Novel Catalytic Fuel Reforming

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Objectives

The ultimate goal of this research project is to develop technology that will produce pure hydrogen from natural gas and logistical fuels using catalytic steam reforming and membrane hydrogen separation.

Phase III is intended to advance the state of InnovaGen™ fuel processing technology to the point of alpha readiness. This means that the fundamental design of key subsystems will evolve to include:

- Mature configurations (geometry and component placement defined)
- Material specifications
- Value engineering, design for manufacturability
- Reliability engineering and modeling.

Phase III includes considerable research, engineering, analysis, design and testing efforts. The result of these efforts will be prototypes capable of successfully completing a multi-unit test program representative of specified operating conditions.

Technical Barriers

This project addresses the following technical barriers from the following sections of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

Fuel Cells

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

Production

- A. Fuel Processor Capital Costs

Approach

- Conduct system analyses and generate design specifications.
- Design and fabricate components.
- Test components.
- Design process configurations.
- Evaluate configurations with model simulation.
- Predict component and operational requirements with model simulation.
- Conduct iterative testing of integrated system.

Accomplishments

- Concluded testing of the Phase II 1-kW diesel fuel processor platform.
- Concluded testing of the sulfur tolerance of a 100-W palladium/copper (Pd/Cu) membrane assembly.
- Concluded long-term catalyst testing for natural gas reforming.
- Disassembled and inspected 100-W membrane module after testing.
- Disassembled and inspected 1-kW fuel processor after testing.
- Developed new reactor and burner design concepts. Developed a prototype micro-channel cross-flow combustor.
- Developed membrane module design concepts. Designed and procured components for a membrane/coupon test fixture.
- Developed improvements to the fuel injector design. Generated an injector nozzle test program. Proceeded with the specification and procurement of equipment for testing the fuel injector and mixer.
- Continued work on heat exchanger design concepts. Established final requirements for heat exchangers.
- Finalized system operating and design parameters.

Future Directions

- Increase system efficiency and reduce system size and weight.
- Further develop hydrogen purification module.
- Improve system packaging.
- Scale up design to at least 60 LPM hydrogen output; enough for a 5-kWe fuel cell.
- Complete micro-channel implementation.
- Automate start-up, operation, and shut-down.
- Perform more complete thermal integration.
- Focus on manufacturability, cost reduction and high-volume production.
- Fully integrate with at least one fuel cell model.
- Thoroughly test reliability.
- Enhance controls - off-site monitoring, data mining, self-diagnostics.
- Complete documentation - drawings, bills of material, manufacturing routers.

Introduction

To be marketable now, fuel cells need to use primary fuel sources from existing production and distribution networks - i.e. natural gas, gasoline, diesel or jet fuels. Fossil fuel-powered fuel cells or refueling stations can form the bridge to a future when renewable resources power fuel cells. When compared to compressed hydrogen, reformed hydrocarbon fuels offer a significant cost advantage in the delivery of power. The high energy density of these fuels will also contribute to increased run times per unit of fuel consumed, and size and weight reductions associated with fuel storage.

To meet this need, InnovaTek is integrating microreactor technology with advanced sulfur-tolerant catalysts and hydrogen membrane technology to create a fuel processor for hydrogen generation. The ultimate goal of this cooperative project is the development of a catalytic reactor heated by the combustion of membrane by-products (raffinate) for the production of clean hydrogen by steam reforming hydrocarbon fuels. Advanced membrane technology is being used to remove CO and CO_2 from the reformate. The fuel processor being developed will provide a pure output stream of hydrogen that can be used without further purification for electrical generation by a PEM fuel cell.

Approach

The ultimate goal of this research program is to develop fuel processing technology that makes it possible for fuel cells to replace internal combustion engines as the power source for electrical generators and auxiliary power units in the 1-5 kW range. The fuel processor developed will produce pure hydrogen from fuels using cost-competitive, highly efficient catalytic steam reforming and membrane separation technology.

The design and optimization of a fuel processing system is complex because of the number of required components and functions (Table 1).

The following objectives (broken down by key subsystems) were identified to achieve our goal.

Overall System Modeling, Analysis and Design

- update model (optimize efficiency, provide design parameters)
- generate and maintain process and instrumentation diagram (P&ID) (revision control and distribution)

Reformer

- burner (convert to diesel start-up)
- vaporizer and superheater (micro-channel alternatives, integration into reactor)
- catalysts (sulfur tolerance, deposition, reforming temperature reduction)
- reformate condensate (recycling, evaporation, disposal)
- reactor design (micro-channel implementation, catalyst deposition, manufacturability)

Fuel Injector

- mixer (develop next generation diesel injector, steam mixer)

Membrane H_2 Purifier

- research contamination causes (investigate Zn, Cd and other contaminants)
- membrane material selection (optimize material form and composition)
- membrane module design (optimize design of membrane module)
- thermal integration (eliminate external heating)

Thermal Management

- condensate cooling/condensing (cooling system design, efficiency improvements)
- other heat exchangers (micro-channel alternatives, integration into the reactor)

Table 1. Primary Components of InnovaTek's Fuel Processor

Component	Function	Product
Catalytic Reactor	Catalytically reforms fossil fuel	Reformate (H_2, CO_2, CO)
Catalyst	Catalyzes the reforming reaction	Reformate
Combustor	Burns raffinate to provide heat for the reforming reaction	Heat, CO_2, H_2O
Fuel injector	Injects and mixes fuel and steam into the reactor	Vaporized steam/fuel mixture
Heat exchangers	Provides the proper temperature for each component	Warmer or cooler gas streams
H-permeable membrane	Converts reformate to pure hydrogen and produces raffinate (membrane reject stream) for combustor	Pure hydrogen, raffinate (H_2, CO_2, CO)

Sulfur Management

- de-sulfurization of reformate (as necessary, preferably re-generative and in-situ)
- desulfurization of fuel (research alternatives)
- thermal integration (eliminate external heating)

Operational Considerations

- safety (failure mode and effect analysis [FMEA], hazard analyses, etc.)
- reliability (reliability modeling, test programs)
- code requirements (research requirements, establish design guidelines)
- manufacturability, maintainability (establish targets, schedule design reviews)

Documentation

- drawings (finalize standards for format, archiving etc.)
- product data management (establish data master, configuration management and other requisite systems)

Physical Layout and Balance of Plant (BoP), including:

- pumping (research and obtain more reliable, less expensive alternatives)
- insulation and shrouds (improve performance and aesthetics)
- valves, orifices, thermocouples, transducers, etc. (integrate control devices)

Sensors and Controls, including:

- metering and flow measurement (eliminate expensive mass flow controllers)
- automation (automated shut-down, start-up and operation)
- hardware, software design (establish requirements for controllers and software)
- diagnostics (implemented as required for troubleshooting)
- data logging (establish requirements, minimize excess data collection)

Results

Catalyst and Membrane Testing

Steam Reforming Catalyst Testing. Over 1,000 hours of catalyst testing was completed using natural gas as a feedstock. The reforming occurs at 850°C with steam/carbon ratio of approximately 3.5. Figure 1 shows the product composition for the last half of the test. Hydrogen concentration is about 75%; the product contains about 1-2% unconverted methane due to the pressure (>80 psig) at which the steam reforming was conducted. This agrees with thermodynamic calculations. The total product flow

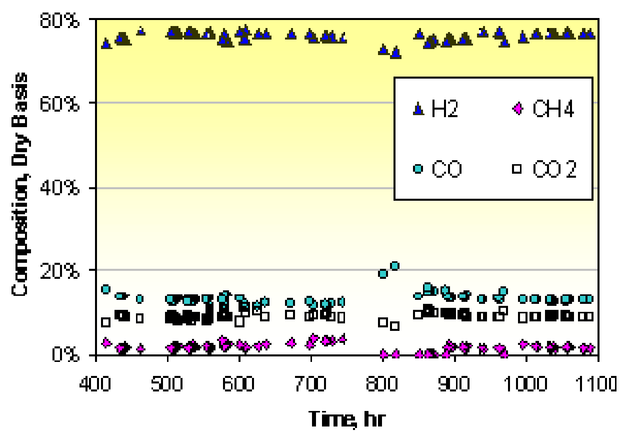

Figure 1. Product Gas (H_2, CO, CO_2, and CH_4) Composition During Steam Reforming of Natural Gas Using InnovaTek's Proprietary Catalyst (ITC #1148); reaction temperature 850°C, water feed rate 1.0 ml/min, natural gas feed rate 380 ml/min, pressure 84.7 psi

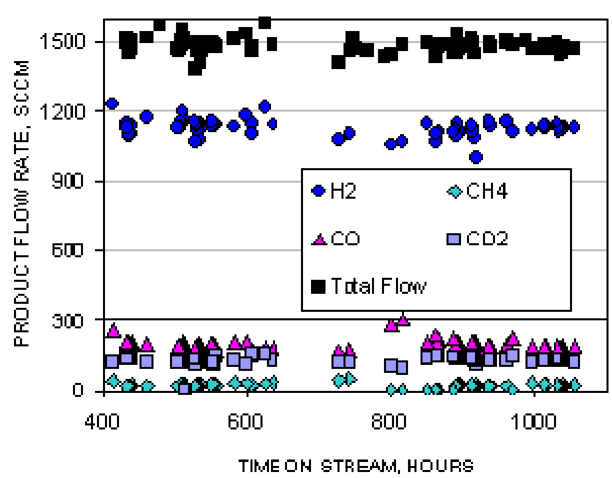

Figure 2. Product Gas (H_2, CO, CO_2, and CH_4) Flow Rates During Steam Reforming of Natural Gas

rate was measured and is plotted in Figure 2 About 1.5 SLM product was produced with a natural gas feed rate of about 380 mL/min, which corresponds to approximately 95% conversion of the natural gas. An 80-hour test with ultra-low sulfur (~5 ppm) diesel, a developmental product obtained from Chevron Phillips Chemical, was also successfully completed (Figure 3).

Membrane Hydrogen Purifier Performance. We designed and fabricated a hydrogen-permeable metal membrane assembly and tested it with simulated reformate with and without sulfur. The 97 ppm concentration of sulfur in the sulfur-containing reformate represents the result of reforming fuel containing approximately 800 ppm sulfur (by weight). Tests were conducted at a pressure of 90 psig. Optimum results were obtained at a membrane temperature of 500°C when sulfur was present and at 400°C without sulfur. Although the sulfur apparently causes some degradation of permeation initially, it appears that performance stabilizes after approximately one hour of run-time. The ultimate recovery with sulfur present is approximately 57% of the recovery without sulfur (Figure 4).The results show promise that a sulfur-tolerant membrane module can be developed but that its surface area will need to be about 1.75 times larger to achieve the same hydrogen permeation rate that is possible when sulfur is not present in the reformate. A visual inspection of the module after disassembly showed no adverse effects from the testing.

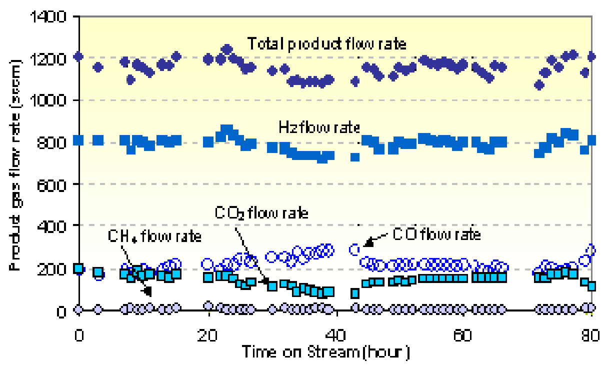

Figure 3. Steam Reforming of Low-Sulfur Diesel Fuel Using InnovaTek's Proprietary Catalyst

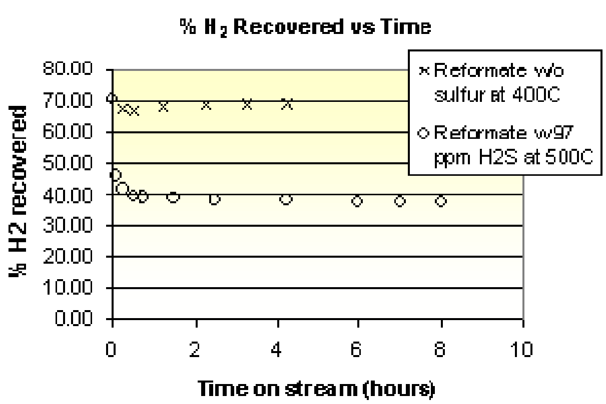

Figure 4. Hydrogen Recovery as a Function of Time and Sulfur Concentration

System Integration

System components were integrated according to the simplified schematic in Figure 5. Table 2 summarizes the operating parameters and system specifications as they currently are defined. We are able to achieve a 49% efficiency using a recuperator to recapture heat from the exhaust to pre-heat combustion air.

Prototype Operation and Testing

We performed continuous testing of the 1-kW prototype using diesel fuel, logging approximately 120 hours of run-time. Over the course of operation, the sulfur content of the fuel was increased incrementally from 50 ppm to 100 and finally to 250 ppm. During these tests, increased understanding was obtained for catalyst and membrane performance in an integrated system. The fuel injector was found to be a critical component that can help eliminate coking, one of the most serious problems associated with reforming heavy hydrocarbon fuels.

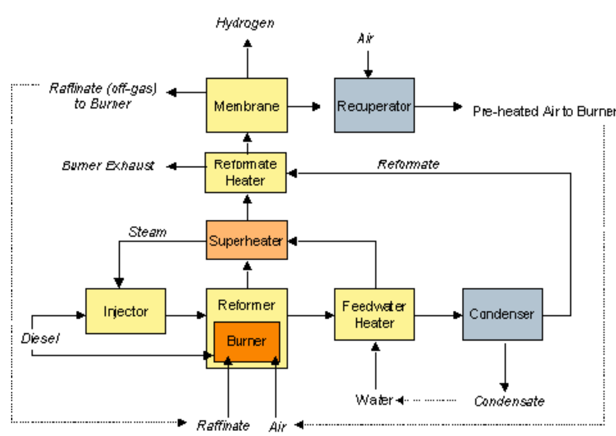

Figure 5. InnovaTek Fuel Processor System Diagram

Table 2. 1-kW System Operating Parameters

Parameter	Value
Diesel Flow Rate to Reactor	3.6 gm/min
Diesel Flow Rate to Burner	2.0 gm/min
Water Feed Rate	23 gm/min
Condensate Collected from Reformate	16 gm/min
Reformer Shell Losses	500 W
Reformate Condensing Temperature	60°C
Reforming Temperature	850°C
Membrane Operating Temperature	400°C
Membrane Surface Area	524 cm^2
Thermal Efficiency	49%

Another finding was that as fuel sulfur content was increased, more frequent catalyst conditioning was required. We also determined that high conversion rates are required during steam reforming to prevent degradation of the membrane system over time.

Hydrogen production of the 1-kW diesel fuel processor was measured over a period of approximately 14 hours of continuous operation at steady-state operating conditions. When compared to the recorded diesel fuel flow rates, an average thermal efficiency was calculated to be at least 36 ±3% (based upon the lower heating values of both the diesel and the hydrogen). This result is short of our target efficiency of 50%, due primarily to higher operating temperatures and steam/carbon ratios, and non-optimized thermal integration. After testing, the prototype fuel processor was disassembled, dissected and inspected. The components were found to be sound and in overall very good condition.

Conclusions

- Our process model was very useful in contributing to the design and establishing the operating parameters of the system.
- Performance tests of InnovaTek's proprietary steam reforming catalyst, conducted in a 100-W test bed and a 1-kW system, indicate that the catalyst can be used for multiple fuel types without the need for prior sulfur removal, although periodic regeneration is required at higher sulfur concentrations.
- A scheme for on-line re-generation of the reforming catalyst has been developed and will be implemented in a modular reactor.
- The hydrogen purification membrane module design is improved, and membrane testing on a custom test fixture indicated that, although the membrane tolerates sulfur, increased surface area is required when sulfur is present in the reformate.
- The fuel injector design continues to improve and is a crucial component to prevent catalyst fouling or reactor plugging during operation.

FY 2003 Publications/Presentations

1. Irving, P.M., T.M. Moeller, Q. Ming, and A. Lee, "Hydrogen Production from Heavy Hydrocarbons Using a Fuel Processor with Micro-Structured Components", presented at the 2002 Fuel Cell Seminar, November 18-21, 2002, Palm Springs, CA.

2. Irving, P.M. "The InnovaGen™ Fuel Processor", presented at the SIRTI Technology Showcase, November 2002, Spokane, WA.

3. Irving, P.M., Q. Ming, and D.R. Stephens, "Development of a Fuel Processor that Generates Hydrogen from Conventional Fuels", In: Proceedings of the 14th Annual U.S. Hydrogen Meeting, March 4-6, 2003, Washington DC.

4. Irving, P.M., "Novel Catalytic Fuel Reforming", Global Climate Energy Project, April 14-15, 2003, Stanford University.

5. Irving, P.M., Q. Ming, T. Dickman, and D.R. Stephens, "The InnovaGen™ Diesel Fuel Processor with Micro-Channel Components", In: Proceedings of the Hydrogen and Fuel Cells 2003 Conference and Trade Show, June 8-11, 2003, Vancouver, BC.