

II.A.4 Integrated Short Contact Time Hydrogen Generator With GE's Staged Catalytic Partial Oxidation (SCPO) Technology

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- Argonne National Laboratory (ANL), Argonne, IL
- University of Minnesota (UMN), Twin Cities, MN

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Objectives

- Develop state-of-the-art, staged catalytic partial oxidation (SCPO) technology that combines catalytic partial oxidation (CPO) and steam methane reforming (SMR) technologies with water-gas shift (WGS) for H₂ production.
- Develop the unique SCPO system with an efficiency of at least 70% on a lower heating value (LHV) basis using natural gas, and cost of hydrogen less than \$3/kg based on the H₂A model.
- Develop high pressure, sulfur tolerate CPO technology.
- Develop active, low temperature, SMR technology.

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) Reformer Capital Costs
- (C) Operation and Maintenance (O&M)
- (D) Feedstock Issues

Technical Targets

This project is integrating three catalysts into a single compact reactor: CPO, SMR, and WGS. This integration will be demonstrated by the fabrication, design and scale-up of prototype units of each key technology. Validation of the technology will address the DOE 2010 cost and efficiency targets for Distributed Production of Hydrogen from Natural Gas:

- Total Energy Efficiency (%LHV) >72%
- Total H₂ Cost <\$2.50/gge H₂

Accomplishments

- Successful construction, failure modes and effects analysis (FMEA)/process hazard analysis (PHA), shakedown, and extensive operation of the High-P CPO unit.
- Baseline CPO catalyst formulation evaluated at various conditions. Screening of optimized catalyst formulations and structures.
- Completed the CPO pre-mixer design, collected preliminary pre-mix CPO data.
- Prepared CPO catalysts and shipped to GE-GRC lab at Niskayuna, NY; completed the preliminary pre-mixer CPO tests. Modified the test rig and prepared the new CPO catalysts for the pre-mixer CPO tests.
- SMR and cooled shift test rig and system control modifications are near completion. The reactor is fabricated and pressure tested.
- Completed the WGS reactor kinetics modeling based on literature kinetics. Completed the preliminary economics analysis.
- ANL and UMN continued to generate test data in support of GE's catalyst selection and scale-up efforts.
- Completed cost analysis using GE's process model and DOE's H₂A model.
- Completed the WGS reactor design and the WGS catalyst literature and intellectual property (IP) analysis.



Introduction

One challenge for the realization of the hydrogen economy is the development of a low-cost, compact reforming technology that is fuel flexible; developed to

operate on both fossil fuels and renewable fuels. GE Global Research is working with ANL and UMN to develop and demonstrate the novel, SCPO technology for hydrogen generation from natural gas (NG). This technology will integrate three catalysts into a single compact reactor: CPO, SMR, and WGS. This integration will be demonstrated via the fabrication prototype scale unit of each key technology. SCPO will meet the DOE and GE cost and efficiency targets for distributed hydrogen generation system.

SCPO is a unique technology based on staging and integrating short contact time catalysts in a single, compact reactor. The use of these novel catalysts allows for greater reformer compactness and therefore lower capital costs than conventional approaches. The unique system design, as well as modular component design will reduce the manufacturing cost after mass production and ease the operation and maintenance for hydrogen production. The project has thus far focused on system and economic analysis, design and optimization, building of experimental facilities and conducting tests of different catalysts and optimized catalysts, operation conditions and reactor design to meet the difficult DOE target for distributed H₂ production. These facilities will allow the testing and verification of vendor catalysts along with catalysts developed by this team.

Approach

In order to meet the technical and economic goals, GE Global Research has been analyzing different reforming system designs to develop the most compact and cost effective reformer system. The analysis provided insight into the fundamental scientific challenges in reforming. These challenges have led the team to work on new catalysts for reforming through inter-team collaboration. In summary, our approach includes:

- Analyze different system designs.
- Design the SCPO hydrogen production system.
- Develop sulfur tolerate catalysts.
- Design and build different pilot-scale reactors to demonstrate each key technology.
- Optimize different operating conditions.
- Develop a control system for safe operation of the hydrogen generator with low O&M cost.
- Quantify the efficiency and cost of the system.

Results

1. Catalytic Partial Oxidation

Early in 2007, final construction of the high pressure CPO test unit was completed and the unit was commissioned for operation. A preliminary standard

operating procedure (SOP) was developed and used in conjunction with the process and instrumentation diagram of the system to perform an in-depth PHA and FMEA. The feed system is designed to deliver gaseous nitrogen, oxygen, steam, and fuel (currently methane) to the CPO reactor at a rate of 200,000 to 1,000,000 gas hourly space velocity (GHSV). The designed hydrogen production capacity of our High-P CPO unit is ~70 kg/day.

High-P CPO testing utilized a low-loading Rh catalyst formulation with significantly reduced metal loading compared to conventional catalysts. This catalyst formulation will be referred to as the “baseline” catalyst. The purpose of starting with this catalyst was to baseline the new high-pressure system and catalyst preparation occurring in another laboratory against known results. Using the baseline catalyst, tests were developed to establish benchmark performance in a small range of O₂/C, steam/carbon (S/C) ratios, and GHSV. The standard catalyst achieves >90% CH₄ conversion at 500,000 h⁻¹ GHSV and above at O₂/C ratios between 0.6 and 0.7 as has been evidenced in UMN and other university research performed at atmospheric pressure. Because limited data exists on performance at elevated pressure, a test plan was developed to first obtain baseline performance at a set of representative conditions followed by process condition effects as pressure is raised.

The experimental results obtained so far include evaluation of the standard catalyst at pressures up to 20 atm at various conditions for baseline data establishment. The design criteria to be included for ongoing testing are the effect of length/diameter (L/D ratio) and pores per inch (PPI) of the catalyst foam. Select elevated pressure results are shown in Figures 1(a) and (b). Methane conversion is more strongly affected by catalyst structure (PPI size of the foam catalyst) at lower pressures and shown in Figure 1(a). However, as pressure is raised, a methane conversion between 92 and 94 percent is obtained over several catalyst structures. The hydrogen yield, Figure 1(b), obtained also appears to reach a maximum or level off near 12 atm at these testing conditions.

Additional catalysts have been prepared to support the on-going pre-mixed tests occurring at Niskayuna, NY. The data collected at GE Fuel Conversion Lab is also used to validate performance on individual catalyst formulations. This included modeling of pressure drop and comparison to experimental data for the substantially larger pre-mix design, up to 800 kg/day H₂ production. Good results between predicted pressure drop and experimental values have been obtained. Preliminary data has been obtained with the pre-mix design at GHSV >1,000,000 h⁻¹ and up to 270 psig using the baseline catalyst formulation. On-going tests focus on demonstration of optimized catalysts under ranges of S/C, pressure, and GHSV.

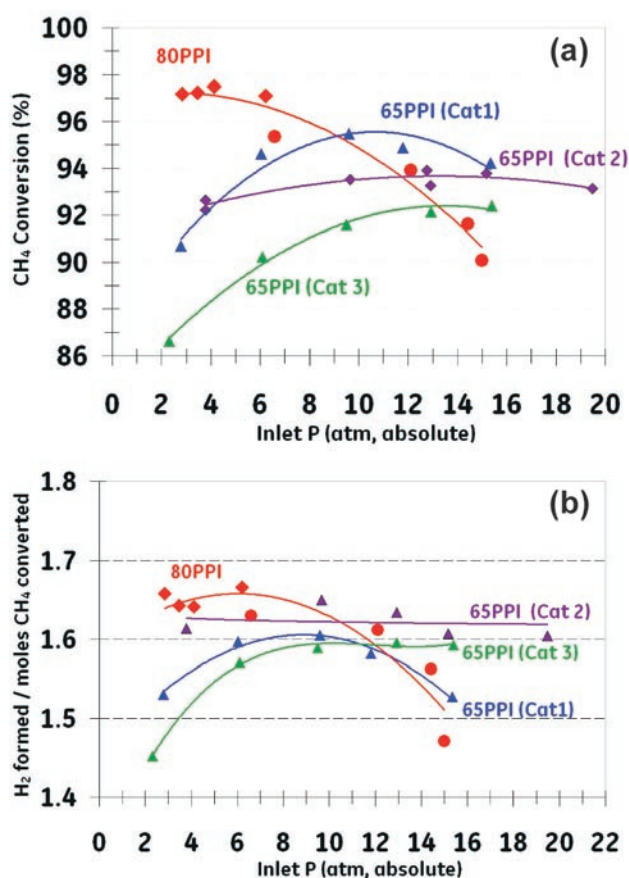


FIGURE 1. High-P CPO Performance of Different Catalyst Structures (a) Methane Conversion (b) Hydrogen Yield, Rh-Baseline Catalyst Formulation, $O_2/C=0.67$, $S/C=1$, $GHSV=500,000\text{ h}^{-1}$

The work performed by UMN in 2007 focused on expanding the operational regime of the capillary technique to include measurements at elevated pressure. The technique consists of inserting a capillary column into the catalyst foam to sample the species as a function of position in the catalyst. Modification has been made to the atmospheric capillary sampling system to allow for steam introduction and a reactor, fabricated at the GE Fuel Conversion Lab, for operation up to 250 psig. Preliminary results were obtained to verify the capability of the experimental setup on an un-optimized Pt-based catalyst at low GHSV. Figure 2 shows the effect of pressure at 3 and 9 atm in the species development. It is striking that the increase in pressure shows a closer approach to equilibrium. This is most likely a function of the increased residence time in the reactor with the increase in pressure since the flow rate was kept constant in this experiment. Much of the CPO reaction occurs in the first 50% of the foam catalyst. Because a significant portion of the foam catalyst does not affect the gas phase concentration of methane near the exit, this technique will be important to understand the contribution to selectivity for a proper evaluation of

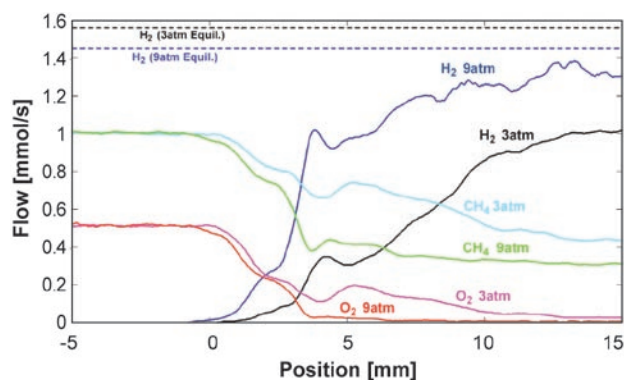


FIGURE 2. Spatial profiles on Pt-coated foam monoliths at 3 atm and 9 atm. Inlet conditions $O_2/C=1$, $S/C=0$, $130,000\text{ h}^{-1}$ GHSV. The start of the 10 mm catalyst is indicated by 0 mm. Equilibrium is calculated under assumption of constant pressure and adiabatic reactor operation.

catalyst lifetime. Thus, continuing capillary sampling efforts are focused on changes with catalyst structure and time-on-steam, as well as special data for kinetic model development.

2. Steam Methane Reforming

GE SMR Reactor Design

The SMR reactor is designed to safely maximize efficiency and flexibility in the experimental SMR system. The reactor specifications are clearly defined including high-pressure operation up to 250 psig and temperatures in excess of 850°C. Pressure drop is minimized, especially on the hot gas side of the heat exchanger. The ability to scale-up is also a factor in the reactor design and it is factored in that all components can be manufactured efficiently. For example, the heat exchanger technology can scale up to the size of large furnaces and then it would be necessary (but definitely acceptable) to modularize the heat exchangers. The reactor is designed to match space velocities with the short contact time catalysts as well as utilize geometries that are conducive to maximizing mixing and minimizing channeling. Test stand instrumentation is matched with the reactor dimensions to allow ease of integration.

Due to the endothermic nature of the SMR reactor, the heat exchanger is integral to efficient operation. A compact heat exchanger minimizes the space and materials needed for this design. Chart Energy and Chemicals worked extensively with GE to meet the required conditions for the heat exchanger. Chart's experience with compact heat exchangers and diffusion bonding enabled GE and Chart to partner in the design phase of this critical section. Along with the heat exchanger block and its integrated channels and manifolds, the reactor is custom designed for process efficiency and reliable operation.

The reactor manufacturing is complete and the reactor is undergoing its final pressure tests. The heat exchanger is connected to two additional zones, which can be filled with catalyst. In this way the reactor includes zone 1 (open volume for catalyst), zone 2 (heat exchanger zone), and zone 3 (final open volume for catalyst). There are multiple configurations for catalyst loadings and GE is confident in several catalyst loadings schemes that will maximize heat transfer into the catalyst to aid the endothermic SMR reaction. A procedure was developed for catalyst loading and change-out which will require approximately 1 day with the current set-up.

The SMR reactor is also designed to function as a WGS reactor. The heat exchanger will function slightly differently as a cooling mechanism for the exothermic shift reactor. The other change will be the catalyst loading. The reactor can go to even higher pressures for the WGS operation due to the lower operating temperatures. The instrumentation is compatible with the test needs of the WGS reactor.

ANL SMR Results

GE worked closely with ANL to define the catalysts with the highest methane conversion and hydrogen yield at the specified conditions. The goal of ANL's testing was to identify the best performing catalysts to use in the SCPO system. Operating parameters included specified temperatures and space velocities while measured outputs were methane conversion, hydrogen yield and reliability of the catalyst. Five precious metal-based SMR catalysts from two commercial vendors (two samples from a vendor designated as Company "B" and three samples from a vendor designated as Company "C"). The SMR activity of these catalysts was evaluated using the low temperature SMR conditions (3:1 H₂O:C, 600-800°C, GHSV of 20,000 to 60,000 h⁻¹) and the high temperature SMR conditions (1% CH₄ in reformat, 800-950°C).

CH₄ conversion was compared in the five commercial catalysts using the low temperature SMR conditions before any high temperature operation and then after exposure to the high temperature SMR conditions. In general, the catalysts from Company C performed better than the catalysts from Company B. The best performing catalyst in terms of activity and stability was C_1. When tested under the high temperature SMR conditions the catalysts from Company B and Company C performed similarly. Catalysts B_1 and C_1 both exhibited the highest conversions and best stabilities at the high temperature SMR conditions. Figure 3(a) demonstrates the high conversion of catalyst C1. The most promising catalysts were the tested long-term for durability and this is shown in Figure 3(b). In catalyst B, the decrease in CH₄ conversion and slight rise in inlet temperature suggests

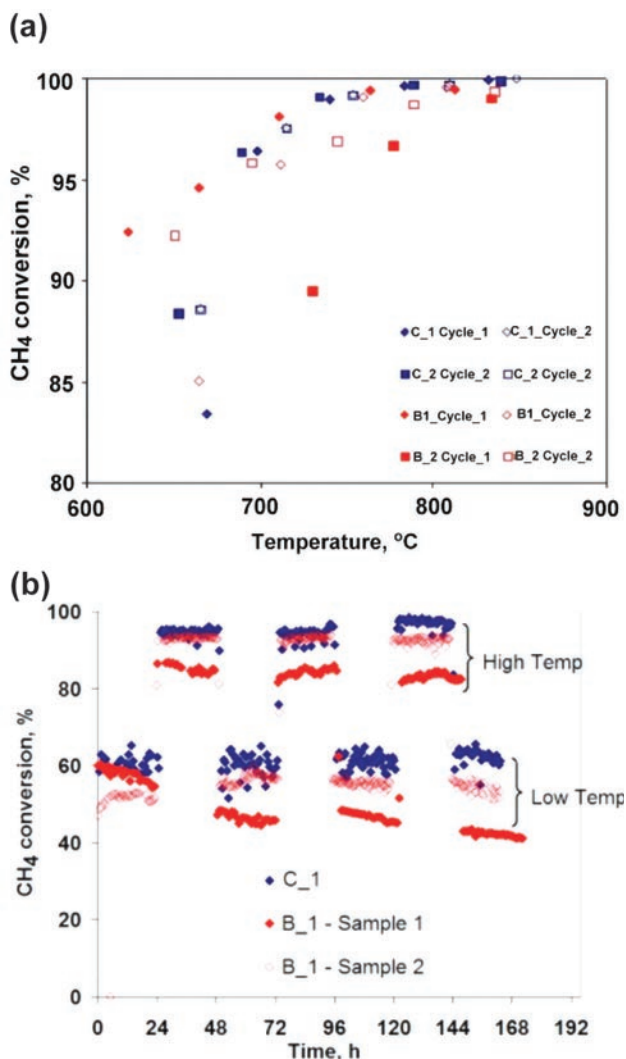


FIGURE 3. (a) Comparison of the CH₄ Conversion as Function of Temperature (b) CH₄ Conversion in Long-Term Testing Performed on the most Promising Catalysts

some deactivation is occurring. The best performing catalyst, C_1, did not show significant degradation at either temperature.

The sulfur tolerance of the five commercial and three Argonne (two formulations, one formulation at two different precious metal weight loadings) SMR catalysts was evaluated at 5 and 20 ppm H₂S using the low temperature SMR conditions. The catalysts were evaluated for sulfur tolerance over a temperature range from 600-800°C. H₂S at concentrations as low as 5 ppm severely poisoned all of the SMR catalysts resulting in a significant decrease in conversion. When the H₂S concentration was increased from 5 to 20 ppm (data not shown), none of the catalysts were active below ~750°C indicating that sulfur had completely poisoned the catalyst. Even at the highest temperature investigated, ~800°C, the best performing catalyst exhibited only a

few percent conversion of CH_4 . Generally, there was little, if any difference, in performance between the various catalysts when H_2S was present in the feed.

Nickel-based catalysts are also being tested by ANL and a recommendation for the less expensive catalyst for SMR operation will be made. This catalyst will then be tested in the SMR system at GE to validate the performance at the larger scale at SCPO conditions.

3. Water-Gas Shift

During 2007, a WGS reactor model was developed based on published WGS kinetic information [1]; a rigorous WGS reactor model was developed for the ICI sour shift catalyst (currently Johnson Matthey). This kinetic model was integrated with two reactor designs: a counter-current cooled WGS reactor and a conventional 2-stage WGS reactor.

Figures 4(a) and 4(b) compare the results of the two models. Preliminary analysis suggests that an actively cooled WGS reactor can effectively reduce the total catalyst loading by as much as 50%, which leads to significant savings in the capital cost of the WGS unit. Other potential benefits of the cooled-WGS reactor also include a lower peak temperature in the catalyst bed, which extends catalyst life and a reduced steam consumption of the WGS synthesis gas, which results in higher system efficiency.

Advanced WGS Reactor Design

A prototype cooled-shift reactor design was completed this year. This reactor design features a 6" outside diameter, 20" long fixed-bed reactor with cooling coils running through the center. A computational fluid dynamics (CFD) analysis was carried out to examine the mass and heat transfer inside of the catalyst zone and help the detailed design of the cooling coils. This CFD model was integrated with the WGS kinetics to accurately describe the mass transfer, reactions, and both convective and conductive heat transfers in the reactor bed, as shown in Figure 5.

Procurement and fabrication of the reactor vessel was initiated in May of 2007. The team also conducted an environmental, health and safety assessment of the WGS experimental system. Safety upgrades and emission issues are being addressed.

IP and Literature Analysis of the WGS Technology

A WGS technology IP landscape analysis was carried out this year. It helped the team identify shift catalyst kinetic information and novel reactor configurations, and provided a basis for the down selection of major catalyst vendors in the U.S. and catalyst of interest from each of these vendors.

The team obtained samples of these down-selected WGS catalysts. Kinetic experiments as well as integrated

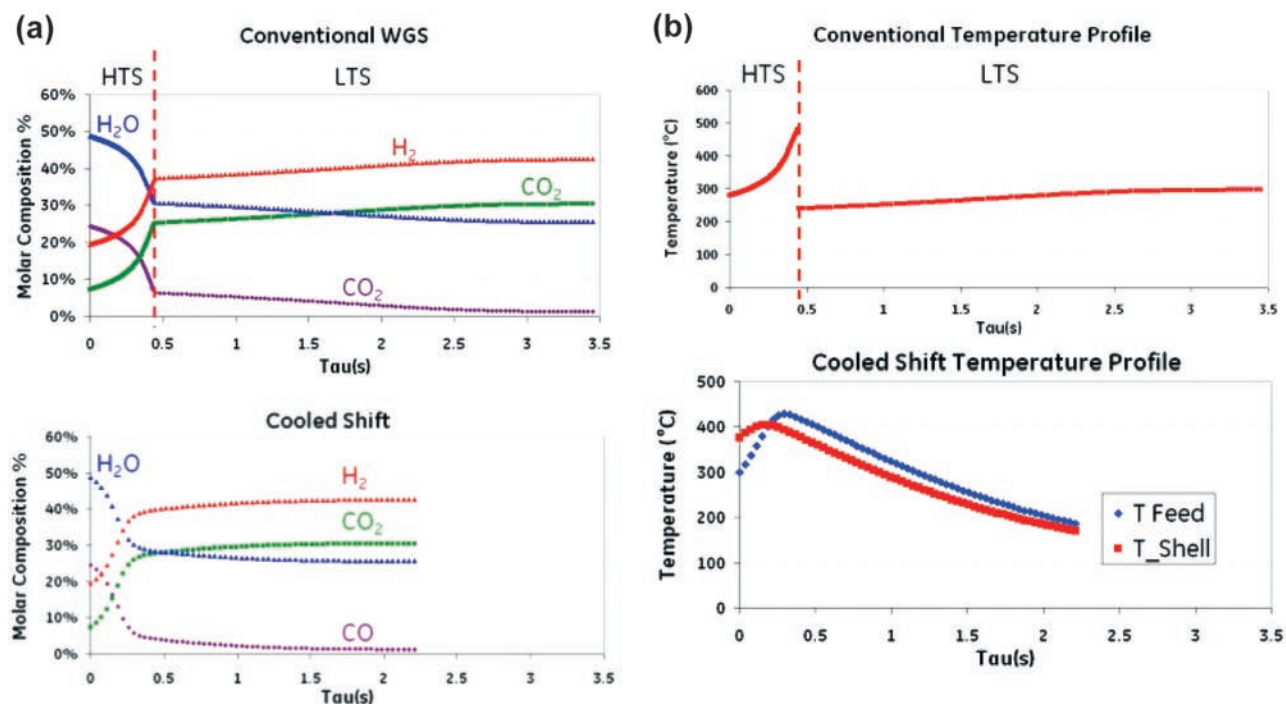


FIGURE 4. Modeling Results of Cooled-Shift Reactor vs. a Conventional 2-Stage Shift Reactor: (a) Composition Profile; (b) Temperature Profile

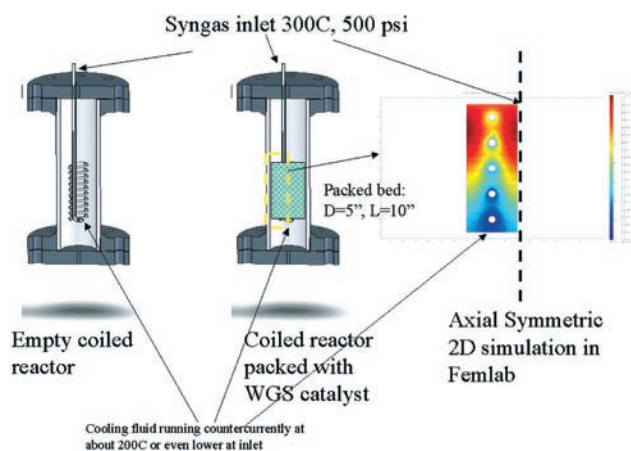


FIGURE 5. WGS Prototype Reactor Design and CFD Analysis Results

shift system testing will be performed with these catalyst samples at the GE-Irvine facility and ANL.

Conclusions and Future Directions

- SCPO will be a leading technology for H₂ production from NG. It is a cost-effective H₂ production technology based on analysis of different H₂ production technologies.
- Minor modification to the feeding system will allow for use of biofuels, gasoline or diesel.
- The key technologies demonstrated in this project have good synergies with other applications including, natural gas combined cycle with CO₂ capture, solid oxide fuel cell systems and syngas production for gas to liquids production.

Future Directions include:

- Conduct High-P CPO test at GE's Fuel Conversion Lab targeting lifetime performance.
- Complete a detailed PHA and FMEA of the SMR/WGS systems and begin operation.
- Continue CPO and SMR supporting tests at ANL and UMN focused on lifetime and model development.
- Conduct SMR and WGS reactor modeling.
- Demonstrate the pre-mix design at GE Global Research's Lab at Niskayuna, New York on optimized catalyst formulations.

FY 2007 Publications/Presentations

1. "Integrated Short Contact Time Hydrogen Generator", 2006 DOE H2 Program Review Meeting, May, 2006, Washington, D.C.
2. 2006 Annual Report to DOE on the "Integrated Short Contact Time Hydrogen Generator".
3. Submitted four quarterly reports.

Special Recognitions & Awards/Patents Issued

1. Two patent applications filed into U.S. patent office, and three patent disclosures filed.

Reference

1. Keiski, R. L., Desponds, O., Chang, Y. .F., and Somorjai, G. A., 1993, Kinetics of the Water-Gas Shift Reaction over Several Alkane Activation and Water-Gas Shift Catalysts, *Applied Catalysis A*, Vol. 101, No. 2, pp. 317-338, August.