Progress on the Development of a Microchannel Steam Reformer for Automotive Applications

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Abstract

A compact, energy efficient steam reforming system for automotive applications has been under development at the Pacific Northwest National Laboratory. At the IMRET 5 conference, results were presented describing the operation of a thermally integrated, energy efficient, compact, microchannel steam reforming system capable of converting a liquid hydrocarbon fuel (isooctane) into a reformate stream sufficient for a PEM fuel cell with >10 kWe capacity (Whyatt et al., 2001). Since this demonstration, the project has focused on performing testing in smaller scale steam reforming reactors to further reduce the reforming reactor volume, demonstrate fuel flexibility and address other issues. A test stand, nominally 1/20th the scale of the previous steam reforming demonstration, was constructed and smaller scale reactors have been used in testing. Significant gains have been made with respect to increasing the volumetric productivity of the reactor, suggesting that the 10 kWe reactor could now be made considerably smaller than the previous prototype. In addition the reformer has been demonstrated on a variety of fuels including methane, methanol, ethanol, propane, butane, isooctane, and a benchmark fuel mix intended to simulate a sulfur-free gasoline. The development effort is being funded by the U.S. Department of Energy's Office of Transportation Technology.

Introduction

A fuel cell powered car provides the potential of greater fuel efficiency and less pollution compared to conventional internal combustion engines. On-board reforming would allow fuel to be stored as a liquid and then processed as needed to produce a hydrogen-rich gas stream suitable for consumption by a fuel cell. Conventional technology for hydrocarbon steam reforming experiences heat transfer limitations resulting in long residence times and large equipment. As a result, most automotive fuel reforming efforts have targeted partial oxidation (POX) and autothermal (ATR) reforming approaches that provide the heat by injecting air along with the reactants. However, steam reforming offers several potential advantages over the POX or ATR approaches, including

1) The hydrogen content in the reformate stream is higher because it is not diluted by nitrogen.
2) High reformate pressures can be efficiently generated by pumping liquid fuel and water as liquids without the need to compress air to the reaction pressure.
3) Steam reforming can combust waste anode gas as fuel to provide the necessary heat input, allowing it to be more efficient. POX and ATR, which are thermally neutral or exothermic, cannot use the waste anode gas in this way.

In May 1999, PNNL successfully demonstrated rapid kinetics for steam reforming in heated microchannels. Based on this observation, a microchannel steam reforming reactor was designed and built capable of providing sufficient reformate to power a PEM fuel cell in the 10 - 20 kWe range. This reactor was

coupled with a network of microchannel heat exchangers that allowed the reformer to operate in an energy efficient manner (Whyatt, et al. 2001). After this demonstration work proceeded to improve the reforming reactor as well as to develop water-gas shift (WGS) and preferential oxidation (PROX) reactors to allow integration of the steam reformer into a fuel processor capable of providing reformate suitable for a PEM fuel cell. The work on WGS and PROX will be presented elsewhere. The current paper focuses on the work performed on the continued development of the steam-reforming reactor itself. A smaller-scale test stand including microchannel reactors and heat exchangers was constructed to allow greater flexibility for testing. Improvements in the reactor performance have been achieved due to design changes, which improved the uniformity of flow distribution within the reactor, as well as due to a significant improvement in the reforming catalyst. The various test reactors will be referred to by their core volume, which includes the heat transfer and steam reforming channels and channel walls as well as the metal needed to seal the channels during diffusion bonding. However, this excludes internal flow distribution headers and the metal enclosing the headers. For clarity, Table 1 provides the core volume and reactor name along with the total reactor volume and the catalyst used in that reactor. This paper will provide results on the improved reformer performance as well as data on the fuel flexibility of the steam reformer.

Table 1. Reactor Names and Critical Values

Reactor Core Volume (assigned name)	Total Volume of Reactor (including headers)	Catalyst Formulation[a] Used in Reactor
2400 cm^3 (2.4 liter)	4900 cm^3	A only
51 cm^3 (51cc)	107 cm^3	Primarily B [b]
26 cm^3 (26cc)	68 cm^3	B only

(a) Development of the catalysts was funded by Battelle Memorial Institute (BMI) and the catalysts are proprietary to BMI. Because the specifics of the catalysts cannot be discussed they will be referred to as "A" for the previous catalyst and "B" for the improved catalyst.

(b) The data presented for the 51cc reactor is obtained using catalyst "B". The only exception is in Table 6 where data using catalyst A in the 51cc reactor is provided in order to compare performance between A and B when reforming benchmark fuel.

Experimental Test Stand and Hardware

The experimental test stand was designed to allow testing of reforming reactors with processing rates in the 50 We to 1000 We range[1]. The network of microchannel heat exchangers provides for vaporization of water and fuel, recuperation of reformate to preheat reactants and for preheating of combustion air using the combustion exhaust. The heat exchangers were fabricated as individual components and then connected via tubing rather than integrating into multi-stream exchangers as was done in the 2.4 liter reactor system. This results in a larger overall volume being occupied, which increases heat losses in the smaller scale test stand. Also, the combustion was configured in a single stage rather than in four stages as was done in the 2.4 liter reactor system which also results in lower efficiency. As a result, while the smaller scale test system has greater flexibility for testing, the overall efficiencies achievable are lower when compared to the 2.4 liter reforming system.

Figure 1 shows the test stand as it appears during use with reactor and heat exchangers insulated. Figure 2 shows a 51cc reactor along with the network of heat exchangers prior to installation into the test stand. Figure 3 shows a 51cc reactor with only a combustor and recuperator attached. Finally, Figure 4 illustrates the flow diagram for the heat exchanger network which supports reactor testing.

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[1] The processing rate is provided in terms of the size of the PEM fuel cell that could be supplied if a WGS and PROX reactor were integrated with the reformer. Currently the WGS and PROX reactors are not integrated with the reactor.

Figure 1. Experimental Test Stand Configured for Propane. The propane is suspended from a hook scale to monitor weight loss. Liquid fuels are placed in a reservoir on the platform scale.
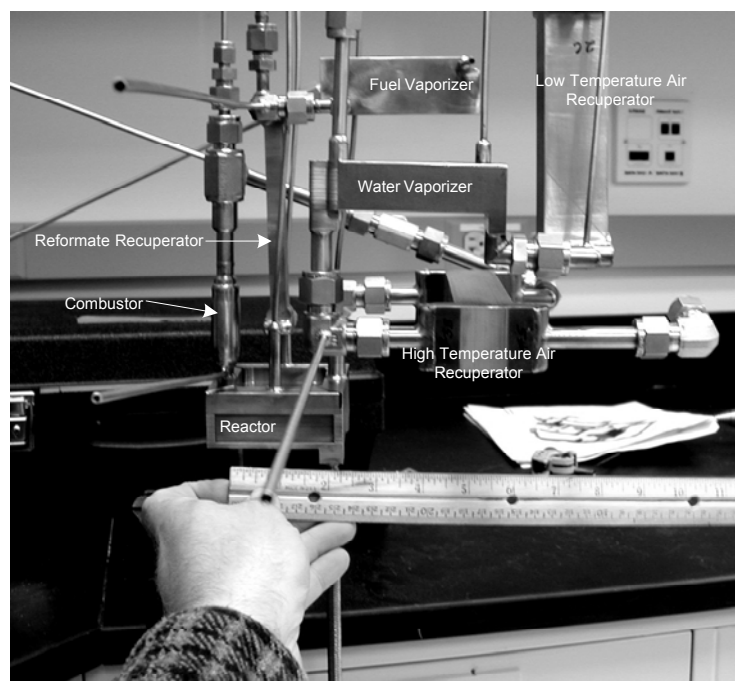

Figure 2. 51cc Stainless Steel Reactor Assembled with Heat Exchanger Network.
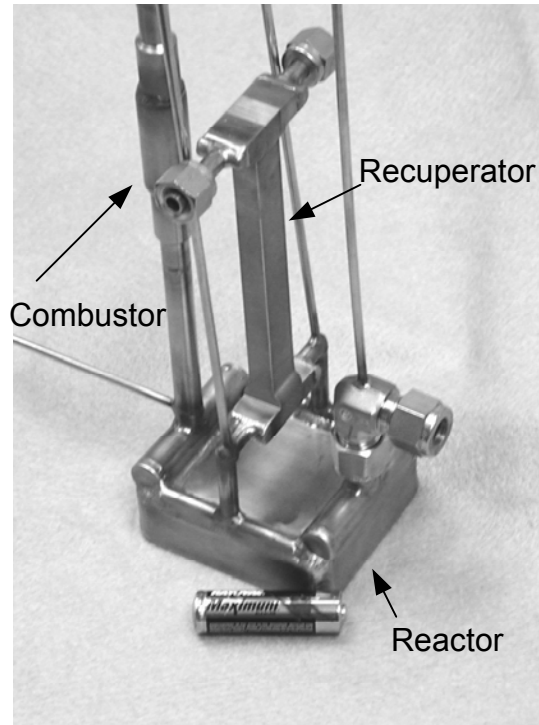
Figure 3. 51cc Reactor with Combustor and Recuperator. This reactor is constructed from Inconnel 625 for increased high-temperature durability. This unit has not yet been tested. (AA battery for scale.)
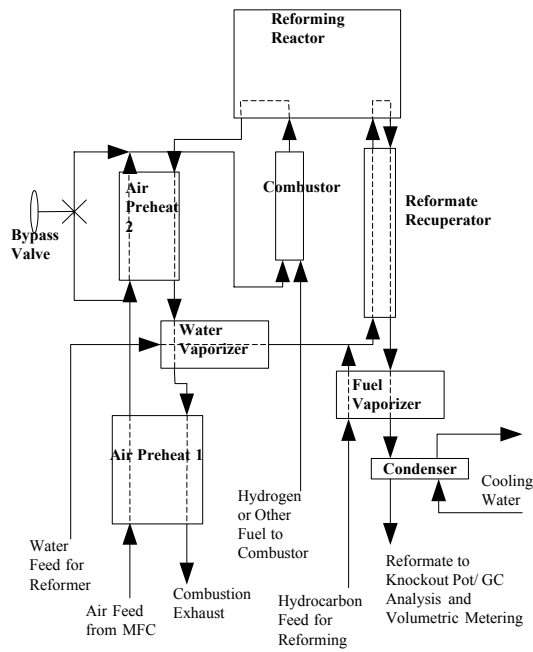

Figure 4. Flow Diagram for Heat Exchanger Network. Bypass valve is used to increase heat delivered to water vaporizer. Fuel vaporizer is omitted when fuel does not require this unit (methane, propane, butane, and alcohols when feeding water-alcohol solution).

Improvement Obtained in Reforming Productivity

The significant improvement in the productivity between earlier 2.4 liter reactor results and current 51cc and 26cc test reactor results is due primarily to improvements in the catalyst. The improvement is illustrated in Figure 5. The most direct comparison is between the isooctane results and the curves. The data points are above and to the right of previous data indicating that higher conversions are being achieved at higher processing rates. The degree of improvement is roughly a factor of 3 (see table caption). Conversion for all fuels except methane is defined as conversion to the single carbon compounds CO, CO_2 or CH_4. For methane it is defined as conversion to CO or CO_2. This tends to bias methane conversions lower than other hydrocarbon feeds due to equilibrium methane levels.
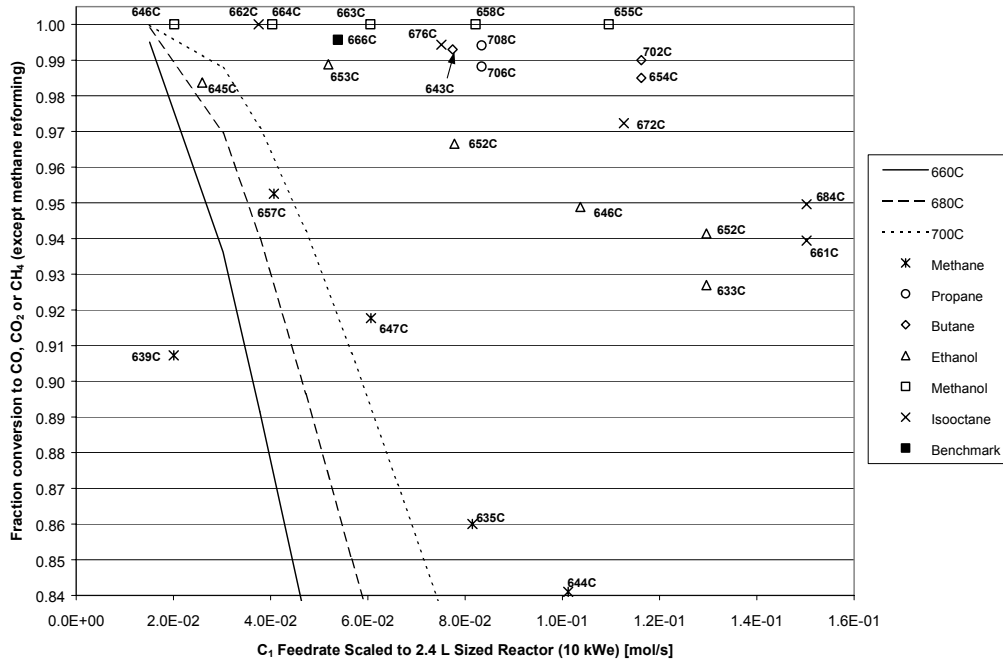

Figure 5. Increased Productivity Achieved in Test Reactors. The lines represent previous data obtained in the 2.4 liter reactor with catalyst "A" reforming isooctane. The data points are results for a variety of fuels using catalyst "B" in the 51cc and 26cc test reactors extrapolated to the 2.4 liter reactor size for comparison. Data labels and line identification refer to the reformate outlet temperature and are an indication of the reaction temperature. The comparison between the curves and the isooctane points illustrate the degree of improvement in reactor productivity. Comparing to the 680°C line at ~97% conversion to the 672°C data point also at ~97% conversion, the improvement in processing rate is about a factor of 3. Data points for other fuels illustrate the degree of fuel flexibility.

Figure 6 provides the same results plotted with the X axis being the size of PEM fuel cell that could be supported by this reforming rate. Examining the isooctane data this illustrates that a reactor core size of 2.4 liters (4.9 liters including internal headers) is capable of supporting a fuel cell at over 40 kWe ouput if conversion in the mid-90s is acceptable. The automotive target for fuel cell capacity is 50 kWe. The degree to which unconverted hydrocarbons can be tolerated downstream is an open issue and one that has a significant impact on the sizing of the fuel processor.
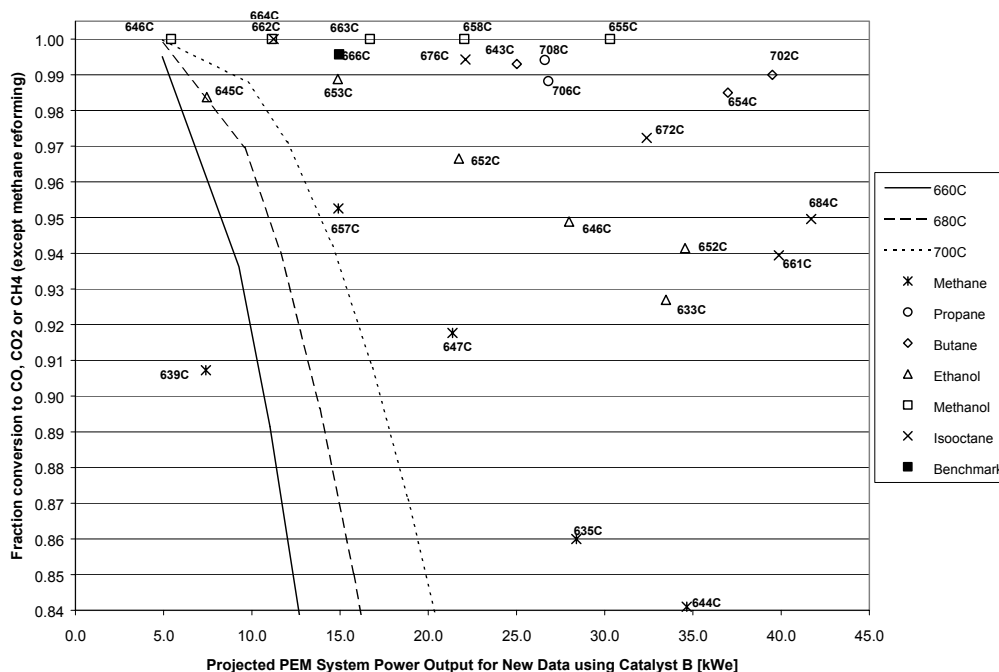
Figure 6. Improved Productivity in Terms of Fuel Cell Size Supported by Reactor with a 2.4 Liter Core Size. The fuel cell power for this plot is calculated assuming a WGS conversion of 90%, neglecting PROX losses and assuming 44% fuel cell efficiency (electrical output/ lower heating value of hydrogen in).

Fuel Specific Results

Tables 2 though 5 include detailed results for a number of steady-state conditions on specific fuels using catalyst B in the 51cc and 26cc test reactors. All of the data presented for hydrocarbon fuels are for a steam to carbon ratio of 3:1. In the case of alcohols, the data presented is for an oxygen:carbon ratio of 3:1 where the oxygen in the alcohol is included in the calculation. Also, all of the data presented are obtained near atmospheric pressure. The data on the 51cc test reactor were collected in a series of consecutive tests reforming ethanol, methanol, methane, isooctane and then benchmark fuel using the same reactor and catalyst[2]. Similarly, the same 26cc reactor and catalyst were used first for butane reforming and then for propane reforming. In both cases the time on stream at the end of testing was on the order of 100 hours. The data demonstrate a high degree of fuel flexibility of the steam reformer system.

In Table 2, conversions of methane tend to be lower than other fuels. This is partially due to the fact that the definition of conversion used for all other hydrocarbons is the percent of the feed compound converted to CO, CO_2 or CH_4 while for methane, residual methane is treated as unconverted. At low processing rates, the residual methane is largely determined by the reformer outlet temperature. For a fuel cell system operating on gaseous hydrocarbons, a lower conversion might be more acceptable than for liquid fuels because they are less likely to cause problems downstream from the reformer. The fuel value of unconverted reformer feed can be recovered when the anode gas is burned to provide heat to the reformer. The potential processing rate using methanol as the reforming fuel is potentially very high. Even at the highest processing rate the volumetric production of reformate was consistent with 100% conversion. In addition, testing with colorimetric tubes (20 ppm detection limit) was unable to detect methanol in the reformate.

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[2] Two days of data on isooctane were collected prior to the starting the series of data points displayed in the tables.

Table 2. Steam Reformer Test Results on Methane with Catalyst B

Reactor Core Volume[1]	51 cc	51 cc	51 cc	51 cc	51 cc
C_1 Feedrate to Reactor [mol/s][2]	4.017E-04	8.133E-04	1.212E-03	1.630E-03	2.024E-03
Productivity[3]	148 We	298 We	427 We	568 We	693 We
Fuel Conversion to C_1 Compounds	90.7%	95.3%	91.8%	86.0%	84.1%
Estimated System Efficiency (Peak/25%)[4,5]	21% / 26%	26% / 33%	29% / 36%	32% / 40%	33% / 41%
Power Density[6]	1120 We/L	2260 We/L	3240 We/L	4300 We/L	5250 We/L
Combustion Temperature	726°C	725°C	726°C	726°C	750°C
Combustion Exhaust Temperature	35°C	35°C	36°C	35°C	37°C
Reactor Reformate Exit Temperature[7]	639°C	657°C	647°C	635°C	644°C
Dry Gas Composition					
	75.2% H_2	75.7% H_2	75.4% H_2	74.4% H_2	74.0% H_2
	12.4% CO	12.7% CO	11.9% CO	10.8% CO	10.8% CO
	10.1% CO_2	10.4% CO_2	10.7% CO_2	11.1% CO_2	11.1% CO_2
	2.3% CH_4	1.2% CH_4	2.0% CH_4	3.6% CH_4	4.1% CH_4

Footnotes (applicable to tables 2 through 5):

1) The core volume is based on the volume of the heat transfer and reaction channels and separating walls along with the metal immediately surrounding the edges of the channels which provides for sealing of the channels. It does not include top and bottom plates and internal headering.

2) The C1 feedrate is feed rate of carbon. To obtain the molar feedrate of a hydrocarbon divide by the number of carbon atoms in the molecule. The steam to carbon ratio (oxygen to carbon for alcohols) is 3:1 for all C1 feedrates listed.

3) Calculated potential power output from a PEM fuel cell is based on assuming 90% CO conversion and 100% selectivity to CO_2 in a downstream water gas shift reactor and a fuel cell with 44% efficiency at peak power (2008 PNGV target).

4) Estimated System Efficiency is calculated as the projected electrical output from the fuel cell divided by the lower heating value of the fuel fed to the system (both for reforming and combustion). Unutilized H_2 (assumed 15% of H_2 fed to fuel cell) and CH_4 in the fuel cell waste anode gas are assumed to be combusted to provide heat to the system. Dual values are based on whether the fuel cell efficiency is selected to correspond to peak power (44% efficiency) or at 25% of peak power (55% efficiency) respectively. Values are lower than what could be achieved in the 2.4 liter system because the combustion is not staged and relative heat loss is greater for the small scale system.

5) The 44% and 55% fuel cell efficiency values correspond to the PNGV 2008 targets for peak power and 25% of peak power respectively.

6) Estimated by extrapolating reactor productivity to 2.4 liter reactor capacity and dividing by total volume of the reactor and associated heat exchangers (4.9 liter for reactor plus 1.7 liters for heat exchangers for a total of 6.6 liters). No scaling of heat exchanger was performed. The PNGV 2004 target for power density in the fuel processor is 700 We/L including water gas shift and PROX. The 2008 goal is 800 We/L. The power density assumes 44% efficiency in the fuel cell. While these densities are not directly comparable to the goal they clearly indicate that that the reformer and associated heat exchangers are only a small fraction of the allowable volume.

7) This is the temperature of the reformate exiting the steam reformer and is used as an indication of reaction temperature.

Table 3. Propane and Butane Reforming (Catalyst B)

	Propane		Butane		
Reactor Core Volume[1]	26 cc	26 cc	26 cc	26 cc	26 cc
C_1 Feedrate to Reactor [mol/s][2]	8.340E-04	8.340E-04	7.744E-04	1.162E-03	1.162E-03
Productivity[3]	266 We	268 We	250 We	370 We	395 We
Fuel Conversion to C_1 Compounds	99.4%	99.8%	99.3%	98.5%	99.0%
Estimated System Efficiency (Peak/25%)[4,5]	29% / 37%	30% / 37%	34 / 43%	35 / 44%	34 / 43%
Power Density[6]	4030 We/L	4060 We/L	3790 We/L	5600 We/L	5980 We/L
Combustion Temperature	775°C	775°C	701°C	700°C	751°C
Combustion Exhaust Temperature	31°C	32°C	36°C	33°C	30°C
Reactor Reformate Exit Temperature[7]	708°C	706°C	643°C	654°C	702°C
Dry Gas Composition					
	72.4% H_2	72.3% H_2	70.5% H_2	70.8% H_2	71.6% H_2
	14.8% CO	14.8% CO	12.4% CO	12.6% CO	14.6% CO
	12.1% CO_2	12.0% CO_2	14.5% CO_2	14.3% CO_2	12.9% CO_2
	0.7% CH_4	0.7% CH_4	2.5% CH_4	2.2% CH_4	0.8% CH_4

Table 4. Methanol and Ethanol Reforming (Catalyst B)

	Methanol			Ethanol		
Reactor Core Volume[1]	51 cc	51 cc	51 cc	51 cc	51 cc	51 cc
C_1 Feedrate to Reactor [mol/s][2]	8.068E-04	1.643E-03	2.191E-03	1.037E-03	1.556E-03	2.593E-03
Productivity[3]	223 We	441 We	606 We	297 We	435 We	669 We
Fuel Conversion to C_1 Compounds	100.0%	100.0%	100.0%	98.9%	96.7%	92.7%
Estimated System Efficiency (Peak/25%)[4,5]	23% / 29%	28% / 35%	31% / 39%	27% / 34%	29% / 36%	31% / 39%
Power Density[6]	1690 We/L	3340 We/L	4590 We/L	2250 We/L	3290 We/L	5070 We/L
Combustion Temperature	725°C	726°C	725°C	724°C	726°C	726°C
Combustion Exhaust Temperature	34°C	36°C	37°C	33°C	36°C	38°C
Reactor Reformate Exit Temperature[7]	664°C	658°C	655°C	653°C	652°C	633°C
Dry Gas Composition						
	70.4% H_2	70.5% H_2	70.1% H_2	70.0% H_2	69.4% H_2	67.6% H_2
	14.1% CO	13.6% CO	13.1% CO	13.7% CO	13.5% CO	11.9% CO
	14.9% CO_2	15.0% CO_2	15.4% CO_2	15.2% CO_2	15.2% CO_2	16.2% CO_2
	0.6% CH_4	0.9% CH_4	1.3% CH_4	0.9% CH_4	1.2% CH_4	3.1% CH_4

Table 5. Isooctane and Benchmark Fuel (Catalyst B)

	Isooctane					Benchmark
Reactor Core Volume[1]	51 cc	51 cc	51 cc	51 cc	51 cc	51 cc
C_1 Feedrate to Reactor [mol/s][2]	7.511E-04	1.502E-03	2.253E-03	3.004E-03	3.004E-03	1.077E-03
Productivity[3]	225 We	442 We	648 We	797 We	834 We	299 We
Fuel Conversion to C_1 Compounds	100.0%	99.4%	97.2%	93.9%	95.0%	99.6%
Estimated System Efficiency (Peak/25%)[4,5]	23% / 28%	27% / 34%	29% / 36%	29% / 36%	29% / 36%	25% / 31%
Power Density[6]	1700 We/L	3350 We/L	4910 We/L	6040 We/L	6320 We/L	2270 We/L
Combustion Temperature	725°C	725°C	725°C	726°C	749°C	725°C
Combustion Exhaust Temperature	35°C	41°C	47°C	47°C	49°C	38°C
Reactor Reformate Exit Temperature[7]	662°C	676°C	672°C	661°C	684°C	666°C
Dry Gas Composition						
	70.9% H_2	71.2% H_2	70.7% H_2	70.2% H_2	70.6% H_2	70.1% H_2
	14.7% CO	14.6% CO	13.9% CO	12.9% CO	14.0% CO	14.9% CO
	13.3% CO_2	13.5% CO_2	14.0% CO_2	14.7% CO_2	13.9% CO_2	14.1% CO_2
	1.1% CH_4	0.7% CH_4	1.3% CH_4	2.0% CH_4	1.3% CH_4	0.9% CH_4

Table 6 provides a single point comparison between catalyst A and B at the same reformate outlet temperature for reforming benchmark fuel. This comparison is made with catalyst B after 9 thermal cycles and 94 hours time on line compared to a relatively fresh catalyst A. This illustrates a clear improvement in performance with catalyst B.

Table 6. Single Point Comparison Between Catalyst A and B for Benchmark Fuel [1]

Catalyst in 51cc reactor	Reformate Outlet Temp/ Productivity	C1 feedrate, mol/s	Overall Conversion to C1 compounds	Isooctane Conversion	Xylene Conversion	Methyl-Cyclohexane Conversion	1-Pentene Conversion
A	666°C/ 200We	7.45x10⁻⁴	88.0%	83.9%	98.3%	90.7%	100.0%
B	666°C/ 299We	1.08x10⁻³	99.6%	99.4%	100.0%	99.1%	100.0%

(1) Both sets of data were collected in 51cc reactors at 3:1 S:C. While the reactor in the catalyst B case included improvements in flow distribution, the major effect is the improvement in catalyst.

The use of higher reaction temperatures will be investigated in the future by utilizing the inconnel 51cc reactor shown previously in Figure 3. It is expected that the reactor can be made substantially smaller if operating at higher temperatures. It is possible that the smaller size and weight my offset the higher cost of higher temperature alloys such as inconnel compared to stainless steel.

Stability of Performance on Catalyst B

The reformer performance appears to be stable when operated at a steady condition. For example, while reforming propane at a steady condition for 37 hours in the 26cc reactor the conversion level averaged 98.83% with a minimum of 98.79% and a maximum of 98.89%. The hydrogen selectivity over this period averaged 98.06% and varied from a minimum of 97.99% to a maximum of 98.14%. Similarly stable results were obtained in the 51cc reactor reforming benchmark fuel at a steady condition for a period of 24 hours. However, over the first 100 hours and multiple startup/shutdown cycles some degradation in reforming

performance can be seen as is illustrated in Table 7. Note that after 8 cycles the conversion is slightly decreased despite a slightly lower processing rate and higher reformate exit temperature indicating a decrease in performance.

Table 7. Decrease in Reforming Performance Over Multiple Startup-Shutdown Cycles

Processing Rate	Startup-Shutdown cycles on catalyst	Time on line for reformer	Reformate Exit Temperature	Conversion to C1 compounds
388 We	1	5 hrs	630	99.95%
340 We	8	70 hrs	669	99.51%

It is next planned to test the 52cc reactor at steady conditions for >1000 hours to establish the stability of the steady-state reformer performance.

Sulfur Sensitivity

Testing with a propane fuel that was determined to be sulfur contaminated resulted in a several percent reduction in conversion per hour of operation. When the reformer feed was changed back to a non-sulfur containing propane the performance was largely recovered over time. Additional work using known sulfur spikes is planned for the future to determine the degree of sulfur sensitivity.

Transient Response

The small volumes and short residence times associated with the micro-channel heat exchangers and vaporizers allow for a system with a rapid transient response. Figure 7 shows the volumetric flow of reformate downstream of the final condenser in response to a step change in the feed rates of isooctane and water to the system. The steps change is from 100% to 10% of the liquid input flows and then from 10% back to 100%. The time for the reformate flow to adjust to the change in liquid input rate is about 5 seconds. The time required for system temperatures to settle to new values after a step change are somewhat longer but it is not expected that this would have any adverse consequences downstream from the reformer.
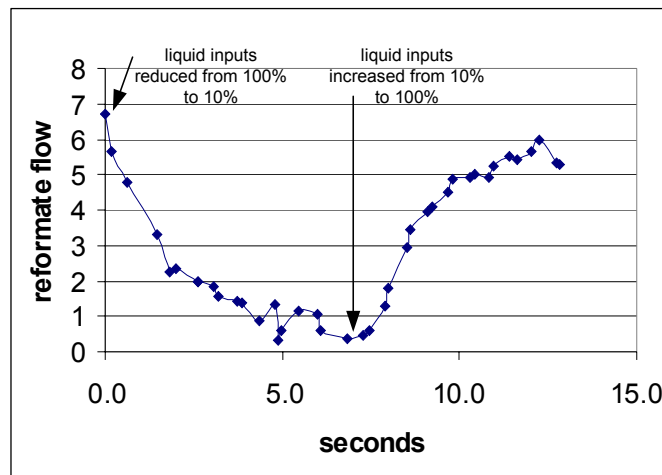

Figure 7. Transient Response in Reformate Flow. The Y-axis represents the relative flow of reformate down stream from the condenser as measured by a flowmeter. The x-axis is elapsed time. Flowrate of liquid fuel and water are cut to 10% of normal at zero seconds and then restored to 100% at about 7 seconds.

Conclusion

Since the demonstration of a microchannel reformer in the 10-20 kWe capacity range, substantial progress in process intensification has been demonstrated on a smaller scale-test stand. The reformer has been demonstrated to be highly fuel-flexible, showing high levels of performance of methane, methanol, ethanol, propane, butane, isooctane and a 4-component liquid hydrocarbon fuel. The reformer performance appears to be stable when operating at steady condition for tens of hours. A moderate decrease in performance has been noted after 70 hours on line, 8 startup/shutdown cycles, and testing with multiple fuels. The ability of the test system to accomplish a 100% to 10% and 10% to 100% change in reformate output in response to step changes in liquid water and fuel feed rates has been demonstrated. Future reformer testing will focus on >1000hr steady state operation to establish stability at steady operating condition, testing at higher temperatures to achieve further process intensification, and investigation of sulfur sensitivity through sulfur spikes. In addition, the reforming system will be integrated with a WGS and PROX reactor to produce reformate suitable for use by a PEM fuel cell.

Reference

Whyatt, G.A., W. E. Tegrotenhuis, J. G. H. Geeting, J. M. Davis, R. S. Wegeng, L. R. Pederson, **Demonstration of Energy Efficient Steam Reforming in Microchannels for Automotive Fuel Processing** Proceedings of the Fifth International Conference on Microreaction Technology, IMRET 5, May 27-30th, 2001.