II.A.4 Autothermal Cyclic Reforming Based Hydrogen Generating and Dispensing System

Ravi Kumar (Primary Contact), Parag Kulkarni, Court Moorefield, and Vladimir Zamansky
GE Global Research
General Electric Company
18 Mason
Irvine, CA 92618
Phone: (949) 859-8851 (159); Fax: (949) 859-3194; E-mail: kumarr@research.ge.com

Michael S. Manning, Safdar A. Baksh, and Andrew C. Rosinski
Praxair Inc.
175 East Park Drive
Tonawanda, NY 14151
Phone: (716) 879-2987; Fax: (716) 879-7030

DOE Technology Development Manager: Arlene Anderson
Phone: (202) 586-3818; Fax: (202) 586-9811; E-mail: Arlene.Anderson@ee.doe.gov

Technical Advisor: Thomas Benjamin
Phone: (630) 252-1632; Fax: (630) 252-4176; E-mail: Benjamin@cmt.anl.gov

Objectives

The overall objective of the project is to develop a reformer-based hydrogen refueling station capable of delivering at least 40 kg/day of hydrogen. The specific performance objectives are as follows:

- Produce proton exchange membrane (PEM) fuel cell grade hydrogen (99.99+% purity);
- Achieve fully automated operation during normal, start-up, shut-down and stand-by modes; and
- Achieve 75% hydrogen generator efficiency (HHV basis).

Technical Barriers

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

- A. Fuel Processor Capital Cost
- B. Operation and Maintenance (O&M)
- C. Feedstock and Water Issues
- E. Control and Safety
- Z. Catalysts
- AB. Hydrogen Separation and Purification

Approach

- Design a pre-commercial 40 kg/day hydrogen generating and refueling system to produce fuel cell grade hydrogen from natural gas based on GE's Autothermal Cyclic Reforming (ACR) process.

- Analyze several process configurations that include ACR reactor, shift reactor, pressure swing adsorber (PSA), and heat exchangers, and select the best configuration that has high efficiency, high reliability and lower capital cost.
- Fabricate and operate the ACR-based hydrogen generator.
- Develop a control system for safe operation of the hydrogen generator with low O&M cost.
- Develop tools to quantify the efficiency, cost and reliability of the system.

Accomplishments

- Operated the low-pressure ACR system for extended periods of time.
- Optimized the operation of the shift reactor to get < 1% of CO in the reformate stream.
- The ACR reactor design was upgraded from low-pressure to high-pressure operation.
- Initial testing of the PSA was completed using simulated reformate.

Future Directions

- Fabricate the high-pressure ACR fuel processor components.
- Optimize the high-pressure ACR fuel processor operation.
- Integrate high-pressure ACR system with PSA, hydrogen compressor, and storage system.
- Safely install and operate the ACR-based refueling system at a demonstration site.

Introduction

GE is developing a hydrogen generation system designed for vehicle refueling. The hydrogen generation system uses a proprietary reformer to convert hydrocarbon fuels to a hydrogen-rich gas that is purified downstream. The ACR process is a unique technology that can be applied for the production of hydrogen or syngas from different fuels. The refueling system also includes a PSA unit to purify the hydrogen, a hydrogen compressor, high-pressure storage tanks, and a dispensing unit to safely deliver the hydrogen to the vehicle. Praxair will develop the PSA unit, hydrogen compressor, storage tanks, and dispenser.

The basics of the ACR process and its advantages over the conventional reforming processes were discussed in the 2003 annual report.[1]

Approach

The major goal of the ACR-based hydrogen generation and dispensing system project is to deliver PEM fuel cell grade hydrogen for vehicle refueling at the hydrogen cost target of $2.50/kg. The project is broken down into three phases: Phase I – Conceptual Design and Analysis, Phase II – Sub-System Development, and Phase III – Prototype Design, Fabrication, and Operation.

In Phase I, a conceptual design of the entire ACR-based refueling system was developed. Phase II is sub-system development. The major task in this phase is ACR reactor and catalyst development. The ACR catalyst will be subjected to detailed evaluation for fuel conversion efficiency and reliability under different operating conditions. Phase III is prototype design, fabrication and system operation. In this phase, the entire system, including the reformer, PSA, hydrogen compressor, and storage tanks, will be integrated, installed and operated at a demonstration site.

Results

The ACR reactors were operated at low pressure for an extended period of time. A continuous 20-hour test was completed successfully without any operator intervention. Figure 1 shows the typical product composition at the ACR reactor outlet. Hydrogen concentration of > 66% on dry volume basis was achieved.

The CO concentration in the reformate was reduced to < 1% on dry volume basis by optimizing

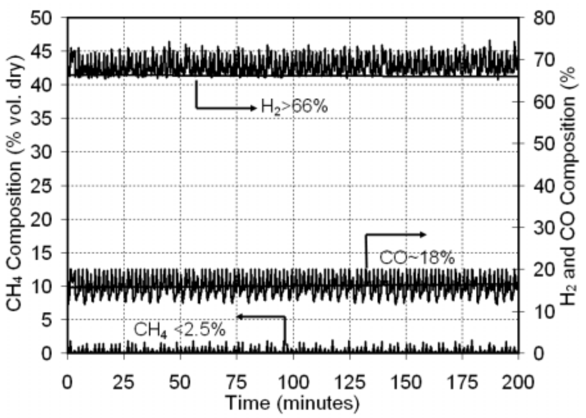

Figure 1. Gas Composition at Low-Pressure ACR Operation

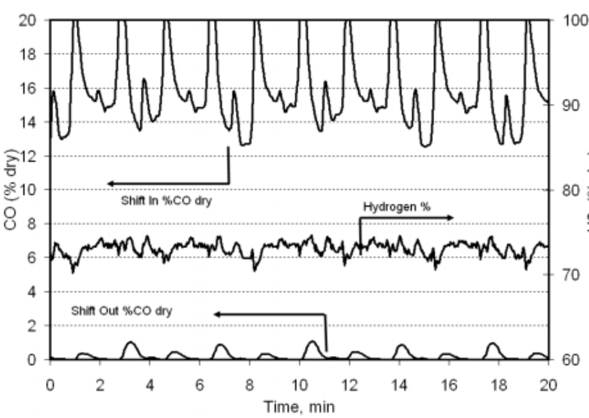

Figure 2. Gas Composition at Low-Pressure Shift Operation

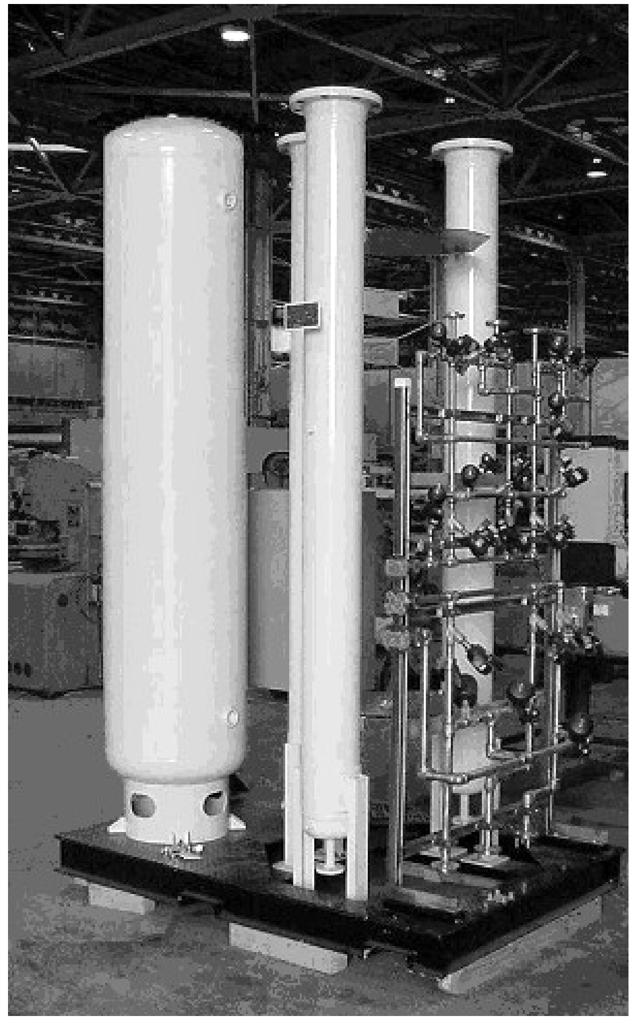

Figure 3. PSA Skid

the operation of the shift reactor. Figure 2 shows the typical CO concentrations at the inlet and outlet of the shift reactor. Figure 2 demonstrates the steady-state ability of the shift to dampen CO fluctuations in the inlet of the shift. In this case, the CO to the shift is fluctuating from 13% to 20% while the shift outlet CO is always < 1.25%. The H_2 concentration out of the shift reactor is typically ~ 72%.

The ACR and the shift reactor are being upgraded for operation at high (> 150 psig) pressure. The high-pressure reforming configuration was chosen after a detailed trade-off-analysis between low-pressure and high-pressure reforming options.[1] The stress and reliability analysis of the high-pressure ACR reactor vessels by means of 3-D thermal and stress modeling was completed. Several reactor components, such as the high-temperature welds in the reactor experiencing the highest mechanical and thermal stresses, were identified and redesigned to increase the reliability. The stress calculations were passed on to Stress Engineering Services for the creep and fatigue analysis that provided quantitative results on cycles to failure. Calculated number of reactor cycles to failure has a safety factor of 2 compared to the projected duration of ACR operation. The analysis of ASME codes and standards applicability validated higher reliability and easier manufacturability of reactor vessels.

Praxair has developed a 3-bed PSA process for integration with the ACR fuel processor, as shown in Figure 3. The 3-bed process developed uses a proprietary 12-step cycle and conventional on/off valves. The 3-bed process results using the reformate flow simulated using industrial grade gases are shown in Table 1. A slip-stream of the product gas was collected in a sample cylinder and analyzed using a Gow-Mac 590 Gas Chromatograph (GC). The lower detection limit for the GC is < 1 ppm. The results show that the PSA produced a H_2 stream with > 99.9% purity and > 75% recovery with reformate pressure > 120 psig.

Table 1. Product Purity vs. Feed Pressure for 3-Bed PSA Pilot Plant

	120 psig Feed Pressure	150 psig Feed Pressure
H_2 Purity (%)	99.996	99.988
CO_2 (ppm)	< 1.0	< 1.0
CO (ppm)	< 1.0	< 1.0
N_2 (ppm)	44.4	122.7
CH_4 (ppm)	< 1.0	< 1.0
Recovery	75%	78%

To compress the H_2 product stream to ~ 6000 psig, a Hydro-Pac hydraulically driven intensifier was chosen for its unique piston design, slower compression stroke, operating flexibility, hydraulic drive method, and past success with Praxair in high-pressure nitrogen and argon compression.

To store the high-pressure H_2, the ACR-based hydrogen fueling station will employ ASME Section VIII, Division I Coded seamless steel vessels. These vessels are designed with a safety factor of 3.0. Praxair has a perfect safety record when employing these vessels for hydrogen service.

Conclusions

The ACR-based fuel processor was operated for extended periods of time. The ACR reactor design was updated for high-pressure operation using extensive 3-D thermal and stress modeling. The remaining fuel processor components are being upgraded to high-pressure operation. Praxair has completed initial testing using simulated reformate stream at > 120 psig that shows that 99.99%-pure hydrogen stream can be produced with > 75% recovery.

References

1. Kumar R., Barge S., Kulkarni P., Moorefield C., Zamansky V., Smolarek J., Manning M., Baksh S., and Schwartz J., AUTOTHERMAL CYCLIC REFORMING BASED HYDROGEN GENERATING AND DISPENSING SYSTEM, DOE Annual Report 2003.

FY 2004 Publications/Presentations (Selected)

1. Kulkarni P., Kumar R., Moorefield C., Barge S., and Zamansky V., “Catalytic Hydrogen Generation Based on Autothermal Cyclic Reforming for Fuel Cells and Vehicle Refueling,” AIChE Annual Conference 2003, San Francisco, CA, November 2003.

2. Kumar R., Moorefield C., Kulkarni P., Barge S., and Zamansky V., “Autothermal Cyclic Reforming Based H_2 Generating & Dispensing System,” Fuel Cell Seminar 2003, Miami Beach, FL, November 2003.

3. Kumar R., Moorefield C., Kulkarni P., Eiteneer B., Reinker J., Zamansky V. and Manning M., “Autothermal Cyclic Reforming and H_2 Refueling System,” DOE Project Review, Philadelphia, PA, May 2004.