

II.A.1 Low-Cost Hydrogen Distributed Production System Development

Franklin D. Lomax
H₂Gen Innovations, Inc.
4740 Eisenhower Avenue
Alexandria, VA 22304
Phone: (703) 778-3121; Fax: (703) 212-4898
E-mail: Lomax@h2gen.com

DOE Technology Development Manager:
Rick Farmer

Phone: (202) 586-1623; Fax: (202) 586-2373
E-mail: Richard.Farmer@ee.doe.gov

DOE Project Officer: Paul Bakke
Phone: (303) 275-4916; Fax: (303) 275-4753
E-mail: Paul.Bakke@go.doe.gov

Contract Number: DE-FG36-05GO15026

Subcontractor:
Süd Chemie, Inc., Louisville, KY

Start Date: July 1, 2005
Projected End Date: September 30, 2009

[LHV] of fuel cell-grade hydrogen out/[LHV of fuel in + electricity in]: 70%.

- Distributed hydrogen cost from natural gas: \$2.50/kg (production capital cost component: \$0.47/kg).
- Distributed hydrogen from ethanol cost: \$3.60/kg (production capital cost component: \$0.50/kg).

Accomplishments

- Based on this extensive test experience at 113 kg/day scale, H₂Gen redesigned the SMR reactor to improve manufacturability, performance and durability.
- Started commercial production of HGM-10000 565 kg/day units.
- Demonstrated 2,700 hours of operation of the reformer on commercially available E-85 fuel in the laboratory microreactor test.
- Started development work for coated wall reformer technology.



Approach

To meet the DOE cost targets, the HGM system must be improved both in terms of higher efficiency (to cut down the cost of natural gas) and also in reduced capital cost. Furthermore, the capacity of the HGM must be increased, both to cut the cost of hydrogen (since many HGM components will scale less than linearly with increased hydrogen capacity) as well as to meet the demands of a full service fueling station. We have therefore designed, built and field-tested an HGM-10000 with five times the capacity of our current system.

While we expect that the HGM-10000 (565 kg/day) technology scaled to 1,500 kg/day will meet or exceed the DOE 2015 cost targets for the hydrogen production and gas cleanup portion of a fueling station, it will still depend on natural gas. To reach the DOE renewable hydrogen goal, we, in collaboration with our catalyst partner, Süd Chemie, also began evaluating the cost and efficiency of reforming ethanol at the local fueling station using the H₂Gen technology. We expect that hydrogen made from ethanol will be the least costly renewable hydrogen option for at least a decade or two.

Results

HGM-10000 Field Testing – Analysis of the first HGM-10000 unit performance over 3,963 hours of field operation followed by inspection and mechanical evaluation of the SMR reactor at the H₂Gen facility led

Objectives

- Design, build and test a steam methane reformer (SMR) system that will achieve the DOE cost and efficiency targets for 2015.
- Demonstrate the efficacy of a low-cost renewable hydrogen generation system based on distributed production of hydrogen from ethanol.

Technical Barriers

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

- (A) Reformer Capital Costs
- (B) Reformer Manufacturing
- (C) Operation and Maintenance (O&M)
- (D) Feedstock Issues
- (E) Greenhouse Gas Emissions
- (F) Control and Safety

Technical Targets

- Total production system (SMR + pressure swing adsorption, PSA) efficiency (lower heating value

to an SMR reactor redesign effort to incorporate all the “lessons learned” from the unit operation. The redesign resulted in higher stress and detonation resistance in the reactor duct flow and improved manufacturability.

Two new reactors were built, one replacing the reactor on the first HGM-10000 unit and another one for the second commercial HGM-10000 unit. Both units were started in the field and went through field testing, which was performed at H₂Gen expense without DOE cost share. H₂Gen now commercially offers HGM-10000 units for sale and is in a process of completing an order for four more HGM-10000 units.

Ethanol Testing – Ethanol reforming testing in 2008/9 concentrated on demonstrating reforming of regular commercially available E-85 (15% gasoline in ethanol) fuel mix. Previous testing of neat ethanol showed very good promise in converting ethanol into hydrogen in a regular HGM SMR reactor, but regulations on distribution of rectified ethanol made this an unlikely fuel candidate. In fact, addition of 5% gasoline to ethanol is required at the point of production and 15% gasoline/85% ethanol mixture is a standard product available at the gas stations across the country. So the objective of testing was to demonstrate feasibility of reforming standard E-85 fuel without further cleaning and pre-treatment.

Two long-term aging tests were performed. The first test had the same sequence of catalysts as that used in HGM units and as previously used in neat ethanol testing. The catalyst bed was 27” long and consisted of four sections. From the top position, the first 6” of the catalyst bed was filled with pre-reforming catalyst, the next 9” catalyst bed was filled with reforming catalyst, followed by 6” catalyst bed of HGUT section (standard HGUT) and finally the bottom 6” catalyst bed was filled with HGHT catalyst (HGHT2). The test was run at 180 psig. This test had to be stopped after about 300 hours due to gradually increasing pressure drop through the tube. Inspection of the catalyst after the test showed that the catalyst severely coked in the reforming section of the catalyst bed, while the pre-reforming catalyst remained clean.

For the second test same tube geometry was used, but all the reforming catalyst was replaced by the pre-reforming catalyst (15” total) which showed good resistance to coking in the first experiment (coke was observed only in the reforming catalyst section). The test was operated under the same conditions with the same E-85 fuel. Stable performance was observed for 2,700 hours (Figure 1 shows the reformat composition, indicating complete conversion of ethanol and high hydrogen yield). After 2,500 hours rapid increase in the pressure drop across the reformer tube was observed and the test was stopped after 2,700 hours. The catalyst was coated with fibrous coke (Figure 2) which was likely

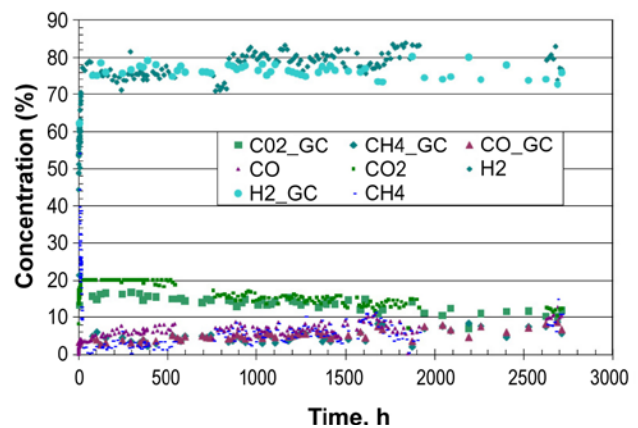


FIGURE 1. Reformat Composition in the E-85 Test

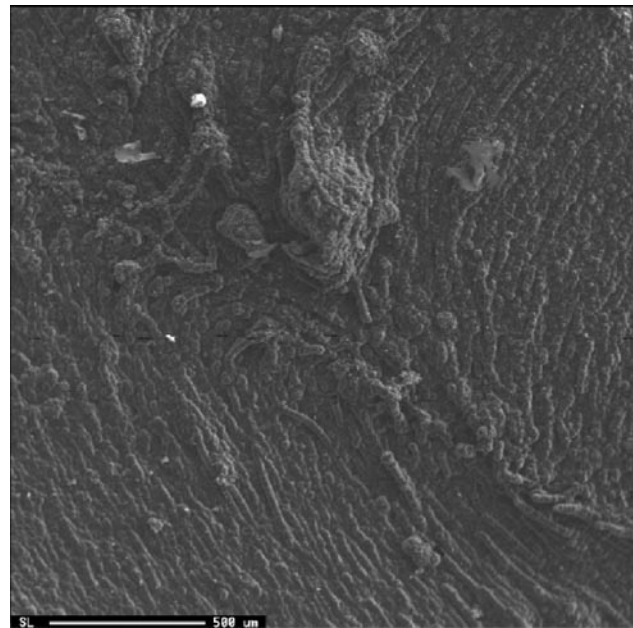


FIGURE 2. Scanning electron microscope image of the coke found in the E-85 reforming tube after the 2,700 hours aging test.

caused by an upset in water feed in the unattended overnight testing.

Dual Fuel Burner Selection – As part of the contract extension for Fiscal Year 2009, we had planned to design a full-scale HGM-type unit to run on ethanol, including any burner tests necessary to validate the design. One major complication in re-designing the HGM unit to operate on ethanol fuel was the fact that in the current HGM design a mixture of the PSA waste gas and the original fuel (natural gas or liquefied petroleum gas) is required to fuel the SMR burner. Furthermore, during the start up the burner is started on the feed fuel alone and is transitioned to burning waste gas when the PSA becomes active. Under steady-state conditions

the SMR burner fuel comprises about 70% H₂/30% CO₂ with small amount of trim raw fuel (natural gas or liquefied petroleum gas). The nozzle mix KromSchroder burners currently used in the HGM units have broad stability range and fit very well for this service as long as gaseous fuel is used for the start up and trim gas.

In the fourth quarter of 2008 we conducted a search for a dual-fuel burner capable of atomizing and firing liquid fuel (ethanol or E-85) and transitioning to operating on gaseous (H₂/CO₂) fuel augmented by liquid ethanol. Unfortunately, no major burner manufacturer would qualify a burner to run on such fuel and/or in the dual-fuel mode operation. Their concern was the potential of detonation in low flash temperature liquids, which presents a substantial safety hazard. Because the problem has safety implications, we believe that an overall change in system design to the use of natural gas or liquefied petroleum gas as a trim fuel during start and operation would be needed, with ethanol only being used to make the hydrogen itself. This obviously has some impact on the greenhouse gas emissions generated by the system, although these might be relatively small, as trim fuel usage is only a few percent of the overall heat flow in the plant. After consultations with DOE the plans for completing the detailed design of an HGM unit prototype running on ethanol were abandoned.

Development of Coated Wall Reformer – To mitigate the coking problem observed in reforming E-85 fuel, after consultation with and approval by the DOE program manager, work was refocused on development of the coated SMR tube approach. In this approach the catalyst is coated onto the wall of the reforming tube instead of being distributed as a packed bed. The potential benefits of this coated tube approach include:

1. Reduced the risk of coking – In most cases coking originates from fuel cracking on the hot, inert wall of the reformer tube. Coke then propagates to encapsulate the catalyst gradually restricting the gas flow and the heat flux through the tube. Coating the catalyst directly onto the wall of the reformer tube will reduce this risk by eliminating the hot, inert surface. In the coated tube reformer, the catalyst will be the hottest surface contacted by the reacting stream, decreasing the likelihood of fuel decomposition and increasing selectivity towards the reforming reaction. Coke formation on the section of the coated wall would result in formation of a hotter catalyst around this spot, likely leading to carbon gasification into CO or CO₂ by excess steam and, thus, reversing of the onset of coking. Higher average temperature of the catalyst coated on the tube wall relative to the packed bed catalyst will also increase tolerance to poisoning.
2. Decrease of required tube size – Direct contact between the reactor tube wall and catalyst gives much better heat transfer rate than a traditional

packed bed reactor. This in turn will result in a higher overall reaction rate and a smaller reformer for the same gas throughput, thereby reducing system cost by reducing the amount of expensive alloy tube required.

3. Minimize the pressure drop at high throughput – Placing the catalyst directly on the tube wall eliminates the flow resistance from the packed catalyst bed which leads to negligible pressure drop and the possibility of running at much higher throughputs.
4. Potential for one-step stream reforming of biomass into syngas – The open tube design of the coated catalyst SMR and high throughput rates achievable for this process can allow the residue from biomass gasification process to pass through the tube without plugging it. This may result in a one-step steam reforming of biomass to produce syngas that can be converted to pure hydrogen. In addition the syngas could also be followed by a synthesis reaction producing liquid fuels (Fischer-Tropsch diesel, methanol or dimethyl ether synthesis).

In the first quarter of 2009 an experimental plan was designed to compare coking resistance of the traditional packed bed and coated SMR tubes. The first step is a series of short-term tests aimed at assessing the risk of coking in steam reforming of natural gas and ethanol in traditional packed bed reactor and in coated wall tube reactor under varying operating conditions. Severe conditions (low steam to carbon ratio and high wall temperature at the reactor inlet) are selected to simulate conditions under which coke is likely to form. The temperature programmed oxidation technique performed on the samples immediately after the steam reforming testing is used to determine onset of coke formation. The second phase includes long-term aging tests, which evaluate long-term structural stability and coking resistance of coated wall tube under steam reforming conditions comparable to that of the regular hydrogen generation process.

Conclusions and Future Directions

Ethanol reforming work continued and long-term steady performance was demonstrated in reforming of commercially available E-85 ethanol fuel. Still coking of the packed bed reactor remained a problem. Further effort was directed towards development of the coated wall reforming reactor which has promise of higher coke resistance, tolerance to poisons, smaller size and lower pressure drop.

FY 2009 Publications/Presentations

1. Presentation to the 2009 DOE Annual Peer Review meeting.