VII.F.8 Plate-Based Fuel Processing System

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Contract Number: DE-FC36-01AL67605

Subcontractor:
National Fuel Cell Research Center, Irvine, CA

Start Date: October 1, 2001
Projected End Date: September 30, 2005

Objectives

- Develop reactor designs and catalyst systems for the direct steam reforming of gasoline to a hydrogen-rich stream for a polymer electrolyte membrane fuel cell.
- Develop computer simulation models of these systems to predict and optimize performance.
- Develop and test prototype reactors in a 1 to 10 kW(e) size range.
- Demonstrate DOE target performance with emphasis on fast start-up and rapid transient response.

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:

- A. Durability
- B. Cost
- I. Hydrogen Purification/Carbon Monoxide Cleanup
- J. Startup Time/Transient Operation

Technical Targets

Catalytica Energy Systems, Inc.'s (CESI's) progress towards meeting several of the DOE on-board fuel processing performance criteria is summarized below in Table 1. Since the project was re-directed, to focus on individual component development instead of integrated system performance, the status presented is based on individual component level evaluations.

Table 1. CESI Progress Towards DOE Technical Targets for Fuel Flexible Fuel Processors

Attribute	Units	DOE Target (2004)	Status
Durability	hours	2000 and >50 stop/starts	80 to 8,000 (a)
Power Density	W(e)/L	700	475 (b)
Start-up Time	s	<60 to 90% traction power	70 (c)
Transient Response	s	<5, 10% to 90% and 90% to 10%	1 (c)
Efficiency	%	78	77(d)
Turndown	ratio	> 20:1	20:1 (c)
Cost	$/kW(e)	n/a	23 (e)

Table Notes:
a) Demonstrated catalyst performance
b) Known reactor volumes plus estimates of balance of plant
c) SR prototype reactor demonstration
d) Complete system simulation (Pro-II/SimSci) with realistic heat exchanger assumptions
e) Noble metal cost only

Approach

- Develop conceptual plate reactor designs for steam reforming (SR), water-gas-shft (WGS) and preferential oxidation (PrOx).
- Assemble detailed computer simulation models for these plate reactor designs.
- Develop and test catalyst washcoat compositions with the required activity, selectivity and durability consistent with the catalyst performance requirements specified by the simulations to determine reaction kinetics.
- Design, fabricate and test prototype plate reactors in the 1 to 10 kW(e) size range.
- Demonstrate plate reactor performance that meets or exceeds DOE technical targets specifically in the areas of fast startup time, rapid transient operation and wide turndown ratio.

Accomplishments

- SR catalyst development has reduced the minimum steam-to-carbon (S/C) ratio from 3.8 to 3.0, reduced the minimum operating temperature from 825 to 785°C and increased initial catalyst activity by 50% while reducing catalyst cost by nearly a factor of 10.
- WGS catalyst durability testing has accumulated ~3,500 hours of total operation with 4 regeneration cycles.
- PrOx catalyst development has increased the < 10 ppm CO operating temperature range from a single operating point (~105°C) to a 25°C window covering 145 to 170°C.
- SR plate reactor prototype test cell upgrades have reduced steady state temperature fluctuations from 90°C to less than 5°C.
- Demonstrated 10% to 100% and 100% to 10% load transients within 1 second on the SR plate reactor prototype.

Future Directions

- Conduct durability testing of the SR and PrOx catalysts.

- Complete fabrication of next generation SR prototype plate reactors.
- Conduct testing of next generation SR prototypes to demonstrate improved start-up performance and transient response and confirm model predictions.
- Evaluate alternative applications (mobile auxiliary power unit, portable power, etc.) for the catalyst and reactor technology developed under this project.

Introduction

On-board reforming of liquid fuels into hydrogen is an enabling technology that could accelerate consumer usage of fuel cell powered vehicles. The technology would leverage the convenience of the existing gasoline fueling infrastructure while taking advantage of the fuel cell's efficiency and low emissions. Commercial acceptance of on-board reforming faces several obstacles that include: 1) start-up time, 2) transient response, and 3) system complexity (size, weight and cost). These obstacles are being addressed in a variety of projects through development, integration and optimization of existing fuel processing system designs. In this project, CESI is directed at investigating steam reforming (SR), water-gas-shift (WGS) and preferential oxidation (PrOx) catalysts while developing plate reactor designs and hardware where the catalytic function is integrated into a primary surface heat exchanger.

The SR process is usually heat transfer limited because of the endothermic nature of the reaction. Therefore, rapid heat transfer to the catalyst is essential to maximize catalyst performance. The CESI steam reforming plate-reactor design maximizes the heat transfer rate by incorporating exothermic catalytic combustion on one side of the plate to drive the endothermic SR on the other side of the plate. The separation of the reforming and combustion streams permits the reforming reaction to be conducted at a higher pressure than the combustion reaction, thereby avoiding costly gas compression for combustion. The separation of the two streams also prevents the dilution of the reformate by the combustion of air in typical autothermal reactor (ATR) and catalytic partial oxidation processes.

Approach

The development of plate reactor designs for conversion of gasoline to hydrogen requires the integration of the reactor design with details of the catalyst's performance. To integrate all of these aspects and optimize the design, this project makes extensive use of reactor modeling that includes the key aspects of the system, for example, convective gas flow, diffusion, catalyst layer structure, heat transfer throughout the structure and detailed kinetics of the catalytic reactions. Because reaction kinetics are not readily available in many cases, initial work was directed at developing catalyst materials with activity in the desired operating range that could be applied as a washcoat layer onto the plate surface. The kinetics of the catalytic reaction were then measured in sufficient detail to allow modeling of the plate reactor design using in-house developed computer codes for each reactor design.

The resulting target reactor design and catalyst system were then used to develop mechanical designs for a plate reactor to be used in laboratory demonstration at the 3 kW(e) size. Test results were fed back into the model to refine assumptions and validate the model. Design improvements were evaluated within the model before redesign and procurement of new prototype hardware.

Results

Catalyst Development

Steam Reforming: SR catalyst development efforts using Argonne National Laboratory Benchmark Fuel I doped with 10 ppmw sulfur were directed at improving performance in terms of activity and operating conditions while reducing the catalyst cost. Table 2 summarizes the performance status of the SR catalyst in terms of S/C, operating temperature, initial activity and catalyst cost. The performance metrics of SR-9 are compared to SR-18 to quantify the level of improvement over the past year. SR development efforts reduced the S/C ratio, reduced the operating temperature and increased the catalyst activity while reducing catalyst cost by nearly an order of magnitude.

Table 2. Summary of Key SR Catalyst Improvements

Metric	Units	SR-9 (2004)	SR-18 (2005)
S/C	mol/mol	3.8	3.0
Lowest T of operation	°C	825	785
Initial catalyst activity	-	1.00	1.57
Catalyst cost	$/kW(e)	20.15	2.56

The improvement in initial catalyst activity did not negatively impact the catalyst's stability. Figure 1 compares SR-9 to SR-18 in terms of hydrogen yield relative to initial yield and demonstrates 50 hours of stable SR-18 performance. This catalyst formulation will be tested in the presence of 10 ppmw sulfur for longer term durability performance.

Water Gas Shift: WGS catalyst work focused on demonstrating catalyst durability of WGS-161 in the wall-coated tubular reactor. The WGS catalyst durability test has accumulated ~3,500 hour of time on-stream. The durability data is shown in Figure 2 as normalized activity (activity relative to initial activity) versus time on stream. The slow but significant increase in activity that was observed during the first 100 hours on stream indicates that preconditioning of the catalyst is important and that a better understanding and control of the pre-conditioning might be an option for increasing the initial activity of the catalyst. After 1,400 hours of operation, it was clear that the catalyst activity was not stabilizing so an oxidative catalyst regeneration cycle was performed. Since catalyst activity fully recovered, the deactivation is not likely the result of sintering and more likely the result of coking.

Since this is a fairly low maintenance experiment, the test has continued with periodic regenerations as necessary. After several regenerations, rate of deactivation increased but appears to have stabilized.

Preferential Oxidation: PrOx catalyst development efforts were focused on increasing the operating temperature range where the single stage PrOx catalyst could achieve < 10 ppm CO. Figure 3 illustrates the performance achieved with the improved PrOx-44 catalyst. When the single stage PrOx catalyst is fed 1% CO, the CO is reduced to < 10 ppm from 145 to 170°C. This is a significant improvement over last year's PrOx-12 catalyst where the 10 ppm CO target was barely met at a single operating temperature.

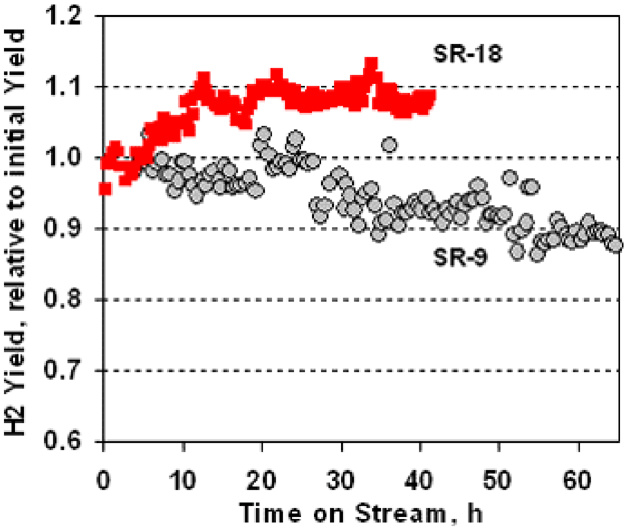

Figure 1. Hydrogen Yield Relative to Initial Hydrogen Yield versus Time on Stream for SR-9 and SR-18

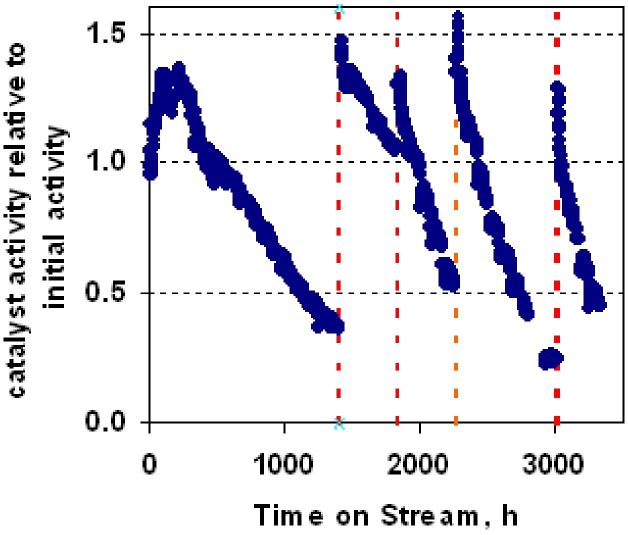

Figure 2. WGS-161 Catalyst Activity Relative to Initial Activity versus Time on Stream

SR Prototype Development

Some of last year's steady-state and transient tests of the prototype plate reactor resulted in undesirable temperature excursions. The temperature excursions were caused by performance

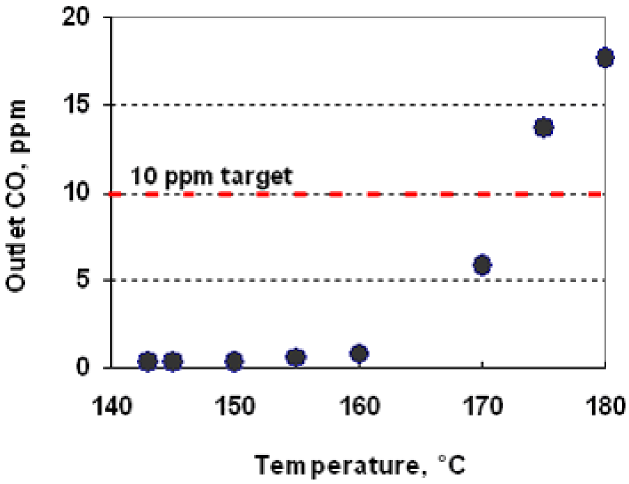

Figure 3. Outlet CO Concentration of PrOx-44 versus Temperature

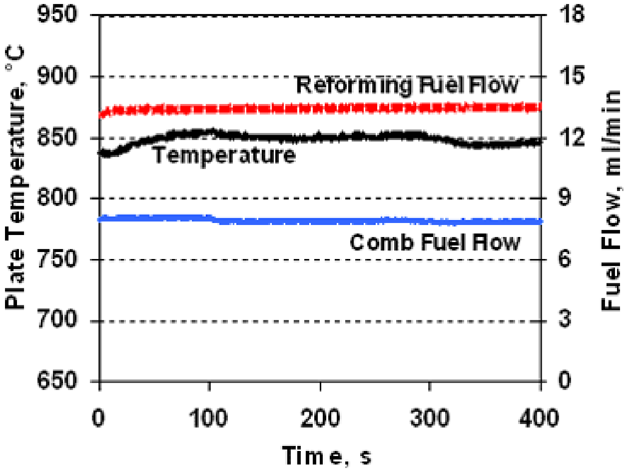

Figure 4. Plate Temperature and Fuel Flow Versus Time

short-falls in the fuel and steam delivery systems. During FY 2005, new fuel and steam delivery systems were installed and tested which allowed the prototype to operate stably at a constant temperature during steady-state reforming conditions (Figure 4).

New control logic that incorporated closed-loop proportional, integral and derivative control of the plate temperature and operated in conjunction with the new fuel and steam delivery systems resulted in rapid and smooth transient performance. Results of a 10 to 100% and 100 to 10% load transient are shown in Figure 5. Each load transient was performed within 1 second and the plate temperature varied by less than 25°C during the transient operation.

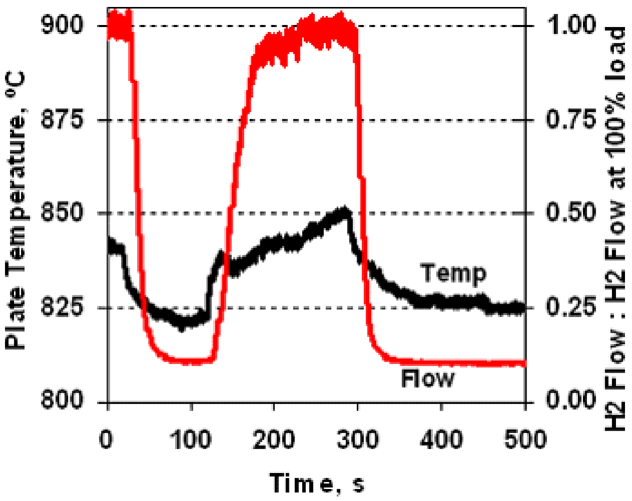

Figure 5. 100% to 10% and 10% to 100% Load Transient Performance

The plate reactor prototype used to collect the presented performance data was fabricated using existing heat-exchanger plates. Lessons learned from this first prototype assembly have been modeled and incorporated into the next prototype designs which utilize custom stamped plates. These custom stamped plates use the available surface area more effectively, thereby increasing the catalytically active surface area per plate and increasing the power density of the plate reactor. The custom plates are fabricated from thinner material which results in a lower thermal mass assembly for improved rapid start-up performance and transient response.

Summary

- Improved SR catalyst performance while reducing catalyst cost by nearly a factor of 10.
- Accumulated ~3,500 hours of WGS operation with 4 regeneration cycles.
- Widened the < 10 ppm CO operating temperature range of the PrOx catalyst.
- Demonstrated very stable operating temperature in the SR plate reactor prototype during steady-state operation
- Demonstrated 10% to 100% and 100% to 10% load transients within 1 second on the SR plate reactor prototype while maintaining the plate temperature perturbation to less than 25°C.

- Modeled and incorporated lessons learned from first plate reactor prototype test results into next generation plate reactor designs.

FY 2005 Publications/Presentations

1. Modeling and Test Results of Plate Reactors for a Gasoline Fuel Processor System – 2004 Fuel Cell Seminar, November 2004, San Antonio, TX.
2. Modeling and Test Results of Plate Reactors for a Gasoline Fuel Processor System – 2005 Meeting of the Pacific Coast Catalysis Society, March 2004, Berkeley, CA.
3. Plate Based Fuel Processing System – 2005 DOE Hydrogen, Fuel Cells and Infrastructure Technologies Program Review Meeting, 23-26 May 2005, Arlington, VA.