IV.F.3 Microchannel Reformate Cleanup: Water Gas Shift and Preferential Oxidation

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Objectives

- Apply microchannel architectures to reduce size and weight, improve fuel efficiency, and enhance operation of fuel processors for transportation and stationary fuel cell power systems.
- Pursue microchannel advantages for CO cleanup, focusing on water gas shift (WGS) and preferential oxidation (PROX) reactors.
  - Demonstrate 90% conversion of CO in a single-stage WGS reactor that scales to less than three liters at full scale (50 kW_e).
  - Evaluate the potential importance of microchannel architectures in reducing the size and weight and improving performance of PROX reactors.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- J. Durability
- L. Hydrogen Purification/Carbon Monoxide Cleanup
- M. Fuel Processor System Integration and Efficiency

Approach

- Demonstrate a compact, differential-temperature, microchannel water gas shift reactor.
  - Select and characterize a high-activity shift catalyst.
  - Calculate the optimal temperature profile.
  - Demonstrate proof-of-concept with a multi-channel microreactor.
  - Design and test a 2-kW_e-scale WGS microreactor.
  - Demonstrate lifetime and durability of the engineered catalyst.
  - Integrate with a steam reforming fuel processor.
- Investigate approaches for PROX reactor enhancements with microchannels.
  - Evaluate industrial PROX catalysts for fast kinetics.
  - Confirm favorable operational characteristics at the 2-kW_e scale.
  - Investigate weight reductions through use of low-density alloys.
  - Investigate transient and start-up characteristics.
  - Integrate with a steam reforming fuel processor.

Accomplishments

- Designed, fabricated, and tested a compact, single-stage, 2-kW_e-scale WGS microchannel reactor.
  - Invented a novel microchannel configuration to increase the fraction of the reactor occupied by catalyst to 52% while maintaining good temperature control.
  - Designed and built a single-stage, 2-kW_e-scale WGS microreactor at a size of <300 mL.
  - Operated the WGS microreactor up to 2.5 kW_e productivity on steam reformate while achieving CO reduction from 12% to <1% (dry basis) at a gas hourly space velocity (GHSV) of 80,000 h^{-1}.
  - Projected a full-scale WGS reactor to achieve 14,700 W_e/L power density (3.4 L) and 6,900 W_e/kg specific power (7.2 kg) at 50 kW_e.
- Operated prototype microreactor as a combined first and second PROX.
  - Selected a Süd-Chemie non-precious metal catalyst for the first stage and an Engelhard precious metal catalyst for the second stage.
  - Decreased CO from 1% to <10 ppm at 2-kW_e throughput with an overall O_2/CO ratio of 1.2 and a combined GHSV of 93,000 h^{-1}.

Future Directions

- Continue catalyst development with focus on durable engineered forms of commercial WGS catalysts.
- Evolve PROX reactor concepts for higher productivity and improved thermal control.
- Integrate WGS and PROX in an integrated steam reforming fuel processor.
- Demonstrate rapid start-up of an integrated steam reforming fuel processor.
- Pursue fabrication alternatives to facilitate low-cost manufacturing targeting low-temperature components.

Introduction

By facilitating point-of-use production of hydrogen from conventional hydrocarbon fuels, fuel processors are important for converting to a hydrogen economy. However, fuel processors must be fuel-flexible, compact, energy-efficient, and, of course, affordable. Attaining DOE fuel-flexible fuel processor targets for size and weight, rapid start-up, rapid transients, and energy efficiency for on-board fuel is made possible by the ability to achieve rapid heat and mass transfer rates in microchannels. This has been demonstrated in the past for the highly endothermic steam reforming reaction in microchannel reactors having integrated heat exchange to supply the necessary heat. This project extends the effort to the areas of reformate cleanup and balance-of-plant in order to identify other elements of a fuel processing/fuel cell system that can benefit from the microchannel architecture.

The water gas shift (WGS) reaction is the conventional processing step after the fuel reformer to convert carbon monoxide to carbon dioxide, thereby reducing CO as a poison for polymer electrolyte membrane (PEM) fuel cells while increasing hydrogen yield. The WGS reaction is exothermic, so that high-temperature operation favors kinetics but equilibrium is more favorable at low temperature. The conventional approach is to operate a high-temperature shift (HTS) reactor above 400°C, followed by a low-temperature shift (LTS) reactor operating below 300°C to achieve the necessary conversion with a heat exchanger in between to cool the reformate. The WGS subsystem, particularly the low-temperature shift reactor, is one of the largest components in the fuel processor. A more optimal temperature profile could reduce the size of the shift subsystem and reduce the amount of catalyst required.

The preferential oxidation (PROX) reactor is used to reduce carbon monoxide to levels that can be tolerated by PEM fuel cells by selectively oxidizing the CO with air. Typically, PROX catalysts have a relatively narrow temperature window where CO conversion and selectivity are high. Conventional approaches typically use up to 4 stages of reactors

with heat exchangers between to control the reaction temperature. Integrating microchannel heat exchange within a PROX reactor will improve temperature control, thereby improving productivity while reducing hydrogen losses.

Approach

For over 10 years, Pacific Northwest National Laboratory (PNNL) has been developing microchannel technologies where heat and mass transfer processes occur very rapidly within arrays of sub-millimeter channels, leading to process intensification—high productivity per unit hardware volume. This approach is very effective for reducing the size and weight of hardware, as is needed for meeting DOE targets for fuel-flexible fuel processors. Microchannel reactors and heat exchangers can also facilitate very high heat exchange effectiveness, giving high energy efficiency, and enable rapid start-up and transient response. One example is catalytic microreactors for highly exothermic or endothermic reactions with rapid kinetics, such as steam reforming with precious metal catalysts. The microreactor approach is also effective with processes that benefit from precise thermal control. Water gas shift is an exothermic, reversible reaction with increasing kinetic rate at higher temperature, but more favorable equilibrium at lower temperature. Consequently, a microreactor that establishes a thermal profile that effectively trades off kinetics and equilibrium as conversion proceeds has the potential to significantly decrease the amount of catalyst required, reduce the size of the WGS system, and simplify the overall system by replacing three components in conventional systems with a single integrated unit.

The requirements for preferential oxidation are high conversion of CO to CO_2 and high selectivity relative to hydrogen oxidation to minimize loss of the desired product. The trade-off between kinetics and selectivity leads to a narrow acceptable operating range for PROX catalysts. Consequently, integrating microchannel heat exchange into the PROX reactor can improve temperature control, leading to higher overall catalyst productivity, improved selectivity, and more effective use of the heat of reaction elsewhere in the system.

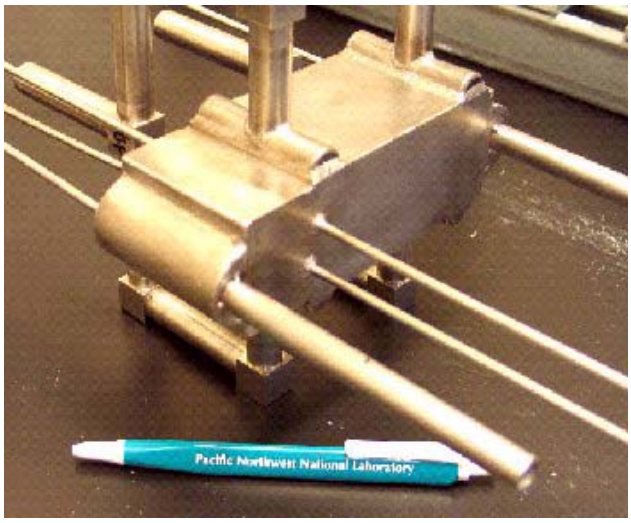

Figure 1. Prototype Differential-Temperature WGS Microreactor Designed for 2-kW_e Scale

Results

The WGS microreactor shown in Figure 1 was designed, built, and successfully operated at 2.5 kW_e equivalent productivity using Süd-Chemie PMS-5B WGS catalyst. The reactor was built with two sections operating in series. The front section operates essentially adiabatically with no active heat exchange embedded and contains copper foam wash-coated with catalyst. The back section, the core of which is shown in Figure 2, has embedded heat exchange channels for establishing a monotonically decreasing temperature profile. Strips of FeCrAlY felt wash-coated with catalyst were loaded into the 125 reaction channels seen on the smaller face in Figure 2. The heat exchange channels, which can be seen on the side of the reactor in Figure 2, were covered with plates and headers on each side to allow for concurrent or counter-current cooling air flow. The catalyst strips accounted for 52% of the reactor volume.

The reactor was operated for over 50 hours at flow rates equivalent to 1-2.5 kW_e fuel cell power levels assuming 44% efficiency in a PEM fuel cell. The CO level was reduced to less than 1% (dry) at 90% CO conversion at the highest reformate flow corresponding to 2.5 kW_e power level. At this level, the catalyst GHSV was 80,000 h^{-1} for the overall reactor. The steam reformate feed was comprised of dry gas having a composition of 12% CO, 14% CO_2,

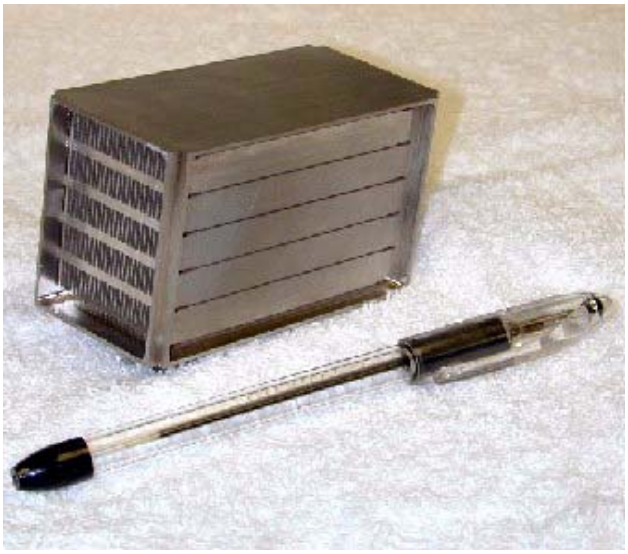

Figure 2. Differential-Temperature Section of the 2-kW_e-Scale WGS Microreactor

and 74% H_2, with water added at a ratio of 0.5:1 steam to dry gas.

Parameters that were varied during testing included the feed flow rate and temperature, and flow and inlet temperature of the cooling air. Results are summarized in Figure 3, showing the outlet CO concentration as a function of outlet temperature for both the adiabatic section (between the sections) and the differential-temperature section. An equilibrium curve is included for comparison. The data show that at the 1-kW_e level, the reformates leaving both the adiabatic and differential sections were at equilibrium, with the lowest measured CO level being 0.36% CO (dry), representing 96.5% conversion. At the 2-kW_e level, the reformate was in WGS equilibrium at temperatures above 260°C, but the reactor became kinetically limited when the cold end dropped below 260°C. At this flow rate, the minimum CO level achieved was 0.67% (dry) at 93.6% CO conversion. Reactor performance was not strongly dependent on the inlet temperature or the cooling air flow and temperature.

Size and weight estimates for a full-scale 50-kW_e WGS microreactor are 3.4 L and 7.2 kg, respectively, which correspond to 14,700 W_e/L power density and 6,900 W_e/kg specific power. The size of a comparable conventional 2-stage WGS system with intermediate heat exchanger utilizing the same

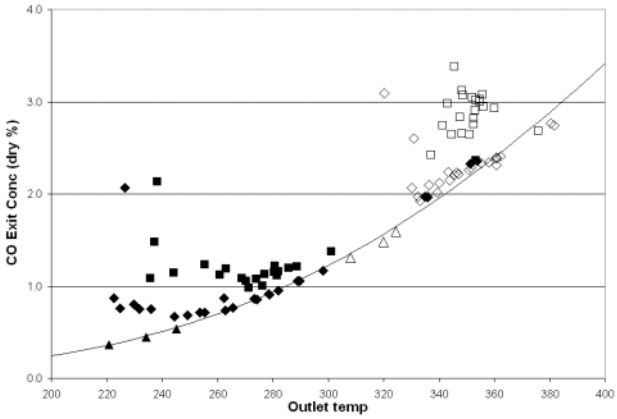

Figure 3. Performance of the prototype WGS microreactor operating with a steam reformate feed (12.4% CO and 14.3% CO_2, dry gas) and 0.5 steam to dry gas ratio showing CO conversion at the outlet of the adiabatic section (open symbols) and from the reactor (filled symbols) versus temperature of the stream at a 1-kW_e equivalent flow rate (▲), a 2-kW_e rate (♦), and a 2.5-kW_e rate (■). The curve indicates the equilibrium conversion.

precious metal catalyst is estimated to be 8.9 L, assuming 350 g/L catalyst loading onto a 600 cpi monolith, total reactor volume 25% greater than catalyst volume, and 5 W_t/cm^3 heat transfer power density in the heat exchanger. The differential-temperature microreactor concept demonstrated in this work represents approximately 2.6 times reduction in hardware volume.

The prototype reactor shown in Figure 4, originally designed and tested as a first-stage PROX, was reconfigured as a combined first- and second-stage PROX with the objective of reducing CO level from 1% to less than 10 ppm in one device. The last chamber of a sequence of four was loaded with Engelhard precious metal PROX catalyst, while Süd-Chemie non-precious metal catalyst remained in the other three. A microchannel heat exchanger within the reactor removes the heat generated from the reaction, and air was added independently into each of the four chambers, providing additional temperature control as well as improved selectivity.

The PROX reactor was operated successfully at a 2-kW_e productivity level, reducing the CO level from 1% to less than 10 ppm, as shown in Figure 5. The

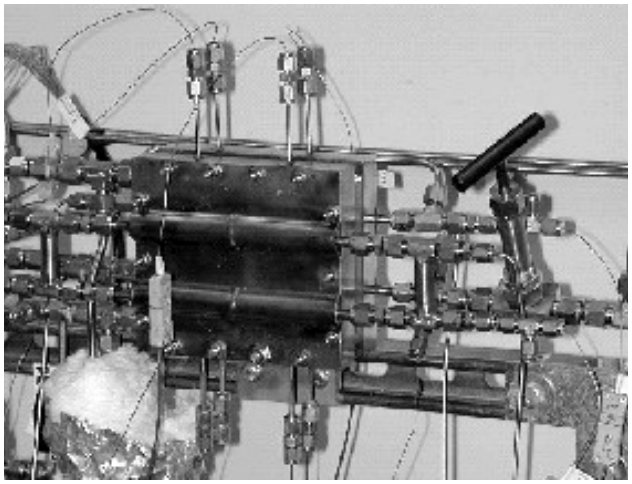

Figure 4. Prototype PROX Reactor with Microchannels for Quasi-Isothermal Operation and Multiple Compartments for Staged Air Injection

reactor was operated isothermally at about 200°C at a steam to dry gas ratio of 0.3 and an overall O_2/CO ratio of 1.2. The combined GHSV, including all of the catalyst, was 93,000 h^{-1}.

Conclusions

The concept of a differential-temperature WGS microreactor was successfully proven at the 2.5-kW_e scale, with greater than 2.5 times reduction in hardware volume over conventional 2-stage approaches. Operating on steam reformate, 90% conversion of CO was achieved, reducing the CO level from 12% to <1% in a single device at an overall GHSV of 80,000 h^{-1} with the Süd-Chemie PMS-5B catalyst. At a reactor volume of less than 300 mL, a power density of 6,900 W_e/L was realized, which will increase as reactor scale increases. Catalyst durability remains an issue for this class of precious metal catalyst, and future work will focus on lifetime and cycle testing and integration within a complete fuel processing system.

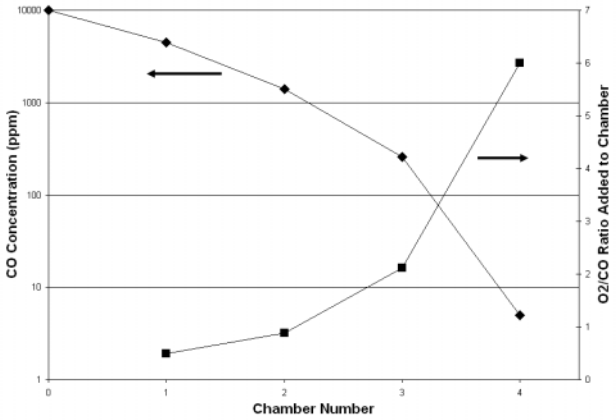

Figure 5. Decrease of CO concentration from chamber to chamber (♦) through the combined 2-stage PROX reactor with integrated microchannel heat exchange operating at a 2-kW_e equivalent flow rate starting from 1% CO and 0.3 steam to dry gas ratio. Air injection into each stage is represented by the O_2/CO ratio (■) with the overall ratio being 1.2.

A prototype reactor was successfully operated as a combined first- and second-stage PROX in a single device. The ability to manage temperature with integrated microchannel heat exchange and distributed air injection enabled a reduction of CO level from 1% to 10 ppm at 93,000 h^{-1} GHSV with an overall O_2/CO ratio of 1.2. This work demonstrates the inherent advantage of microchannel architectures for superior thermal control.

Special Recognitions & Awards/Patents Issued

1. TeGrotenhuis, W.E., R.S. Wegeng, G.A. Whyatt, V.S. Stenkamp, P.A. Gauglitz, "Microsystem Capillary Separations", U.S. Patent 6,666,909, 2003.