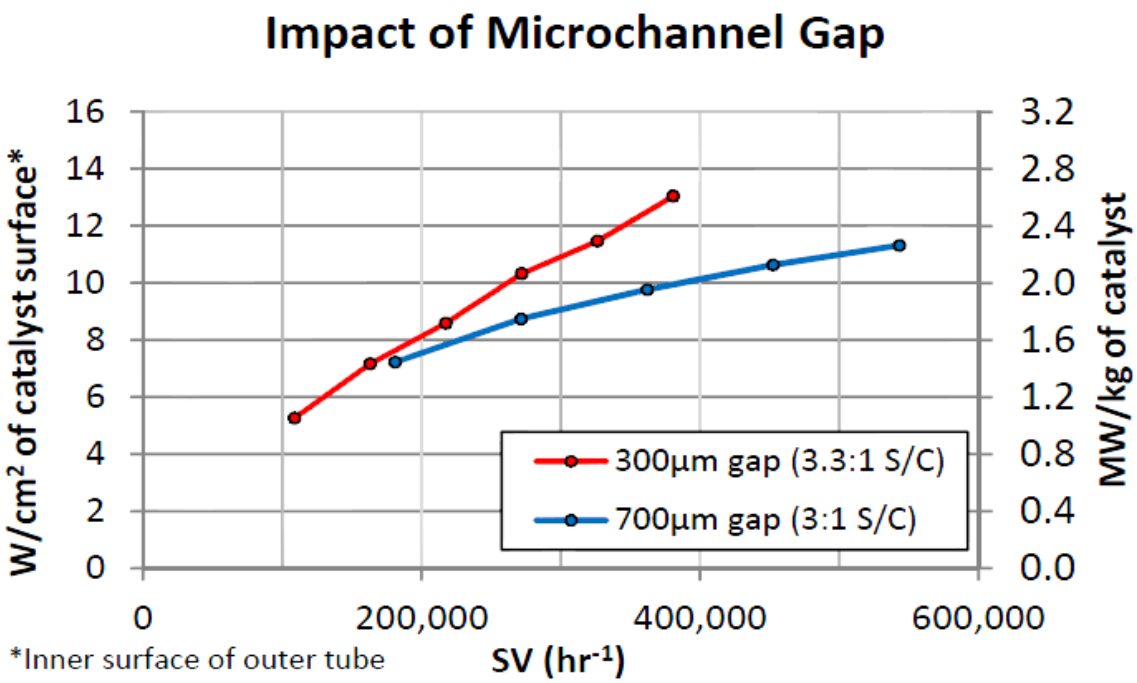

Figure 9: Comparison of measured heat flux for two RMR gap distances.

Discussion

The calculated equilibrium distribution of a 3.3:1 steam-methane mixture at 750 °C and 11 bar is:

H_2 45.8%, H_2O 36.99%, CO 6.365%, CO_2 6.681% and CH_4 4.14%

Barring any coking, this comes down to an equilibrium composition in the dry raffinate of 72.7% H2, 10.1% CO, 10.6% CO2 and 6.6% CH4.

These equilibrium values are very close to measurement results such as the 73 % hydrogen in dry raffinate shown in figure 5 and the CO, CO2 & CH4 percentages in figure 6. This, and the linearity shown in the various figures show that the 300 micron gap system achieved an equilibrium distribution over the measured fuel flow range. Consequently, it achieved maximum conversion and catalyst used at least up to the highest measured flow rate. To put these results in perspective, based on the obtained numbers, a projected performance of a system with a volume less than 1 ft3 system is shown in figure 10.

Parameter	Value
Number of RMR channels	1600
Envelope dimensions	8.63" OD x 20" L (~ 0.68 ft^3)
Total reforming catalyst area	31,800 cm^2 , Length ~ 25cm
Estimated mass	< 100 kg, Adequate open space between RMRs for air and fuel ignition and smooth transition to catalytic combustion
Endothermic power transferred	300 kW
Hydrogen output (@90% CH_4 conv.)	500 Nm^3/hr , ~ 1,000 kg/day
Total catalyst content	< 0.2 kg

Figure 10: RMR parameters and projected performance example.

The simulations performed at TAMU based on the experimental results obtained on the 700 micron RMR measurements did forecast a 20 – 100% improvement in volume heat flux for a 300 micron gap. Though obtained at different s/c ratios, the experimental results shown in figure 9 seem to confirm this predicted trend illustrating the value of such simulations for further RMR development.

The Pd membrane partial pressure hydrogen gauge used in this experiment proved highly valuable. This technique is non intrusive and in steady state operation does require taking hydrogen gas out of the reformate stream. In a transient condition only a small amount of hydrogen is taken out of, or put, in the reformate stream, depending on whether the partial pressure of the H_2 in the reformate stream is increasing or decreasing. A measured value for the power absorbed in the reaction and the partial pressure of hydrogen determine the extent of the two chemical reactions involved, the methane steam reforming and the water gas shift.

Conclusions

The present work investigates a radial microchannel reactor (RMR) system for achieving breakthroughs in heat utilization and thermal efficiency in steam reforming of methane. An experimental analysis of a prototype RMR system capable of isolating microreactor heat consumption by catalytic reaction indicates significant improvements in volumetric heat fluxes over existing planar microreactor designs are achievable using this radial architecture. A comparison of system geometry between the RMR prototype and an industrial planar microreactor illustrates a 1000-fold reduction in sealing requirements for the RMR architecture. Computational fluid dynamic (CFD) simulations of the RMR prototype are shown capable of predicting qualitative and quantitative trends in steam reformer performance, providing an invaluable design tool for rapidly evaluating changes in RMR design. Simulations over a range of RMR geometries indicated a significant improvement in volumetric heat fluxes for a reduced channel widths from 0.700mm to 0.300mm which was confirmed by experiments. These improvements correspond to 200 – 400% improvements in heat transport rates in the RMR architecture, as compared to planar microreactor designs. The resulting design tool is expected to facilitate the design and analysis of next-generation RMR systems integrating catalytic steam reforming of methane with catalytic methane combustion for autothermal hydrogen and/or synthesis gas in support of the petrochemical and natural gas industries.

The large space velocity and the near equilibrium reached by the reaction indicates' that the chemical reaction are very fast and that in typical S.R. reformers the catalyst is starved for energy and the principle issue is the distance and medium separating the heat source and the reforming reaction. The RMR technology is nearly stress free, can easily handle the required pressures, is scalable from small to large capacities in a much smaller foot print and lower cost manufacture process. The RMR technology greatly reduces if not eliminating the heat transport as a limiting factor when operating at temperatures of 750C. The process can be extended to handle diesel and biofuels for a compact and low cost method of generating syngas for SOFC and other processes that require low cost and a small foot print.

Report End.