

Microchannel Chemical Reactors for Fuel Processing

Anna Lee Y. Tonkovich[‡], Daniel M. Jimenez, Jennifer L. Zilka,
Mike LaMont, Yong Wang, Robert S. Wegeng

Pacific Northwest National Laboratory^(a), Battelle Boulevard, Richland WA 99352

Abstract

A fuel processor is a critical component for the deployment of PEM-based fuel cells for both portable and stationary applications. The fuel processor produces hydrogen rich streams from hydrocarbon-based feedstocks in a multi-step process. Conventional fuel processing technology is based on fixed-bed reactors, which do not scale well with the small modular nature of fuel cells. Microchannel reactor-based fuel processors, however, are small, efficient, modular, lightweight, and potentially inexpensive. One step of the multi-component fuel processor, the fuel vaporizer, was developed and demonstrated at both a bench and full-scale for an automotive application using a microchannel chemical reactor.

Introduction

The fuel processor produces a hydrogen rich stream from a hydrocarbon fuel that is suitable for use in a PEM or other fuel cell. Fuels of interest include methanol, gasoline, methane, and others. The fuel processor contains multiple reactors in series. A primary conversion step produces synthesis gas from either partial oxidation, steam reforming, or autothermal reforming. A second step -- the water gas shift reactor -- converts carbon monoxide (in the presence of hydrogen) and water to carbon dioxide and hydrogen. An additional gas clean-up reactor preferentially oxidizes the remaining carbon monoxide to carbon dioxide with exiting CO levels below 10 ppm (required for the PEM fuel cell). The final step in the integrated fuel processor system is a fuel vaporizer for liquid hydrocarbon feedstocks. This latter component was demonstrated using a microchannel reactor.

Microchannel reactors reduce the size of conventional chemical without lowering the throughput. Heat and mass transport limitations slow the observed reaction rates in conventional reactors, but are minimized in microchannel reactors. A much smaller boundary layer is found within each microchannel than that found in the bulk flow of a conventional reactor. As the boundary layer shrinks, the corresponding contribution of slow conduction and diffusion to the heat exchange or catalyst surface is reduced. Fast heat and mass transfer increase the process efficiency which permits process miniaturization without sacrificing productivity.

A microchannel fuel vaporizer was demonstrated at both a bench-scale and full-scale for automotive applications at the 50-kW size. The technology is based upon combusting the waste hydrogen from the fuel cell anode to provide the fuel's latent heat of vaporization. The anode effluent stream is comprised primarily of nitrogen, carbon dioxide, water, and hydrogen (6-8% by volume).

[‡] author to whom all correspondence should be addressed

^(a) PNNL is operated by Battelle for the U.S. Department of Energy.

Background

Several fuel processor systems are currently under development. One example of a complete fuel processor system is described in Figure 1. Different primary conversion reactors are also under investigation. The options for the production of synthesis gas from either methanol, ethanol or gasoline include catalytic partial oxidation, non-catalytic partial oxidation, steam reforming, and autothermal reforming. The other system processing steps (water gas shift reactor, the preferential oxidation reactor, and the fuel vaporizer) remain unchanged.

A comparative paper on the attributes of partial oxidation versus steam reforming is reported by Argonne National Laboratory (Kumar and Ahmet 1995). A complete system description of the fuel processor and fuel cell is presented by Delphi (Delphi 1996). A third fuel processing system configuration is under development at Arthur D. Little (ADL 1994). Each of the reported systems are based upon conventional fixed-bed reactor technology, which does not scale linearly with throughput because of inefficient heat transfer.

The conventional fuel processors, which are based upon fixed-bed technology, are expected to be at least an order of magnitude larger than the microchannel reactor fuel processor. Heat transport limitations which dramatically increase the size of the conventional technology (Kumar and Ahmet 1995) are mitigated with the emerging technology described in this paper. The results from the first step of the multi-sequence fuel processor, the vaporizer, show that this component is more than an order of magnitude smaller than the competing fuel vaporizer (ADL, 1997).

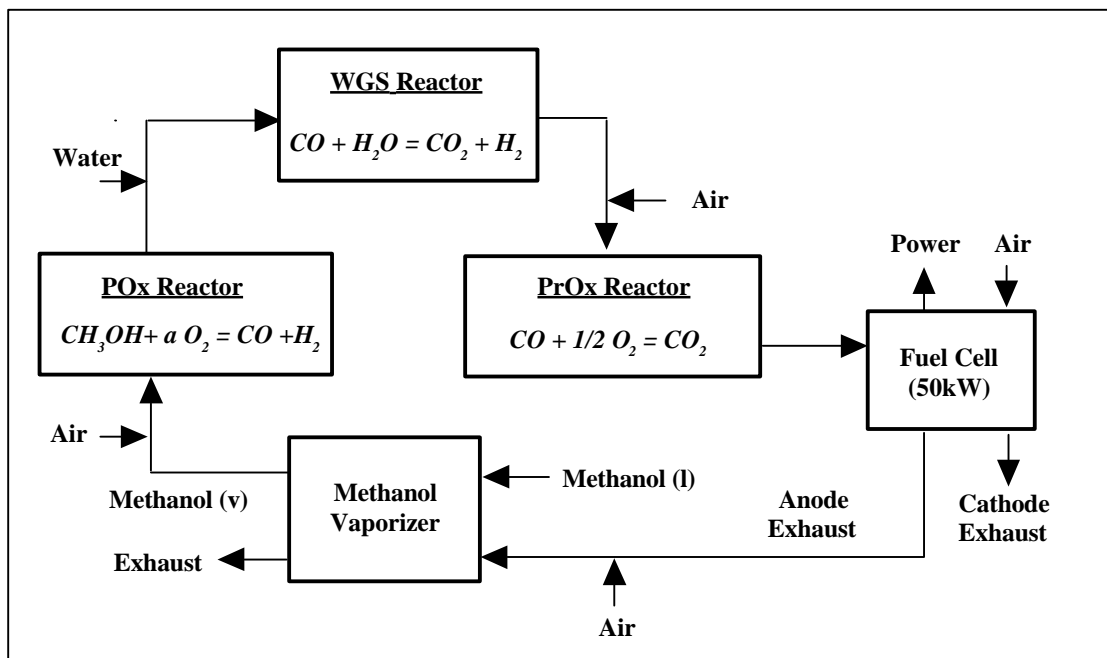


Figure 1. Fuel processor and fuel cell system for transportation applications

Experimental

Each fuel processor concept requires a vaporizer to prepare liquid fuels for their primary conversion to hydrogen and carbon oxides. The fuel latent heat of vaporization is provided by combusting the dilute hydrogen remaining in the fuel cell anode effluent stream. If there were insufficient heat content remaining in the anode effluent, then a microcombustor can be embedded within the vaporizer to provide additional heat. A small fraction of the liquid fuel stream would be diverted and combusted to supply the necessary vaporization energy.



Catalytic combustion of the dilute hydrogen (6 to 8%) remaining in the anode effluent stream is a facile reaction using a palladium catalyst supported on a porous ceramic foam, metal monolith, or silica powders. No pre-heating is required because hydrogen combustion initiates at room temperature.

The initial bench-scale reactor consisted of using active catalyst powders. The powders were prepared by incipient wetness impregnation of powdered PQ SiO₂ with a Pd(NO₃)₃ solution. The Rh loading was varied between 1 and 10% by weight. A solution of palladium nitrate (Pd(NO₃)₂ (14.57 wt% assay from Engelhard) of appropriate concentration was prepared, corresponding in quantity to the total pore volume of the SiO₂ powders, or slightly less. The palladium nitrate-impregnated silica powders were dried at 100 °C in vacuum overnight and then calcined at 350 °C for at least one hour. The PQ silica supported Pd catalysts were reduced with 10% H₂/He at 100 °C for at least one hour.

While the use of catalyst powders demonstrates the microchannel vaporizer technology concept, they are not well suited for scale-up. After operating for several days, thermal cycling and the corresponding drying cycles changed the macroscopic morphology of the catalyst bed, which in turn affected both the pressure drop and performance. Subsequent bench scale tests were conducted using a monolithic catalyst made from both a ceramic and a metal support.

The bench-scale vaporizer consists of two plates (reactor and heat exchanger) and is shown in Figures 2 and 3. The plates are 5.7-cm wide and 7-cm long. The size of the single microchannel cell on both sides of the heat exchanger plate is 5-cm wide and 4.5-cm long. The plates are constructed from aluminum or stainless steel (first bench-scale only). The top plate (reactor sheet) has a well (0.63 cm deep) for the catalytic monolith. Gas enters in the top plate, reacts in the monolith, and travels down through a hole in the footer to the header of the heat exchanger plate below. The heat exchanger sheet has microchannels on both sides. Heat is transferred from the hot gas on the top side of the plate through microchannels to the microchannels on the back side of the heat exchange plate where methanol is vaporized. The microchannels on the gas side are 254-microns wide, the fins are 304-microns wide, and the depth is 1016 microns (in the first bench-scale tests only). The microchannels on the cooling fluid side are the same.

The catalytic monolith was prepared with a substrate (Ni monolith with 60 pores per inch) purchased from Astro Melt, Inc. The monolith was washed in a sonicator successively with acetone, chloroform, and water over 10-minute intervals. The Ni monolith was then etched in a 0.01M HNO₃ solution for 30 minutes at 60 °C and was washed thoroughly with water. The treated monolith is saturated with a dilute

Pd nitrate solution followed by air-drying at room temperature. The saturation process was repeated several times until the desired Pd loading was achieved. The Ni monolith supported Pd catalysts were finally dried at 100 °C in vacuum overnight followed by calcination at 350 °C for one hour. The catalysts were activated with 10% H₂/He at 100 °C for at least one hour prior to the catalytic testing.

Several design iterations on the bench-scale reactor were completed and the microchannels on the gas-side were changed (shown in Figure 3). The channel width is maintained at 254 microns, but the depth is varied to achieve aspect ratios of 4, 7, 10, and 18:1. The aspect ratio is defined as ratio of the channel height to the width.

The full-scale vaporizer was similar to the bench-scale process, and is shown in Figure 4. Two sheets -- reactor plate and heat exchanger plate -- are stacked between cover plates. Each plate is 7.6-cm x 10.2-cm x 0.64-cm or 3" x 4" x 0.25". The reactor plate has four parallel microchannel reactors. The inlet gas stream enters at the center of the top plate and segregates between the four reactive monoliths. The split-gas flows through four parallel slits in the four monolith footers to the parallel headers of the four cells in the heat exchange plate below. A cell is defined as a cluster of parallel microchannels that operates in parallel to other cells. After passing through the heat exchanger plate, the gas flows back up through a hole in the monolith plate and out the top of the vaporizer. The cooling fluid (evaporating methanol) enters in two ports in the bottom plate. Each fluid stream divides and flows countercurrent to the gas stream through four parallel cells. Fluid streams recombine in two exit ports in the bottom plate.

Each monolith has a cross section of 7.2 cm² and each heat exchanger has a cross section of 7.2 cm². The channels on the gas side are 254 microns wide and have an aspect ratio of 18:1. The fins are 304 microns wide. The channels on the vaporizing side of the heat exchanger plate are 254-microns wide and have a 7:1 aspect ratio.

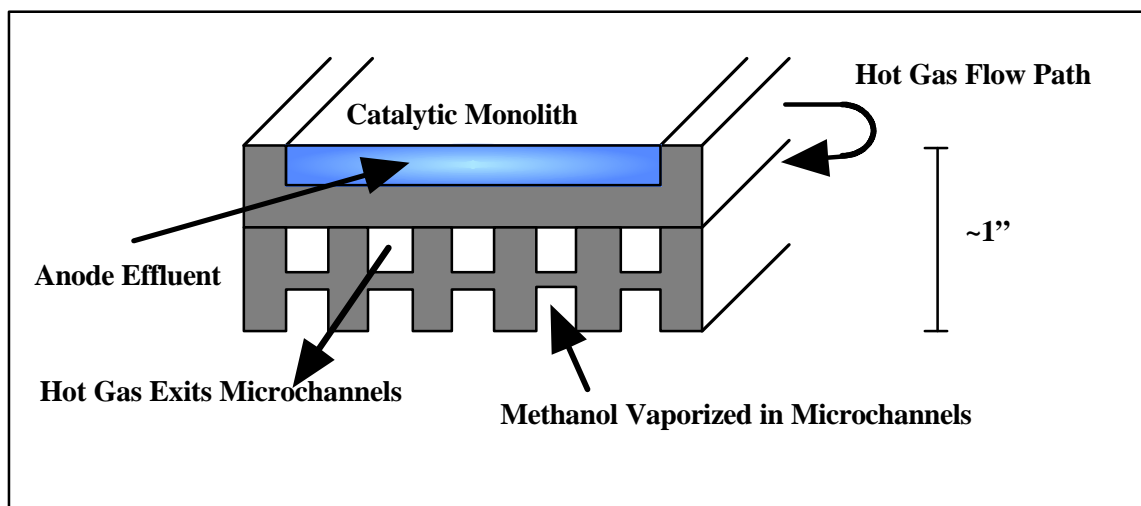


Figure 2. Bench-scale microchannel vaporizer

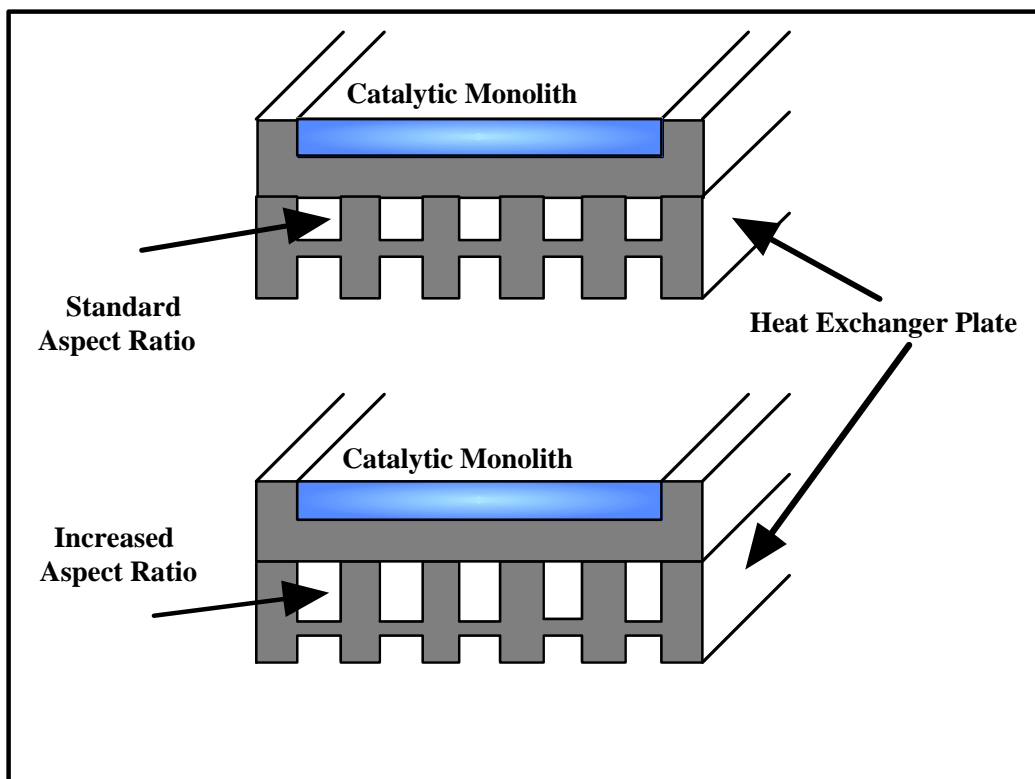


Figure 3. Effect of aspect ratio on reactor design

Temperature measurements are taken using thermocouples placed at the exit of each of the four monoliths, in the footer region of each of the four evaporating methanol cells, in the gas inlet, at the two gas outlets, in the two methanol inlets, and in the two recombined methanol outlets. Temperature measurements give insights on the flow uniformity and potential maldistributions. The variance across the four monoliths is typically less than 20 °C. The temperatures on the methanol side have a greater variance, and manual flow control is required for both inlets and outlets.

The tests conducted with vaporizing methanol required the use of a microchannel methanol condenser to collect the vapors. A bench-scale condenser process (4:1 aspect ratio on both sides) was designed with only a heat exchanger plate (from the bench-scale vaporizer) sandwiched between cover plates. The hot vapor flowed countercurrent to cooling water (6 °C) set between 550 and 580 mL/min on the back side of the heat exchanger plate. The outlet temperature of the liquid methanol stream from the condenser was 35 °C during the full-scale tests.

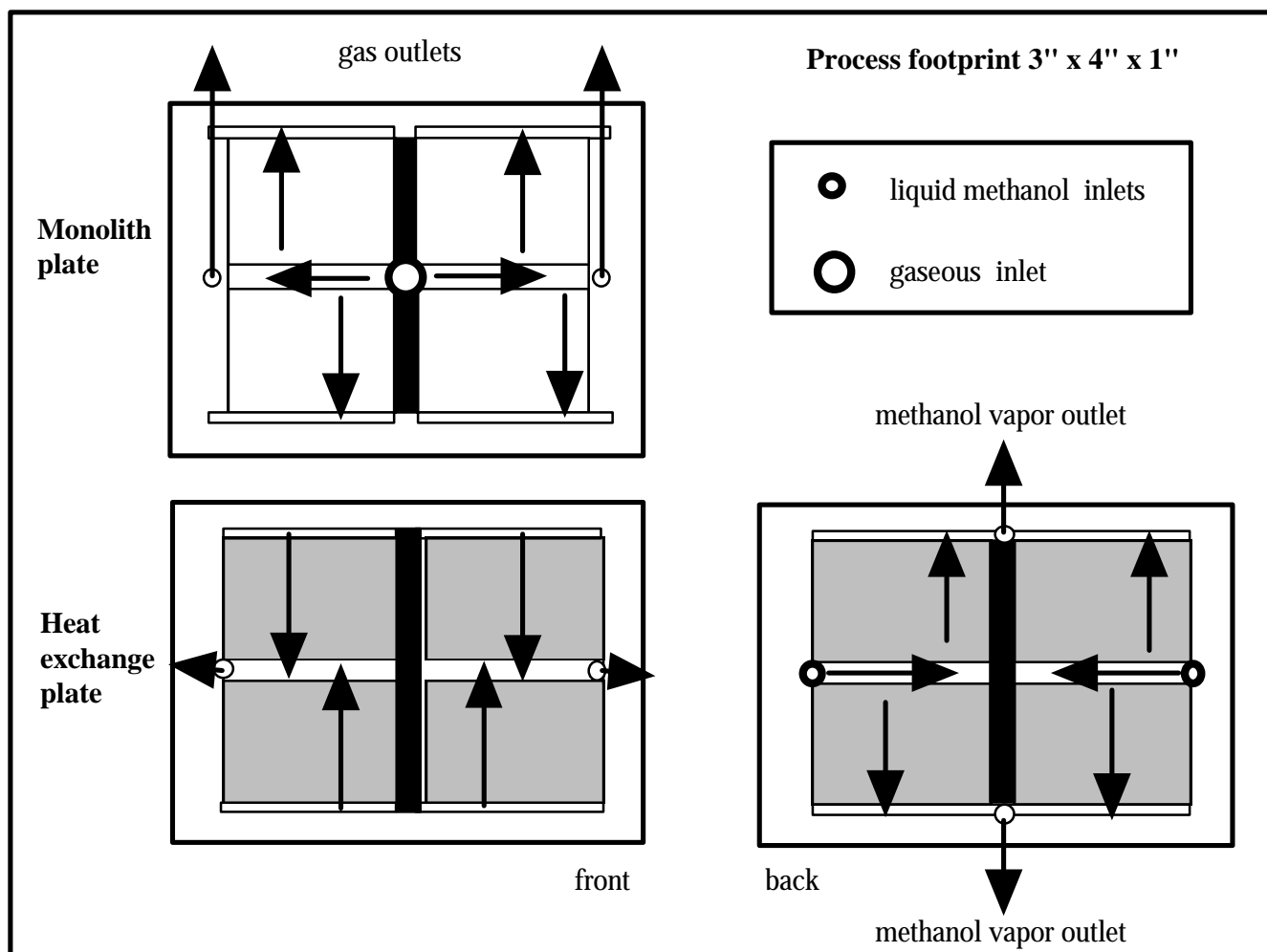


Figure 4. Full-scale reactor with four reactor and heat exchanger cells

Results and Discussion

The development and scale-up of a microchannel vaporizer as part of a fuel processor for automotive applications was completed in 10 months. The feasibility of the technology was demonstrated initially with the use of catalyst powders. In subsequent trials, catalyst scale-up issues were addressed and ceramic and metal monoliths were investigated in a single-cell bench-scale vaporizer. Finally, a full-scale vaporizer was built, tested, and demonstrated (patent pending). This device contains four cells per plate and shows the linear scaling laws for microchannel reactors.

The initial proof-of-principle experiments were conducted with catalyst powders packed within the header or channels of a microchannel reactor. The active catalyst for hydrogen oxidation was independently determined to be palladium in fixed-bed experiments. Light-off occurs at room temperature and adiabatic reactor operation is required to sustain the reaction.

The vaporizer performance with 5 wt% Pd/SiO₂ catalyst powders (42.5 mg) packed in the header is shown in Figure 5. Comparative tests were conducted with catalysts packed in the channels, but the system would not self-sustain in the presence of a countercurrent cooling fluid. The results shown in Figure 5 were collected during one week with increasing hydrogen flowrates as a function of time. The system was shut down completely each day and restarted the next. Over the course of five thermal cycles, considerable catalyst degradation occurred. During the final runs, the catalyst activity dropped significantly and hydrogen conversions below 50% were achieved. Visual inspection of the catalyst after the series of tests revealed that it had become compacted and by-pass flow paths were observed.

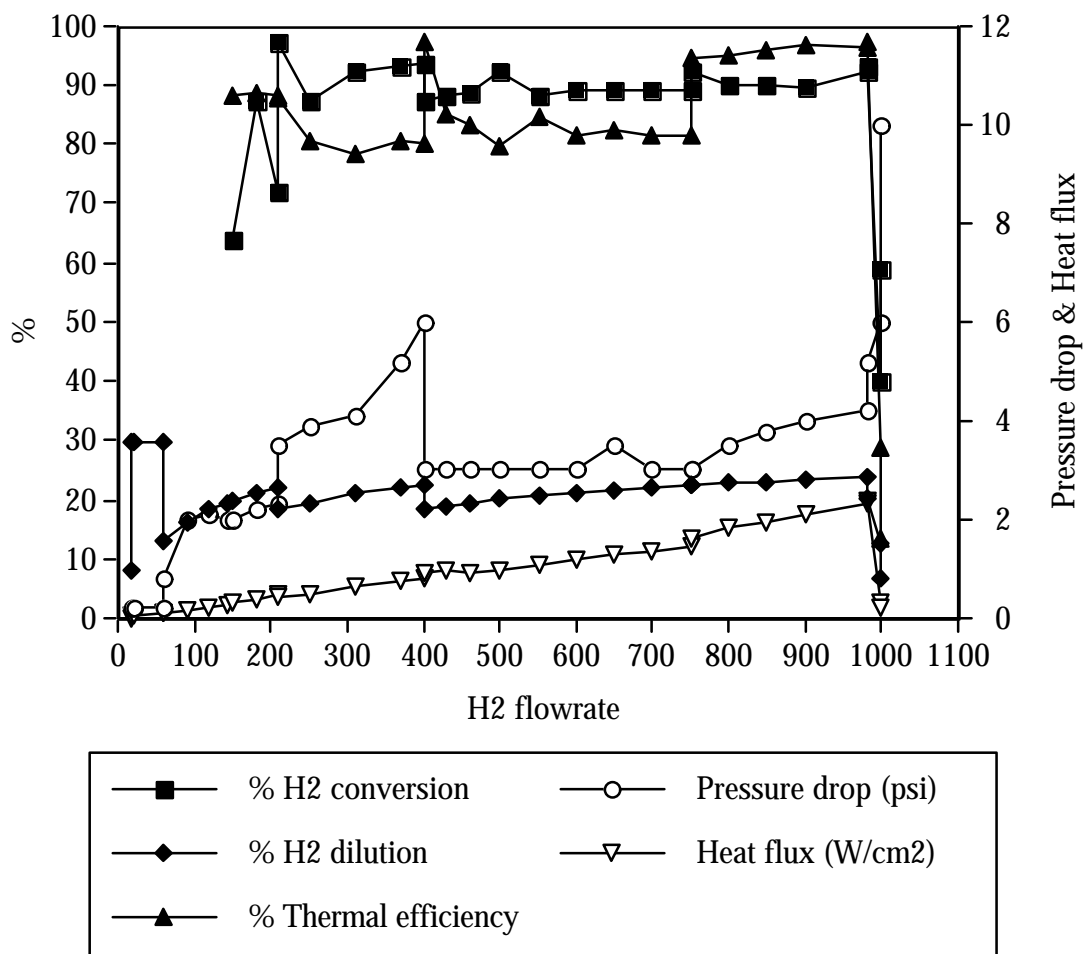


Figure 5. Microchannel vaporizer with catalytic powders

While powders are not the method to scale-up microchannel reactors, they did conclusively show that the microchannel vaporizer technology concept is feasible. In Figure 5, the hydrogen conversion was typically greater than 90% until the final series of tests with a high hydrogen dilution rate. The feed consisted of hydrogen (with the sccm given on the x-axis) and a stoichiometric rate of oxygen (fed as air) in a balance of nitrogen. The hydrogen dilution percent is shown with the diamond symbol. The system operating constraints for the fuel processor vaporizer consist of a 6-8% hydrogen stream and these early

tests worked toward reaching that goal. The other parameters reported are the thermal efficiency which reveals how much of the thermal energy generated from hydrogen oxidation is transferred to the cooling water. The gas phase pressure drop is reported along with the heat flux transferred to the cooling water below the reactor.

The results of the powder catalyst tests lead to a redesign of the reactor with a catalyst that is highly active and with low pressure drops for high throughputs. The bench-scale reactor shown in Figure 2 is constructed from aluminum using conventional machining. A series of catalytic monoliths were tested in the vaporizer. The catalyst weight loading is important and must be greater than 5% Pd to achieve rapid light-off. A series of ceramic monoliths were tested and the performance shown in Figures 6 and 7. These catalyst supports gave adequate performance except for pressure drop which exceeds 20 psig with flowrates less than 10 L/min. In all tests, the feed gas mixture was maintained at 6.7% H₂, 3.35% O₂, and balance N₂. The total gas flowrate was varied until complete vaporization of methanol (Figure 6) or water (Figure 7) was achieved. Complete vaporization was determined when the temperature measurement in the outlet port reached 20 °C above the vaporization temperature. During a typical test, the outlet temperature of the partially vaporized two-phase flow remained constant until sufficient heat was added to achieve rapid superheat.

In these tests, the fraction of monolith loaded with catalyst was varied to determine the minimum amount of catalyst required. Of the coated portion of the monolith, the weight percent is always 5%. In the methanol tests, the monolith was quarter coated. In the water tests, the monolith was completely coated.

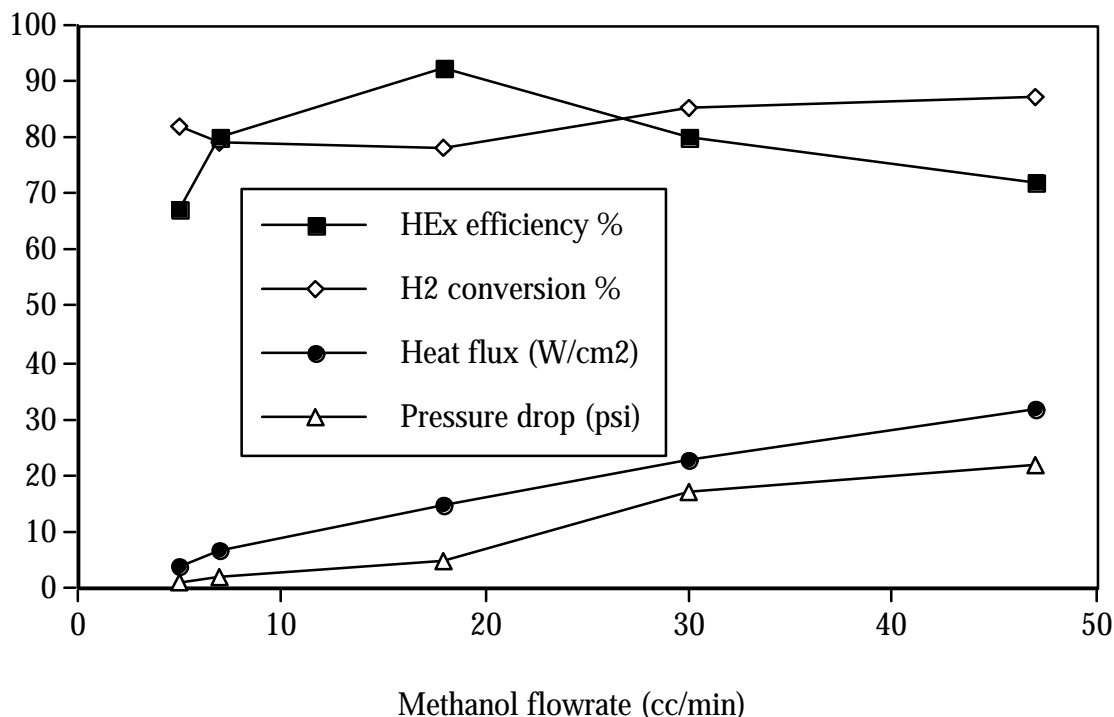


Figure 6. Bench-scale microchannel vaporizer with catalytic monolith for methanol

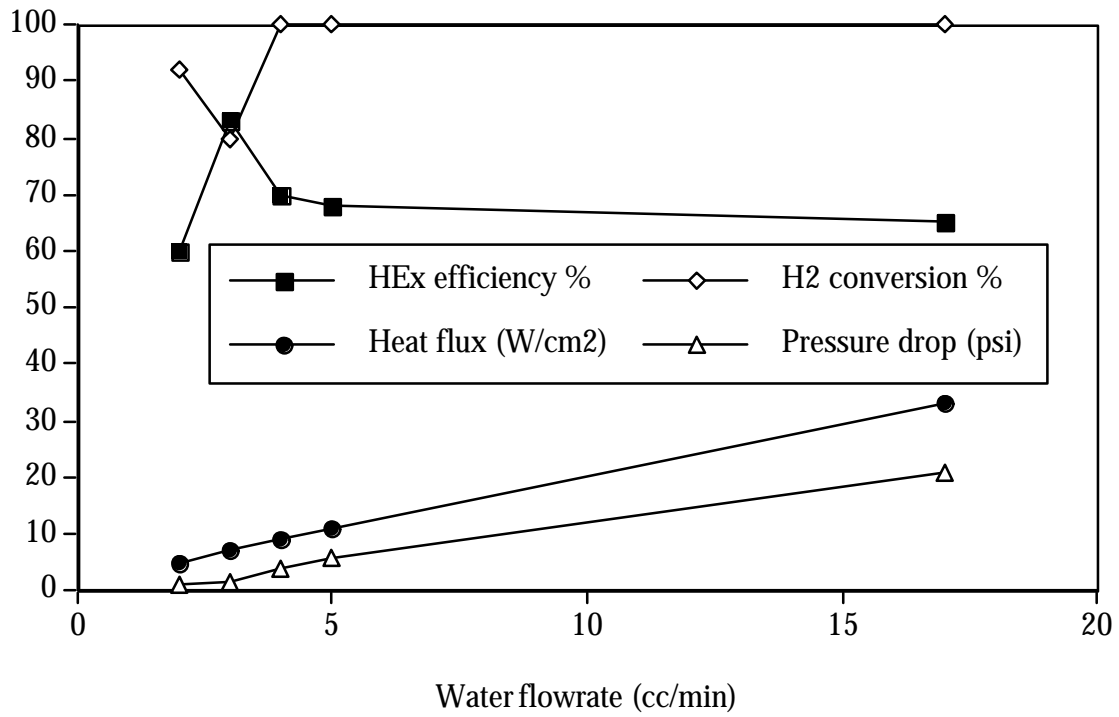


Figure 7. Bench-scale microchannel vaporizer with catalytic monolith for water

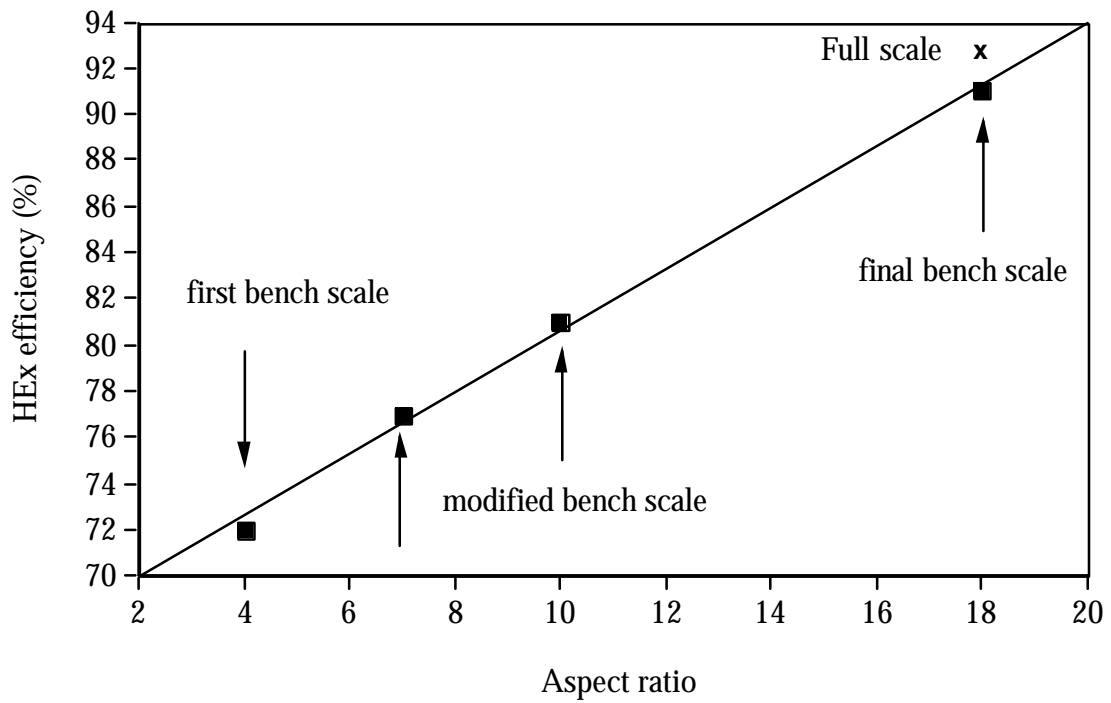


Figure 8. Effect of aspect ratio on performance

In each of these preliminary bench-scale tests, the microchannels on the gas-side have an aspect ratio of 4:1 and the corresponding thermal efficiency ranges between 70 and 80%. This efficiency is sufficient for the automotive fuel vaporizer application, which has a critical efficiency requirement of 63%, but higher efficiencies are desired. The aspect ratio (channel height to width ratio) is varied on the gas side to determine the effect on efficiency. For a methanol flowrate of 50 mL/min and the corresponding total mixed gas feed flowrate, the thermal efficiency was measured for different aspect ratios and shown in Figure 8. A near linear relationship between aspect ratio and thermal efficiency is measured in the region explored. It is expected that this function will approach an asymptotic limit at some higher aspect ratio. Also shown in Figure 8 is the corresponding heat efficiency that was measured in the full-scale tests.

The design and fabrication of the heat exchange plate with different aspect ratios required different methods. The first bench-scale reactor was fabricated from both stainless steel and aluminum using EDM. It is not possible to achieve higher aspect ratios using this machining technique. Conventional machining can achieve higher aspect ratios, but only in soft metals like aluminum. The highest possible aspect ratio achievable with conventional machining was 18:1.

The full-scale reactor is shown in Figure 5. This four-cell device is 3" x 4" x 1" and two of these units operating in parallel are required for a full-scale methanol vaporizer for an automotive fuel cell. Table 1 shows the operating conditions and results for the full-scale testing.

Table 1. Full-scale reactor operation performance

Parameter	Value
Methanol flowrate	208 mL/min
Hydrogen flowrate	25 L/min
Total gas flowrate	373 L/min
% H ₂ conversion	100%
% HEx efficiency	93.2%
ΔP - reactor (measured)	1.5 psi
ΔP - reactor (calculated)	1.0 psi
ΔP - HEx (calculated)	0.27 psi
ΔP - system (measured)	14 psi
ΔP - methanol side (measured)	< 1.0 psi
Heat flux (W/cm ²)	145.4 W/cm ²
Average gas temperature-monolith exit	298.8 C
Average temperature - methanol vapor exit	203.4 C

Channel fouling and subsequent regeneration is a consideration for real-world fuels. A pre-vaporizer in-line filter will prevent particulate fouling much like an air or oil filter in automobiles today. Additional fouling may result from a number of organic and inorganic impurities contained within each fuel. Periodic channel regeneration is envisioned to remove foulants.

An evaporative residue of organic and/or inorganic material may build up on the walls of the microchannels after operating for a fixed period of time. For long duration use, a typical regeneration cycle may include switching the air feed away from the catalytic monolith and consuming the oxygen to burn out the organics left on the channel walls. The liquid fuel may be used under non-evaporative conditions to resovlate and remove inorganic residues within the channels. The resulting liquid mixture would be combusted off-line to provide additional heat for the system.

The advantage of using a microchannel fuel vaporizer rises from the efficient use of the dilute hydrogen in the anode effluent. This stream is not currently used in many fuel processor concepts. The specific design is chosen to provide a robust conversion technology. Traditional non-catalytic flame combustion schemes are sensitive to the hydrogen content in the feed stream and may have difficulties sustaining a flame during system transients

Conclusions

The microchannel vaporizer for use in an automotive fuel cell fuel processor was designed, tested, and demonstrated at both a bench and full-scale. The full-scale process is 4" x 6" x 1" (roughly the size of a paperback novel) and can process nearly 1000 L/min of gas (at STP) to vaporize the required fuel for an automobile. The total system pressure drop after optimization should be less than several psi with thermal efficiencies approaching 90%. Similar performance is expected for other microchannel reactor components in the complete fuel processor system.

Acknowledgments

This work was supported by the Office of Transportation Technology in the US Department of Energy. PNNL is operated by Battelle for the U.S. Department of Energy under contract DE-AC06-76RLO 1830.

References

ADL (Arthur D. Little), 1994, Multi-fuel reformers for fuel cells used in transportation, DOE/CE/50343-2.

ADL (Arthur D. Little), 1997, private communication.

Delphi, 1996, Research and development of a proton-exchange membrane (PEM) fuel cell system for transportation applications, DOE/CH/10435-02

Kumar, R., and S. Ahmed, 1995, Fuels processing for transportation fuel cell systems, presented at the First International Symposium on New Materials for Fuel Cell Systems, Montreal Canada, ANL/CMT/CP--84932.