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Novel Catalytic Fuel Reforming with Advanced Membrane Technology

P. Irving, W.L. Allen, Q. Ming, and T. Healey
InnovaTek, Inc.
350 Hills Street
Richland, WA 99352

Abstract

InnovaTek is developing a hydrogen generator that processes multiple fuel types to create hydrogen directly for fuel cells or indirectly for refueling stations for fuel cell-powered vehicles.

Our ultimate goal is the development of a micro channel catalytic reactor that produces pure hydrogen through catalytic reforming of methanol, diesel fuel and natural gas. Advanced membrane technology is incorporated to remove carbon dioxide and detrimental co-products such as CO from the reformate stream. Our technology provides a pure output stream of hydrogen that can be used in a compatibly-sized PEM fuel cell for electrical generation or at refueling stations for vehicles equipped with hydrogen storage tanks.

A thermal and process system model that was developed as a system simulator was used to optimize the design of our micro channel reactor and heat exchangers. With iterative testing and further refinement, the model will be used to provide a sound basis for improved reactor design and process engineering.

On-going tests indicate that hydrogen production is maximized and CO production is minimized by proper selection of 1) temperature-dependent reaction equilibria, 2) ratio of fuel to steam, and 3) catalyst activity. The use of micro-reactor and micro-heat exchanger components helps optimize these processes. Milestones achieved include catalyst testing with sulfur present in the fuel and fabrication of a hydrogen-permeable membrane that is less than 10 micrometers thick. On-going work includes the development of a mini-plasmatron and a micro-fuel injection system.

Introduction

Although fuel cells have been around for years, it wasn't until recently that advances, such as those made in fuel processing technology, promise to make fuel cells economical and reliable enough for use in a multitude of commercial applications.

The InnovaTek H2GEN™ hydrogen production system, currently under development, uses advanced technology to provide a pure hydrogen stream to fuel cells for stationary, portable, and mobile applications. The technology conveniently uses today's standard fuels such as natural gas, gasoline or diesel to generate hydrogen for clean on-site electrical power production.

Our portable power reformer (Fig. 1) can generate enough hydrogen for a 100 Watt fuel cell. Our development plans include systems to generate hydrogen for equivalent sub-kW, kW, and multi-kW power production devices. We report here on our development and testing of the primary sub-components of the H2GEN™ system and results from testing.

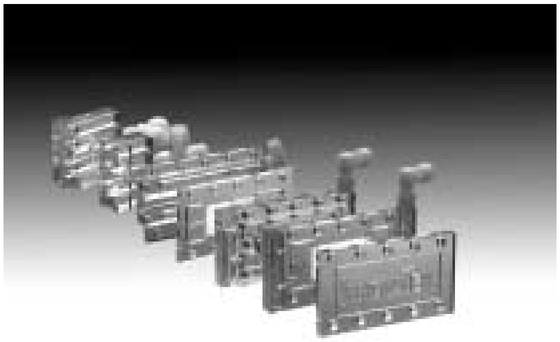

Figure 1. Model of InnovaTek's H2GEN Fuel Processor

System Components

InnovaTek's fuel processor is based on catalytic steam-reforming coupled with hydrogen separation membrane technology, and incorporates various proprietary and licensed components. The technology can reform gasoline, diesel, methanol and natural gas. We are developing and integrating the following critical enabling technologies into components (Fig. 2) that create a system offering significant advantages over traditional reactors:

- Sulfur-tolerant reforming catalyst that eliminates the requirement for extra components for sulfur removal
- Sulfur-tolerant H-separation membrane that yields 100% hydrogen product (no CO, H_2S or CO_2 to poison fuel cell or dilute hydrogen) thereby producing higher fuel cell current densities
- Fuel Injector Micro-Nozzle that eliminates catalyst coking
- Micro-channel reactor and heat exchanger for compact high-efficiency system design
- Plasmatron for fast start-up and catalyst regeneration.

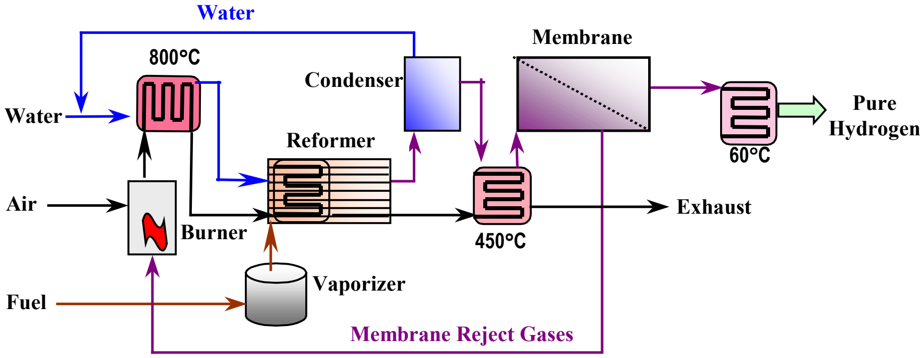

Figure 2. Process Flow Diagram For Hydrogen Generation System

A thermal and process system model that was developed as a system simulator was used to optimize the design of our micro-channel reactor. With iterative testing and further refinement, the model will be used to provide a sound basis for improved reactor and process engineering.

The process starts with water, air, and fuel, which are injected into two subcomponents – the burner unit and the vaporizor/fuel injector unit. The burner unit combusts the membrane reject gases to convert the water to steam and create enough heat for fuel vaporization and reforming processes.

Micro-channel heat exchangers transfer the energy to the catalytic micro-channels of the reformer where the vaporized fuel and steam are injected. The catalytic reaction occurs at about 800°C producing reformate that consists primarily of hydrogen (H_2), carbon monoxide (CO), and carbon dioxide (CO_2). Small amounts of hydrogen sulfide are produced from fuels with sulfur content.

The reformate is cooled through the use of microchannel heat exchangers and water is condensed and recycled. The dry reformate is heated to 450°C and then purified by the membrane component. Only hydrogen can pass through the membrane thereby producing a stream of pure hydrogen that is delivered to the fuel cell after additional cooling. The gas that does not pass through the membrane, known as the “reject stream” is sent back to the burner where the cycle continues.

Experimental Results

Catalyst Testing

The performance of InnovaTek’s catalyst ITC-3 for reforming commercial-grade “regular” gasoline was evaluated using a tube reactor. Gasoline normally contains some sulfur compounds in the concentration range between 50 and 300 ppm, The results (Figure 3) indicate that the catalyst maintains its activity with no deactivation for 50, hours at which time the experiment was terminated.

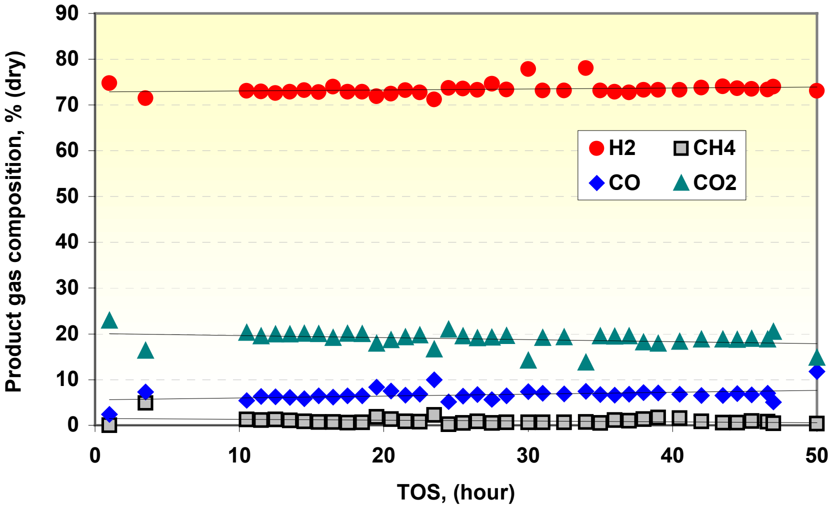

Figure 3. The product gas composition vs. the reforming time using InnovaTek catalyst ITC-3 for commercial gasoline; feed rate was about 0.1 g/minute; the ratio of steam:C varied from 5 to 8 and the temperature was 800°C.

Tests were also conducted using iso-octane feed containing 1000-ppm sulfur (Figure 4). The catalyst, ITC-3, has maintained its high activity and hydrogen selectivity for over 100 hours of testing; the reactor is still operating and data continues to be collected. The hydrogen concentration was maintained at about 70% during the testing period and no deactivation was observed. We believe the slight decrease (from 75% to 70%) after the first 30 hours was the result of some initial coking in our reactor that reduced the volume of active catalyst. The presence of H_2S in the reformate was detected (by lead acetate paper) shortly after the reaction started indicating that sulfur was reduced (and not absorbed by the catalyst bed, which would deactivate it).

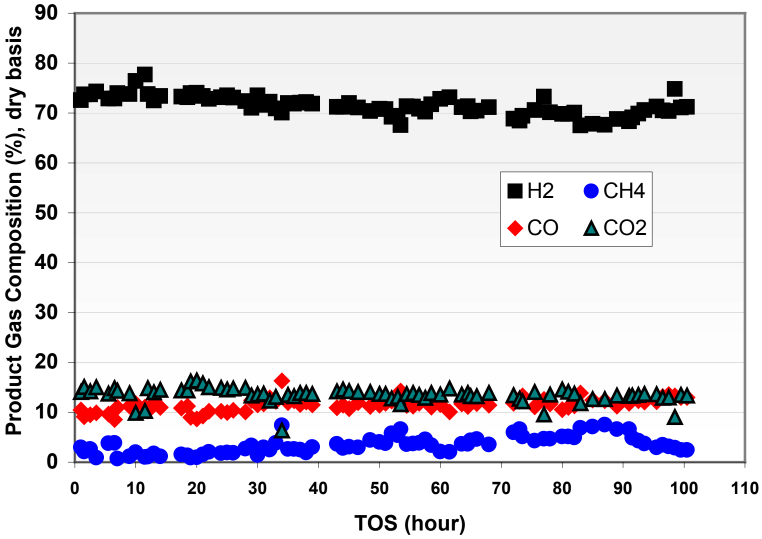

Figure 4. Product gas composition vs reforming time using InnovaTek catalyst ITC-3 for iso-octane with 1000 ppm sulfur; feed rate of iso-octane was about 0.1 gram/minute; steam/C ratio was about 4; and temperature was 800°C.

Microchannel Reactor Design and Fabrication

A micro-channel reactor was designed and fabricated from stainless steel and ceramic. The device consists of four layers performing separate functions: heat source (burner), fuel mixing, heat exchange, and catalytic reforming (Figure 5). The burner plate serves as the heat source for the reactor and the preheater for the fuel and water. The combustion of the fuel and air in the burner generates heat, a portion of which is transferred to the other plates by conductive heat transfer. Another portion of the heat is carried by the exhaust through micro channels generating convective heat transfer.

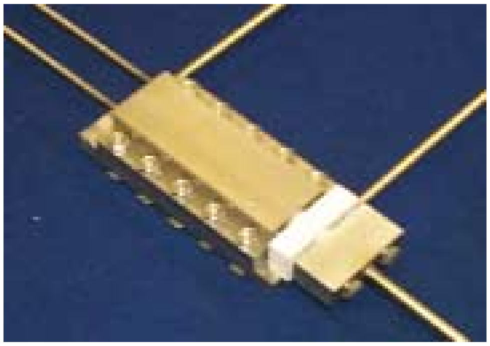

Figure 5. Integrated micro channel fuel reformer and burner 6"x 2.5"x 2".

Both mixing and reactor plates (Fig. 6) have micro channels on top and bottom. This provides advantages in reducing mass and blocking unnecessary heat transfer to other regions. The mixing plate sits directly on top of the burner and the reactor plate is separated from the mixing channel by a thin stainless steel foil and graphite sheet. The top side of the reactor plate is enclosed by the cover plate. The plates and burner are fastened by bolts that prevent leakage but are removable for inspection of components or to install new catalyst.

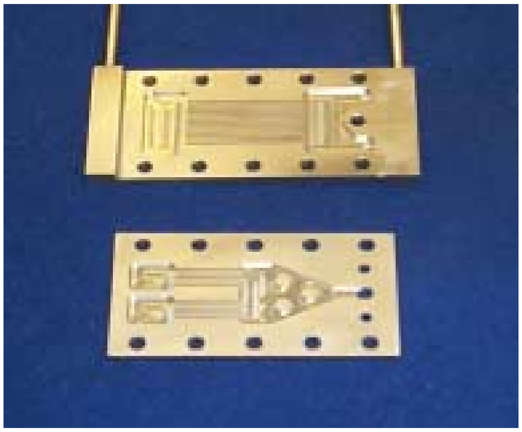

Figure 6. Catalytic reactor (top) and fuel mixer components (bottom).

Tests were conducted with the catalyst packed into the micro-channel reactor that had heat supplied to it by an integrated micro-burner. The burner supplied heat, steam and vaporized fuel to the micro-channel reactor. A more complex fuel mixture consisting of isoctane, toluene, dodecane, and about 500 ppm sulfur was used to simulate gasoline. Our results for steam reforming indicate that the catalytic micro-reactor produced greater than 70% hydrogen at a constant level for 65 hours (Figure 7).

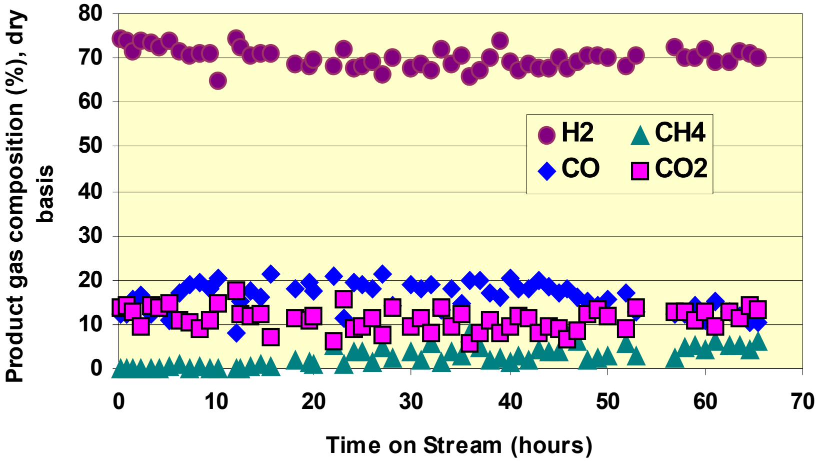

Figure 7. Steam reforming of simulated gasoline with about 500 ppm sulfur using InnovaTek's proprietary catalyst ITC-2 at 800°C.

Heat Exchange

Counter-flow micro-channel heat exchangers made of 316 SS (Fig. 8) were tested to determine efficiency and effectiveness. Heat exchanger size for a gas flow rate up to 9 LPM is approximately 12.3 x 1.4 x 0.9 cm. Pressure drop at 5 LPM was 0.6 psi. The core volume of the device is approximately 12 cm^3.

Figure 8. Micro-channel heat exchanger.

Results indicate that at 400°C heat exchange efficiency was greater than 80% and decreased to about 50% as flow rates were reduced to 2 LPM (Fig. 9). Room temperature (25°C) air was used for the counter-current side for these tests. Micro-channel heat exchangers will be used to maintain optimum temperature conditions for each stage of our fuel processing system (see Fig. 2). Tight temperature control is essential to maintaining maximum chemical conversion and thermal efficiencies in the system.

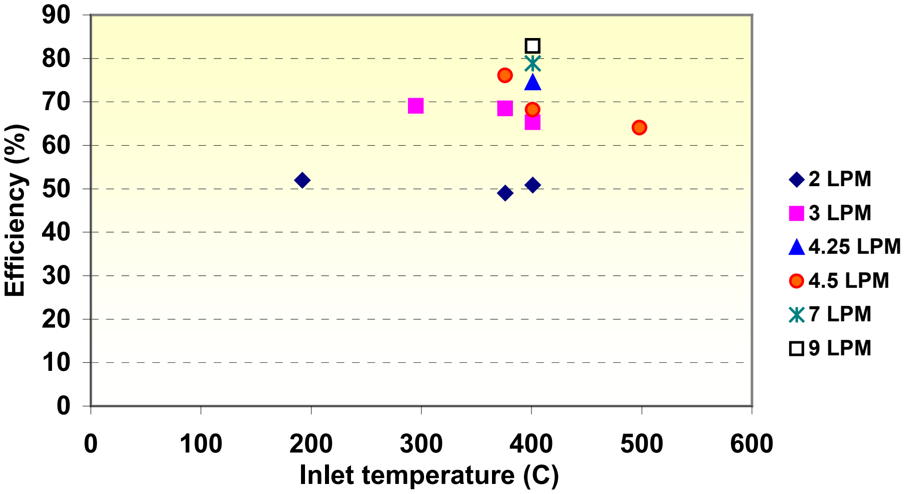

Figure 9. Heat Exchanger Efficiency as a Function of Inlet Temperature (hot side) and Flow Rate.

Hydrogen Separation

An apparatus to test the hydrogen membrane was constructed to measure performance under various temperature and pressure conditions. For simplicity a compressed cylinder of gas containing 65% H_2, 20% CO_2 and 15% CO (simulating our reformate composition) was used as the feed gas for separation tests. The membrane was fabricated on the inner surface of a support structure with 7 mm ID and 22 cm in length, with an effective surface of about 53 cm^2 and a membrane thickness of about 10 μm. Membrane development is continuing with the goal of further reducing membrane thickness and incorporating a composition that is sulfur tolerant.

Tests were conducted by changing the pressure (P_2) on the feed side of the membrane, while the pressure (P_1) at permeation side was at atmospheric pressure. As the pressure P_2 increases, the hydrogen permeation rate increases (Fig.10). Results are shown for varying pressures and temperatures.

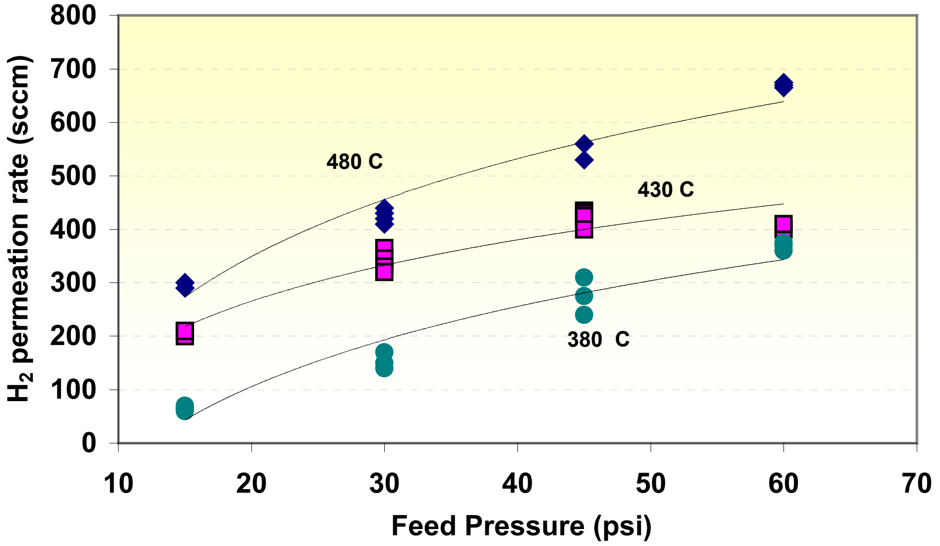

Figure 10. The hydrogen permeation rate vs. pressure of membrane feed gas at different testing temperatures; the pressure at permeate side (pure hydrogen) is atmospheric; the composition of feed gas is 65% H_2, 20% CO_2, and 15% CO.

Composition of the membrane permeate stream (which is the system output) is pure hydrogen with >80% recovery at a temperature of 450°C and pressure of 60 psi (Table 1). The reject gas stream is recycled to the system burner to vaporize fuel and water for the reformer and achieve the temperatures needed for catalytic reforming. This approach creates a very efficient system with little thermal and chemical losses.

Table 1. Composition and Flow Rate in Membrane Stream at 60 psi and 450 °C

Reformate Compound	**% Composition Membrane Component**		
	Feed	**Reject**	**Permeate**
Hydrogen	65	25	100
Carbon Dioxide	20	43	0
Carbon Monoxide	15	32	0
Hydrogen Recovery			82

Future Research

Further research is being conducted to develop additional micro components to optimize system design. These include micro-nozzles for fuel injection to reduce coking in diesel fuel systems and a micro-plasmatron for fast start-up and possible catalyst regeneration. System components will be integrated and tested.

Summary

We have successfully engineered novel micro-technologies in developing a fuel processor that offers the following competitive advantages:

- Reforms multiple fuel types without the need for prior sulfur removal. This greatly expands the market potential to include 1) military logistical fuel and 2) those areas of the world with high sulfur content fuels.
- Produces nearly pure hydrogen output thereby enabling higher fuel cell voltages and power densities with no potential for electrode poisoning.
- Utilizes a steam reforming process that yields higher hydrogen product per volume of fuel consumed.
- Incorporates micro-technology for reactor, heat exchanger, and fuel vaporizer components to improve system efficiency through optimized thermal management and fluid dynamics.

Acknowledgements

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Papers in Proceedings

Irving, P.M., W. L. Allen, T. Healey, W.J. Thomson, “Catalytic Micro Reactor Systems for Hydrogen Generation”, invited presentation at the 5th International Conference on Microreaction Technology, Strasbourg, May 2001.

Patricia M. Irving, W. Lloyd Allen, Quentin Ming, and Todd H. Healey, “The H2GEN™ gasoline/diesel processor for portable fuel cell hydrogen production.” In: Proceedings of the 2001 Conference on Small Fuel Cells, April 2001, Washington DC, sponsored by The Knowledge Foundation, Brookline MA.