

A Compact Steam Reforming Reactor for Use in an Automotive Fuel Processor

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Abstract

Steam reforming was evaluated as a method for generating the hydrogen-rich gas stream needed for automotive polymer electrode membrane (PEM) fuel-cell applications. Tests were conducted on the steam reforming of a gasoline analogue, isooctane, in a compact microchannel reactor using a proprietary catalyst that enables a residence time of 2.3 milliseconds. Microchannels were used to add heat efficiently to the strongly endothermic reaction. A compact steam reformer unit with a volume less than 30 cubic centimeters was demonstrated to produce enough hydrogen gas to power a 1-kWe fuel cell. The unit was tested over a number of hours and thermal cycles with no perceptible change in performance. Based on these results, a full-scale, 50-kWe gasoline-based steam reforming system would have a volume less than 4 L, and a complete 50-kWe fuel processor is expected to be smaller than 8 L.

Introduction

Fuel-cell technology has the potential to improve both the efficiency and the environmental impact of automobile travel. A fuel cell can achieve a much higher overall system efficiency (45%) than an internal combustion (IC) engine (20%). The improvement in efficiency on that order will decrease significantly the fuel consumption of automobiles per mile traveled, slowing the drain on our fuel resources. The other virtue of the fuel cell is that its output is more environmentally benign than the IC engine. The waste stream from the fuel cell is a mixture of water and air, a tremendous improvement over the high temperature combustion products such as NO_x, SO_x and particulates that exit with the effluent from an IC engine.

The key to implementing automobile-based fuel-cell technology is to establish an on-board hydrogen gas source. The hydrogen gas reacts electrochemically in the membranes of the fuel cell to produce electrical current. At this time there is no infrastructure available to supply either gaseous or liquid hydrogen to fuel cell-based automobiles. Another option is to deploy a fuel processor upstream of the fuel cell that takes a liquid hydrocarbon fuel and chemically processes it into a hydrogen-rich gas stream suitable for the fuel cell. Liquid fuels are easy to pump into automobiles and are widely available. Of all the liquid fuels to be used in a fuel processor, gasoline has several advantages. Gasoline has the largest number of processing plants, the largest deployed capacity, and the largest distribution infrastructure. It is the authors' belief that making a gasoline-based fuel processor is the key to making fuel cells a commercial reality, and the work discussed in this paper, steam reforming of a gasoline analogue (isooctane), gives us reason to expect it is a realistic expectation.

The fuel processor is a chemical plant that uses multiple unit operations such as reactors, heat exchangers and separation units to produce the hydrogen gas stream, a fact that is a concern to those looking to commercialize this technology. Both the size and weight of a fuel processor are important design considerations for automobile deployment. Conventional chemical processing unit operations tend to be large and bulky, a consequence of the realities of mass and heat transfer limitations. The size of conventional chemical processing technology has created an opportunity for microchannel technology to enter the field of fuel processors. Microchannel devices shrink the dimensions through which energy and chemicals must travel to their desired location, and, consequently, heat and mass transfer are dramatically improved. These efficiencies are a tremendous advantage over conventional chemical

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reactor technology and design. Many reactions need to be run at slower residence times than their kinetics allow because the conventional technology cannot supply the heat and reactants quickly enough. Microchannel-based unit operations have the ability to keep up, allowing them to process the same amount of mass with a decisively smaller volume.

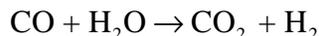
This paper discusses the results of testing a microchannel isooctane steam reformer as the primary conversion reactor, the chemical reactor in the fuel processor that converts the majority of the fuel into hydrogen and oxidized carbon. PNNL has built and demonstrated the first piece of the gasoline-based fuel processor, the gasoline vaporizer (Zilca-Marco et al. 1999; Tonkovich et al. 1999).

Background

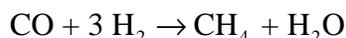
The steam-reforming reaction uses steam to oxidize hydrocarbons into CO and H₂. For the case of isooctane steam reforming, the reaction stoichiometry is



and the standard heat of reaction is strongly endothermic ($\Delta H_r^\circ = +1275$ kJ/mole of isooctane). Isooctane was chosen to simulate gasoline because it represents the mid-range molecular weight of gasoline's hydrocarbon mixture. The steam reforming reaction is often run at steam concentrations higher than the reaction stoichiometry shown above to avoid coke formation and to improve conversion. The steam concentration is usually given in the form of the steam-to-carbon ratio (S:C), the ratio of steam molecules per carbon atom in the reactant feed. A ratio greater than 1 points to a greater than stoichiometric steam concentration, and under those conditions the water-gas shift (WGS) reaction also takes place as a secondary reaction:



It is only slightly exothermic ($\Delta H_r^\circ = -41$ kJ/mole CO). The WGS reaction does two good things for the fuel processor: It produces additional hydrogen gas and converts carbon monoxide, a poison for PEM fuel cells, into carbon dioxide. An unwanted secondary reaction is the methanation reaction, which consumes hydrogen:



Steam reforming has not received much attention as the primary conversion reaction for fuel processors, mainly because steam reforming has the reputation of being a kinetically slow reaction with residence times on the order of one second. Its large endothermic heat load exacerbated the consensus. However, some system-level advantages to steam reforming intrigued us, so we decided to investigate steam reforming. First, because most PEM fuel cells run above atmospheric pressure, it is important that a fuel processor's primary conversion reaction run at a pressure higher than the fuel cell. Pressurizing liquid water and fuel for the steam reforming reaction is technologically straightforward and incurs a relatively small parasitic energy cost. Second, current fuel cell technologies do not consume all of the hydrogen produced, and, as presumed, a fuel processor cannot use all of the fuel fed to it. Thus the fuel-cell effluent steam should have both hydrogen gas and fuel, which could be combusted to provide a heat source for a steam reformer reactor. Third, a highly endothermic reaction has the advantage that if the reactor should lose its heat transfer fluid, it would self-quench. The endothermic reaction makes the steam-reforming reactor a safer reactor. If the kinetics of steam reforming could be greatly accelerated, a steam reformer reactor would be reduced in size and become attractive for use in a fuel processor.

Experimental Results and Analysis

Catalyst testing

Steam reforming catalysts were synthesized with the intention of achieving high conversion of isooctane and high selectivity to hydrogen while dramatically lowering the reactant residence times. Through powder catalyst screening, a strong candidate was chosen for isooctane steam reforming. This proprietary catalyst was put into engineered form and tested with a steam-to-carbon ratio of 6:1 and residence times of 7.4 ms. The extraordinary results are illustrated in Figure 1. At 650°C, the conversion of isooctane reached almost 100%, while the selectivity to hydrogen was on the order of 92%. The selectivity to CO₂ was 65%, by far more favored than CO and smaller hydrocarbons, with selectivities of 27% and 8%, respectively. The engineered catalyst was tested for more than 90 hours online under similar conditions without noticeable deactivation.

Based on these engineered catalyst results, the volume of an isooctane steam reformer can be reduced by three orders of magnitude over conventional reactors. This thousand-time reduction in reactor size means the primary conversion reactor for a fuel processor can conceivably be a steam reformer reactor. The key to implementing this engineered catalyst on the reactor scale was to devise a way to get the reaction heat into the reactor zone. And that is where microchannel technology comes in.

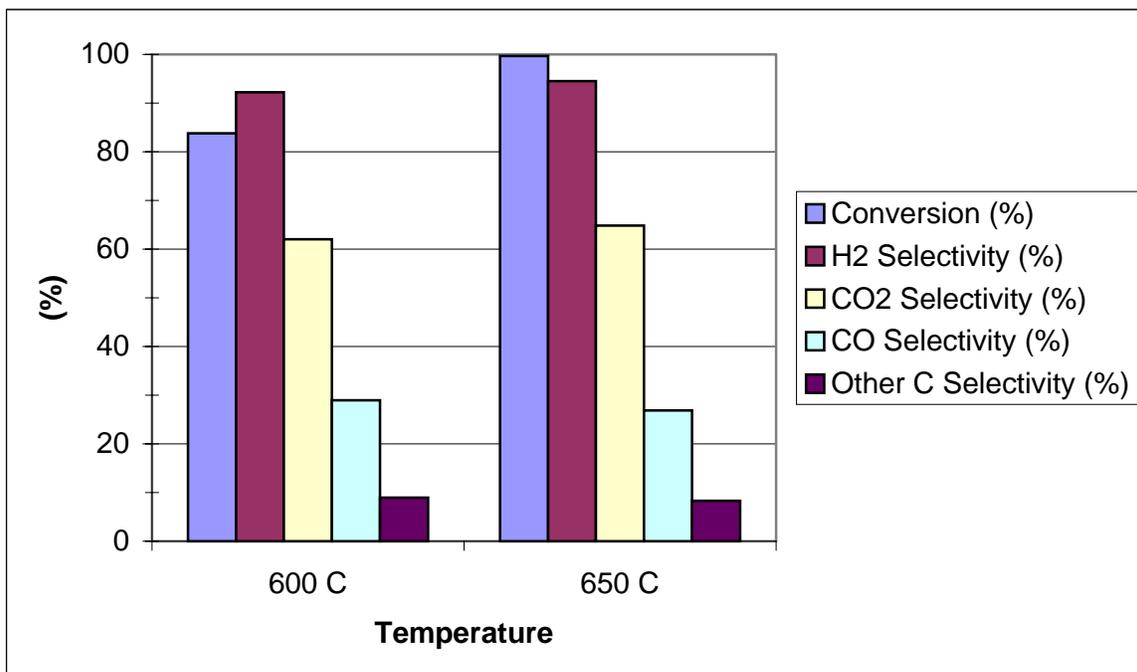


Figure 1. Engineered Catalyst Results for Isooctane Steam Reforming at 600 and 650°C. The steam-to-carbon ratio for both temperatures was 6:1 with a residence time of 7.4 ms.

Reactor testing

A microchannel isooctane steam reformer was built with a total volume of 30 cubic centimeters. This reactor has integrated heat exchange to add the heat needed for this highly endothermic reaction. The heat-exchange fluid used to heat the reactor zone was combustion gas. This design was built to process a hydrogen gas stream large enough to produce 1.0 kilowatt electric (kWe) power in a PEM fuel cell.

The data from the microchannel isooctane steam reformer's first hour of operation are shown in Figure 2. The reactor zone was operated at 650°C and one atmosphere. The reactants had a 6:1 steam-to-carbon ratio and a 2.3 millisecond residence time in the reactor. The reactor was able to reach isooctane conversions ranging from 86.5% as a minimum to 95% at a maximum. The hydrogen selectivity was in the 85 to 90% range as well. These results

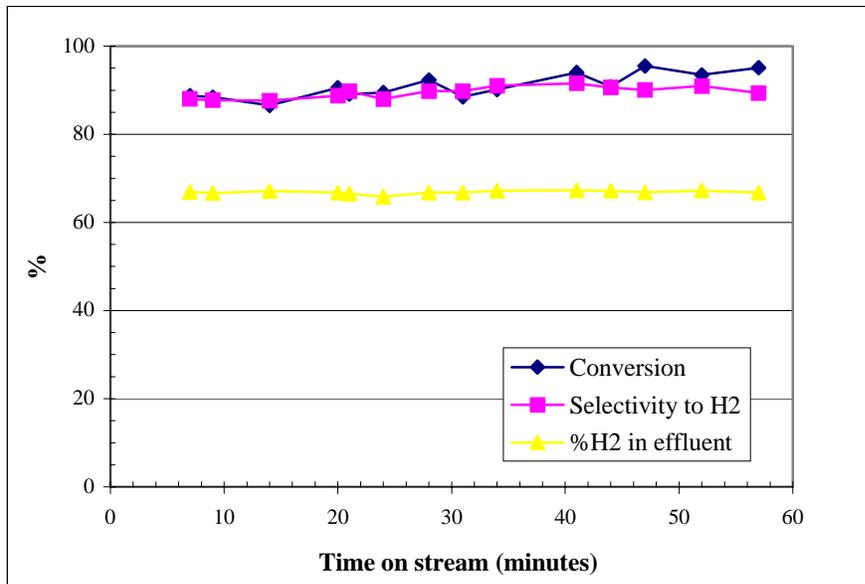


Figure 2. Isooctane steam reformer's first hour of operation: Temperature = 650°C, 1 atm, 6:1 steam-to-carbon ratio, 2.3 ms residence time

are not as high as the engineered catalyst data shown earlier, but they are also at a shorter residence time and are still very close to those presented. More importantly, the results show that this microchannel isooctane steam reformer reactor can supply the heat necessary to sustain this reaction for such a fast flow rate. The reactant side pressure drop through this device was roughly 6.9 kPa (1.0 psi). The expected fuel cell output under these conditions was 0.5-kW_e. This demonstration was continued for another hour and then shut down.

Another three demonstrations were run using this device, putting the device through four thermal cycles. These four thermal cycles put the device through over 12 total hours of on-line service. The results of the final three thermal cycles in bar chart form in Figure 3. All of the results in Figure 3 are at 1 atm, a 630 to 670°C temperature range, and a 2.3 millisecond residence time. The results for the 0.5-kW_e power output and the 6:1 steam-to-carbon ratio for these tests are consistent with the values shown in Figure 2.

As the steam-to-carbon ratio is lowered from 6:1 to 5.7:1, 5:1, 4.06:1, and finally to 2.97:1, the isooctane conversion decreases but the hydrogen selectivity remains steady. At constant residence time, the effect of reducing the steam-to-carbon ratio is the same as increasing the isooctane flow rate. So while the conversion decreases with decreasing steam-to-carbon ratio, the amount of isooctane being converted increases, resulting in a net increase in hydrogen generation. This is seen in the higher electrical power output listed with these values. The last set of bar data on the far right side of Figure 3 is taken with a 5.7:1 steam-to-carbon ratio and a 1.1 millisecond residence time, resulting in a 1.0-kW_e power output. The conversion and hydrogen selectivity results at 1.1 millisecond are not much lower than the corresponding values at 2.3 milliseconds; these results show that there may be more isooctane steam reforming capacity available in this reactor.

Conclusions

A microchannel steam reformer was demonstrated using a gasoline simulant, isooctane. The results show that this reactor can achieve 90% conversion of isooctane and 90% selectivity to hydrogen at a 2.3-ms residence time, 3 orders of magnitude faster than conventional technology. The major achievement of this reactor is that it can match the performance of a small, engineered catalyst while producing enough hydrogen gas to power a 1.0-kW_e PEM fuel processor. The reactor was able match the catalyst performance by efficiently delivering the needed heat load to keep up with the millisecond residence time. The overall

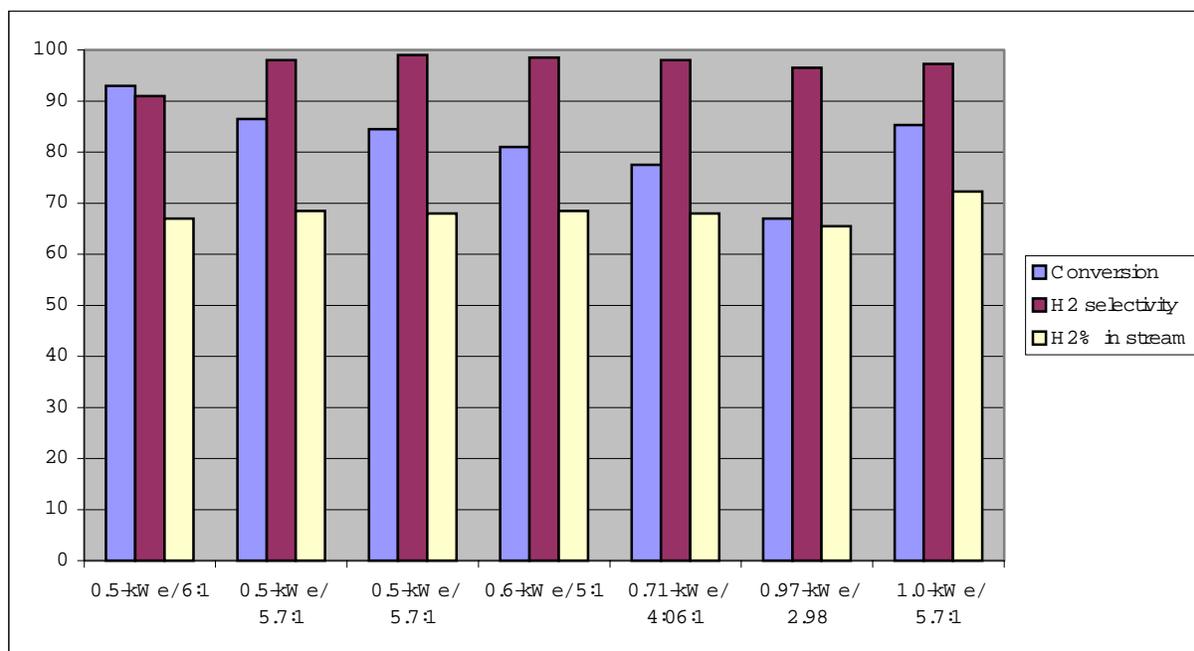


Figure 3. Isooctane Steam Reformer Reactor Performance at Higher Power Outputs/Lower Steam-to-Carbon Ratios

volume of the isooctane steam reformer is 30 cubic centimeters, leading us to believe that a 50-kWe fuel processor's steam reformer unit will be less than 4 liters and the entire fuel processor less than 8 liters.

Acknowledgments

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