

Novel Catalytic Fuel Reforming Using Micro-Technology with Advanced Separations Technology

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Abstract

InnovaTek is integrating microreactor technology with advanced sulfur-tolerant catalysts and hydrogen membrane technology to create a portable-sized hydrogen generator. The ultimate goal of this 4-year cooperative project is the development of a catalytic reactor heated by the combustion of membrane raffinate for the production of clean hydrogen by steam reforming natural gas. Advanced membrane technology is being used to remove CO and CO₂ from the reformat. The fuel processor that we are developing will provide a pure output stream of hydrogen that can be used without further purification for electrical generation by a PEM fuel cell. This report presents the results of work accomplished in the period, February 2001-May 2002.

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.

Objectives

The goal of our research is to produce pure hydrogen from infrastructure fuels using cost-competitive, highly efficient catalytic fuel reforming and membrane separation technology. The following strategies are used to achieve this goal.

- Catalytic steam reforming of natural gas -- optimize catalyst composition and evaluate reforming conditions.
- Hydrogen purification using advanced membrane technology -- optimize membrane composition and operating procedures and compare to water gas shift (WGS) approach for CO clean-up.
- Thermal management using microchannel heat exchangers and internal burner.
- Process and component integration to achieve smallest size and most efficient thermal management.

System Analysis and Design Specification

The design and optimization of a processing system is complex because of the number of required components and functions. The first step is to develop an optimal system design by evaluating different process configurations using process simulation. Another objective is to develop the specifications for the design of the components used in the system. Special attention is paid to thermal management and water management, two of the most technically challenging issues of effective system operation and integration.

In our process, there are two hot streams (reformate gas and combustion gas), and two cold streams (feed water and combustion air). Accordingly, there are several different process configuration options and trade-offs. These options affect the cost, efficiency, complexity, reliability, and operating flexibility. Figure 1 is a process configuration that we are testing. In this design, the hot reformate gas is first cooled down by feed water at heat exchanger II (HTX II) and then condenses water at the water knockout box. The cool and dry reformate gas is then heated by the combustion exhaust gas at HTX III to the temperature at which the membrane module operates. A ZnO₂ canister may be added prior to the membrane module to adsorb any H₂S in the reformate, preventing membrane poisoning by H₂S. The rejected gas (raffinate) from the membrane module is fed with air into the combustor providing the heat for the reforming reaction. The combustion exhaust gas exiting from the reformer will further heat steam/water (from HTX II) in HTX I, and then heats the cold dry reformate gas at HTX III. Finally, the combustion exhaust gas heats the feed air at HTX IV before it is vented to the atmosphere.

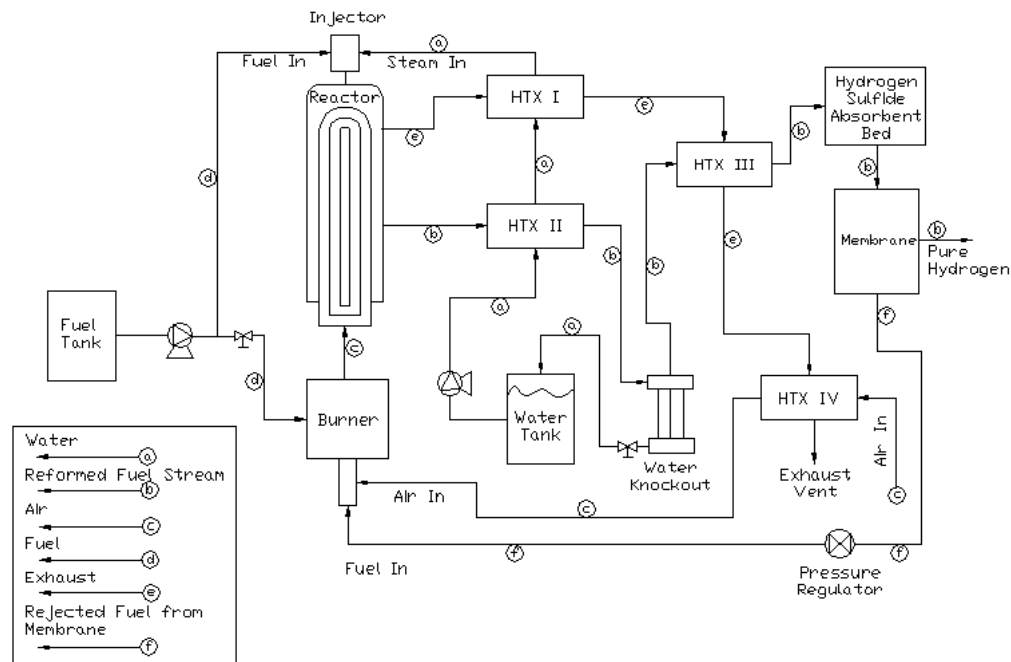


Figure 1. Process Configuration for InnovaTek's Fuel Processor

Excess water is used in the reforming reaction to avoid carbon deposition that consequently leads to the deactivation of the catalyst; therefore, there is vapor/water in the reformate stream that is removed prior to HTX III.

We are conducting process simulation and analysis for all possible system configurations to obtain an optimal system design and a complete mass and energy balance for every individual component of the system. These include flow rates, flow compositions, and temperatures for every stream in the system. The information provides a solid foundation for the design, fabrication, and testing of the reactor, heat exchangers, and combustor. The information will also guide us during the integration and demonstration of the complete system throughout the entire project period.

Testing Facility

System testing takes place in a reaction chamber that is a vented area 3.5 ft deep, 6.5 ft wide and 7 ft tall. Instrumentation support for tests in the chamber includes gas chromatography, thermocouple probes and a positive displacement electronic flow meter. Safety measures were installed to automatically shut down test systems if hydrogen concentration in chamber air or the temperature exceeds pre-selected limits. A second chamber is used for integrated reformer system testing and demonstration. Both units are supported by two SRI gas analyzing GC systems, one with the capability of determining sulfur. A Dri-Cal digital positive displacement flowmeter is used to determine gas production rates.

The National Instruments LabVIEW basic software for graphical process monitoring and control is used along with Field Point modules for sensor interfacing and computer display. This system permits us to design a computer based, virtual screen display of the output from thermocouples, pressure transducers and flow meters. Control modules will be added as the system evolves in line with assembly of the laboratory demonstration system.

Component Development

Proprietary components have been developed to achieve a technically superior fuel processor by solving specific problems related to several of the fundamental processes associated with fuel processing (Figure 2). These components will produce a more efficient system that is sulfur tolerant and produces pure hydrogen while remaining compact and lightweight.

The individual components have been tested and results of key tests are summarized below. The components are now being integrated into a bench-top system that will undergo additional testing that will culminate in a prototype demonstration in late 2002 that produces 12 LPM of pure hydrogen.

Steam Reforming Results

Steam reforming reactions were conducted in a packed bed reactor. Typically, about 3-5 grams of reforming catalyst was packed in a ½ inch Inconel 600 or 316 stainless steel tube with a K-type thermocouple inserted in the bottom of the tube. The thermocouples contacted the catalyst bed to ensure the accurate measurement and control of the temperature at the catalyst bed. The temperature of the catalyst bed was set and maintained using a temperature controller.

Raw reformat from the reactor output is cooled to remove water and the dry product gas is then sent to either a gas chromatograph (SRI 8160C) equipped with both TCD and FID detectors to determine the reformat composition or a gas collection setup to measure the gas flow rate.

Component	Problem Addressed
Catalyst	Conversion Efficiency Sulfur tolerance
Microchannel Reformer	Heat Exchange Conversion Efficiency System size
Fuel Injector	Uniform Vaporization & mixing Coke Formation
H Permeable Membrane	Hydrogen Purity Sulfur tolerance System size

Figure 2. Fuel Processor Components and Problem Addressed

Initial tests were conducted to investigate the effect of reaction temperature on the product gas composition and conversion using our proprietary catalyst ITC-3. The first set of tests with methane was conducted at different temperatures. The H₂O/C ratio was three, and methane gas hourly space velocity was about 12,000 hr⁻¹. At 750° C, nearly complete conversion of methane was obtained, while only 30% conversion was achieved when the reaction temperature decreased to 550° C. The product gas composition for steam reforming of methane at different temperatures is shown in Figure 3. At 750° C, hydrogen concentration of about 77% reaches its equilibrium composition. At the same temperature, the equilibrium composition for CO and CO₂ are 14% and 8.5 %, respectively. These equilibrium concentrations are very close to the experimental ones we obtained.

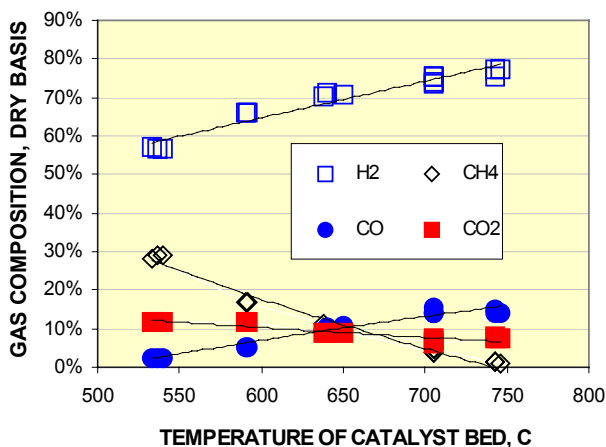


Figure 3. Product composition (H₂, CO, CO₂, and CH₄) for steam reformed methane at different temperatures using 1.45-gram ITC-3 catalyst, ratio of H₂O/C was 3.0, methane feed rate was 300 ml/min.

Additional testing was conducted to optimize the catalyst for specific fuel types. After catalyst optimization, long-term tests for reforming natural gas were successfully conducted using

InnovaTek's proprietary catalyst ITC #1148. The reaction temperature was set to be 850°C and H₂O/C ratio was 3.0. The GHSV of this test was 19,200 hr⁻¹. The hydrogen concentration was over 74% on a dry basis. CO and CO₂ concentrations were about 19% and 6%, respectively. No methane was detected, indicating 100% conversion during the entire testing period. The test was continuously conducted for 341 hours at the same conditions (850°C, H₂O/C =3.0). The catalyst shows very high and stable activity (Fig. 4). The reactor temperature was then set to 800° C and the tests were continued for another 100 hours with very stable performance (Fig.4). These results indicate that our catalyst composition has great potential for stable hydrogen generation from natural gas.

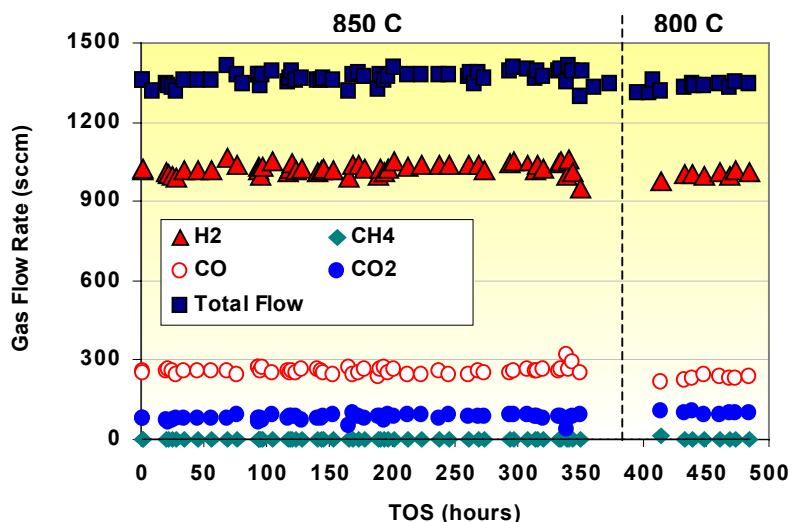


Figure 4. Steam Reforming of Natural Gas with InnovaTek's Proprietary Catalyst, ITC-1145.

An 80-hour test with ultra-low sulfur diesel, a developmental product obtained from Chevron Phillips Chemical, was also conducted. The chemical composition of the diesel fuel was: >65 % paraffinic, <5% olefinic, >20% aromatic hydrocarbons, with less than 5 ppm sulfur. The use of this product will permit us to add controlled amounts of sulfur for future testing. Due to variations in the feed rate, measured reformate flow rates were corrected to a constant diesel-feeding rate of 0.25 ml/min. At this feed rate, about 800 ml/min hydrogen was produced (Fig. 5).

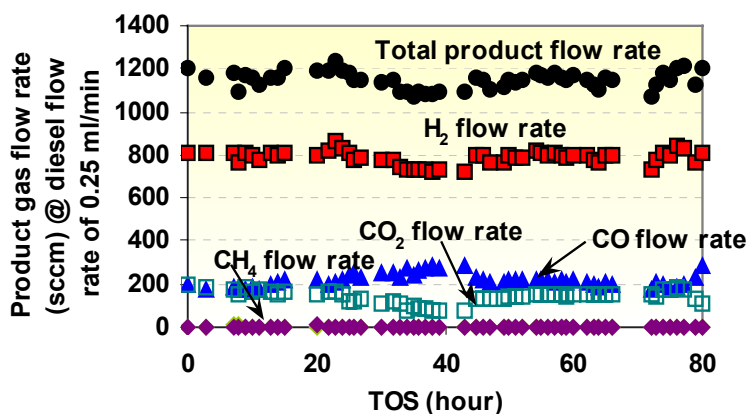


Figure 5. Steam Reforming Results for Low-Sulfur Diesel Fuel using InnovaTek's ITC-1145 Catalyst.

Total gas flow rate was about 1.2 liter/minute. At 40 hours into the test, the H₂O/C ratio was changed. The test results indicate that our ITC catalyst #1145 has very high catalytic activity and selectivity to hydrogen production. The sulfur concentration existing in this ultra low sulfur fuel did not affect (poison) our catalyst during the 80-hour test.

Membrane Purification

The development of a S-tolerant H-permeable membrane is continuing. Figures 6 and 7 show the results of membrane testing with simulated reformat. The composition of simulated reformat used was 65% H₂, 15% CO and 20% CO₂ by volume. As reformat feed rate and pressure increase, the rate of hydrogen permeate through the membrane increases (Fig. 6). For this size membrane, a feed rate of about 2 LPM is optimum for 80-90% hydrogen recovery (Fig. 7). However, our system design requires only about 70% recovery, so that there is enough hydrogen in the raffinate for burner operation. A reformat feed rate of about 5 LPM at 100 psig and 450°C will result in the production of about 2.4 LPM of pure hydrogen, enough to provide 200 Watts of electrical power from a PEM fuel cell. No pin-hole or seal leakage was observed when this membrane was pressurized with inert gas. The composition of this membrane material is not sulfur tolerant. However, we are currently fabricating a scaled-up membrane with a composition that we have previously tested and determined to be sulfur tolerant.

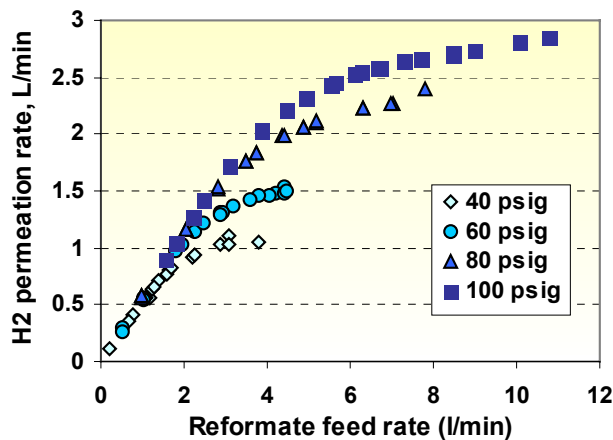


Figure 6. Hydrogen Permeation Rate as a Function of Reformat Feed Rate and Pressure at 450°C.

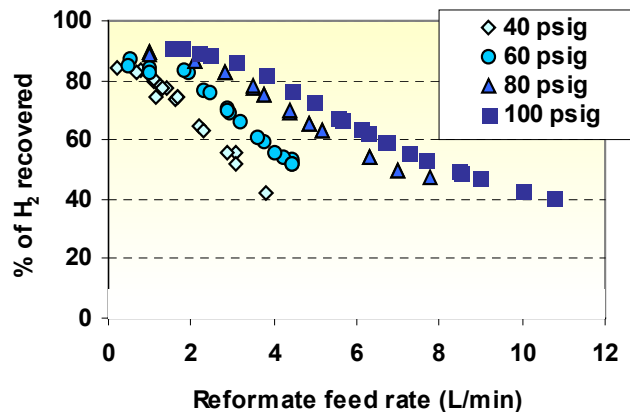


Figure 7. Percent Hydrogen Recovered from Reformat as a Function of Feed Rate and Pressure at 450°C.

Reactor/Combustor Design and Fabrication

A radial concept is used for the integration of the combustor and catalytic reactor where concentric functional chambers build outward from a central core (Figure 8). The innermost sections comprise the combustor unit where air is carried to the interior and raffinate gas from the membrane penetrates through the wall to form a combustion flame along the inner wall of the reaction chamber. Preheated and mixed steam and fuel enter the reaction chamber from the right. Reformate exits through the flange at the center where it is then sent to the membrane (not shown). Exhaust gas from the combustion chamber is carried back so that the hot gas passes over the outside of the reaction chamber, thereby providing uniform thermal conditions. This reactor, which is about 12 inches long, has a capacity for a 1 kWe fuel cell. It is currently being used for integrated system testing.



Figure 8. At left, disassembled view with fuel injector in foreground. At right, assembled view.

Development Milestones

System components have been developed and are being integrated. A demonstration of a prototype system that reforms natural gas at a rate sufficient to power a 1 kWe fuel cell will be performed late in 2002 with scaled-up systems in 2003 (Figure 9).

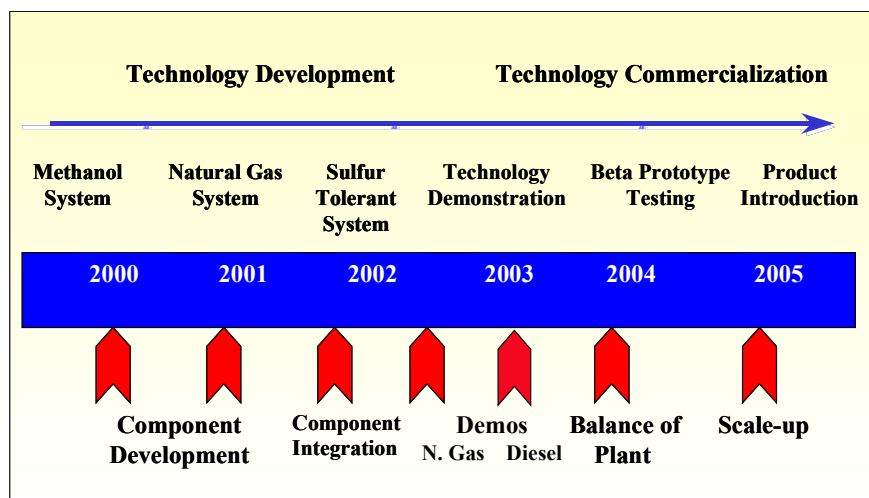


Figure 9. InnovaTek Technology Development Milestones