Demonstration of Energy Efficient Steam Reforming in Microchannels for Automotive Fuel Processing

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Abstract

A compact, energy-efficient microchannel steam reforming system has been demonstrated. The overall volume of the reactor is 4.9 liters while that of the supporting network of heat exchangers is 1.7 liters[1]. The reactor contains alternating reaction and combustion gas channels, arranged in crossflow, to provide heat to the reaction. Use of a microchannel configuration in the steam reforming reactor produces rapid heat and mass transport which enables fast kinetics for the highly endothermic reaction. The microchannel architecture also enables very compact and highly effective heat exchangers to be constructed. A network of microchannel heat exchangers allows recovery of heat in the reformate product and combustion exhaust streams for use in vaporizing water and fuel, preheating reactants to reactor temperature and preheating combustion air. As a result of the heat exchange network, the system exhaust temperatures are typically ~50°C for the combustion gas and ~130°C for the reformate product while the reactor is operated at 750°C. While reforming isooctane at a rate sufficient to supply a 13.7 kWe fuel cell, the system achieved 98.6% conversion with an estimated overall system efficiency after integration with WGS and PEM fuel cell of 44% (electrical output / LHV fuel). The efficiency estimate assumes integration with a WGS reactor (90% conversion CO to CO_2 with 100% selectivity) and a PEM fuel cell (64% power conversion effectiveness with 85% H_2 utilization for an overall 54% efficiency) and does not include parasitic losses for compression of combustion air.

Introduction

A fuel cell powered car provides the potential of greater fuel efficiency and less pollution compared to conventional internal combustion engines. Although on-board hydrogen storage technology is being pursued, an alternative approach

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[1] The heat exchanger volume of 1.7 liters includes a low-temperature air preheater (0.7 liter) although this exchanger may not be required upon integration within a fuel cell system where cathode air is combusted. The volume excludes the low temperature water preheater (~0.1 liter) which was not utilized in generating the data presented.

is to process a liquid hydrocarbon fuel 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 system was designed and built with the key objectives being to demonstrate productivity sufficient to support a 10 kWe PEM fuel cell[2], to demonstrate conversions >90% and to demonstrate a reformer efficiency sufficient to support a >40% efficiency for an integrated PEM fuel cell system[3].

The experimental system demonstrated a capacity of 13.7 kWe capacity at 98.6% conversion with an estimated 44% overall system efficiency, exceeding the design objectives. In addition, productivity >20 kWe was demonstrated while maintaining conversion >90% and estimated system efficiency >40%. This paper describes the system and the results obtained.

System Configuration

The experimental system prior to application of insulation is shown in Figure 1. The Figure 1 caption explains the function of the various exchangers. A schematic of the system flows is shown in Figure 2 for the combustion side and in Figure 3 for the reaction side. The controls required to operate the system include metering pumps for each isooctane and water inlet, a controller to

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[2] The kWe capacity is calculated using an assumed WGS reactor performance (90% conversion, 100% selectivity to CO_2) and a 54% efficient PEM fuel cell (64% fuel conversion effectiveness with 85% fuel utilization).
[3] Efficiency is defined as (electrical output from fuel cell)/(lower heating value of input fuel).

maintain the desired air flow rate on the combustion side and 4 temperature controllers tied to hydrogen flow controllers used to control combustion temperatures at the primary combustor and each of the 3 secondary combustion points just prior to each of the reactor cells. In addition, there is a manual valve that allows incoming combustion air to be diverted around the high temperature recuperator if more heat is needed in the water vaporizor. This is used to operate at higher capacities when a proportional increase in combustion air flow is not available.
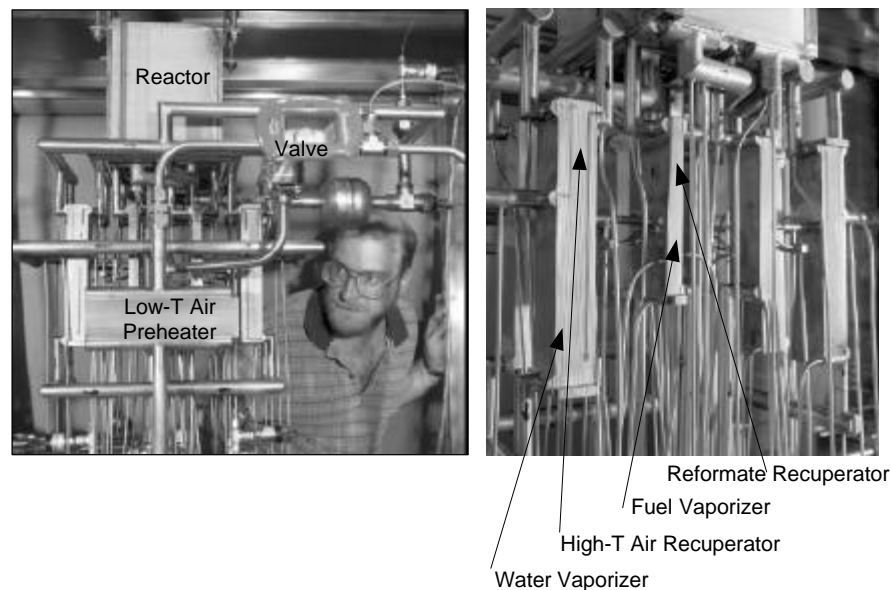
Fabrication Approach

The individual microchannel components are fabricated from 316L stainless steel in a process that includes photo-chemical etching of thin metal sheets which are then stacked and diffusion bonded to form a laminated structure with microchannels. The laminated fabrication approach is discussed in more detail in Reference 1.
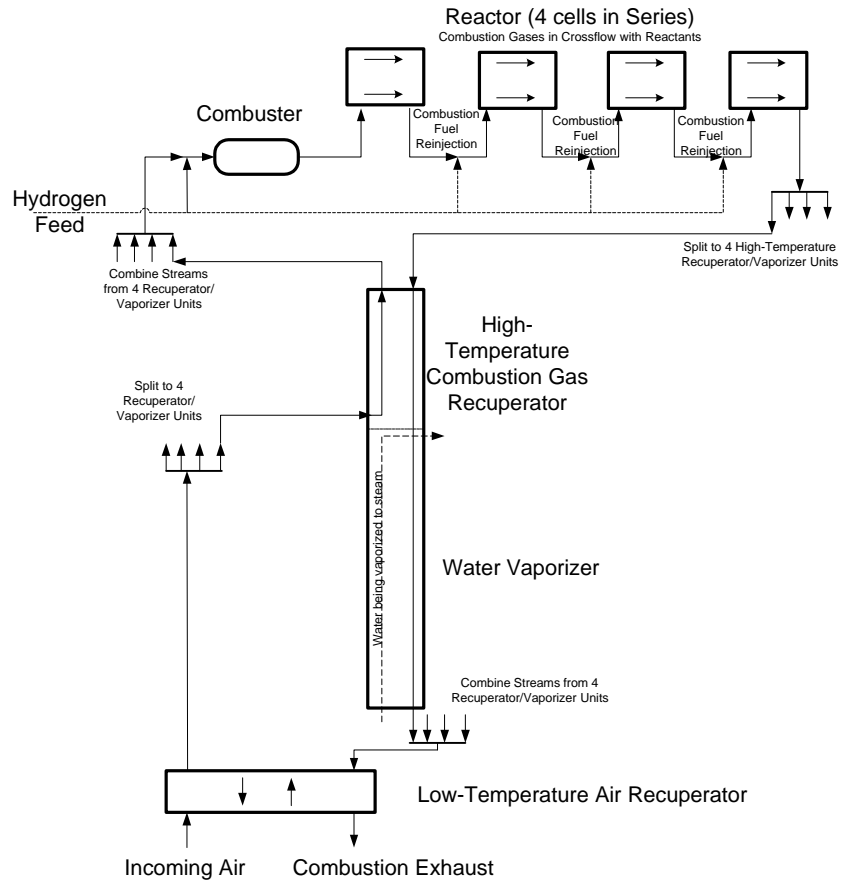
Experimental Results

A summary of operational data for 2 steady-state operating points is shown in Table 1. The reforming system is capable of achieving 98.6% conversion operating at 13.7 kWe capacity. In addition, the system can exceed 20 kWe capacity with conversions greater than 90%. The appropriate operating capacity of the system will depend on the level of conversion required to avoid problems due to unconverted fuel in components downstream from the reformer. The energy efficiency values in Table 1 take no credit for the fuel value of unconverted multi-carbon components that may show up in the anode gas (effectively assuming they are removed prior to the fuel cell). If unconverted fuel components can pass through downstream components and return with the waste anode gas the high output energy efficiency would be improved and the system could operate efficiently at the high end of its capacity. Alternatively, it could be smaller at a lower capacity level.

A plot of data for various operating points is shown in Figure 4. The reaction rate has an approximate Arrhenius temperature dependence which allows a simple model of the reactor to be formulated to predict productivity and conversion as a function of the reformate exit temperature. For a fixed level of conversion, the plot indicates a strong dependence of productivity on temperature. Alternatively, at a given hydrocarbon feed rate the conversion level is strongly dependent on temperature.

Reactor

Valve

Low-T Air
Preheater

Reformate Recuperator

Fuel Vaporizer

High-T Air Recuperator

Water Vaporizer

Figure 1. 10 kWe Microchannel Steam Reforming System. The picture on the left shows the reforming system with 4-cell reactor at top, and the low-temperature air preheater in front. The low-temperature air preheater uses the combustion exhaust leaving the water vaporizer to preheat incoming combustion air. This exchanger may not be necessary after system integration if air enters from the cathode of the fuel cell. The picture at right provides a closeup of the multistream exchangers directly below the reactor. To the outside are exchangers that include (in a single block) a high-temperature air preheater and water vaporizer. This exchanger takes the combustion exhaust from the reactor and uses it to first preheat incoming combustion air from the low-temperature air preheater and then to vaporize water. Toward the inside are exchangers that include (in each block) a reformate recuperator, a fuel vaporizer, and a water preheater. These exchangers take the hot reformate product from the reactor and use it to first heat vaporized water and fuel to near reactor temperature and then to vaporize the liquid fuel. The exchangers also include a section for preheating water when operating at high pressure. The vertically orientated exchangers are designed so that they can all be combined into a single integrated, multi-stream exchanger. However, to accommodate instrumentation the exchangers were bonded as separate units. The large number of small diameter tubes provide for detailed monitoring of temperature and pressure. When opened, the manual valve (left picture) allows some fraction of incoming air to bypass the high temperature combustion gas recuperator, thus leaving more combustion gas heat for use in the water vaporizer.

Reactor (4 cells in Series)
Combustion Gases in Crossflow with Reactants

Combuster

Combustion Fuel Reinjection

Combustion Fuel Reinjection

Combustion Fuel Reinjection

Hydrogen Feed

Split to 4 High-Temperature Recuperator/Vaporizer Units

Combine Streams from 4 Recuperator/Vaporizer Units

High-Temperature Combustion Gas Recuperator

Split to 4 Recuperator/Vaporizer Units

Water being vaporized to steam

Water Vaporizer

Combine Streams from 4 Recuperator/Vaporizer Units

Low-Temperature Air Recuperator

Incoming Air   Combustion Exhaust

Figure 2.   Flow Schematic for Combustion Gas Side of Steam Reformer System. Combustion gas flows through the four reactor cells in series and then through the four high temperature air recuperator/water vaporizors in parallel. The combustion gas then recombines before passing through the single low temperature air preheater. In this system, hydrogen is burned for fuel since the system is not yet integrated with a fuel cell and waste anode gas is not available. Most of the combustion occurs in the main combustor. However, additional fuel is burned after each pass through the reactor to restore the desired temperature before reentering the reactor.
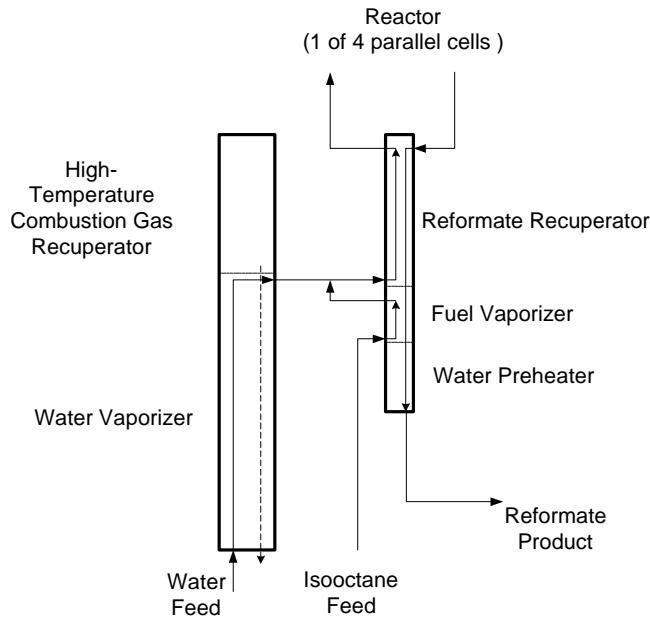
Figure 3. Schematic of Reaction Side Flows. There are 4 independent reaction cells in the reactor that operate in parallel. Each cell has a dedicated water and fuel vaporizer and reformate recuperator. Since each cell is independent, the processing rates of each cell can be independently varied. The water preheater is only used at high pressure. Near ambient pressure, the water preheater is bypassed and water is fed directly to the vaporizer as illustrated in the figure. .

Table 1. Steam Reformer System Performance at Two Conditions

Productivity[1]	13.7 kWe	22.2 kWe
Fuel Conversion to C1	98.6%	93.6%
Estimated System Efficiency[2,3]	44%	41%
Power Density[4]	2100 We/L	3500 We/L
Combustion Temperature	750°C	775°C
Combustion Exhaust Temperature	43°C	50°C
Reformate Exit Temperature	129°C	115°C
Dry Gas Composition	70.6% H_2	69.7% H_2
	14.6% CO	16.1% CO
	13.7% CO_2	12.3% CO_2
	0.9% CH_4	1.3% CH_4

1) 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 54% efficiency (85% H_2 utilization and 64%

fuel conversion efficiency). These assumptions are also used to calculate system efficiency.

2) Efficiency is calculated as 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 and CH_4 in the fuel cell waste anode gas are assumed to be combusted to provide heat for the system.

3) The PNGV 2000 target for system efficiency at 25% of system capacity is 40%. The 2004 goal is 48%.

4) The PNGV 2000 target for power density in the fuel processor is 600 We/L. The 2004 goal is 750 We/L. The goals include the volume of the water gas shift and CO cleanup as well as the reformer. However, the current reformer consumes only a fraction of the volume goal making it likely that an integrated system including WGS and CO cleanup can be made to meet the goal.
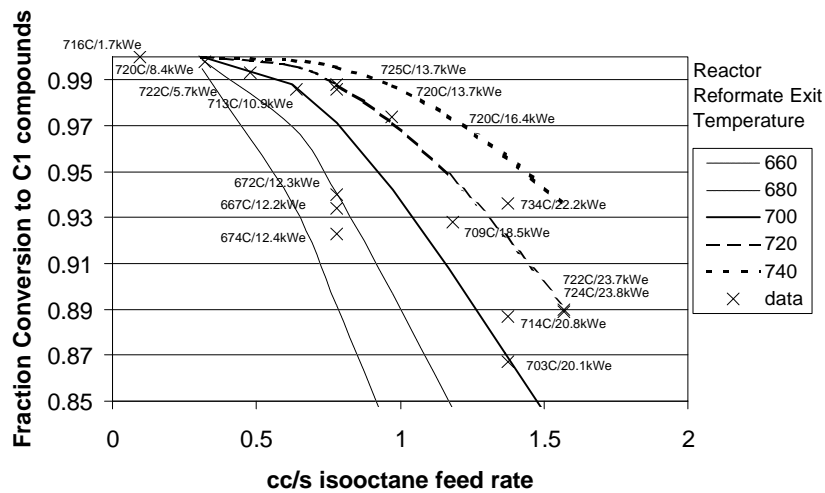
Figure 4. Relationship Between Fuel Reforming Rate and Conversion at Various Temperatures. The horizontal axis indicates the rate at which isooctane is being fed to the system while the vertical axis indicates the fraction converted to single carbon species. The curves show model predictions for conversion as a function of isooctane feed rate and reformate outlet temperature. Actual observed operating points are shown with labels indicating the reformate outlet temperature and calculated productivity. The productivity ratings in kWe are calculated as described in Table 1, footnote 1. The data plotted above are restricted to a steam to carbon ratio of 3 and to operating points where reaction pressure was not intentionally increased.

Thermal Efficiency vs. Processing Rate

In Table 1, a 44% efficiency is estimated for a system consisting of the steam reformer plus an assumed water gas shift reactor, CO cleanup and PEM fuel cell. The steam reformer within the integrated PEM system increases system efficiency because roughly half of the heat input required by the reformer is provided by the fuel value of the waste anode gas. However, this efficiency value tends to mask the efficiency of the network of microchannel heat exchangers in the reformer system. A theoretically obtainable efficiency for the reformer system can be calculated by summing the lower heating value (LHV) of the hydrogen and carbon monoxide leaving in the reformate for 100% conversion and equilibrium gas composition and dividing this quantity by the LHV of the isooctane fed to the reformer plus the net heat input required to sustain the reaction, vaporize fuel/water, and preheat reactants while recovering heat from the reformate sufficient to cool it to its dewpoint[1]. By replacing the net heat term in the denominator with the actual LHV of hydrogen burned as fuel to provide heat during an experiment the percent of theoretically obtainable efficiency can be evaluated. This quantity is shown in Figure 5 as a function of the processing rate of the system. The system is capable of >90% of theoretical efficiency over a range of 5 to 15 kWe capacity. At high processing rates the efficiency decreases due to lower conversion. At low processing rates longitudinal conduction in the heat exchangers begins to reduce efficiency.

## Heat Exchanger and Vaporizer Heat Transfer Densities

The efficient operation of the steam reforming system depends on a number of diffusion bonded microchannel heat exchangers. The heat exchanger network was sized to operate up to a processing rate of ~20 kWe in order that the heat exchangers would not limit the system productivity. The heat exchanger volumes and observed heat transfer duties and densities for the conditions reported in Table 1 are summarized in Table 2.

Transient Response

The system has a rapid warm transient response due to the very short residence time. The current manually adjusted metering pumps limit the rate at which process changes can be made. However, doubling the reformate output can be accomplished within 20 seconds, limited by the pump adjustment. The 2004 PNGV goal for warm transient from 10 to 90% is 1 second.

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[1] This definition penalizes the theoretical efficiency value for the heat required to vaporize water, which is needed as vapor downstream in the WGS reactor in any case. However, theoretical obtainable efficiency is only used as a point of comparison to evaluate the relative efficiency of the reforming system.
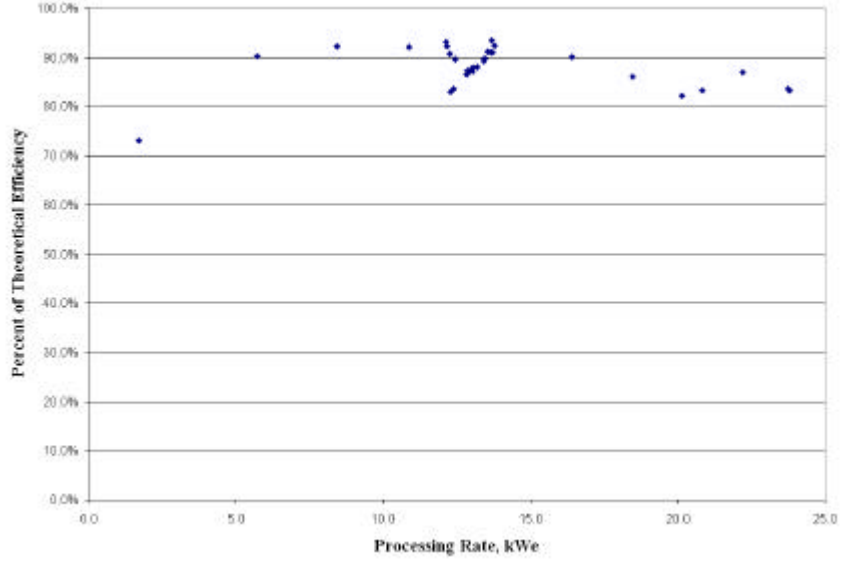
Figure 5. Fraction of Theoretical Efficiency Observed in Various Experiments. Test conditions shown are limited to 3:1 S:C and reformate exit temperature between 650 and 750°C. A value of 100% would indicate complete conversion of fuel to single carbon compounds, zero heat loss, recovery of heat from reformate stream sufficient to bring it to the dewpoint, and complete utilization of the LHV of the fuel combusted for heat.

Table 2. Heat Exchanger Duties for Conditions Reported in Table 1.

Exchanger	Bonded Stack [a]	Heat Exchanger Duty [b]		Bonded Stack Heat Transfer Density	
	cm^3	13.7 kWe Reformate	22.2 kWe Reformate	13.7 kWe Reformate	22.2 kWe Reformate
		Watts	Watts	W/cm^3	W/cm^3
Reformate Recuperator	41.3	705	1087	17	26
High-T Air Preheater	74	1517	1119[c]	21	15[c]
Low-T Air Preheater	726	1228	1346	1.7	1.9
Fuel Vaporizer	10.3	55	98.5	5	10
Water Vaporizer	125	1346	2344	11	19

See next page for footnotes

TABLE 2 FOOTNOTES

a- Volume within integrated exchangers apportioned between different heat exchange functions. The reactor system contains 4 of each heat exchanger with the exception that there is only 1 low temperature air preheater. Volume is taken as the volume of the diffusion bonded stack which includes the volume of the internal flow distribution headers.

b- Duties are for a single exchanger. For all units except the low temperature air preheater the total system duty can be determined by multiplying by 4.

c- The air flow available to the system was limited and was only increased by 12% in going from the 13.7 kWe condition to the 22.2 kWe condition. A control valve intentionally bypassed incoming air around the high temperature air recuperator to reduce its duty and increase heat available in the vaporizer section.

Conclusions

The current steam reformer system has successfully demonstrated that a microchannel steam reformer can achieve a significant capacity in a compact package while achieving high conversion of the hydrocarbon feed. In addition, a highly integrated system of microchannel heat exchangers and vaporizors has been demonstrated to allow the system to operate in an energy efficient manner. Although work remains to develop the system sufficiently for operation in an automotive setting, the current demonstration is a major step towards that goal.

Acknowledgement

References

1) Matson, D. W., P. M. Martin, D. C. Stewart, A. Y. Tonkovich, M. White, J. L. Zilka, G. L. Roberts. *Fabrication of Microchannel Chemical Reactors Using a Metal Lamination Process.* Microreaction Technology: Industrial Prospects. IMRET 3: Proceedings of the Third International Conference on Microreaction Technology. W. Ehrfeld, ed.