II.A.9 Integrated Short Contact Time Hydrogen Generator (SCPO)

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Argonne National Laboratory, Argonne, IL
University of Minnesota, Twin Cities, MN

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Objectives

- Develop the state-of-the-art, staged catalytic partial oxidation (SCPO) technology that combines catalytic partial oxidation (CPO) and steam methane reforming (SMR) for H_2 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 Production section (3.1.4.2.1) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Fuel Processor Capital Costs

(C) Operation and Maintenance (O&M)

(D) Feedstock Issues

Technical Targets

- Total Energy Efficiency (LHV) > 70%
- Total H_2 Cost <$3.00/gge H_2

Accomplishments

- System analysis/design completed
- System design for six sigma (DFSS) pressure trade-off analysis completed
- Base case catalysts identified and tested
- Reactor sizing/design completed
- Heat exchanger technology DFSS trade-off completed
- Heat exchanger technology selected, design completed
- Control strategy, start-up and shut-down procedures developed
- Completed cost analysis using GE's process model and DOE's H2A model
- Prototype and lab unit design/budgeting completed
- Argonne National Laboratory (ANL) and University of Minnesota (U of Mn) worked closely with GE and delivered catalyst test results
- Conducted preliminary failure mode effects analysis (FMEA), major risks identified

Introduction

One challenge for the realization of the hydrogen economy is the development of a low-cost, compact reforming technology that is fuel flexible, and developed to operate on both fossil fuels and renewable fuels. GE Global Research is working with ANL and U of Mn to develop and demonstrate the novel, staged catalytic partial oxidation (SCPO) technology for hydrogen generation from natural gas (NG). This technology will integrate three catalysts into a single compact reactor: catalytic partial oxidation (CPO), steam reforming (SMR), and water-gas-shift (WGS). This integration will be demonstrated via the fabrication of prototype scale key technologies. 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: 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. The project has now moved into the building of experimental facilities where catalysts will be tested and created to meet the difficult demands of SCPO. 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 lead 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 pilot-scale reactors
- 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. DOE Tech Team Review of SCPO Project at GE

The team conducted a DOE Tech Team review at GE's Fuel Conversion Lab, which is also the time when the DOE made a go/no go decision based on current results of the project. A team of reviewers from DOE and industry visited the Global Research Center (GRC) Fuel Conversion Lab at Irvine on March 16th to review the progress on the SCPO project. Both DOE and the tech team were satisfied with the progress of the SCPO project thus far. DOE indicated that the SCPO is one of the most important projects in DOE's H2 Production Program, and DOE agreed to continue the project as planned based on the progress made. The plan forward is to spend most of the effort to develop core CPO and SMR technologies. These were some of the key challenges identified for low-cost reformer technologies. The tech team reviewers left the meeting with a realistic appraisal of the timeline when a reformer based on this technology to be ready for deployment.

The tech team asked for the following to be addressed in the future.

- GE's experience in pre-mixing of natural gas and air for CPO
- Contaminants accumulation over the long term
- Catalyst durability
- Heat integration strategy and its cost-effectiveness at scale-up
- Diffusion bonded heat exchangers long term stability and delamination

GE proposed building and testing only the most important components, instead of a full demonstration style pilot plant. The largest effort will now focus on development of core CPO and SMR technologies. DOE agreed to the plan proposed by GE.

2. System & Reactor Design and Heat Integration

2-1. System Design & Heat Integration

A system analysis using Aspen has been conducted to optimize the energy efficiency while limiting the number of components for the SCPO system. Many configurations were analyzed to find the optimal energy usage for this system. It is important to understand that efficiency is only one factor that affects the cost of a hydrogen generation system. During the system analysis, it was found that some configurations had a higher than expected system efficiencies; however, these systems also had more components. The additional number of components leads to higher capital cost and lower reliability. The most critical factor in a system design for a new technology is to reduce the capital cost. The current SCPO system design tries to balance the cost of hydrogen (using the DOE's H2A model as a guide) and the overall system efficiency. At the end of 2005, we have completed most tasks on the system analysis, optimization and design.

In addition, a preliminary internal safety design review has been completed. Vendors of various systems have been contacted and some quotes have been received. Notice that the change in completion dates for the first few tasks are tied with delay in funding for the sub-contractors. Most of the GE GRC tasks are progressing on target and on time.

2-2. Reactor Design

A preliminary reactor design was completed using vendor quotes for guidance. Various vendors for catalysts and heat exchangers were contacted. The particular specifications from GE GRC, along with internal discussion with technical staff allowed for completion of the preliminary design. Further heat transfer calculations and design must be completed before construction could begin, but the approximate dimensions have been ascertained.

3. Catalyst work

The Fuel Conversion Lab catalyst test apparatus is currently being modified to allow for high-pressure operation. This apparatus will be capable of testing the catalysts at temperatures and pressures similar to those calculated for use in the pilot-scale unit. The 1 ft to 2 in catalyst test reactor is larger than the units at ANL and U of Mn. This should allow for lower heat losses to the environment and thus simulate the SCPO reformer conditions better. We plan to start tests during the third quarter of 2006.

3-1. ANL Results

ANL has received two samples of partial oxidation (POX1 and POX2) and one steam reforming (SR1) catalysts from catalyst manufacturers. Tests were initiated to investigate the long-term durability and sulfur tolerance of these catalysts for the test conditions provided to us by GE using natural gas.

Partial Oxidation Catalysts

Two different partial oxidation catalysts were evaluated for long-term testing for the autothermal reforming (ATR) of natural gas, one for approximately 450 h and the other for approximately 100 h at a space velocity of 50,000 h^{-1}. Yield is presented in Figure 1, during the long-term test using the POX1 catalyst. The second catalyst, POX2, was tested for a shorter time. During the tests, the catalyst was cooled down to perform some light-off tests. A higher space velocity was then used, i.e., 150,000 h^{-1}. The furnace temperature was raised slowly and the bed temperatures were monitored. There was a slight deactivation between the first two tests as observed with an increase furnace temperature at light-off. However, for both POX1 and POX2 catalysts, there was no evidence of significant loss in activity.

Steam Reforming Catalysts

One steam reforming catalyst has been evaluated for almost 500 h with no evidence suggesting a significant loss in activity (Figure 2). The methane conversion was only 60%. Deactivation was observed due to the presence of steam at low temperatures that may re-oxidize the active phase of the catalysts and promote metal volatilization.

Steam Reforming Tests

The SR1 catalyst was also tested for the steam reforming of natural gas in the absence and in the presence of 5 and 10 ppm H_2S. The results are still preliminary, however it can be stated that the effect of sulfur is significant, reducing both conversion and selectivity to an unacceptable level for the SCPO reactor. The vendor has been contacted in order to produce a catalyst that is more sulfur tolerant. This remains a challenge for the project 2006.

3-2. Results from University of Minnesota

The work at the University of Minnesota continued the catalyst development started in 2005. Based on the previously reported results, the catalyst loading was kept to 0.5 wt% Rh and different additives was tested (Re, Cu-Fe, Y-K, and Ce for comparison) as well as a Ni-Ce-K. All catalysts were prepared by the incipient wetness technique. The support used was 80 ppi α-Al_2O_3 with 3 wt% γ-Al_2O_3.

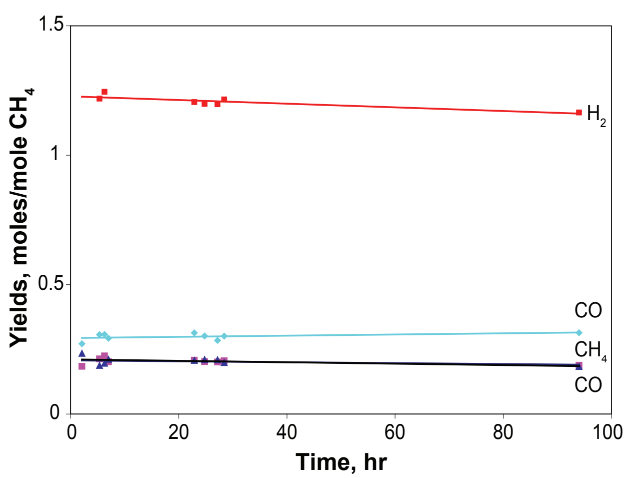

FIGURE 1. H_2, CO, CO_2 and CH_4 Yield during the Autothermal Reforming of Natural Gas using the POX2 Catalyst

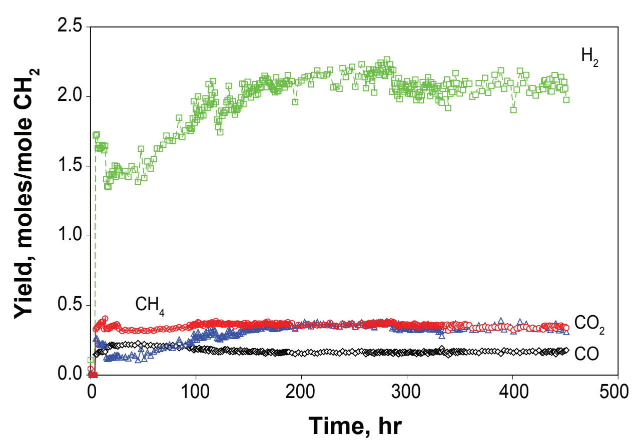

FIGURE 2. H_2, CO, CO_2 and CH_4 Yield during the Steam Reforming of Natural Gas using the SR1 Catalyst

The results for Rh-Ce and Rh-Re are shown in Figures 3 and 4 comparing the two catalysts. From Figure 3 it is seen that the two catalysts are almost identical in hydrogen selectivity at low temperatures, however, at higher temperatures the Rh-Ce catalyst shows a higher selectivity.

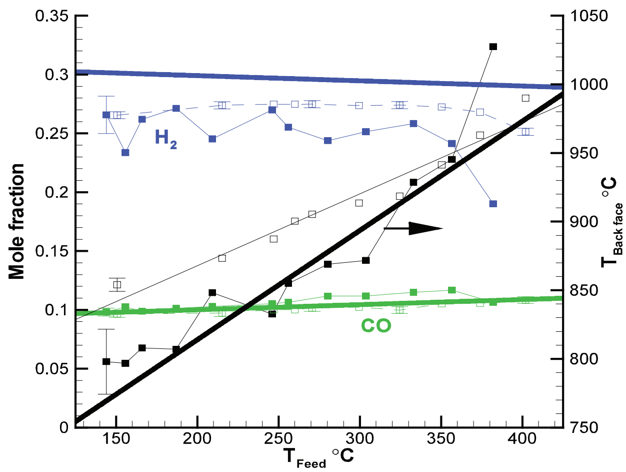

FIGURE 3. Comparison of Rh-Ce (open symbols), and Rh-Re (closed symbols) showing the mole fraction produced from the CPO of methane as a function of preheat temperature of hydrogen and carbon monoxide along with the measured temperature of the catalyst; solid thick lines are adiabatic equilibrium.

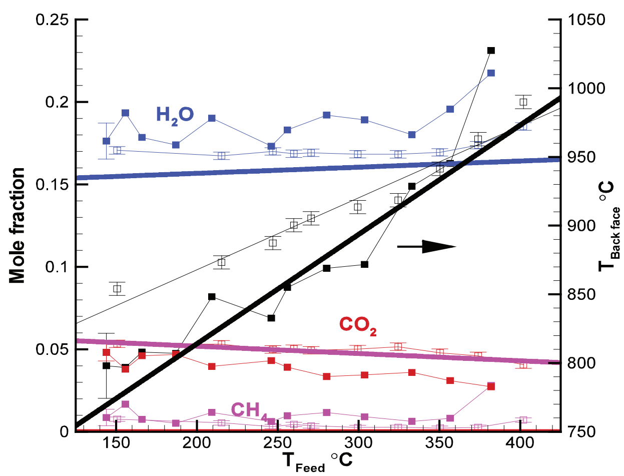

FIGURE 4. Comparison of Rh-Ce (open symbols), and Rh-Re (closed symbols) showing the mole fraction produced from the CPO of methane as a function of preheat temperature of water, carbon dioxide and methane along with the measured temperature of the catalyst; solid thick lines are adiabatic equilibrium.

Conclusions and Future Directions

- SCPO will be the leading technology for H_2 production from NG. It is the most cost-effective H_2 production technology based on analysis of different H_2 production technologies
- Minor modifications will allow 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 CO_2 capture, solid oxide fuel cell systems and syngas production for making liquid fuels from natural gas
- Design and build CPO and SMR reactors in 2006 and conduct testing in 2006 and 2007

Special Recognitions & Awards/Patents Issued

Two patent applications filed with the US patent office.

FY 2006 Publications/Presentations

1. 2005 DOE H2 Program Review Meeting, May 23-26, Washington, D.C.

2. 2005 Annual Report to DOE on the "Integrated Short Contact Time Hydrogen Generator".

3. "SCPO Toll Gate 3 Design Review", November 16, Niskayuna, NY, 2005.