

II.A.5 Integrated Hydrogen Production, Purification and Compression System

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Contract Number: DE-FG36-05GO15017

Subcontractors:

Membrane Reactor Technologies, Vancouver, BC,
Canada (MRT)
HERA USA, Ringwood, NJ (HERA)

Start Date: April 1, 2005

Projected End Date: June 30, 2008

Objectives

- To demonstrate a low-cost option for producing fuel cell vehicle (FCV)-quality hydrogen to meet DOE cost and efficiency targets for distributed hydrogen production.
- To develop a hydrocarbon fuel processor system that directly produces high pressure, high-purity hydrogen from a single integrated unit by combining a fluidized bed membrane reactor (FBMR) and a metal hydride-based compressor (MHC).

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section (3.1.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan related to hydrogen production:

- (A) Fuel Processor Capital Costs
- (C) Operation and Maintenance (O&M)
- (L) Durability
- (P) Operating Temperature

(Q) Flux

(S) Cost

In addition, the project addresses the following technical barrier from section 3.2.4.2 related to hydrogen delivery:

(B) Reliability and Cost of Hydrogen Compression

Technical Targets

TABLE 3.1.2. Technical Targets: Distributed Production of Hydrogen from Natural Gas^{1,2}

Characteristics	Units	2010 Target ³	Current FBMR-MHC Projection ⁴
Total Energy Efficiency ⁵	%(LHV)	66.0	56
Production Energy Efficiency	%(LHV)	70.0	73.3
Storage, Compression, and Dispensing Energy	%(LHV)	94.0	70.3 (82.0) ⁶
Total Hydrogen Cost	\$/gge H ₂	2.50	2.81

¹ The H2A Production tool (http://www.hydrogen.energy.gov/systems_analysis.html) was used for the cost modeling. Economic parameters used were for a production design capacity of 1,500 kg/day of hydrogen: 20 yr. analysis period, 10% internal rate of return after taxes, 100% equity financing, 1.9% inflation, 38.9% total tax rate, and modified accelerated cost recovery system 7-year depreciation for 2005, 2010, and 2015. A 70% capacity factor was used for 2005, and 2010. A 75% capacity factor was used for 2015. The results for 2005, 2010, and 2015 are in 2005 dollars.

² The natural gas cost and electricity cost used for 2005, 2010, and 2015 were \$5.00/MMBTU (LHV) and \$0.08/kWh respectively based on the EIA 2005 Annual Energy Outlook High A case projection for 2015 in 2005\$. The natural gas cost assumes industrial gas cost is available for distributed production of hydrogen.

³ For the 2005, 2010, and 2015 analysis it was assumed that Design for Manufacture and Assembly (DFMA) would be employed and that on the order of 500 units per year would be produced.

⁴ Cost based on the Advanced Prototype design, 1,500 kg/d, 6,515 psia hydrogen pressure, 10% internal rate of return after taxes, 2.5% inflation, 38% total tax rate, 83% capacity factor, \$6.00/MSCF natural gas cost, \$0.075/kWh electricity cost.

⁵ Energy efficiency is defined as the energy of the hydrogen out of the process (LHV) divided by the sum of the energy into the process from the feedstock (LHV) and all other energy needed. The electrical energy utilized does not include the efficiency losses from the production of the electricity.

⁶ These figures are for the MHC only and do not include efficiencies for "Storage and Dispensing". MHC outlet pressure is 6,515 psia for filling a fuel tank to 5,000 psig. Since most of the energy input to the MHC is heat, not electricity, the efficiency of 70.3% cannot be directly compared to the target efficiency quoted for traditional mechanical compression. For a more direct comparison, the MHC efficiency figure in parenthesis can be used; it is based on multiplying the heat energy input by 0.35 to offset inefficiencies associated with electrical generation and distribution.

Accomplishments

- Various reformer-membrane configurations and options were analyzed, resulting in the selection of integral, planar membranes in a fluidized bed reactor.
- Auto thermal reformer (ATR) and steam methane reformer (SMR) systems were compared using modeling techniques and in laboratory experimentation, with ATR exhibiting advantages over SMR.
- Different options for heat integration between the FBMR and MHC modules were explored using process simulation; over 25% of the compression energy is derived from excess energy in the FBMR.
- Experimental evaluation of a combined FBMR-MHC system demonstrated stable operation, with the MHC maintaining sub-atmospheric suction pressure at all times and hydrogen flux responding proportionally to variations in suction pressure.
- Detailed design of reformer/compressor components completed to allow a techno-economic analysis of the FBMR-MHC integrated system.
- Efficiency versus capital cost calculations and economic analysis of the system were completed using the H2A model and proprietary analysis tools, showing the potential to approach the DOE forecourt technical targets.

Introduction

The DOE has determined that the delivered cost of hydrogen must be in the \$2 to \$3/gge range for hydrogen to be competitive with gasoline as a fuel for vehicles. For small, on-site hydrogen plants being evaluated for refueling stations (the “forecourt”), capital cost is the main contributor to delivered hydrogen cost. This project is based on achieving the target hydrogen cost by combining unit operations for the entire generation, purification, compression and delivery system. It uses a membrane reformer developed by Membrane Reactor Technologies (MRT) which has elevated temperature, H₂ selective, Pd-alloy membrane modules immersed in the reformer vessel, thereby directly producing high purity hydrogen in a single step. The continuous removal of hydrogen from the reformer pushes the equilibrium “forward” thereby maximizing reactor productivity. Additional gains are envisaged by the integration of the novel hydride compressor developed by HERA, whereby H₂ is compressed from 0.5 bar (7 psia) to 350 bar or higher in a single unit with little or no electricity. Excess energy from the reformer provides over 25% of the power used for driving the hydride compressor so that system integration can provide further efficiency improvement. Hydrogen from the membrane reformer is

of very high quality (purity over 99.99%) and therefore is uniquely suited to feeding the hydride compressor.

Work during this first year of the project centered on a techno-economic analysis that included the following elements: 1) the feasibility of various membrane, reformer and compressor configurations; 2) a preliminary system design using the preferred configurations; and 3) evaluation of system performance and costs against the DOE targets using internal and H2A models. In addition, a pilot scale membrane reactor-hydride compressor combination was assembled and tested to validate compatible operation. The techno-economic analysis indicated that the DOE technical targets are achievable with scale up and volume production. As a first step toward that goal, it was decided to build, test and operate a 15 m³/h, proof-of-concept (POC) prototype.

Approach

The project team will integrate the membrane reformer developed by MRT and the hydride compression system developed by HERA in a single package. This is expected to result in lower cost and higher efficiency compared to conventional hydrogen productions technologies.

Lower cost compared to conventional fuel processors will be realized by:

- reduced component count and sub-system complexity
- tight thermal integration of all reactions/processes in a single package
- thermal metal hydride compression without rotating machinery, which should result in high reliability, low maintenance and low electricity usage

High efficiency will be achieved by:

- producing high-purity hydrogen using high temperature, hydrogen selective membranes
- improved heat and mass transfer due to inherent advantages of fluidized catalyst bed
- equilibrium shift to enhance hydrogen production in the reformer by lowering the partial pressure of hydrogen in the reaction zone
- improved thermal efficiency and lower compression energy by integrating compression with the reactor system

Results

Membrane Configuration - Hydrogen perm-selective membranes are normally made from palladium alloys, as Pd is well known for its hydrogen separation properties. The challenge is to use the thinnest membranes possible in order to maximize hydrogen flux

while reducing cost. Composite membranes consisting of lower cost substrate(s) materials together with thin metallic Pd layers are often the preferred route as they have the potential for greatest cost reduction. Substrate materials are frequently porous sintered stainless steel, other metals or porous ceramics. The composite membranes are usually one of two architectures: planar or tubular. Key evaluation factors include surface area per module, surface area per unit volume, foil-to-substrate bond geometry, differential pressure crush support, and mounting support. A review determined that planar membranes were the most economical and practical choice for this project. In addition, a modular design has been developed, which facilitates membrane replacement.

Catalyst Bed Design – Traditional industrial reformers usually employ catalyst pellets in a fixed bed, but a fixed bed may not be optimal for a membrane reactor. The selection of fixed vs. fluidized catalyst beds was evaluated. Key evaluation factors included heat flux, catalyst particle size, effectiveness factors, heat transfer coefficients, temperature profiles, particle entrainment and attrition, abrasion, and gas flow distribution. A review concluded that a fluid bed catalyst system offered advantages in performance, footprint and ease of maintenance.

Reactor Heating Method – The membrane reactor can be operated in either the steam methane reformer (SMR) or auto thermal reforming (ATR) mode. Conventional fixed bed catalyst reformer systems usually employ SMR because all feed gas is converted to product without “parasitic” partial oxidization, combustion of waste gases to generate the heat can be done at atmospheric pressure, independent of reactor pressure, and nitrogen dilution of the reactants does not occur, as it does for air-supplied ATR reactors. Reactant concentrations are kept higher and flow rates smaller.

Fluid bed membrane systems are different because the fluidized, moving catalyst provides an extra degree of freedom, allowing the heat generation reaction to occur in situ, but physically separated from the membrane area, where the reforming and water-gas-shift reactions take place. This allows heat to be delivered without a limiting transfer surface while maintaining high hydrogen partial pressure and allows ATR reactor performance to approach SMR.

Further benefits accrue to ATR when thinner membranes are used to increase hydrogen flux. In SMR, increased hydrogen flux requires additional heat transfer area; whereas that heat is internally available in the ATR process requiring no additional hardware changes.

SMR and ATR reactor designs were modeled, showing a possible slight advantage for ATR. Subsequent laboratory tests were conducted in MRT’s facility. With the membrane reactor run in both SMR

and ATR modes, performance favored ATR and the POC unit will employ the ATR operating mode.

Metal Hydride Compressor - Different heat integration options for the MHC and the fluidized bed membrane reactor systems were explored using process simulations. It was determined that, even when using excess energy from the membrane reactor, compressor thermal efficiency (on an isothermal basis) must be kept high to allow the integrated system to approach the DOE technical targets. The thermal efficiency for the fluid-heated compressor that was originally anticipated for use in this project was in the 7% to 12% range. HERA developed a gas-heated compressor system where thermal efficiency could be increased to more than 20%, resulting in an overall lower heating value (LHV) efficiency predicted to be more in line with the technical targets.

Experimental Validation of the FBMR-MHC integration - In order to verify that the MHC can maintain suction pressure of less than one atmosphere and that variations in suction pressure associated with compressor thermal cycling does not cause operating problems in the membrane reactor, a pilot scale, gas heated MHC was built and successfully tested with an MRT membrane. Permeate pressure was maintained below one atmosphere at all times, hydrogen flux responded proportionally to suction pressure variations and reactor operation remained stable.

Efficiency – The FBMR cycle was optimized to result in an LHV efficiency of approximately 73%. When coupled to the MHC, LHV efficiency for the integrated system is calculated to be approximately 58%.

Hydrogen Cost – Detailed designs and cost estimates were prepared based on the 15 m³/h POC unit. The design and costs were scaled to reflect production quantities of 20 and 200 units per year and capacity increases to 1,500 kg/day using accepted scaling techniques. Cost calculations using the non-optimized POC design indicate the FBR-MHC will deliver high pressure, pure hydrogen for a cost of \$3.97/gge. Improvements expected with the next phase advanced prototype are expected to bring the projected hydrogen cost to within the \$2 to \$3/gge range.

POC Progress – Detailed process engineering and mechanical design work has commenced for the 15 m³/h POC unit in anticipation of a Hazards and Operational Safety Analysis (HazOp) scheduled for June 2006.

Conclusions and Future Directions

The main experimental findings are as follows:

- The 25-micron membranes, catalyst, and reactor conditions proposed for the POC delivered acceptable performance, and produced 99.99+% H₂ purity in pilot-scale tests.

- A fluid bed membrane reformer was successfully operated at steady-state with sub-atmospheric H₂ discharge supplied to a hot gas heated MHC.

The main conclusions with respect to system economics are as follows:

- A technically viable design has been developed for a single POC unit producing 15 Nm³/hr H₂ at 1,500 psig.
- Based on this and by using the DOE H2A approach, the cost of hydrogen from a scaled up version (670 Nm³/hr at 6,500 psig) of the POC unit in volume production (200 units/yr) is estimated to be \$3.97/kg.
- The MHC cost accounted for between 18-27% of the total direct material and labor costs for 15-50 Nm³/hr hydrogen.
- Ancillary, balance-of-plant equipment (BOP) costs account for 38 to 55% of the equipment cost, indicating further efforts to reduce BOP cost are necessary.

Based on a decision to proceed, a POC unit will be built, installed and tested to validate the concept and to obtain design data for scale up and optimization.

FY 2006 Publications/Presentations

1. Presentation to DOE Hydrogen Delivery Tech. Team – September 21, 2005.
2. Presentation to DOE Hydrogen Production Tech. Team – February 21, 2006.
3. World Hydrogen Technologies Conference, Singapore, October 2005.
4. Nordic Hydrogen Seminar, Oslo, Norway, February 2006.
5. CHA Workshop on Infrastructure, Toronto, Canada, April 2006.
6. IEA-HIA Task Group on Small-Scale Reformers, Brussels, Belgium, June 2006.
7. Presentation at the DOE Hydrogen Program 2006 Merit Review meeting, Arlington, VA, May 2006.