IV.F.10 Development of a 50-kW Fuel Processor for Stationary Fuel Cell Applications Using Revolutionary Materials for Absorption-Enhanced Natural Gas Reforming

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Objectives

Develop distributed hydrogen production technology with significant cost advantages in:

- Reduced reformer + proton exchange membrane (PEM) fuel cell system operating costs through improved fuel efficiency
- Reduced capital costs through reduced system complexity

Technical Barriers

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

- I. Fuel Processor Start-up and Transient Operations
- J. Durability
- K. Emissions and Environmental Issues
- L. Hydrogen Purification/Carbon Monoxide Cleanup
- M. Fuel Processor System Integration and Efficiency
- N. Cost

Approach

The technical approach is based on conversion of natural gas to hydrogen using an absorption-enhanced reformer (AER) that combines steam reforming, water gas shift, and purification processes into one reactor. This approach combines the expertise of Chevron Texaco Technology Ventures in fuel processing and reformer systems engineering with the unique ability of Cabot Superior MicroPowders to produce materials with the necessary microstructure and composition required to achieve absorption-enhanced reforming.

- Develop calcium-based materials that are capable of fixing and releasing carbon oxides over thousands of cycles
- Build reactors and control systems that take advantage of process simplification
- Conduct process modeling and testing to demonstrate significant savings in operating expense (OPEX) and capital expense (CAPEX) of these systems

Accomplishments

- Three tube reactors and one 2-kg H_2/day reactor operational
- Additional 2-kg H_2/day reactor is in construction
- 10-kg H_2/day reactor design has been started
- Over one hundred sorbents synthesized and screened with multiple cycle thermal gravimetric analysis (TGA) testing
- Over thirty sorbents extruded and tested in microreactor
- Over twenty integrated-function materials synthesized
- Over twenty steam reforming catalysts synthesized
- Three sorbent powders manufactured in >10 kg scale
- Sorbent material in operation for over 1500 hours and still meeting CO_2 fixing specification
- Efficiency and cost studies estimate CAPEX savings of 40% and fuel savings of 20% compared to conventional steam methane reformer + pressure swing absorption system

Future Directions

- Remainder of 2004 Fiscal Year
  - Continue material synthesis and testing
  - Conduct dynamic modeling using experimental kinetic data
  - Complete cost study
  - Operate four installed reactors
  - Design and fabricate 5-kW reactor
- Remaining Two Years of Project
  - Install & operate 5-kW reactor
  - Design and fabricate stand-alone 50-kW fuel processor
  - Operate processor for 10 months continuous operation

Introduction

Many of the operating characteristics of PEM fuel cells, such as high fuel efficiency and low emissions, are good matches for distributed generation of electricity. For widespread use it is important that PEM fuel cell distributed generation systems operate on commonly available hydrocarbon fuels rather than bottled hydrogen. To accomplish this goal, the hydrocarbon feed must be "reformed" or converted to a hydrogen-rich product gas called "reformate" in a reactor called a "reformer". A "fuel processor" is a device that includes all components needed to produce hydrogen for a fuel cell. These components include a reformer, a control system, water gas shift reactor(s), blowers, sulfur traps, condensers, etc. The goal of this project is to produce a stand-alone fuel processor capable of converting natural gas to hydrogen for a 50-kW PEM fuel cell.

Approach

The fuel processor being developed in this project is based on absorption-enhanced reforming (AER). The AER process (Reaction 4) combines steam methane reforming (Reaction 1), the water gas shift (Reaction 2), and CO_2 sorption (Reaction 3) to produce a synthesis gas with relatively high hydrogen purity and low CO_2 and CO content. The theoretical benefits of AER are relatively well known[1,2,3].

(Reaction 1) $CH_4 + H_2O \text{ --> } 3H_2 + CO$

(Reaction 2) $CO + H_2O \text{ --> } H_2 + CO_2$

(Reaction 3) $CaO + CO_2 \longrightarrow CaCO_3$

(Reaction 4) $CaO + CH_4 + 2H_2O \longrightarrow 4H_2 + CaCO_3$

Important characteristics of a fuel processor are efficiency, durability, cost, and product gas purity. The current generation of fuel processors is too mechanically complicated, too costly, and produces hydrogen not sufficiently pure to meet DOE goals for fuel cell based distributed generation. AER can reduce mechanical complexity by combining reforming, water gas shift, and reformate purification into a combined, adiabatic reactor. The reformate has a much higher concentration of hydrogen than conventional reforming processes such as partial oxidation and steam reforming, which should lead to a reduced-cost PEM fuel cell stack and higher system efficiency.

During this project, materials capable of reforming natural gas, water gas shifting carbon monoxide, and reversibly reacting with carbon dioxide over many thousands of cycles will be developed and tested. Several small AER reactors will be built and used to test the AER materials developed. A 5-kW-scale reactor and a stand-alone 50-kW fuel processor will be designed, constructed, and tested for durability. The project also includes dynamic process simulation, cost studies, and efficiency studies of several process configurations.

Results

During the first year of the project, over 100 CO_2 sorbents, 20 steam reforming catalysts, and 20 materials with integrated reforming, water gas shift, and CO_2 sorption materials were synthesized. Figure 1 shows the CO_2 fixing capacity over multiple cycles. The line in Figure 1 has been fitted to the data points using a model developed by Mai and Edgar.[4]

Using this model, the asymptotic absorption capacity of this material is about 82% of the theoretical maximum. This compares to about 5% for natural calcites. We have materials that have retained high CO_2 sorption capacity for over 1500 hours.

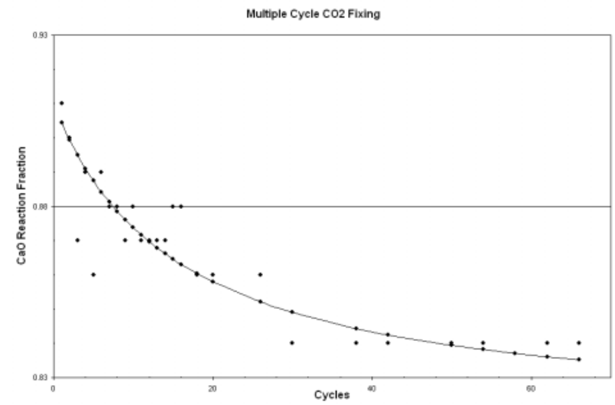

Figure 1. Multiple Cycle CO_2 Fixing

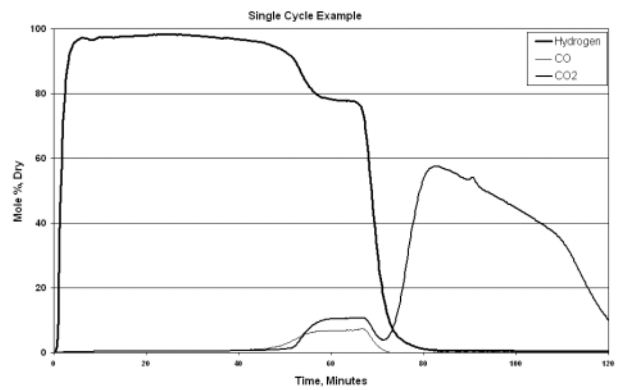

Figure 2. Single Cycle Example

We currently have two micro-reactors and one 2-kg H_2/day reactor in operation. Figure 2 shows an example of one cycle of one of the micro-reactors using materials developed in this project. During the initial part of the cycle, methane is converted to hydrogen, carbon monoxide, and carbon dioxide, but the carbon oxides are retained in the reactor. Once the sorbent capacity is reached, the methane conversion drops, and carbon oxides appear in the reformate. The last portion of the cycle shows CO_2 being released as the sorbent is regenerated by heating.

We have completed initial efficiency and cost model studies using simulation models and cost estimation tools. The results of these studies indicate a potential 20% decrease in natural gas required to produce a unit of hydrogen and a 40% decrease in capital cost when compared to a conventional steam methane reformer + pressure swing absorption process.

Conclusions

- Extradites made with materials synthesized with a spray process are capable of retaining a high CO_2 sorption capacity over many reforming/ calcination cycles lasting over 1500 hours.
- AER-based fuel processors have the theoretical potential for meeting DOE cost and reformate quality goals.
- Small-scale reactor tests show performance consistent with theory-based simulations.
- AER reactors are relatively inexpensive and easy to design compared to conventional steam methane or autothermal reactors.

References

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2. Balasubramanian, B.; Lopez Ortiz, A.; KaytaKoglu, S.; and Harrison, D.P., Chemical Engineering Science, 54, 3534, 1999.
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FY 2004 Publications/Presentations

1. James Stevens, Jerry Rovner, Alex Kuperman, Charles Wilson, Paolina Atanassova, Jian-Ping Shen, Mark Hampden-Smith, Julie Cao, “Development of a Fuel Processor Using Revolutionary Materials for Single Step Absorption-Enhanced Natural Gas Reforming”, 2004 National Hydrogen Association Conference, Los Angeles, California

Patents Issued

1. James F. Stevens, USP 6,682,838, “Integrated Fuel Processor, Fuel Cell Stack, and Tail Gas Oxidizer with Carbon Dioxide Removal”