

II.A.13 Integrated Short Contact Time Hydrogen Generator (SCPO)

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- Argonne National Laboratory (ANL), Argonne, IL
- University of Minnesota (U of M), Minneapolis, MN

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Objectives

- Develop state-of-the-art, staged catalytic partial oxidation (SCPO) technology that combines catalytic partial oxidation (CPO), steam methane reforming (SMR) and water-gas shift (WGS) technologies in one unit 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 via the fabrication, design and scale-up of prototype units of each key technology. Validation of this technology will be applied toward the DOE and GE cost and efficiency targets for distributed hydrogen generation systems, specifically toward the DOE 2010 hydrogen storage targets:

- Total energy efficiency (%LHV) >70%
- Total H₂ cost <\$3.0/gasoline gallon equivalent (gge) H₂

Accomplishments

- Successful set-up and shake-down of the SMR and cooled shift test rig, and the system integration, instrumentation and control were completed.
- SMR catalyst testing based on precious metal based catalyst and nickel based catalyst completed.
- A scalable WGS prototype fixed-bed reactor (6" outside diameter [OD], 4" inside diameter [ID], 20" length) was fabricated in-house that features a cooling coil with multiple thermocouple and gas sampling taps.
- Prototype WGS reactor coupled with active cooling demonstrated preferred temperature profile and achieved improved WGS activity.
- High-pressure reaction vessel was fabricated and provided temperature and gas phase species profile of fresh and aged CPO catalysts.
- Completed high pressure, pre-mixed CPO tests at GE-GRC's lab at Niskayuna, NY and demonstrated the scale-up of the CPO at pressures higher than 100 psig.
- CPO tests were performed to evaluate the effect of catalyst pores per square inch (PPI) size and length/diameter (L/D) ratio on CPO catalyst performance. The commercial CPO catalyst formulation was evaluated and compared to our in-house prepared rhodium-based baseline formulation.
- Short-term life tests (~75 hours) on the CPO were completed to elucidate any degradation for both the commercial and in-house CPO catalyst formulations.
- CPO catalyst performance with sulfur level was evaluated and 200 hours of CPO test with sulfur was conducted for CPO catalyst lifetime, start/stop behavior and performance.

- DOE's H2A model was modified to reflect demonstrated catalyst (reactor) performance and cost analysis based on H2A model was updated.



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 Argonne National Laboratory and the University of Minnesota 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 of a prototype scale unit of each key technology. SCPO will meet the DOE and GE cost and efficiency targets for a 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 1) reduce the manufacturing cost after mass production, and 2) 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. CPO

High pressure CPO testing utilized a low-loading Rh catalyst formulation with significantly reduced metal loading compared to conventional catalysts. Development of low metal loading CPO catalyst formulations that allow acceptable methane conversion into syngas was continued during this project year.

Several catalysts were prepared based on additives to the baseline CPO catalyst formulations, which is a low-loading Rh catalyst over alumina foam and serves to baseline high pressure CPO catalyst performance against known results. The additives were aimed at increasing combustion activity, steam reforming activity and rhodium metal dispersion, respectively. Tests were conducted at 500,000/hr gas hourly space velocity (GHSV) and the feed composition was controlled for O₂/C of 0.67 and H₂O/C of 1.0. Overall, a slight increase in hydrogen production was observed over a wide operation pressure range for the steam reforming and metal dispersion additives to the CPO catalyst.

A commercial catalyst was acquired from a vendor under a non-disclosure agreement with a catalyst company. This catalyst formulation was prepared on 45 PPI foams. The commercial catalyst performance was compared to a 45 PPI foam with the baseline composition. In Figure 1(a), the commercial catalyst was found to give about five conversion efficiency points higher over a range of pressures compared to the baseline formulation. Additionally, Figure 1(b) shows that a greater syngas yield is also achieved with the commercial catalyst. The improvement in performance over our baseline composition is considered tangible, although modest. This is especially true considering that we were able to slightly improve the syngas yield of our baseline catalyst by adding modifiers as mentioned above.

A number of tests were followed to understand the effect of CPO catalyst structure (L/D ratio at 0.5 and 1 and pore size of foam support at 45, 65 and 80). Based on these results and previous results at GE's combustion laboratory on the pre-mixed CPO performed, we have determined the optimized support for high pressure CPO operation in terms of high methane conversion and near-equilibrium output.

Additional catalysts have been prepared to support the on-going pre-mixed tests occurring at Niskayuna, NY. The experiments measured the SCPO product stream at pressures up to 240 psig, typical of modern heavy-duty gas turbine combustors. The fuel and the air were independently preheated before entering the

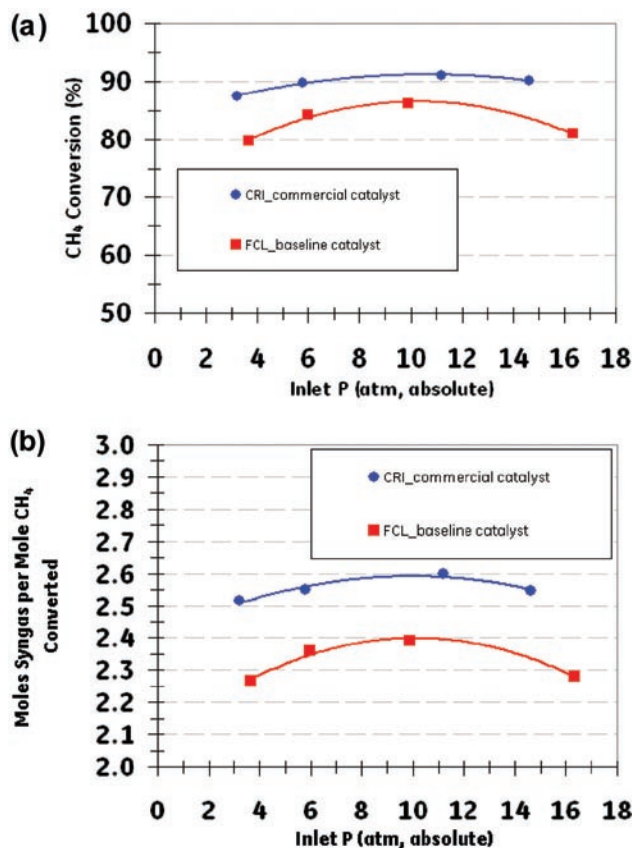


FIGURE 1. Commercial CPO catalyst evaluation compared to Fuel Conversion Lab prepared baseline catalysts, 45 PPI, L/D = 1; Conditions: 500,000/hr GHSV, S/C = 1, O₂/C = 0.67.

rig, and the mixture was maintained at a temperature at or slightly greater than 350°C for optimal catalyst performance and comparison to smaller scale data. In the experiments described, the fuel and air are introduced in rich proportions, O₂/C = 0.65. The scale of the experiment focused on the processing of 25 to 37 kg of NG/hr and a space velocity of 200,000 or 300,000 h⁻¹. The maximum fuel flow rate was 41 kg/hr under dry conditions. The conversion of the NG to H₂ was at least 96% of the calculated equilibrium levels at all pressures. The conversion is highest at low pressure, and the influence of pressure appears to be small. For the large-scale catalyst this is a very encouraging result because it demonstrates the potential of the catalyst over a wide range of gas turbine operating conditions. It is important to note that these results were obtained without the addition of water. The measured CO concentrations showed a similar trend of being higher at the low-pressure condition, but again the effect of pressure was very small. Alternatively, the methane concentration increased with pressure, but the levels remained below 0.7 % in all cases. In the second set of experiments the impact of steam addition on catalyst emissions was studied. The higher space

velocity, 300,000 hr⁻¹, and the highest pressure, 270 psia, conditions were maintained. The higher heat capacity of the steam and thermal losses in the system made maintaining the mixture temperature more of a challenge. The 350°C preheat condition for the catalyst was met in every case except one, and in all cases the temperature fell in the range of 337°C and 410°C. The catalyst outlet temperature showed a distinct decrease with steam addition. This is to be expected as the steam shifts the equilibrium temperature.

U of M's effort focused on obtaining spatial profiles at elevated pressure. The method allows obtaining species and temperature composition with a resolution of 300-400 μm. This technique has been developed at U of M as part of this project and holds promise to be a versatile technique to analyze high temperature short contact time reactors. The feed stoichiometry was fixed at O₂/C=0.5 and no preheat was applied.

Figure 2 shows the effect on temperature over a ten-fold increase in pressure. It is interesting to note that the curves do not change in this range. The effect of pressure on the temperatures seems to be smaller than what can be measured if present at all. This is also seen in other tests where the differences observed are within the experimental uncertainty. Temperature and species compositional profiles through a catalyst sample that had been aged for 75 hours were obtained. The other sample was a completely fresh sample with only 15 minutes on stream. It is seen that the temperatures are higher for the 75 hours sample, however, in line with data previously obtained on a catalyst aged for 2 hours, it appears that there is an initial deactivation of the catalyst over the first few hours. After the initial deactivation, the catalyst remains constant. It is also noted that the catalyst seems to be losing steam-reforming capability, which leads to lower synthesis gas yields. The decrease in activity is most likely due to loss of surface area due to phase transformations in the γ-alumina wash coat.

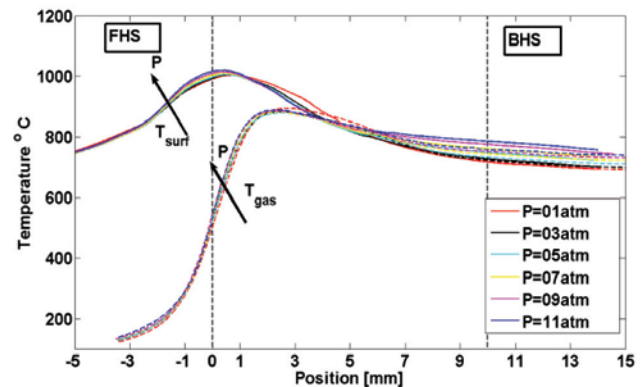


FIGURE 2. Effect of pressure at a constant GHSV of 164,000/hr, O₂/C = 0.5, Rh catalyst on 80 PPI α-Al₂O₃. (FHS: Front Heat Shield; BHS: Back Heat Shield)

CPO catalyst life test in the presence of sulfur was conducted using a simulated NG mixture containing three sulfur species. Common sulfur compounds that may be found in the gas supply are tetrahydrothiophene (THT), tertiary butyl mercaptan (TBM), dimethyl sulfide (DMS), and hydrogen sulfide (H_2S). Environmental Protection Agency criteria for pipeline NG dictate that sulfur concentrations are not to exceed 8 ppm by volume on a time averaged basis. A gas source containing three sulfur compounds of 100 ppm hydrogen sulfide, 250 ppm dimethyl sulfide, and 250 ppm methyl mercaptan in nitrogen was obtained for blending into our CPO feed stream to simulate a NG containing total sulfur at various levels. Starting from sulfur-free NG, the sulfur level in simulated natural gas was increased in a stepwise manner for high pressure CPO tests. Methane conversion, pressure and both inlet and back face temperature of the catalyst are shown in Figure 3. Introduction of sulfur into sulfur-free feed mixture showed instant change in both CH_4 conversion and catalyst back face temperature. Total sulfur content of 1.2 ppm in the CPO feed stream (which corresponds to 6 ppm sulfur in natural gas) led to an instant drop in CH_4 conversion by 14% and was accompanied by an increase in catalyst back face temperature by approximately $100^\circ C$. Subsequently, sulfur content in the CPO feed mixture was increased to 2.4 ppm and 4.8 ppm and only marginal increase in both CH_4 conversion and CPO catalyst back face temperature resulted as shown in Figure 3. One possible explanation for the change brought in by sulfur compounds is that sulfur species accumulate selectively over the surface of the catalyst, thereby blocking sites for carbon and maintaining a higher O_2/C ratio on the surface than is present in the gas phase.

A number of CPO tests of 10 hours to 200 hours of runtime on sulfur-free and sulfur-bearing CPO feed streams were conducted. Methane conversion, syngas selectivity and catalyst back face temperature were

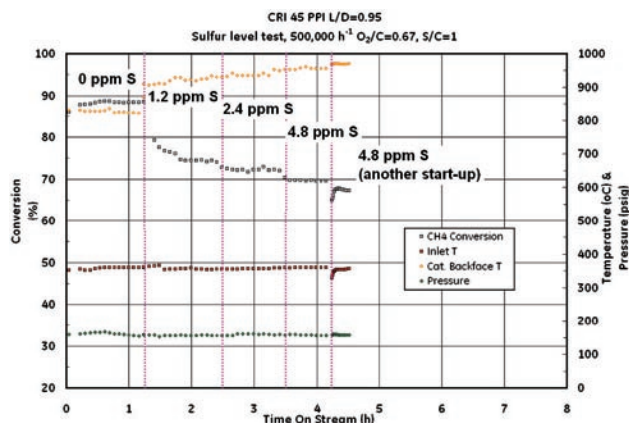


FIGURE 3. Changes in CH_4 conversion and catalyst temperature (inlet and catalyst backface) with introduction of sulfur compounds.

monitored for any sign of CPO catalyst degradation and to understand durability issues involved with sulfur poisoning. The test results obtained so far indicate that there is no clear sign of accelerated CPO performance degradation incurred by sulfur compounds present in CPO feed stream.

2. SMR

GE SMR Results

SMR reactor fabrication for high-pressure operation up to 250 psig and temperatures in excess of $850^\circ C$ was completed. The reactor was 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. Full integration of the reactor with process control, heat, and gas analysis, safety, and steam generation systems were followed by shakedown tests and comprehensive environmental, health, and safety review. The system was loaded with an extruded precious metal catalyst for the first set of tests as identified previously in ANL screening tests. Full test status was achieved and the following milestones were reached:

- Tests were performed at three different space velocities under pre-reforming (low temperature) conditions ($GHSV=15,000\ h^{-1}$, $20,000\ h^{-1}$, and $25,000\ h^{-1}$). These tests were operated up to $700^\circ C$.
- The system was operated successfully up to pressures of 225 psig.
- Methane conversion at the pre-reforming condition reached as high as 68%.

Figure 4 demonstrates the activity of the precious metal catalyst in the compact heat exchanger. The blue curve is equilibrium conversion at the given temperatures. The data are at these same conditions unless otherwise noted on the chart. It was expected that the conversions would be at or near equilibrium due to the activity of the catalyst and the good heat transfer characteristics of the reactor. Although there is a slight variation in the space velocities the conversion remains at or near equilibrium. It is noted that the outlet temperatures of the reactor were measured by a thermocouple in the gas stream and due to heat loss the thermocouple may be reading slightly lower than the actual temperature at the catalyst outlet. A pressure of 225 psig equilibrium will not allow the high conversions seen at ambient pressures so the goal of these experiments was to see how close to equilibrium the process would achieve. This increase in conversion with a decrease in pressure is demonstrated in Figure 4 where the methane conversion at 175 psig is well above the equilibrium curve of 225 psig. It is also noted that the lower steam to carbon decreased the methane conversion but, as expected with the precious metal

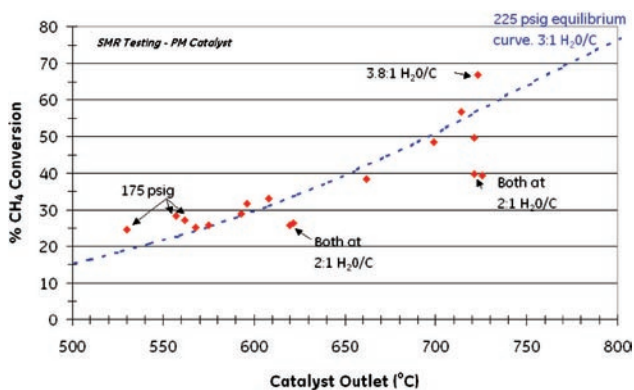


FIGURE 4. SMR methane conversion on precious metal catalyst compared to equilibrium methane conversion at varying outlet temperatures. (The blue curve is equilibrium conversion at the given temperatures. The data are at these same conditions unless otherwise noted.)

catalyst, the catalyst did not show any signs of coking after this low steam to carbon operation.

ANL SMR Results

Sulfur tolerance of a commercial precious metal SMR catalyst was evaluated under partial oxidation conditions over a period of 720 hours. This test was conducted to verify the catalyst's reported sulfur tolerance at temperatures above 900°C. Previous studies by ANL suggested that this SMR catalyst deactivated rapidly by 5–20 ppm H₂S at temperatures ranging from 650–800°C under steam reforming conditions. It is believed that the reported sulfur tolerance of the catalyst may be attributable to a hot catalyst surface under partial oxidation reactions, which makes adsorption of sulfur species less favorable.

The catalyst was evaluated for its sulfur tolerance by being exposed to sulfur-free and sulfur-bearing partial oxidation feed streams. Upon exposure to 23 ppm H₂S, the catalyst deactivated slowly over the first 200 hours with the fractional conversion of methane decreasing from 0.55 to 0.37 and the H₂/(CO+CO₂) yield decreasing from 0.80 to 0.20. When H₂S was dropped from the feed stream for sulfur-free partial oxidation, partial recovery of catalyst performance was observed to follow. An attempt to regenerate the catalyst by exposing to air at temperatures above 800°C appeared to bring the sulfur-poisoned catalyst back to the performance of fresh catalyst. However, a subsequent test showed that the catalyst's sulfur-tolerance after hot air exposure for recovery became worse and the catalyst showed noticeable deactivation on feed streams with 1.5–3.0 ppm H₂S. Overall, the catalyst was not able to tolerate H₂S at concentrations as low as 1.5–3.0 ppm, which is typical of the concentration of H₂S in pipeline NG.

3. WGS

A scalable WGS prototype reactor design was finalized, as shown in Figure 5, and the reactor hardware was fabricated. This reactor design features a fixed bed reactor (6" OD, 4" ID, 20" length) with cooling coils running through the center. The reactor has 28 thermocouples and five gas sampling ports at various locations inside the WGS catalyst bed for kinetic information. WGS system simulation was developed using Pro/II software. This simulation provides vital information that helps the design of experimental process, sizing of equipment, identifying experimental parameters, estimating experimental results and assessing the waste gas emissions from the test cell. Also, 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.

WGS tests were conducted using commercial shift catalyst extrudates and required pre-reduction and post-oxidation process to remove pyrophoric hazard. No coke deposition was observed to occur by analyzing effluent stream of the post reaction oxidation processing. Baseline WGS test results at 50 psig indicates that the CO conversion reached over 80%, which is very close to thermodynamic limit, suggesting good catalyst activity.

4. Cost of Hydrogen Estimation with H2A Model

The first iteration cost analysis began with a conceptual design of a SCPO base distributed hydrogen fueling station. This design was then translated into a system model in Aspen and was used to generate the input data to the H2A model for cost of hydrogen analysis. This preliminary cost of hydrogen analysis and sensitivity analysis results provided critical performance targets for each component in the SCPO system.

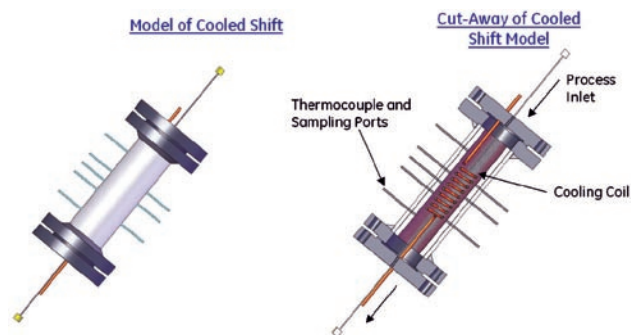


FIGURE 5. Cooled WGS prototype reactor design and CFD analysis results.

This year we completed two iterations of the cost of hydrogen analysis with H2A. As experimental data become available, SCPO process efficiency was derived using an updated SCPO system model in Aspen Plus. The H2A model cost of hydrogen analysis was then modified in Q1 2008 to reflect demonstrated SCPO performance including both CPO and SMR performance as well as supporting equipment design for distributed generation. Table 1 lists the CPO and SMR conversion assumptions used in the first H2A model analysis and the experimentally demonstrated conversion data. As a result, the cost of hydrogen was modified from \$3.052/kg hydrogen to about \$3.025/kg in Table 2. The slight cost reduction is primarily due to a higher than expected SMR conversion.

TABLE 1. SCPO Performance Assumption and Experimental Data

| | Prior Assumption | Experimental |
|-------------------------------------|------------------|--------------|
| SCPO Conversion | 99.56% | 98.18% |
| SMR Conversion | 74.16% | 79.10% |
| Production Unit Hydrogen Efficiency | 73.00% | 75.40% |
| Production Step Efficiency | 70.30% | 72.50% |
| Total System Efficiency | 66.50% | 68.50% |

TABLE 2. Updated Cost of Hydrogen Using the H2A Model

| Hydrogen Selling Price and Cost Contributions (Year 2005 \$) | | |
|---|--------------|-------------|
| | Previous H2A | Updated H2A |
| Required Hydrogen Selling Price (\$2005/kg of H ₂) | \$3.05 | \$3.03 |
| Capital Costs (\$/kg of H ₂) | \$1.38 | \$1.38 |
| Fixed O&M (\$/kg of H ₂) | \$0.58 | \$0.58 |
| Feedstock Costs (\$/kg of H ₂) | \$0.83 | \$0.80 |
| Other Raw Material Costs (\$/kg of H ₂) | \$0.00 | \$0.00 |
| Byproduct Credits (\$/kg of H ₂) | \$0.00 | \$0.00 |
| Other Variable Costs (including utilities) (\$/kg of H ₂) | \$0.26 | \$0.26 |

This cost analysis needs to be modified for effective removal of sulfur compounds that may be found in pipeline NG in addition to H₂S: THT, TBM, and DMS. The additional project months will be used to determine if the CPO catalyst itself can be used as part of the sulfur removal by converting these species selectively to H₂S and allowing for a simplified and likely cheaper H₂S removal option based on sorbents or membrane technologies. Viable options will be included in a sensitivity analysis of the H2A cost of hydrogen model we have developed for the SCPO system.

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, NG combined cycle with CO₂ capture, SOFC systems and syngas production for gas-to-liquids.

Future Directions

- Continue sulfur tolerance evaluation on CPO catalysts, focused on sulfur poisoning mechanism and its related kinetics.
- Conduct durability testing on sulfur-bearing feed streams for long-term sulfur poisoning effect and quantify its rate.
- Continue CPO and SMR supporting tests at ANL and U of M focused on lifetime and model development.
- Continue to update H2A model based on improvement in catalyst and reactor design.

Special Recognitions & Awards/Patents Issued

1. Three applications pending.

FY 2008 Publications/Presentations

1. “Integrated Short Contact Time Hydrogen Generator”, 2008 DOE H2 Program Review Meeting, June 9-13, 2008, Arlington, Virginia.
2. “SYSTEM AND METHOD FOR HYDROGEN PRODUCTION” patent applications filed into US patent office, Ke Liu et al, 2007.
3. 2007 Annual Report to DOE on the “Integrated Short Contact Time Hydrogen Generator.”
4. Submitted four quarterly reports.
5. A. Bitsch-Larsen, N. J. Degenstein, L.D. Schmidt. Effect of Sulfur in Catalytic Partial Oxidation of Methane on Rh-Ce. *Journal of Applied Catalyst B: Environmental* (September 2007).
6. A. Bitsch-Larsen, R. Horn, B. Michael, N. J. Degenstein, L. D. Schmidt, “Spatial profiles at elevated pressure in millisecond contact times reactors for production of syngas” *Preprints of Symposia - American Chemical Society, Division of Fuel Chemistry, 2007, 52(2), p. 603-604.*
7. R. Horn, K. A. Williams, N. J. Degenstein, A. Bitsch-Larsen, D. D. Nogare, S. A. Tupy, L. D. Schmidt, “Methane Catalytic Partial Oxidation on Autothermal Rh and Pt

Foam Catalysts: Oxidation and Reforming Zones, Transport Effects and Approach of Thermodynamic Equilibrium”.
Journal of Catalysis, v 249, n 2, Jul 25, 2007, p. 380-393.

8. A. Bitsch-Larsen, N. J. Degenstein and L.D. Schmidt.
“Catalytic Partial Oxidation of Methane: Sulfur & High Space Velocity”. NACS 20th North American Meeting, June 17-22, 2007, Houston, TX, U.S.A.