Bio-Derived Liquids to Hydrogen Distributed Reforming Working Group (BILIWG), Hydrogen Separation and Purification Working Group (PURIWG) & Hydrogen Production Technical Team Research Review

November 6-7, 2007

2007 Annual and Merit Review Reports

Tuesday, November 6, 2007

9:00 DOE Targets, Tools and Technology

10:00 Research Review

12:30 Research Review Continued

Wednesday, November 7, 2007

10:00 Research Review

12:30 Research Review Continued

II.B.7 Cost Analysis of Distributed Bio-Derived Liquids Reforming

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Contract Number: DE-AD36-07GO27018

Project Start Date: May 9, 2007
Project End Date: February 9, 2008

Objectives

- Assess the capital cost, performance and resulting total hydrogen cost for three different configurations of 1,500 kgH_2/day distributed hydrogen production systems:
  - A current technology ethanol reformer system.
  - An advanced technology ethanol reformer system.
  - An aqueous phase reformer glycerol reformer system.
- Conduct basic sensitivity analysis on the above reformation systems to assess the impact on hydrogen cost ($/kg).

Technical Barriers

This project addresses the following technical barriers from the “Hydrogen Production: Distributed Hydrogen Production from Natural Gas or Renewable Liquid Feedstocks” section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Reformer Capital Costs
(B) Reformer Manufacturing

Technical Targets

This project is conducting configuration and cost analysis of current and future technology distributed bio-derived liquids reforming systems for the on-site production of hydrogen. Insights gained from these studies may be applied toward future system development that can meet the DOE 2012 hydrogen production from bio-derived liquids targets:

- Production Unit Energy Efficiency: 72%
- Production Unit Capital Cost (uninstalled): $1M
- Total Hydrogen Cost: <$3.80/gge

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Approach

This project seeks to quantitatively assess the projected cost of hydrogen produced by advanced configuration bio-derived liquids reformer systems. To achieve this objective, several bio-derived liquids (ethanol and glycerol) reformation system configurations will be defined and evaluated for expected performance and capital cost. All systems will be sized to produce 1,500 kg/day of purified hydrogen. While the focus of the work will be determination of the capital cost and performance of the production system, the results will be combined with the standard DOE assumptions for hydrogen compression, storage and dispensing to arrive at the total delivered hydrogen cost for comparison with DOE targets.

A baseline ethanol gas-phase reformation system using current technology catalysts and configuration will be examined to serve as a benchmark. The baseline will utilize steam reforming and employ discrete unit reactors (reformation, water-gas shift, pressure swing adsorption, etc.). Catalyst beds will be sized by experimental data and/or kinetics modeling to the extent possible. System performance will be evaluated using HYSYS® simulations and system cost estimated by a combination of scaling factors, previous estimates, and additional Design for Manufacture and Assembly-style calculation. The expected total delivered cost of hydrogen will be evaluated using DOE’s H2A cost model which provides a discounted cash flow methodology and standard assumptions regarding H_2 compression, storage, and dispensing at the forecourt dispensing station.

Advanced technology on-site ethanol reforming systems will next be examined. Emphasis will be placed on unitized operations to achieve tighter heat integration, smaller reactor volume, enhanced efficiency, and lower capital cost. Integrated reformer/shift beds and integrated reformer/shift/membrane purification beds will be examined. Advanced catalysts for lower temperature operation will be considered. Like the baseline configuration, performance will be evaluated in

HYSYS®, capital costs by a variety of methods, and total hydrogen cost by the H2A model. Sensitivity analysis will be conducted on all configurations to assess the impact on hydrogen cost. The impact of ethanol with water dilution and ethanol/gasoline mixtures will be assessed.

A low temperature aqueous phase reformer system utilizing glycerol as the bio-derived liquid feedstock will next be configured. Reactor sizing will be based on a combination of published developer data and first principles reaction rates. Capital costs will be estimated based on a variety of methods as described above. Production systems performance and capital costs will be entered into the H2A model to obtain estimated delivered hydrogen cost for the total dispensing station.

Accomplishments

- Defined the baseline ethanol system to consist of pre-reformer, steam reformer, water-gas shift, and pressure swing adsorption.
- Initiated capital cost analysis of the baseline configuration.
- Conducted literature reviews and preliminary configuration analysis of several advanced configuration systems.

II.A.2 Low-Cost Hydrogen Distributed Production System Development

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Contract Number: DE-FG36-05GO15026

Subcontractor:
Süd Chemie, Inc., Louisville, Kentucky

Start Date: July 1, 2005
Projected End Date: September 30, 2008

Objectives

- Design, build and test a steam methane reformer 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

Technical barriers from the Hydrogen Production section (3.1.4.2.1) 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

Distributed Production of Hydrogen from Natural Gas

	2010	2015	H_2Gen Status
Production Unit Energy Efficiency, %(LHV)	72.0	75.0	67.4[a]
Production Unit Capital Cost (Uninstalled)	900K	580K	742K[b]
Total Hydrogen Cost $/gge	2.50	2.00	2.33[c]

[a] Based on the current HGM-2000
[b] 1,500 kg/day system at 500/year production rate
[c] Using 7-year MACRS depreciation

Accomplishments

- Collected over 42,000 hours of field test data (multiple units) on the 113 kg/day commercial H_2Gen SMR systems to verify system efficiency and reliability, exceeding the original goal of over 2,500 hours field test experience.
- Based on this extensive test experience at 113 kg/day scale, H_2Gen redesigned the reactor and flow sheet for a 565 kg/hr platform, including:
  - Low pressure drop burner
  - Compact, low stress steam generator
  - Linear combustion air supply system
- Designed the SMR plus PSA skid to industry standards including B31-3, VIII-1, API 618, NFPA 70A, 497, 496 and CSA 5.99.
- Built and tested the major sub-systems including the burner and steam generator systems, and redesigned the boiler system to improve performance.
- Completed fabrication of the first 565 kg/day reformer and PSA system.
- Completed the ethanol catalyst screening tests and successfully demonstrated reforming of neat ethanol in micro-reactor tests.
- Started the long-term (>1,000 hours) catalyst life testing with ethanol, and prepared for testing of ethanol reforming with gasoline additives found in E-95 used in commercial ethanol fuel transport.

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Introduction

Achieving the DOE cost targets will require improved efficiency and also larger hydrogen capacity compared to the current hydrogen generation module (HGM)-2,000 system (2,000 scfh or 113 kg/day capacity). We are also reducing catalyst cost while improving SMR, shift and PSA performance and increasing feedstock diversity.

Approach

To meet these 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 will begin field-testing an HGM-10,000 with five times the capacity of our current system.

While we expect that the HGM-10,000 (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, working with our catalyst partner, Süd Chemie, will also evaluate the cost and efficiency of reforming ethanol at the local fueling station using the H_2Gen technology. We expect that hydrogen made from ethanol will be the least costly renewable hydrogen option for at least a decade or two.

Results

Water-Gas Shift (WGS) Catalyst Development. Süd-Chemie continued working on the development of improved WGS catalysts which are stable under high pressure conditions of HGM operation, has high activity towards WGS reaction, low activity for methanation and suppress formation of any by-products. Modifications to existing WGS reactors at Süd-Chemie were necessary to operate at H_2Gen pressures of interest. Upgrades to existing equipment included pressure gauges, mass flow controllers, and relief value spring kits. Other modifications included back pressure regulators for the reaction tubes as well as a regulator to step down the pressure before continuing to the analytical equipment.

Süd Chemie ran multiple tests on several WGS catalysts under H_2Gen operating conditions. A number of different supports were also prepared and tested. A new support was identified, and the best support/catalyst combination was optimized by detailed studies of support properties and promoter concentrations and types.

Pre-Reforming Catalyst Development. Süd-Chemie and H_2Gen identified an opportunity to develop a high performance pre-reforming catalyst to extend to fuels such as liquefied petroleum gas (LPG) and ethanol. The pre-reforming of natural gas, LPG and ethanol required a stable fuel flexible catalyst that is matched to H_2Gen's operating parameters. In addition to being stable this catalyst needed to be sulfur and carbon tolerant.

Süd-Chemie has developed stabilized oxide support for the pre-reforming catalysts. The initial sample sent to H_2Gen was prepared on a 100 cc scale using R&D lab equipment. After receiving positive feedback from initial trials at H_2Gen, the scale-up of the material was investigated. Initial trials were not successful in the pilot plant using industrial equipment. Upon further investigation and equipment optimization, successful trials were carried out by making several tens of kilograms. The results need to be confirmed in actual plant equipment.

HGM-10,000 Fabrication. The primary work for 2007 was the full-scale testing of the burner and steam generator sub-systems, completion of the detailed HGM-10,000 design including a new control system architecture, and the fabrication of the first HGM-10,000 that was completed in June 2007.

The HGM-10,000 burner has a much lower pressure drop than the burner used in the HGM-2,000. This lower pressure drop significantly reduces the power draw required from the air blower, which increases the overall electrical efficiency of the SMR system. The burner mechanical design was augmented by a computational fluid dynamic (CFD) analysis of the burner uniformity as shown in Figure 1. This burner system was then fabricated and tested at our Alexandria test facilities as shown in Figure 2.

The full HGM-10,000 system is shown during construction in Figure 3. This system will be shipped to a field test site in July 2007 to begin initial system testing. Our goal is to demonstrate more than 2,500 hours of field operation to gather information on system efficiency and reliability.

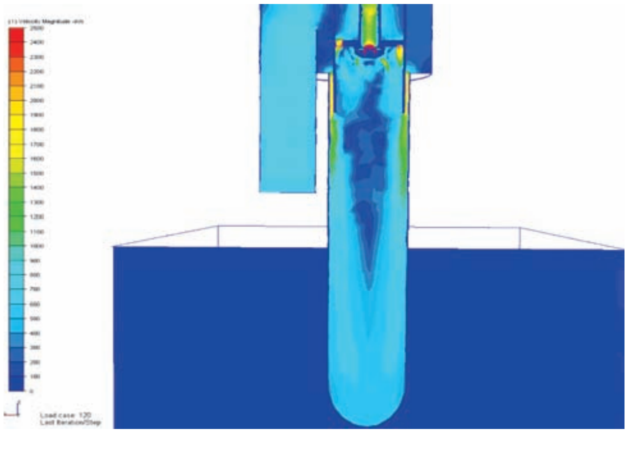


FIGURE 1. CFD Analysis of Mixing Region for HGM-10,000 Burner

FIGURE 2. HGM-10,000 Burner Test Setup

FIGURE 3. HGM-10,000 During Construction

SMR/PSA Cost Reduction. The total material cost (excluding fabrication labor and general and administrative expenses associated with ordering, shipping and receiving parts) will meet our $350,000 goal without any further cost reductions. Hence, the economies of building multiple units with vendor price reductions should reduce the material costs below our target of $350,000.

The current HGM-10,000 will be optimized through the design for manufacture and assembly processes. In the current unit to save project costs, we used the same reformer tubes that are in our HGM-2,000 reactor. Future costs could be reduced by optimizing the diameter and lengths of these reactor tubes. Other cost savings are anticipated with future designs incorporating the lessons learned in the field test.

Conclusions and Future Directions

To ready the HGM-10,000 for actual deployment in commercial situations, the following key tasks must be completed:

(a) Complete the development of the first version of the operating software for the HGM-10,000, including field testing.
(b) Commissioning procedures, installation, operations and maintenance manuals for the HGM-10,000.
(c) Map the operation of the HGM-10,000 as built, establishing the operating envelope and characteristics.
(d) Identify areas for improvement.

These tasks will naturally lead to the completion of a second prototype plant at the 565 kg/day capacity. This plant will help remedy shortcomings identified in the first plant while the first plant continues to accumulate operating hours to demonstrate durability. A second site has been secured for testing; this second plant and construction and delivery to the site are expected to be completed by Q1 2008.

We will continue screening of ethanol catalysts and complete long-term durability tests. A key focus will be testing with real ethanol blends with impurities present.

Special Recognitions & Awards/Patents Issued

1. We received a 2007 DOE Hydrogen Program R&D Award "in recognition of outstanding achievement in technology innovation" at the annual review meeting.

FY 2007 Publications/Presentations

1. Presentation to the 2007 DOE Annual Peer Review meeting.

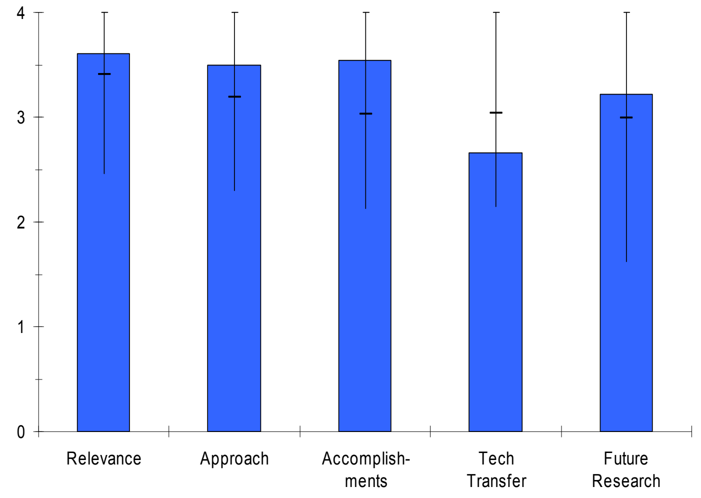
Project # PD-02: Low-Cost Hydrogen Distributed Production Systems

Frank Lomax; H2Gen Inno. Inc.

Brief Summary of Project

H2Gen Innovations is conducting the development, fabrication and testing of an advanced steam methane reformer and pressure swing adsorption (PSA) system that will produce ~10,000 scfh (565 kg/day) of 99.999% pure hydrogen at over 200 psig, to meet the DOE 2010 interim cost target of $2.50/kg. A catalyst suite suitable for use with fuel grade ethanol to facilitate renewable hydrogen production is also being developed.

Overall Project Score: 3.4 (5 Reviews Received)



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.6** for its relevance to DOE objectives.

- Strongly supports natural gas distributed reforming goals; more feedback concerning performance versus goals necessary.
- Project clearly meets the DOE Hydrogen Program targets.
- Good concept to achieve high reliability and cost.
- Meets the need for renewable hydrogen production from ethanol.
- Management understands and appreciates the requirement to achieve the DOE cost targets and is on track to meet them.
- Can be used for distributed and stationary applications.
- A demo of the natural gas to hydrogen process is appropriate for the near-term.
- H2Gen is not a catalyst company. Not clear about their novel concept for ethanol catalysis.
- This project addresses barriers such as fuel processor capital cost, manufacturing, O&M, feedstock issues, and control and safety in the Multi-Year RD&D plan.

Question 2: Approach to performing the research and development

This project was rated **3.5** on its approach.

- Development of natural gas reforming is well designed; addition of ethanol research, primarily the conversion from ethanol to methane is questionable.
- Well conceived, staged approach; sufficient testing of individual components.
- Good design and operations estimates.
- Could not tell if there were independent analyses on cost.
- Ethanol R&D looks promising.
- The process approach is good and makes sense for a refueling center.
- Fuel process capital cost, manufacturing costs, O&M, feedstock issues, and control and safety barriers are addressed in this project.
- This team has perfect approach.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.5** based on accomplishments.

- Strong accomplishment towards achieving cost targets; more performance parameters versus goals required.
- Impressive accomplishment to complete 565 kg/hr platform.
- Good progress and cost reduction.
- Materials of construction - limited data on reliability.
- Compression related work not clear to achieve cost.
- Good performance of reformer as demonstrated by data.
- New PSA designed to increase capacity.
- Not much data to evaluate technical progress.
- Unclear on Slide 8, where a plot is shown without any y-axis, what is being measured.
- Cost analysis is promising.
- Ability to convert ethanol is not very meaningful. Unclear how much H_2 and what else is produced.
- This team has made excellent progress toward meeting their overall objectives.
- Based on test experience at 113 Kg/day scale, they have redesigned reactor and flowsheet for 565 Kg/day platform. This system has low pressure drop burner, compact and low stress steam generator and linear combustion air supply system.
- To reduce risk and cost this team has tested the burner, steam generator, and air supply system at full 565 Kg/day scale.
- Designed skid to industry standards.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **2.7** for technology transfer and collaboration.

- Minimal collaboration; nearly all technology in-house.
- Good coordination, but commercialization and service support were unclear.
- Team roles unclear once R&D goals are achieved.
- Unclear how IP shared in the next generation technology.
- Partners have been identified for future site location.
- Sud-Chemie is a good partner, possibly in catalysis research.

Question 5: Approach to and relevance of proposed future research

This project was rated **3.2** for proposed future work.

- Scale-up of approximately 115 kg/day unit to 565 kg/day will provide useful information and potential path to 1500 kg/day.
- Need to (eventually) have clear reasons/objectives for building the 2nd generation plant; should be based on a clear need with significant performance benefits.
- Good focus on research goals, accelerated reliability studies should be considered to validate longer term cost projections.
- The 565 Kg hydrogen generator will be tested at field site as well as building and testing a second 565 Kg hydrogen generator at a second field site.
- Based on test data, they will identify areas for improvement – excellent plan.
- In addition to the primary objective of reforming natural gas, H2Gen has secondary objective of using ethanol as a feedstock. They have plans to demonstrate the durability of ethanol reforming catalyst.
- They will make go/no-go decision based on durability tests.

Strengths and weaknesses

Strengths

- Simple design, skid mount approach useful.
- Good team with strong technical expertise. Past experiences have influenced current project and management oversight is good.

- Natural gas to hydrogen plant demonstration is promising with respect to cost targets.
- Very good project planning and execution.

Weaknesses

- Requires integration into overall production, compression, and storage system to determine transients, turndown, etc.
- Scale up from 113 to 567 was not clearly defined as to risk both on a market penetration basis and reliability of performance. Unclear whether the availability of components is within their current analysis or if a new evaluation will be undertaken since there is limited performance data available.
- Catalyst development strategy does not fit with this project.
- Unclear if it is necessary to pre-reform ethanol.
- No safety and code analysis for the installation of the hydrogen generator at the field site.

Specific recommendations and additions or deletions to the work scope

- Continue to complete this project to benchmark progress to goals.
- Add task to track hydrogen quality and its impact on cost of hydrogen.
- Maybe they should focus on their primary objective which is the development of hydrogen generator for distributed production of hydrogen using natural gas as feedstock. Would like to see more of these hydrogen generators built instead of redirecting their effort on reforming ethanol.
- It is a good idea for DOE to fund H2Gen for ethanol reforming.

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

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Contract Number: DE-FG36-05GO15023

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

Start Date: May 30, 2005
End Date: May 30, 2008

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 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 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 H_2 Cost <\$2.50/gge H_2

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.

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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 H_2 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 O_2/C, steam/carbon (S/C) ratios, and GHSV. The standard catalyst achieves >90% CH_4 conversion at 500,000 h^{-1} GHSV and above at O_2/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 H_2 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.

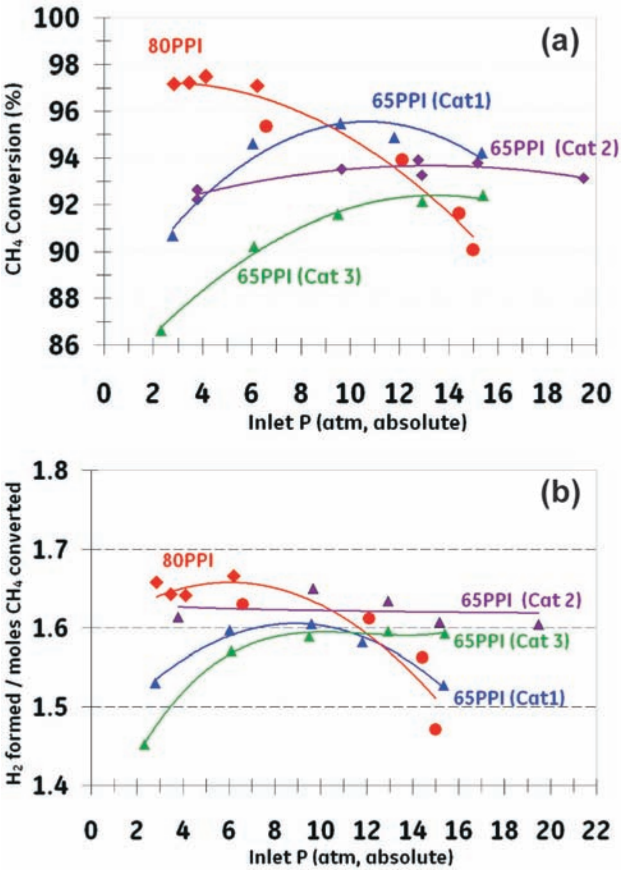


FIGURE 1. High-P CPO Performance of Different Catalyst Structures (a) Methane Conversion (b) Hydrogen Yield, Rh-Baseline Catalyst Formulation, $O_2/C=0.67$, $S/C=1$, $GHSV=500,000\ h^{-1}$

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 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.

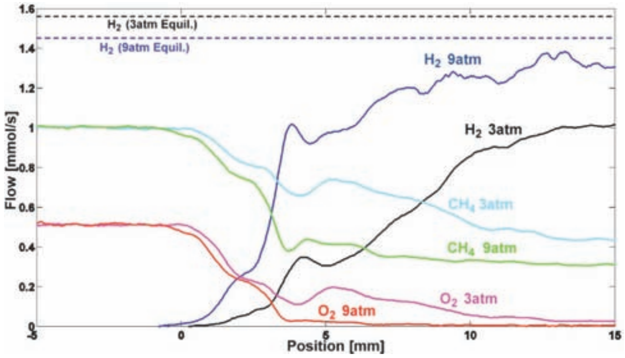


FIGURE 2. Spatial profiles on Pt-coated foam monoliths at 3 atm and 9 atm. Inlet conditions $O_2/C=1$, $S/C=0$, $130,000\ h^{-1}$ GHSV. The start of the 10 mm catalyst is indicated by 0 mm. Equilibrium is calculated under assumption of constant pressure and adiabatic reactor operation.

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 H_2O:C, 600-800°C, GHSV of 20,000 to 60,000 h^{-1}) and the high temperature SMR conditions (1% CH_4 in reformate, 800-950°C).

CH_4 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 CH_4 conversion and slight rise in inlet temperature suggests some deactivation is occurring. The best performing catalyst, C_1, did not show significant degradation at either temperature.

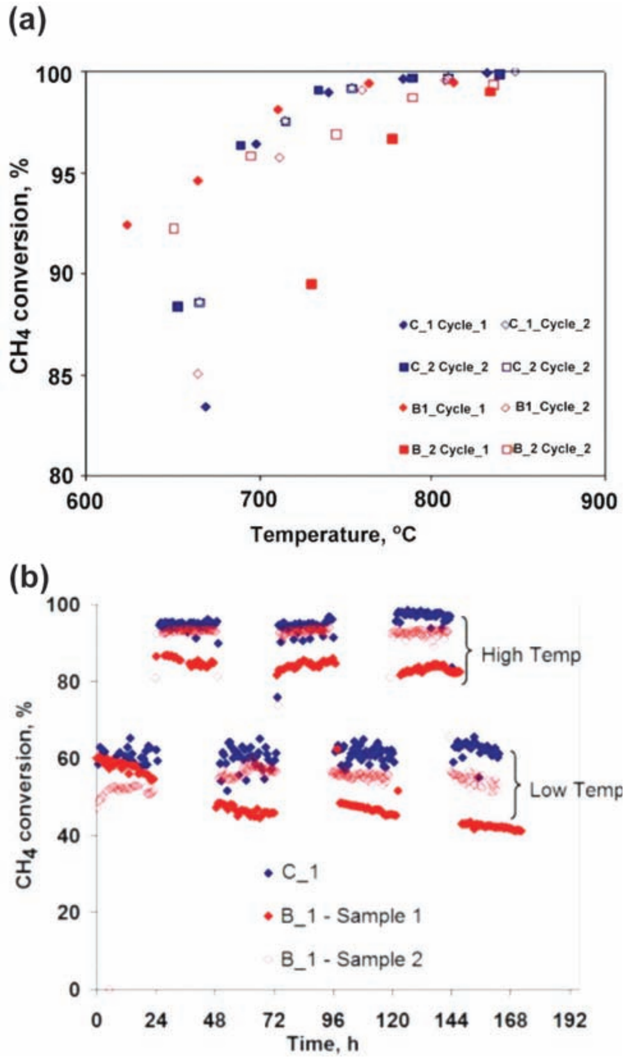


FIGURE 3. (a) Comparison of the CH_4 conversion as function of temperature; (b) CH_4 Conversion in long-term testing performed on the most promising catalysts.

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 H_2S using the low temperature SMR conditions. The catalysts were evaluated for sulfur tolerance over a temperature range from 600-800°C. H_2S at concentrations as low as 5 ppm severely poisoned all of the SMR catalysts resulting in a significant decrease in conversion. When the H_2S 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 4a and 4b 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 venders in the U.S. and catalyst of interest from each of these venders.

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

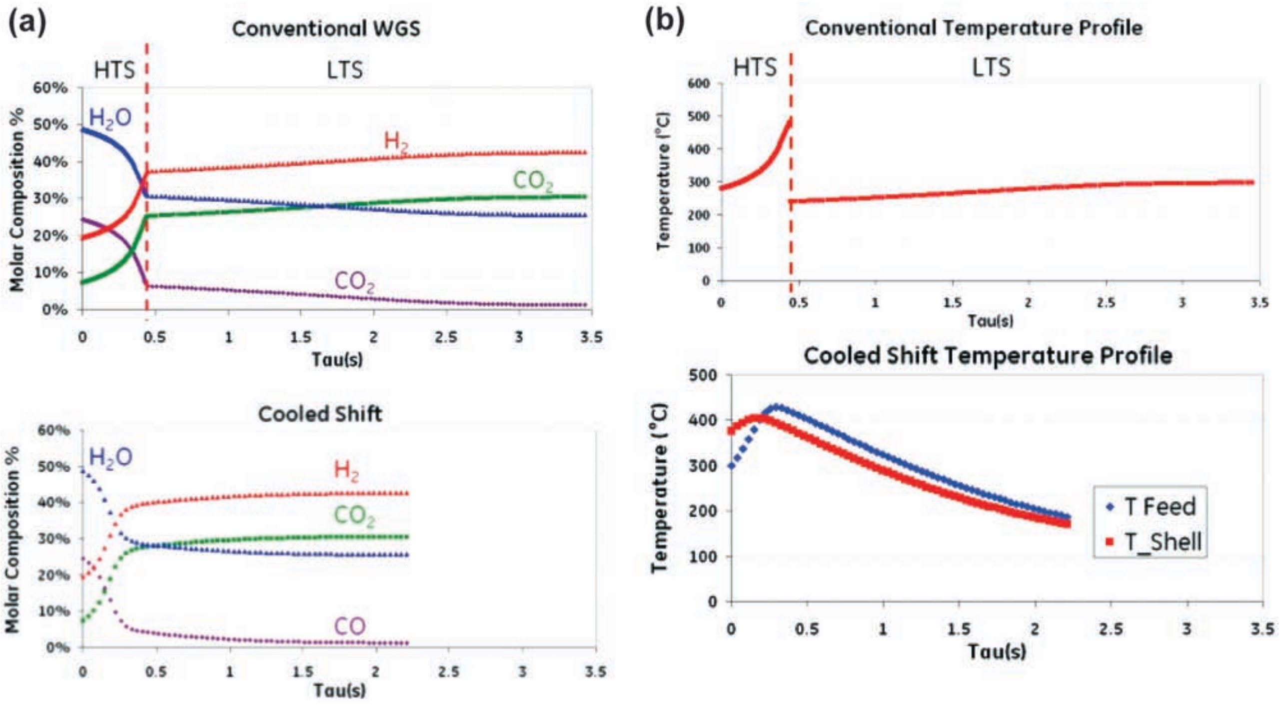


FIGURE 4. Modeling Results of Cooled-Shift Reactor vs. a Conventional 2-Stage Shift Reactor: (a) Composition Profile; (b) Temperature Profile

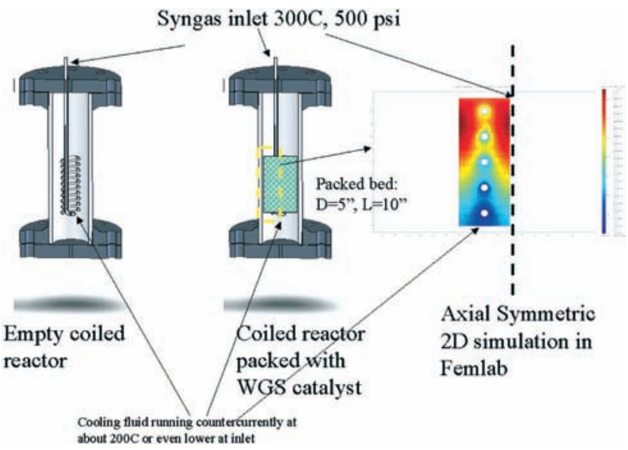


FIGURE 5. WGS Prototype Reactor Design and CFD Analysis Results

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 H_2 production from NG. It is a cost-effective H_2 production technology based on analysis of different H_2 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 CO_2 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, DC.
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.

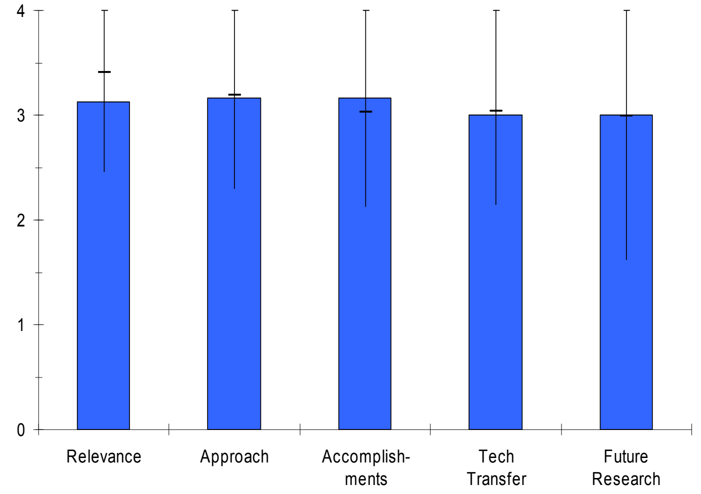
Project # PDP-09: Integrated Short Contact Time Hydrogen Generator (SCPO)

Ke Liu; GE Global Research.

Brief Summary of Project

Both short contact time and steam methane reforming catalysts are being developed and a compact reforming system was designed. An interim (2006) hydrogen production cost target of $3.00/gge for distributed reforming from natural gas was achieved based on GEGR SCPO technology economic projections and those of other distributed natural gas research efforts. This project received an independent assessment verifying that the interim target was met. Specifically, GEGR is working with the University of Minnesota to: 1) discover sulfur-tolerant catalytic partial oxidation (CPO) catalysts; 2) develop sulfur-tolerant CPO catalysts; and 3) characterize CPO catalysts using X-ray diffraction and X-ray photoelectron spectroscopy. Argonne National Laboratory objectives include catalyst discovery, screening, durability testing, and characterization.

Overall Project Score: 3.1 (4 Reviews Received)



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.1** for its relevance to DOE objectives.

- Development of simplified reformers, particularly multi-fuel reformers is a significant step towards meeting the DOE H_2 cost goals.
- Directly relevant to the economic production of H_2 in line with DOE Hydrogen Production targets.
- Reformer technology is critical to the initiative, but this technology doesn't appear to solve any problems or improve market penetration.

Question 2: Approach to performing the research and development

This project was rated **3.2** on its approach.

- Concept seems similar to other CPO configurations.
- Partial oxidation offers a path to compact, on site reformers, but has historically suffered from inability to operate reliably and safely at high pressure. (Good) focus on this problem as well as the identification of S-tolerant catalysts.
- Excellent leveraging of academia / national lab expertise in catalyst technology and characterization.
- Strong experimental program with impressive in-situ characterization of the reactor.
- Nothing new or innovative.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.2** based on accomplishments.

- Team has good experimental results with high space velocities.
- Great progress in operating at high pressure...a longstanding problem in this technology.
- Lots of work in evaluation of S-tolerant reforming catalyst...though not much progress towards a breakthrough.
- Successfully demonstrated applicability of short contact time hydrogen generation.

- Would be helpful to show SCPO overall process integration to produce pure hydrogen.
- Not much data presented; no comparison to conventional ATR performance.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.0** for technology transfer and collaboration.

- Impressed with strong record of collaboration with partners at U. Minnesota and Argonne National Labs. Poster clearly laid out contributions from both institutions and work processes they are using to collaborate.
- Effective collaboration between industry, national lab, and academia.
- Unclear what is being done.
- Limited publications.

Question 5: Approach to and relevance of proposed future research

This project was rated **3.0** for proposed future work.

- Testing at 1M space velocity is good goal.
- Not clear how practical 400psi operating pressure is: good from H_2 purification viewpoint but bad if one has to compress air/oxygen to that pressure.
- Clear path forward for natural gas reforming, and they are thinking about attacking more ambitious liquid feeds derived from renewable resources.
- Proposed future research needs to be more clearly stated.
- Would like to see a plan to commercialize this technology (start by building a prototype hydrogen generator).
- Question whether this technology can compete with conventional SMR; should capitalize on the potential to reform complex hydrocarbons which can't be done with steam reforming.
- Limited in scope and value.
- Uncertain how large cost reductions were derived.

Strengths and weaknesses

Strengths

- This is the best project I had the opportunity to review. It is using novel science and engineering to attack a difficult problem, and there is clearly a great deal of interaction and collaboration amongst the industry, national laboratory, and university participants. This is the poster child of how industry, universities, and national labs should work together in developing novel science and engineering to attack a national challenge.
- GE corporate involvement.
- Potential to handle multiple feedstocks.

Weaknesses

- Innovation.
- Independent review.
- Market study.

Specific recommendations and additions or deletions to the work scope

None

II.B.3 Distributed Bio-Oil Reforming

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Start Date: October 1, 2004
Projected End Date: Project continuation and direction determined annually by DOE

Objectives

- By 2012, develop and demonstrate distributed reforming technology for producing hydrogen from bio-oil at \$3.80/kilogram (kg) purified hydrogen.
- By 2011, develop a prototype that incorporates the key operations: high-pressure bio-oil injection, homogeneous partial oxidation, and catalytic autothermal reforming.
- Develop the necessary understanding of process chemistry, bio-oil compositional effects, catalyst chemistry, and deactivation and regeneration strategy to form a basis for process definition for automated distributed reforming to meet DOE targets.
- In fiscal year (FY) 2007, demonstrate bio-oil performance consistent with distributed reforming system concepts including volatilization, carbon management, partial oxidation, and catalytic auto-thermal reforming.

Technical Barriers

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

(A) Reformer Capital Cost
(C) Operation and Maintenance (O&M)
(D) Feedstock Issues
(F) Control and Safety

Technical Targets

Distributed Production of Hydrogen from Bio-Derived Renewable Liquids

	2012	2017	NREL Status
Production Unit Energy Efficiency, %(LHV)	72.0	65-75g	50
Production Unit Capital Cost (Un-installed)	1.0M	600K	1.5M
Total Hydrogen Cost \$/gge	3.80	<3.00	4.50

Accomplishments

- Improved bio-oil volatilization by enhancing the ultrasonic nozzle and reducing the methanol content to 10%.
- Demonstrated model development for methanol under oxidative-cracking process conditions (under subcontract to CSM).
- Validated oxidative cracking of bio-oil at temperatures less than 650°C and with high CO/CO_2 ratio.
- Introduced catalysts to the process and demonstrated equilibrium syn-gas composition over a 0.5% rhodium-supported on alumina catalyst.

◆ ◆ ◆ ◆ ◆

Introduction

More than 500 million tons of biomass could be available in the United States at less than \$50/ton. This biomass can be converted to over 50 million tons of hydrogen (H_2) [1]. The challenges for the variety of feedstocks include handling and drying, regional and seasonal availability and variability, and the impurities inherent in biomass or/and generated in the process. Such impurities could impact conversion technology and hydrogen purity. Processes must be feedstock-flexible and minimize costs for feedstock collection, transport, and processing. Given the near-term technical barriers to hydrogen storage and delivery, technologies that can be distributed at or near the point of use are attractive.

This work addresses the challenge of distributed hydrogen production with a targeted hydrogen cost of \$3.80/kg by 2012 [2]. Pyrolysis is used to convert biomass to a liquid that can be transported more efficiently and has the potential for automated operation of the conversion system [3]. "Bio-oil" can then be converted to hydrogen and carbon dioxide (CO_2) in a distributed manner at fueling stations. The thermally reactive compounds (e.g., anhydro-sugars, phenolics) in bio-oil do not evaporate cleanly. They tend to decompose and react, and may form carbonaceous deposits or be converted to aromatic hydrocarbons, which are thermally stable and more difficult to convert to hydrogen. Thus, conventional fixed-bed reformers have not been proven efficient for this highly reactive feedstock. Reactors that fluidize or circulate the catalyst are much more suited for this application, but have not been proven for small-scale and unattended operation.

Approach

A system has been developed for volatilizing bio-oil with manageable carbon deposits. It uses ultrasonic atomization to control physical properties and modifies bio-oil properties, such as viscosity, by blending or reacting bio-oil with alcohol. Homogeneous partial oxidation of bio-oil is then used to achieve significant conversion to carbon monoxide (CO) with minimal aromatic hydrocarbon formation by keeping the temperature at 650°C or lower and the oxygen (O_2) at a low and steady level. Model compounds are used to establish the underlying chemical understanding of the process and identify optimized conditions. The product gas is converted via heterogeneous auto-thermal reforming with precious metal catalysts to complete the conversion to hydrogen [4].

The reactor is shown in Figure 1. The reactor system is based on ultrasonic nebulization. A fine mist of oil is generated at ambient conditions and heated to the target temperature, typically 650°C, at which point a bio-oil vapor residence time of 300 ms is achieved. A catalyst bed is located at the bottom of the tube. The initial testing of homogeneous cracking used a bed of quartz particles to capture any deposits that formed in the volatilization and cracking zones. Performance of the bio-oil injection system was tested with a 50% bio-oil solution in methanol. The system allowed steady-state operation.

Molecular Beam Mass Spectrometry (MBMS). The study of pyrolysis by MBMS has been described previously [5]. The gases exiting the reactor are expanded through an orifice on the apex of a sampling cone into the stage 1 vacuum at 40 mtorr. The free-jet expansion quenches the products and allows light gases, high-molecular-weight compounds, and reactive products to be sampled. A molecular beam, collimated through a second expansion, enters an ion source, where 25- to 50-eV electron-impact ionization is used to form ions that are analyzed by a quadrupole mass filter.

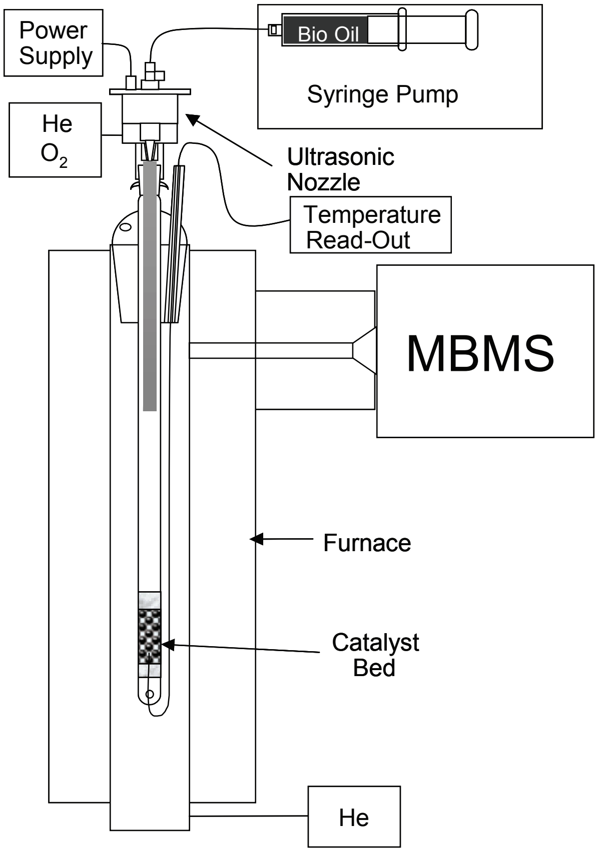

FIGURE 1. Auto-Thermal Bio-Oil Reforming Reactor

Results and Discussion

Experiments were performed in FY 2006 and FY 2007 without catalysts to determine the extent of low-temperature oxidation of the volatilized bio-oil. Variables were temperature and O_2 level. The objective was to break carbon-carbon bonds and avoid oxidation to carbon dioxide (CO_2) and water (H_2O) as well as aromatic hydrocarbon formation. The temperature was varied from 500 to 650°C. The oxygen level was varied from that of the methanol/bio-oil feed (no oxygen added) to the maximum level that could be added in the gas phase without the onset of flaming combustion.

The effects of the oxygen-to-carbon ratio (O/C) and temperature on CO and CO_2 yields are shown in Figures 2 and 3. Bio-oil was converted to CO at a greater than 50% yield on a carbon basis, with only 10% CO_2 yield. The most important variable in the range between 550 and 650°C is the O/C, with experiments at different temperatures following the same trend line. Runs below 550°C are affected by both O/C and temperature. The most significant conclusion here is that the oxidative cracking effect is observed at temperatures as low as 550°C. The lower temperatures allow higher O_2 levels to be introduced before the

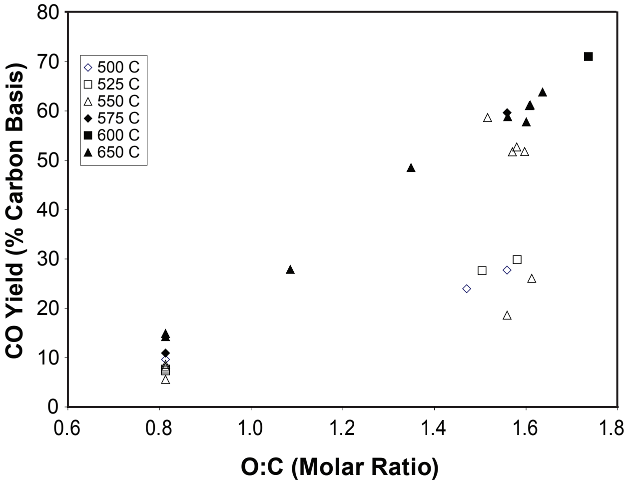

FIGURE 2. The Effect of O/C, Varied by the Introduction of O_2, and Temperature on the Gas-Phase CO Yield at Different Temperatures for a 50% Bio-Oil in Methanol Solution

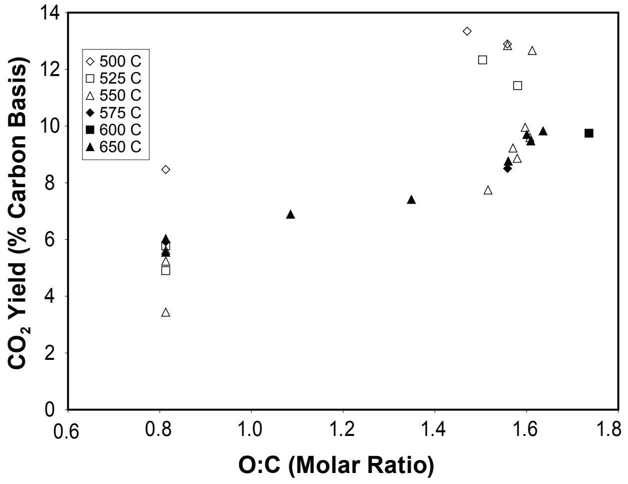

FIGURE 3. The Effect of O/C, Varied by the Introduction of O_2, and Temperature on the Gas-Phase CO_2 Yield at Different Temperatures for a 50% Bio-Oil in Methanol Solution

onset of flaming combustion. The 600°C experiment was at the highest O/C and resulted in a CO yield of 70%. In the best case at 600°C, the conversion of bio-oil carbon to CO and CO_2 was comparable to the rate of conversion of methanol, which was around 80%. However, there was aromatic hydrocarbon formation and carbon deposited in the reactor approximately equal to 15% of the bio-oil, which was subsequently oxidized by the O_2 no longer consumed in the gas phase after feeding was suspended.

Catalytic Auto-Thermal Reforming. The products from oxidative cracking include some residual oxygenates and low-molecular-weight hydrocarbons, such as benzene. The oxidation and reforming of these products followed by the water-gas shift reactions will be accomplished by low-temperature auto-thermal catalysis. Commercially available catalysts have been used to initiate catalyst testing experiments. A comparison of packed beds of 0.5% rhodium, palladium, platinum, and ruthenium catalysts on alumina was performed as a benchmark to establish the competitive reaction pathways for syngas reactions, such as oxidation, water-gas shift, and steam reforming. The major product traces are shown in Figure 4 for a typical catalyst experiment using 0.5% Rh on an alumina-packed bed for 50:50 methanol/bio-oil fed at 6.7 g/hr with a gas-phase residence time of 300 ms at 650°C prior to the catalyst bed. Oxygen is added to give an O/C of 1.33. The bio-oil is fed from 13 to 100 minutes. The CO_2, water, and CO signals continue after the feed is stopped due to the residual material that is oxidized by the available oxygen. These traces are considered the raw data and are not corrected for differences in response factors. The results for different catalysts and conditions are shown in Tables 1 and 2. The equilibrium values and gas-phase-only results are shown for comparison. The amount of oxygen and water in the systems was the same as for the gas-phase reaction, which means that only steam was available as a reactant gas on the catalyst since all O_2 was completely used in the gas-phase section. The reaction with residual hydrocarbons on the catalyst was complete, although conversion to carbon is a likely reaction pathway. As with the gas-phase studies, the solid carbon was quantified when the feed was turned off and the oxygen became available for carbon burn off. To date, no attempt has been made to characterize

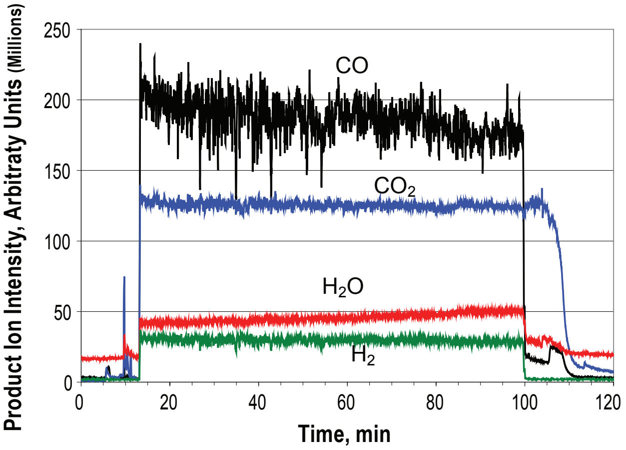

FIGURE 4. A typical catalyst experiment using 0.5% Rh on an alumina-packed bed showing the major product gases for 50:50 methanol/bio-oil fed at 6.7 g/hr with a gas-phase residence time of 300 ms at 650°C prior to the catalyst bed. Oxygen is added to give an O/C of 1.33. The bio-oil is fed from 13 to 100 minutes. The CO_2, water, and CO signals continue after the feed is stopped due to the residual material that is oxidized by the available oxygen. These traces are considered the raw data and are not corrected for differences in response factors.

TABLE 1. Results of Catalyst Experiments with O/C = 1.3

	Equil.	Gas	Alumina	Rh	Pd	Pt	Ru
CH_3OH conversion	100.0	49.1	38.7	99.6	82.1	88.2	75.4
CO	68.7	38.6	36.0	61.1	50.9	45.5	48.4
CO_2	23.8	7.2	7.5	23.2	9.6	11.6	9.3
H_2	80.3	13.1	9.2	83.7	34.1	31.2	27.6
H_2O	13.5	38.5	38.0	17.8	40.6	45.3	40.7
CH_4	3.9	5.2	5.3	5.9	7.7	8.2	9.5
Carbon deposition	3.6	1.0	1.6	4.4	7.7	10.4	6.9
Benzene	0.0	1.3	1.0	1.4	4.4	2.3	2.0

TABLE 2. Results of Catalyst Experiments with O/C = 1.7

	Equil.	Gas	Rh
CH_3OH conversion	100.0	87.5	100.0
CO	57.0	60.3	52.9
CO_2	41.8	11.3	37.6
H_2	72.3	27.7	74.1
H_2O	25.8	54.3	31.7
CH_4	1.2	6.5	5.0
Carbon deposition	0.0	0.9	1.4
Benzene	0.0	2.7	0.5

the carbon that accumulates on the catalyst. The conversion on Rh catalyst was the closest to equilibrium conditions. The challenge for the integrated system will be to selectively reform the residual hydrocarbons and catalyze the water-gas shift reaction without catalyzing methanation and CO oxidation. The goal will be to attain equilibrium levels of hydrogen, CO, H_2O, and CO_2 at the exit of the catalyst bed and to maintain steady-state conditions, which requires adequate carbon conversion in the first phase of the catalyst bed.

Conclusions and Future Directions

These results show that a low-temperature oxidative cracking stage will reduce the required catalyst load in the reforming of bio-oil and that a clean syngas can be produced without high gasification severity conditions, namely temperatures higher than 650°C and excessive H_2O to drive the carbon reforming reactions to completion. Only trace amounts of methane and benzene are detected in the product gas when the catalyst is in place. Ongoing developments in the project are examining the parametric effects of variation in process variables (temperature, oxygen, and steam), the removal of CO_2 from the system by adsorption within the catalyst bed, and the impact of variations in the composition of the bio-oil. Model compounds are being studied to develop mechanisms of homogeneous oxidative cracking, which will add insight to the chemistry of the gas-phase reactions. Catalysis studies will be expanded to determine optimum materials to minimize costs and the formation of aromatics and other syngas contaminants.

FY 2007 Publications/Presentations

1. Marda, J, Czernik, S., Evans, R., French, R., and Dean A. *Hydrogen from Biomass; Distributed Production by Steam Reforming of Biomass Pyrolysis Oil*, 4th Annual World Congress on Industrial Biotechnology and Bioprocessing, March 21-24, 2007, Orlando, Florida.

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1. Milbrandt A. A Geographic Perspective on the Current Biomass Resource Availability in the United States, National Renewable Energy Laboratory: Golden, CO, TP-560-39181, 2005.

2. U.S. Department of Energy. Hydrogen, Fuel Cells, and Infrastructure Technologies Program, Multi-Year Research, Development, and Demonstration Plan, Section 3.1 Hydrogen Production, 2007. U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy: Washington, D.C.

3. Czernik, S., Elam, C., Evans R., Milne, T. Thermochemical Routes to Hydrogen from Biomass – A Review. In Science in Thermal and Chemical Biomass Conversion, Bridgwater AV, Boocock DGB, eds., CPL Press: Newbury, UK, 2006, pp.1752–1761.

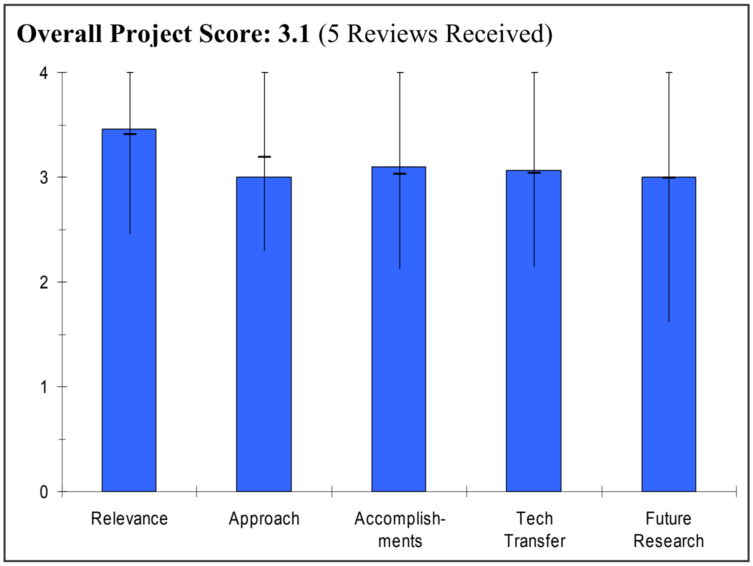
4. Evans, R.J., Czernik, S., French, R., Marda, J. Distributed Bio-Oil Reforming, DOE Hydrogen Program FY 2006 Annual Progress Report, 2006.

5. Evans, R. J., Milne, T. A. Energy & Fuel, 1987, 1,123.

Project # PDP-07: Distributed Bio-Oil Reforming

Bob Evans; NREL

Brief Summary of Project



The National Renewable Energy Laboratory is developing the necessary understanding of the process chemistry, feedstock compositional effects, reactor configuration, catalyst chemistry, deactivation, and regeneration strategy as a basis for process definition and assessment for automated distributed reforming of whole bio-oil. The objective in 2012 is to produce hydrogen for less than $3.80/gge. The objective for 2007 is to demonstrate integration of bio-oil atomization, partial oxidation, and catalytic conversion to obtain equilibrium syngas composition at 650°C.

Question 1: Relevance to overall DOE objectives

This project earned a score of **3.5** for its relevance to DOE objectives.

- Important to further the understanding of biomass pyrolysis interactions.
- Developing a viable pathway to achieve a renewable forecourt production system is a major step forward.
- Good focus on conversion of biomass to liquid fuel to hydrogen.
- Key source of renewable hydrogen.
- Provides cost effective syngas for bioproducts.
- Supports MYPP gasification / pyrolysis technology development.
- The program focuses on developing autothermal reformer for bio-oil processing to meet DOE 2012 hydrogen cost targets for biofuel production of hydrogen. However, focus is on methanol currently not other more relevant alcohols like ethanol, sorbitol etc.

Question 2: Approach to performing the research and development

This project was rated **3.0** on its approach.

- Use of modeling in parallel with experimentation is good.
- Good focus on bio-oil conversion; unclear on whether path from biomass to bio-fuel to hydrogen makes sense from an energy cycle viewpoint.
- Addresses key thermochemical barriers to low cost syngas.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.1** based on accomplishments.

- Scale up of ultrasonic nozzle atomization not well understood/explained.
- Need to better quantify extent of sooting and degree to which it can be burned-off/cleaned.
- Reasonable progress, yet unclear if cycle is viable.
- Good accomplishments for limited budget.
- Focused on major barriers.
- Successful in developing needed analytical instrumentation / methods.

- Developed atomizer, cracking process and autothermal bench scale reactor. Validated the need for oxidation to increase CO production.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.1** for technology transfer and collaboration.

- Focused primarily on NREL activities.
- (Should) link work to thermochemical research in the Office of Biomass Programs at DOE to produce (bio)-products.
- Good representation from national lab, academic and industrial partner, yet more collaboration with industry is needed.
- Papers will be given at ACS and other public forums to share results.
- Partnership with Chevron further demonstrates project merit.
- University of Minnesota performing systematic catalyst study.

Question 5: Approach to and relevance of proposed future research

This project was rated **3.0** for proposed future work.

- Reasonable project but limited benefit as hydrogen pathway.
- More fundamental research should be proposed on mechanism of reactions, efficiency and catalytic selection.
- Investigators have considered contingency paths.
- Addition of WGS and parametric studies just need to broaden focus beyond methanol.

Strengths and weaknesses

Strengths

- Tests with Rh show promise of equilibrium reaction with reversible/recoverable sooting.
- Good data on particle oxidation.

Weaknesses

- Currently requires biomass mixing with methanol. Would prefer that MeOH mixing was not needed.
- Needs more innovation and support.
- Consider an integrated bio-refinery approach to reforming bio-oils.

Specific recommendations and additions or deletions to the work scope

- Need to evaluate energy cycle.
- Independent review by company such as ADM which is heavily involved in products from oils.

II.B.5 High Pressure Distributed Ethanol Reforming

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Project Start Date: October 1, 2004
Project End Date: Project continuation and direction determined annually by DOE

Objectives

- Evaluate the high-pressure steam reforming of ethanol as an option for the distributed production of hydrogen.

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) Fuel Processor Capital Costs
(E) Greenhouse Gas Emissions
(H) System Efficiency

Contribution to Achievement of DOE Distributed Reforming Milestones

This project will addressthe following DOE Hydrogen Production milestones from the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- Down-select research for distributed production from distributed renewable liquids. (4Q, 2010)
  - This project is evaluating the technical feasibility of reforming ethanol, a renewable bio-derived liquid, at an elevated pressure to save on downstream hydrogen compression costs for a distributed hydrogen production facility.
- Down-select separation technology for distributed bio-derived renewable liquid feedstocks reforming. (4Q, 2010)
  - The pressurized reforming pathway offers the advantage of a larger driving force in separation processes that rely on partial pressure gradients. The project will further evaluate other separation and purification membrane options.
- Demonstrate pilot-scale use of integrated separation (membrane) reactor system for renewable feedstocks. (1Q, 2012)
  - If the initial results from the pressurized reforming in a membrane reactor appear sufficiently promising, the concept may be demonstrated at the pilot scale in collaboration with industrial partners.

Accomplishments

- Designed and fabricated a membrane reactor and apparatus to study the effectiveness of hydrogen extraction on the kinetics and hydrogen yield during the steam reforming of ethanol at an elevated pressure.
- Measured the hydrogen transported across the membrane to establish the hydrogen flux as a function of temperature and pressure differential. The results were fitted to models to obtain the activation energies. The analysis indicated a change in transport mechanism at ~300°C.
- Initiated catalytic reaction studies and mathematical modeling of the reactor that is being set up to extract global kinetic parameters.

✧ ✧ ✧ ✧ ✧

Introduction

Distributed hydrogen production facilities will need to store and transport hydrogen at pressures in excess of 5,000 psig. This is typically achieved by compressing the product hydrogen, where the compression (from 150 psig) consumes ~18% of the lower heating value of the hydrogen produced, a significant parasitic load on the overall process efficiency. In this project, we are investigating the option of steam reforming ethanol at elevated pressures, since this pathway can eliminate or greatly reduce the energy cost of compression by feeding a pressurized liquid stream into the reformer.

The challenges in high-pressure reforming of ethanol include: (1) high hydrocarbon and low hydrogen yields (at a given temperature and steam-to-carbon ratio) favored at thermodynamic equilibrium; (2) an increased tendency to form coke deposits; and (3) the potentially higher capital cost associated with pressurized equipment. On the other hand, the high-pressure process offers the advantages of a more compact system (greater reactivity) and higher driving force for pressure-based separation/purification systems. The system design needs to balance these diverse characteristics to meet an efficiency target (for calendar year 2012) of 72%, to produce hydrogen at a cost of $3.80 per gallon of gasoline equivalent.

Approach

An experimental apparatus has been set up to study the ethanol steam reforming reaction as a function of the catalyst formulation, space velocity, steam-to-carbon ratio, temperature, and pressure. The catalytic reactor has been redesigned to include a hydrogen transport membrane for the removal of hydrogen from the reaction zone to promote the kinetics and shift the equilibrium towards higher hydrogen yields. The hydrogen permeation can be stopped by shutting off a valve on the permeate side, thereby enabling an evaluation of the yields with and without hydrogen separation within the reactor. A model of the micro-reactor is being developed, which will be used to determine the kinetics of hydrogen transport and the reforming reaction, and to identify the mechanisms that limit the reaction rate, conversion, and product selectivity. The experiments will be conducted at reaction temperatures and pressures up to 800°C and 1,000 psig, respectively.

Results

The experimental reactor was redesigned to incorporate a hydrogen transport (Pd-alloy) membrane. The 3.2-mm (1/8-in) outside diameter, 25.4-mm (1-in) long membrane tube was purchased from REB Research and Consulting. The apparatus has been modified to enable measurement of the amount of hydrogen permeating across the membrane. Initial tests have been conducted to measure the hydrogen flow across the membrane and to calculate the flux as a function of the reactor temperature and pressure. For these measurements, the permeate side was maintained at 1-atm pressure. Figure 1 plots the hydrogen permeation rate as a function of temperature and pressure; as expected, the permeation rate increases with temperature and pressure. The hydrogen flux (J) was calculated from the permeation rate. The maximum hydrogen permeation rate for this membrane, with its 30-µm-thick Pd-alloy film on a 43-µm-thick support layer, was measured at 32 ml/min (at 1 atm, 25°C), which corresponds to a calculated flux of 12.7 ml/cm^2-min, at 650°C and 300 psig feed pressure. The permeation tests were limited to 300 psig because the maximum hydrogen partial pressure in the catalyst zone is expected to be less than 300 psig, when the reaction is conducted at 1,000 psig. The highest flux achievable in these tests is lower than DOE's target value of 101 ml/cm^2-min at a pressure difference of 20 psig across the membrane.

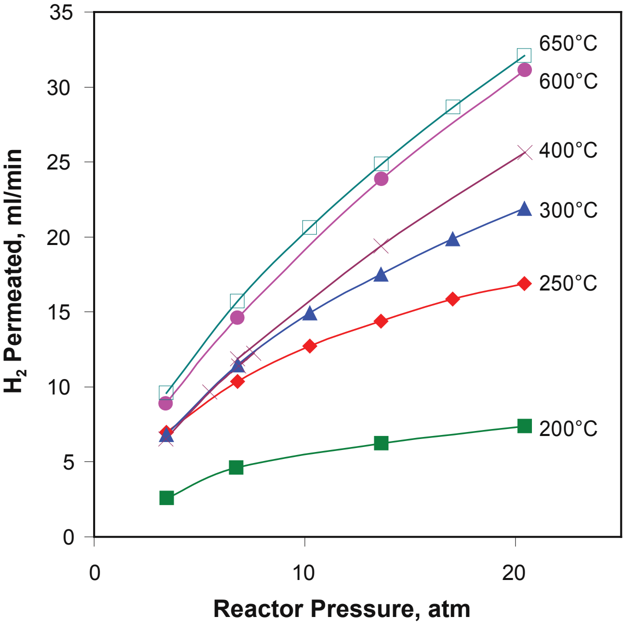

FIGURE 1. Hydrogen permeated across a Pd-alloy membrane tube as a function of the upstream pressure. Permeate side pressure was maintained at 1 atm.

The hydrogen flux was fitted to an equation of the form of Sievert's law,

$$J = k\,[(P_{H2,hi})^{½} - (P_{H2,lo})^{½}], \quad \text{where, } k = A_o\, e^{(-E/RT)}$$

to determine an apparent activation energy (E) for the rate of hydrogen transport through the Pd membrane. Figure 2 shows the flux of hydrogen plotted as a function of the partial pressure driving force. Figure 3 is used to extract the apparent activation energy and shows that the data are best fitted with two straight lines. Below 300°C, the activation energy is 24.8 kJ/mol; above 300°C, the calculated apparent activation energy is 4.7 kJ/mol, which is somewhat lower than that reported in the literature [1]. It has been reported [2] that above 300°C, the surface sorption and dissociation of the hydrogen molecule are fast and the rate is controlled by the diffusion of the hydrogen atoms through the metal. In this temperature region, the hydrogen transport follows Sievert's law. At lower temperatures, the sorption and dissociation steps control the hydrogen transport, which is then not predictable per Sievert's equation.

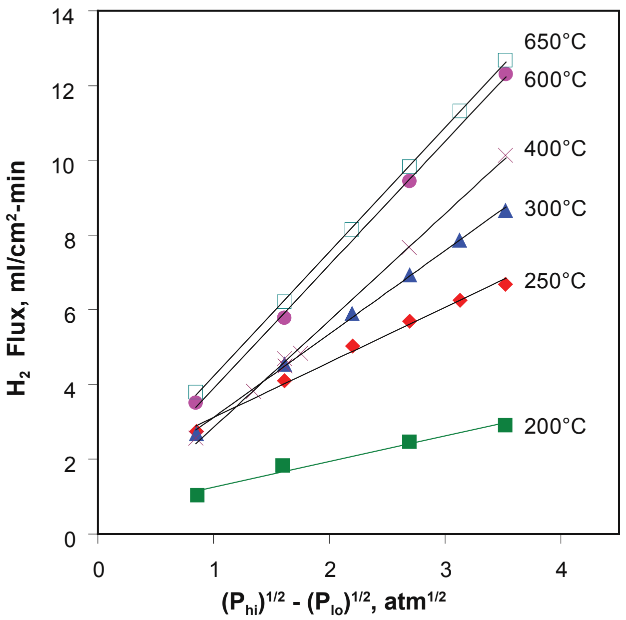

FIGURE 2. Hydrogen Flux across the Membrane as a Function of the Driving Force, to Determine the Value of Sievert's Constant (k)

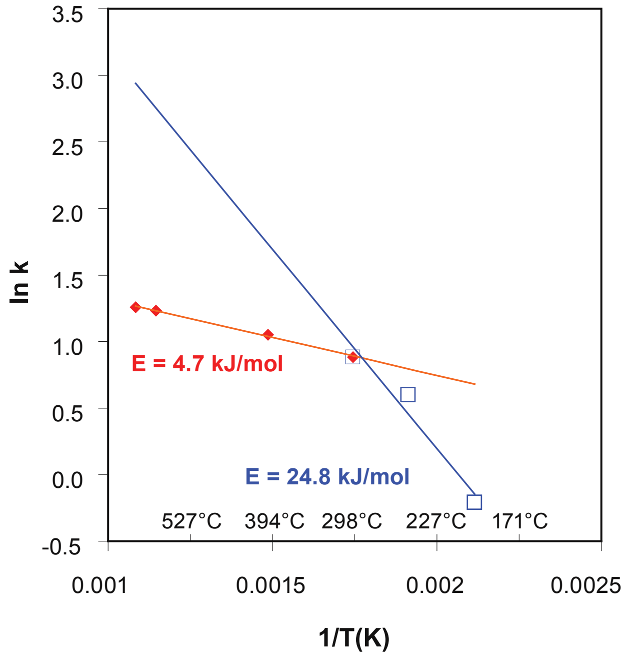

FIGURE 3. Estimation of the Activation Energy (E) using the Arrhenius Equation

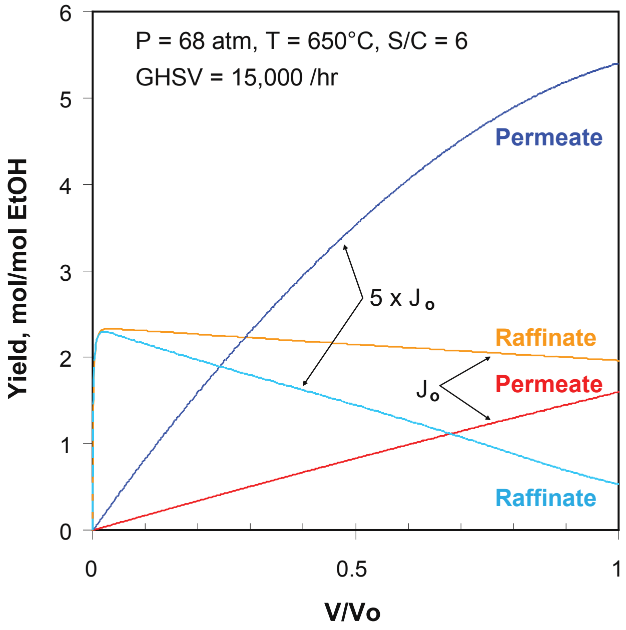

FIGURE 4. Simulation results showing the hydrogen yield that may be expected assuming fast reforming kinetics. J_o represents the flux based on the experimental data in Figures 1-3. The curves for $5xJ_o$ show the effects of achieving higher permeation rates.

A model of the membrane reactor is being developed to extract the global kinetics and to delineate the controlling mechanisms. The model was exercised to evaluate the effect of hydrogen permeation, obtained from the permeation experiments discussed above, when the reforming kinetics are very fast. The use of fast kinetics is reflected in the curves for the hydrogen yields in the raffinate streams (see Figure 4), where the hydrogen yield rises to ~2.5 mols/(mol of ethanol) very near the reactor inlet. The rest of the reactor essentially serves to permeate the hydrogen, which in turn leads to additional hydrogen production via methane reforming and water-gas shift reactions. For the permeation rates corresponding to current data (J_o) and under the conditions specified, 1.6 mols of hydrogen permeate across while ~2 mols leave with the reformate in the raffinate stream. If the permeation rate can be increased by a factor of five, then that case is represented by the curves indicated by ($5xJ_o$). That scenario would lead to the recovery of 5.5 mols of high purity hydrogen, from a theoretical maximum achievable of 6 mols per mol of ethanol, according to the reaction:

$$C_2H_5OH + 3H_2O = 2CO_2 + 6H_2$$

Conclusions and Future Directions

- A membrane reactor and a mathematical model for it have been set up to evaluate the effect of hydrogen removal on the pressurized steam reforming of ethanol.
- The hydrogen permeation rate has been measured as a function of temperature and pressure.
- The hydrogen permeation rate with current membrane dimensions is an order of magnitude lower than the DOE target. The use of thinner

membranes to increase the rate can significantly improve the hydrogen yield.

- The reaction kinetics and achievable hydrogen fluxes will be used to assess, from a fuel processing system perspective, the prospects for continuing R&D on a hydrogen-permeation membrane-reactor.

FY 2007 Publications/Presentations

1. S.H.D. Lee, S. Ahmed, R.K. Ahluwalia, "Steam reforming of ethanol at elevated pressure for hydrogen production," poster presentation at the 2006 Fuel Cell Seminar, Honolulu, HI, November 13-17, 2006.

References

1. Basile, A., Gallucci, F., Paturzo, L,. "A dense Pd/Ag membrane reactor for methanol steam reforming: Experimental study," *Catalysis Today*, **104**, pp.244–250, 2005.

2. Baker, R.W, Membrane Technology and Applications, McGraw Hill, 2000.

II.B.2 Investigation of Reaction Networks and Active Sites in Bio-Ethanol Steam Reforming Over Co-Based Catalysts

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Contract Number: DE-FC36-05GO15033

Start Date: May 1, 2005
Projected End Date: April 30, 2009

Objectives

Acquire a fundamental understanding of the reaction networks, active sites and deactivation mechanisms of potential bio-ethanol steam reforming catalysts so that the work to develop precious metal free catalysts that can operate at lower temperatures with high yields and selectivities for hydrogen steam reforming from bio-ethanol can be guided by this knowledge. More specifically:

- Determine the effect of catalyst synthesis methods on oxidation state, structure, metal dispersion, and particle size of cobalt-based bio-ethanol reforming catalysts using the following techniques:
  - Aqueous or organic impregnation
  - Co-precipitation
  - Sol-gel synthesis
  - Organometallic synthesis
  - Control of calcination and reduction conditions
- Determine oxidation states and chemical structures that are present in active catalysts that are exposed to:
  - Varying pre-treatment protocols
  - Differing levels of steam-to-carbon ratio during reaction
  - Oxidative and auto-thermal operation
  - Different space velocities
- To study how the observed catalyst characteristics influence the reaction pathways for:
  - Oxygenate formation
  - Reverse water-gas shift
  - Alkane and olefin formation
  - Coke deposition
- Determine how the chosen support material can influence metal dispersion and structure, and how it participates in:
  - Alcohol and water adsorption
  - Spillover of species
  - Intermediate and product formation
- Determine methods that can tailor the catalyst surface for optimum selectivity and activity by:
  - Site blocking
  - Chemical promotion
  - Active site density control
- Determine factors that degrade catalyst stability and optimize regeneration methods:
  - Pathways and active sites for coke formation
  - Loss of surface area under reaction
  - Metal-support compound formation
  - Sintering

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
(C) Operation and Maintenance (O&M)
(D) Feedstock Issues

Technical Targets

Bio-ethanol steam reforming over Co-based catalysts:

This project is a systematic and detailed study aimed to provide fundamental answers to questions that are not readily solved in an industrial setting. The results of this study will prevent interpreting erroneous information resulting from the screening of a large catalyst matrix by characterizing the parameters that lead to or inhibit the formation of active sites for reforming. The information obtained from the proposed study will address many common problems associated with catalyst development, such as choice of materials, pre-treatment conditions, and factors controlling active site distribution, stability, and selectivity. Insights gained from these studies will be applied toward the design and synthesis of cost-effective and efficient reforming technologies that meet the DOE 2010 technical targets for hydrogen from bio-derived renewable liquids. Specific technical targets that would benefit from this study are the following:

- Production Energy Efficiency: 70%
- Contribution of Production to Capital Cost: 0.50 ($/gge)

Accomplishments

- Understanding the reaction mechanism by exploring a complex network of reactions and reaction intermediates.
- Studying the deactivation mechanisms and developing strategies, based on catalyst formulation and modification, to improve stability while maintaining activity.
- Developing catalyst formulations that can achieve H_2 yields over 90% and no liquid by-products. No deactivation was observed in a 70-hour run.
- Developing novel catalyst synthesis techniques by changing the impregnation medium. Resulting catalyst much higher yields (83%) at much lower temperatures (350°C) compared to catalysts prepared in aqueous media.

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Introduction

For hydrogen energy to fulfill its potential for protecting the environment, providing more efficient energy sources, and decreasing our nation's dependence on foreign oil, we need economical and efficient technologies for hydrogen production from renewable energy sources. Hydrogen production from ethanol through steam reforming solves issues involved in hydrogen storage and infrastructure and lends itself very well to a distributed hydrogen production strategy. The bio-ethanol produced by fermentation of biomass can yield an ethanol-water mixture already ideal for reforming without additional distillation steps. A review of the ethanol steam reforming literature shows that there is no consensus about an optimal catalyst, and a fundamental understanding of the relationships between catalytic properties and how these properties are affecting various reaction steps involved in this complex network is lacking.

The development of non-precious metal catalysts in this project will reduce the catalyst cost, while the lower operation temperatures will reduce the material cost for reactor systems and will also reduce the energy requirement for heating the feed mixture to high reaction temperatures. The catalyst will have high steam reforming activity, while being non-selective for various undesired side reactions, such as methanation, dehydration, dehydrogenation, coking, and reverse water-gas shift reaction. The high yields to be achieved will help increase the production energy efficiency. The catalytic system will have high stability and well-understood regeneration mechanisms. High stability will reduce catalyst cost by prolonging the active life span of the catalyst. The regeneration mechanisms will be useful in reactivating the catalyst, rather than discarding the deactivated catalyst. The design of such catalysts will not be possible without a thorough understanding of the relationships between the catalyst preparation parameters, their structural and molecular characteristics and their reaction performance. The understanding acquired through this study will eliminate the need for costly trial-and-error efforts and will enable design of catalytic systems with the desired characteristics.

Approach

The project is structured into seven tasks occurring over the four-year project period. Each task is accompanied with milestones on a yearly basis. As a Go/No decision point at the end of Phase I (year two) technical progress must be shown in achieving the milestones set forth for the development of safety standards and catalyst preparation/initial characterization efforts. Additionally, catalyst performance with respect to temperature and gas hourly space velocity at the end of year two must warrant feasibility based on the initial economic analysis performed based on the DOE Distributed Hydrogen Production Technologies target goals. Scientific merit must be demonstrated by at least one peer reviewed publication to warrant the advanced studies in the following years.

Results

Based on the temperature-programmed desorption (TPD) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) results illustrated in the quarterly reports of this year, a tentative reaction pathway for ethanol steam reforming over Co-based catalysts is proposed in Figure 1. In Scheme 1, the reactants (EtOH and water) molecules diffuse from gas phase to the surface of the catalyst. Then as demonstrated in Scheme 2, the ethanol molecules adsorb dissociatively on the Co sites, forming ethoxide species. Water, on the other hand, adsorbs on the

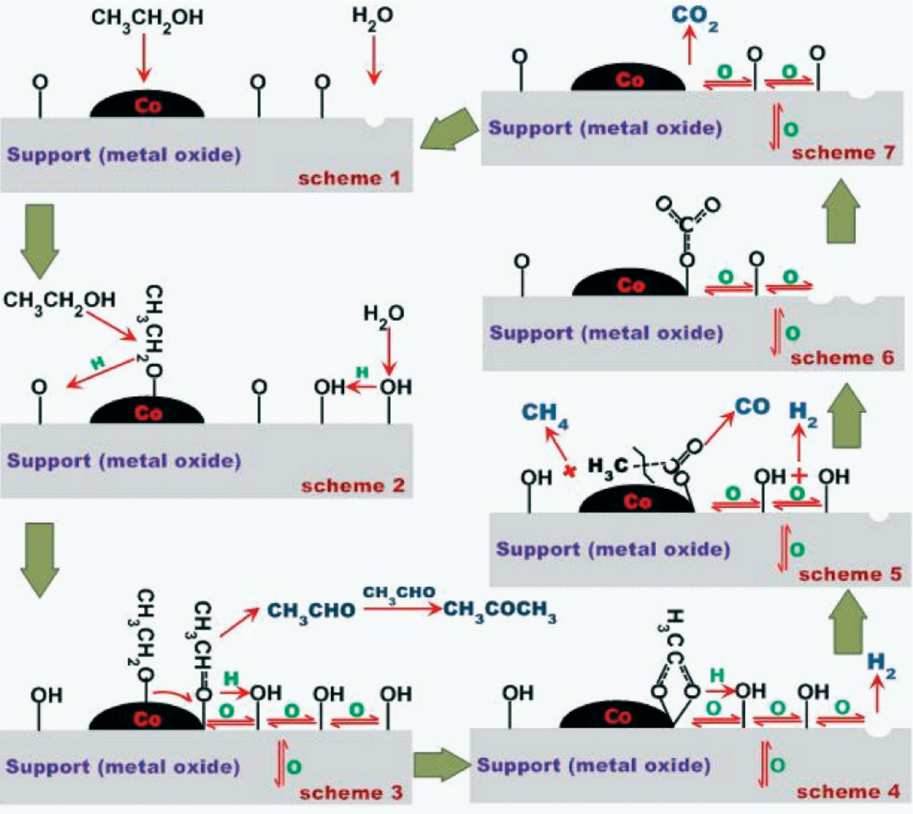
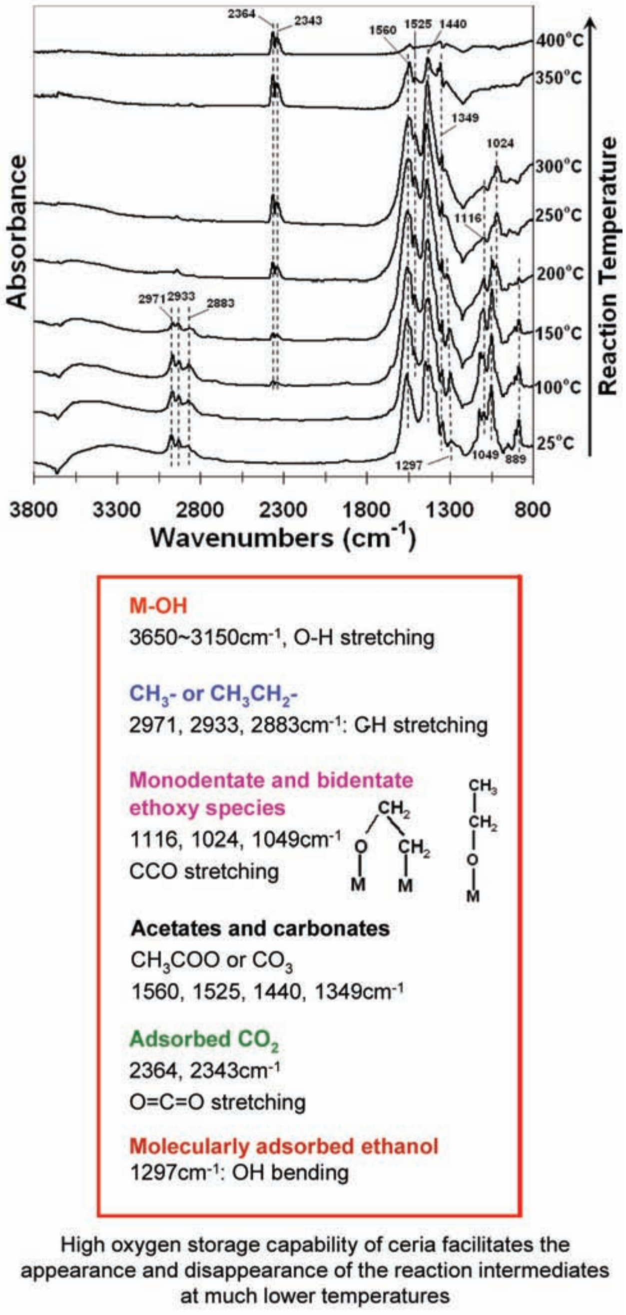


FIGURE 1. Proposed Reaction Mechanism for Ethanol Steam Reforming

support, forming hydroxyl groups. Subsequently, the ethoxide species will move to the interface of metal and oxide support and be oxidized by an additional hydrogen abstraction. Oxygen species from the surface are thought to be involved in forming acetaldehyde formation as shown in Scheme 3. Acetaldehyde molecules may lead to the formation of acetone through an aldol-condensation type reaction. Acetaldehyde species on the surface may further oxidize to acetate species, which can be facilitated by surface OH groups. The metal may be involved in C-C bond cleavage leading to the formation of single carbon species (Schemes 4-5). This step may account for the appearance of methane in the gas phase. The carbon-oxygen surface species may desorb or further oxidize to give carbonate species, especially on supports with high oxygen storage capacity (Scheme 6), which can desorb as CO_2 (Scheme 7).

Although Co/ZrO_2 had promising activity, time-on-stream experiments showed coke formation at high temperatures (500°C and above). The deactivation mechanism was examined by incorporating X-ray diffraction (XRD), laser raman spectroscopy (LRS), X-ray photoelectron spectroscopy (XPS), and thermo-gravimetric analysis-differential scanning calorimetry/mass spectrometry (TGA-DSC/MS) techniques. From the results of LRS, two broad peaks centered at 1340 and 1590 cm^{-1} are observed over 10%Co/ZrO_2 sample after time-on-stream experiment. These bands are characteristic of disordered carbonaceous deposits [1]. The band located around 1340 cm^{-1} is known as the D line and the band at 1590 cm^{-1} is recognized as the G line, which is very sensitive to the extent of two-dimensional graphitic ordering. With the insight gained through the deactivation studies, new catalyst formulations were developed incorporating ceria and other lanthanide elements. These new formulations provided much higher activity at lower temperatures, with no coking on the surface. *In situ* DRIFTS experiments provided an explanation for the enhanced activity at low temperatures. A comparison of DRIFT spectra taken during ethanol TPD or ethanol+water TPD experiments showed that over the ceria-containing samples, the appearance and disappearance of surface species took place at much lower temperatures. This can be explained by the high oxygen storage capacity of ceria. DRIFT spectra taken during ethanol TPD over Co/CeO_2 catalyst is presented in Figure 2 as an example. Time-on-stream experiments over these catalysts showed no sign of coking on the surface, even after 110 hours on stream.

A strong promotion effect has been observed after making modifications to the 10%Co/ZrO_2 catalyst



M-OH
3650~3150cm^{-1}, O-H stretching

CH_3- or CH_3CH_2-
2971, 2933, 2883cm^{-1}: CH stretching

Monodentate and bidentate ethoxy species
1116, 1024, 1049cm^{-1}
CCO stretching

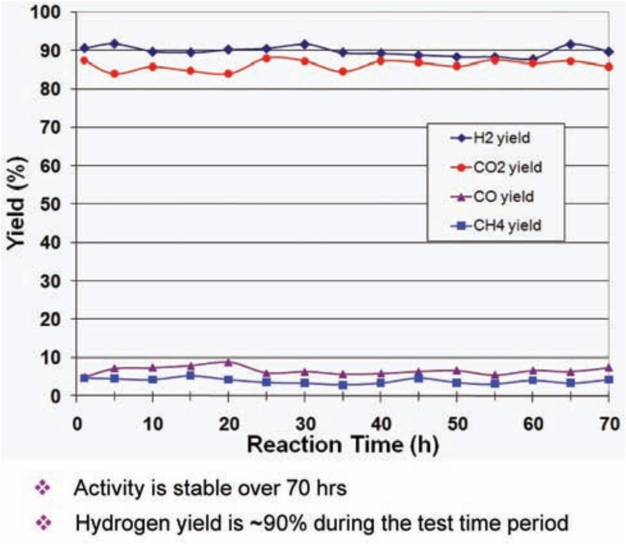
Acetates and carbonates
CH_3COO or CO_3
1560, 1525, 1440, 1349cm^{-1}

Adsorbed CO_2
2364, 2343cm^{-1}
O=C=O stretching

Molecularly adsorbed ethanol
1297cm^{-1}: OH bending

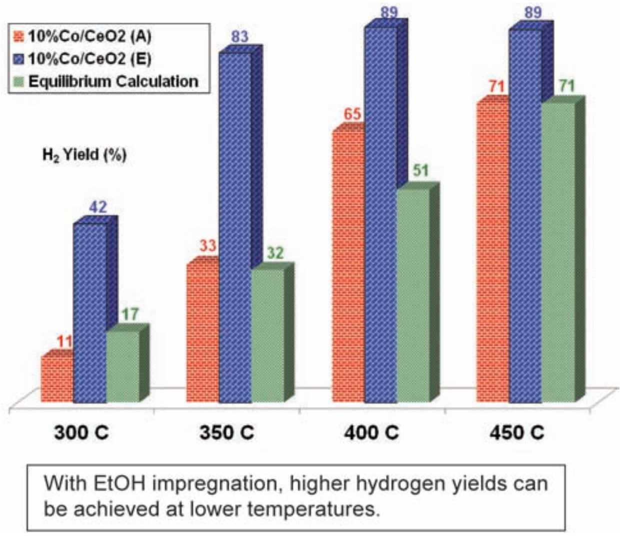
High oxygen storage capability of ceria facilitates the appearance and disappearance of the reaction intermediates at much lower temperatures

FIGURE 2. *In situ* DRIFTS during Ethanol TPD over Co/CeO_2 Catalyst



- Activity is stable over 70 hrs
- Hydrogen yield is ~90% during the test time period

FIGURE 3. Best Performing Catalysts: Product Distribution and Time-On-Stream Performance on 10%Co/20%La_2O_3-CeO_2



With EtOH impregnation, higher hydrogen yields can be achieved at lower temperatures.

FIGURE 4. Effect of the Impregnation Medium on Activity (Aqueous vs Ethanol) H_2O:EtOH=10:1(molar ratio) WHSV=0.48gEtOH/gCat/h, GHSV=~20,000h^{-1} C_{EtOH}=2%

system. Figure 3 shows the product distribution and time-on-stream performance of 10%Co/20%LaO_2-CeO_2 catalyst at 450°C. Over this catalyst, a hydrogen yield over 90% was maintained for over 70 hours. At this temperature and using the same feed conditions, the hydrogen yield that would be obtained at equilibrium is only 71%, showing that we are clearly in the kinetically controlled regime. The only other products formed besides H_2 and CO_2 are CH_4 (less than 5%) and CO (less than 8%). It appears that this catalyst is very promising both for activity and stability performance it has exhibited and will be further investigated in the coming year.

Figure 4 shows the results from a recent set of experiments where the catalysts synthesis was modified by changing the impregnation medium. Two Co/CeO_2 catalysts prepared in aqueous versus ethanol solutions were compared for activity. The most exciting aspect of this set of results is the very high activity (83% H_2 yield) at temperatures as low as 350°C obtained over the catalyst prepared in an ethanol solution. At this temperature, the catalyst which was prepared in an aqueous medium gives only 33% hydrogen yield.

Conclusions and Future Directions

- CeO_2 supported cobalt catalyst is shown to be a promising candidate for bio-ethanol steam reforming (BESR) with excellent activity and stability.
- A catalyst system with high cobalt dispersion and oxygen mobility is crucial for achieving high activity and stability.
- Primary mode of deactivation over Co-based catalyst is coking on the surface.
- Ceria has high oxygen storage capacity and oxygen mobility which can prevent carbon deposition resulting in higher stability.
- Re can favor the C-C bond breakage which can facilitate formation of single-carbon products.
- The proposed reaction mechanism will be further investigated and supported by additional characterization techniques.
- The economic analysis will be completed and updated with the modified catalyst formulations and a better understanding of the kinetic and mechanistic behavior of the corresponding catalyst system.
- A more robust catalyst system will be developed to afford more stringent reaction conditions.

FY 2007 Publications

1. Song, H., Zhang, L., Watson, R.B., Braden, D., Ozkan, U.S., "Investigation of Bio-ethanol Steam Reforming over Cobalt-based Catalysts" *Catalysis Today*, *in press*.

2. Song, H., Zhang, L., Ozkan, U.S., "Effect of Synthesis Parameters on the Catalytic Activity of Co/ZrO_2 for Bio-ethanol Steam Reforming", *Green Chemistry*, 9(2007) 686-694.

3. Song, H., Zhang, L., Ozkan, U.S., "Promotional Effects on Co-Based Catalysts in Bio-ethanol Steam Reforming", submitted to *International Journal of Hydrogen Energy*.

Presentations

1. Song, H. and Ozkan, U.S., "Fuel Cell Grade Hydrogen Production from the Bio-Ethanol Steam Reforming over Co-based Catalysts: An Investigation of Reaction Networks and Active Sites" *Ohio Fuel Cell Symposium*, Canton, Ohio, May 2006. (Poster Presentation)

2. Song, H., Zhang, L., Ozkan, U.S., "Investigation of bio-ethanol system reforming over cobalt-based catalysts", *232nd ACS National meeting & exposition*, San Francisco, CA, September 2006. (keynote lecture)

3. Song, H., Zhang, L., Ozkan, U.S., "Investigation of bio-ethanol steam reforming over cobalt-based catalysts", *U.S. Department of Energy Bio-derived Liquids to Hydrogen Distributed Reforming Working Group Kick-Off Meeting*, Baltimore, MD, October 2006.

4. Song, H., Zhang, L., and Ozkan, U.S., "Catalytic Hydrogen Production from Renewable Sources" *OSU-Honda Research Forum*, Columbus, Ohio, February 2007. (Poster Presentation)

5. Song, H., Zhang, L., Ozkan, U.S., "Investigation of Reaction Networks and Active Sites in Steam Reforming of Bio-ethanol over Cobalt based Catalysts" *233rd ACS National Meeting*, Chicago, IL, March 2007.

6. Song, H., Zhang, L., Ozkan, U.S., "Hydrogen Production from Renewable Sources over Cobalt-based Nanocatalyst", Ohio Nanosummit 2007, April 2007, Akron, OH. (Poster Presentation)

7. Song, H., Zhang, L. and Ozkan, U.S., "Hydrogen Production from Bio-ethanol Steam Reforming over Cobalt-based Catalysts" *20th North American Meeting of North American Catalysis Society*, Houston, TX, June 2007.

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2. Llorca, J., Homs, N., Sales, J., Piscina, P.R. *J. Catal.* 209(2002) 306.

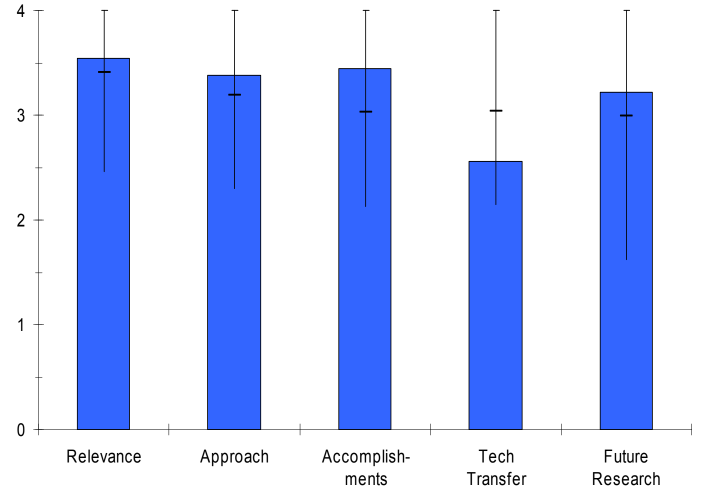
Project # PDP-06: Investigation of Bio-ethanol Steam Reforming over Cobalt Based Catalysts

Umit Ozkan; Ohio State U

Brief Summary of Project

The overall objective of this project is to acquire a fundamental understanding of the reaction networks and active sites in bio-ethanol steam reforming over Co-based catalysts that would lead to 1) development of a precious metal-free catalytic system which would enable low operation temperature (350-550°C), high ethanol conversion, high selectivity and yield of hydrogen, and minimal byproducts such as acetaldehyde, methane, ethylene, and acetone; 2) understanding of the catalyst deactivation and regeneration mechanisms; and 3) low cost for commercialization.

Overall Project Score: 3.3 (8 Reviews Received)



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.5** for its relevance to DOE objectives.

- Development of a precious-metal free, low temp. Ethanol catalyst would significantly reduce H_2 cost.
- Directly related to goals; good initial analysis of catalysts; supports effort to reform bio-derived liquid fuels.
- Project supports DOE program goal of hydrogen production from renewable resources.
- Seeks to reduce cost for ethanol steam reforming by identifying base metal catalysts and thereby eliminating need for platinum-group metal catalysts.
- Project has excellent relevance to DOE H_2 Production goals.
- Identification of inexpensive (non-precious metal) catalyst is critical.
- Ethanol is only a transition fuel to the hydrogen future which cannot meet all (domestic) transportation needs and lignocellulosic ethanol production has (many technology barriers).
- Suggest looking at other biomass-derived liquids (e.g., dimethyl ether).
- Unclear as to the cost reductions achieved with $CoZrO_2$ catalyst and low temp processing but assume costs are lower than precious metal so likely helpful in reducing capital costs.
- Useful empirical validation.
- Important effort to find a metal free catalytic system.

Question 2: Approach to performing the research and development

This project was rated **3.4** on its approach.

- Too much experimental data is presented: specific approach to optimizing performance is obscured. Needs an overview to explain differences between tests conducted.
- Good initial start; good focus on reaction mechanisms.
- Sound approach based on fundamentals of heterogeneous catalysis: identify active catalytic phase(s) and synthetic techniques to optimize population of those sites; identify reactive intermediates, reaction networks and desired reaction pathways. Identify deactivation pathways and regeneration methods.
- Outstanding systematic approach to catalyst characterization and structure/property relationship.
- Firm fundamental scientific approach; strong application of catalyst characterization techniques.
- Excellent catalyst R&D. Excellent presentation of results (albeit with too many slides).
- Need systems analysis to determine if this is a viable project and to define research objectives.
- Good use of thermogravimetric and infrared analysis to follow reaction mechanism.

- Logical and well thought out approach.
- Fuel processor capital costs, O&M, and feedstock issues are addressed by this project.
- This is a university project. The approach is to select few materials, prepare catalyst, carry out reforming reaction, and study deactivation/regeneration characteristics. This seems to be quite appropriate for university-led research.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.4** based on accomplishments.

- Hard to quantify significance of test results since no longevity testing.
- Achievement of high H_2 yield at <500C is significant.
- Lifetime testing is missing. Although unknown, the performance may decline precipitously. Good initial progress, but less than half complete; quality data presented.
- Identified very active, selective cobalt-based catalyst as well as preferred support and methods of preparation.
- Comprehensive studies on characterization of bulk catalyst as well as surface intermediates.
- Good body of work on catalyst evaluation for activity, selectivity.
- Impressive property-activity correlation completed to maximize catalyst performance with minimal trial and error.
- Modified catalyst formulation has outstanding H_2 selectivity with minimal CO production.
- Outstanding application of basic science to achieve a promising commercial solution to EtOH reforming.
- Excellent understanding of catalyst performance.
- Excellent set of experiments.
- Catalyst reaction mechanism and selectivity well understood under varying temperatures.
- Need more stability data; they only have 70 hrs.
- Need a purification scheme.
- Good data; useful information to other reformer studies.
- (Good) understanding (of) the competing reaction networks in steam reforming of ethanol.
- (Good) identification of active (reaction) sites.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **2.6** for technology transfer and collaboration.

- No evidence of any collaboration.
- Not clear on partner roles/activities to date.
- Not at all clear what the supporting organizations (NexTech, PNNL) have contributed to this work.
- Good collaboration with catalyst manufacturer and PNNL for economic analysis.
- As catalyst technology is considered close to commercially ready, need to add an industrial collaboration.
- Could use a reactor design and reforming commercial partner.
- Should work to identify 'industrial partnerships' for catalyst scale-up.
- Industry interest is missing. Lacking active collaborations with other groups.
- Good coordination.
- Excellent body of publications and presentations. Glad to have this knowledge in the public domain.
- Teaming with NexTech Materials for catalyst manufacturing scale-up.
- Teaming with PNNL for economic analysis & catalyst deactivation studies.

Question 5: Approach to and relevance of proposed future research

This project was rated **3.2** for proposed future work.

- Need to add long term testing.
- Strong plan, especially deactivation/regeneration studies.

- Good plans for the future builds on the group's strengths: kinetics and mechanistic studies, in-situ characterization of working catalyst surfaces, and identification of deactivation pathways. This is a new catalytic system and needs to build the fundamentals in order to advance to a commercial process.
- Must assume project partners (NexTech and PNNL) will be involved in the catalyst scale up and economic evaluation.
- Future work properly focused on deactivation/regeneration, catalyst production considerations, and overall economic analysis.
- Should develop overall process design in which to use this catalyst.
- Could this catalyst technology be used for reforming of other bio-liquids?
- Would be useful to see economics of the processor and hydrogen production (costs) as calculated using DOE's H2A model.
- Although not included on poster, assume there are plans to process other feedstocks beyond ethanol.
- Well thought out and appropriate
- Research plan for future work is very reasonable.
- Kinetic and mechanistic investigations (well) coupled with in-situ characterization.
- Economic analysis based on updated catalyst system knowledge database.

Strengths and weaknesses

Strengths

- Research may have an ethanol catalyst breakthrough but it's too early to tell.
- Good focus on reaction mechanisms.
- Excellent R&D effort.
- World-class catalyst research.
- Comprehensive reporting.
- Strong basic fundamental understanding of reaction sites. Availability of graduate students and post-docs at OSU. Lower overhead rate compared to industry and national labs.
- At this point (only 40% complete), no glaring weaknesses.

Weaknesses

- Needs description of catalyst optimization approach. What is strategy beyond experimentation?
- Needs catalyst life testing.
- No systems understanding demonstrated.
- Poster presentation did not adequately provide the means to address all the issues.
- Stronger coordination with partner(s) needed.
- Too much data presented. This much technical detail is not needed for this type of review.

Specific recommendations and additions or deletions to the work scope

- Add catalyst lifetime testing.
- Add testing of contaminants.
- Suggest construction of integrated process development unit.
- Economic analysis should be an integral part of research in order to quantify effect of R&D achievements and steer R&D objectives.
- Continue to support the work.

II.B.1 Bio-Derived Liquids Reforming

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Arlene Anderson
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Project Start Date: October 1, 2004
Project End Date: Project continuation and direction determined annually by DOE

Objectives

- Quantify hydrogen production rate from bio-derived liquids and determine the reaction mechanisms involved.
- Optimize catalyst and catalytic process that maximize the volumetric hydrogen production rates from bio-derived liquids.
- Demonstrate hydrogen production from bio-derived liquids can meet the DOE 2017 targets of <$3.00/gge with 65-75% production unit energy efficiency.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section (3.1) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Reformer Capital Costs
(D) Feedstock Issues
(E) Greenhouse Gas Emissions

Technical Targets

This project focuses on the reformation of biomass-derived liquids for the production of hydrogen. Both aqueous phase reformation and vapor phase reformation are studied. The focus of aqueous phase reformation is on producing hydrogen from bio-derived liquids such as glucose and mixed sugars, and ultimately expanding the knowledge to less refined lignocellulosic biomass feedstocks. These feedstocks are too unstable and insufficiently volatile for conventional steam reforming, but are amenable to low-temperature aqueous phase reforming. The goal is to maximize reactor volumetric productivity toward hydrogen production while maintaining high hydrogen selectivity, facilitating development of a commercially viable process. The focus of vapor phase reformation is on developing a catalyst and reactor system that can efficiently convert ethanol to hydrogen. A particular effort will be made to maintain moderate reforming temperatures (~500°C) in order to eliminate the need for costly high temperature alloys for reformer fabrication. A related objective is to develop the forming process so that it can be readily integrated with water-gas shift (WGS) or hydrogen separation to realize process intensification. Insights gained from these studies will be applied toward the development of a catalytic process that can potentially meet the DOE 2017 targets of <$3.00/gge with 65-75% production unit energy efficiency.

Accomplishments

- Developed a Pt-Re/C catalyst and demonstrated that hydrogen productivity from a 10% ethylene glycol feed increased from ~500 to ~2,000 STD L H_2/L-cat/hr.
- It was found that the addition of KOH can significantly increase the hydrogen productivity by suppressing alkane formation.
- It was found that the degradation products of ethanol are insignificant at temperatures <600°C and our future studies should limit to temperatures <600°C to avoid the catalyst deactivation induced by ethanol thermal degradation.
- Developed a Pt-Re/C catalyst for ethanol vapor phase reformation which shows improved stability over the Rh/CeO_2-ZrO_2 catalyst due to its favored ethanol dehydrogenation-decarbonylation reaction pathways at low temperatures such as 350°C.

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Introduction

Biomass sources include forest resources, agricultural resources, municipal solid waste, and animal waste. Our target biomass-derived feedstocks for hydrogen production include ethanol, sugars, sugar alcohols, and polyols, and less refined hemicellulose or cellulose. The cost of these feedstocks decreases as ethanol>sugar alcohols>sugars>hemicellulose or cellulose. Likewise the ease of conversion of these feedstocks also decreases in a similar order. Even for the most expensive bio-derived liquids under our consideration such as ethanol, it may still be an attractive bio-derived feedstock for distributed hydrogen production. In general, poly-hydroxylated molecules such as sugars and sugar alcohols are thermally unstable at conventional reforming temperatures, but are good feedstocks for low temperature aqueous phase reforming. Ethanol, on the other hand, is thermally more stable, and reforming at higher temperatures in the gas phase becomes possible. Ethanol reforming therefore provides an opportunity for high reactor productivity, although at too high temperatures materials of construction become of concern and integration with WGS becomes less efficient. The major objective of this project is to research the options of aqueous and vapor phase reforming and develop feedstock flexible reformers for distributed hydrogen production.

Approach

Both aqueous phase reformation (APR) and vapor phase reformation are studied in this project. APR has the potential to produce a product rich in hydrogen and CO_2, at elevated pressure, facilitating subsequent separation and recovery of hydrogen. It also appears possible to capture and sequester the byproduct CO_2, making APR potentially a net reducer of CO_2 from the environment. Despite significant progress in APR over the past several years, challenges remain in developing a process that can meet the economic targets identified in the DOE Hydrogen, Fuel Cells, and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan. The challenges that we intend to address in our work include identification of catalyst and reaction conditions for optimizing activity, selectivity and stability; and reactor design to address heat and mass transport resistances, with the goal to improve volumetric productivity for the process.

Ethanol, on the other hand, needs to be activated at higher temperatures than polyols and sugar alcohols, and vapor phase reforming may be more practical and economic. Reaction pathways and mechanisms of ethanol steam reforming are fairly complicated and there has been no general agreement. Methane is one of the major side products and is favored thermodynamically at lower temperatures. In addition, coke deposition precursors such as ethylene, acetaldehyde, and acetone are also thermodynamically favored at low temperatures. Therefore, the majority of literature has been focusing on high temperature ethanol steam reforming (>500°C) to reduce the coke deposition due to the formation of coke precursors. Even high temperature reforming may introduce different carbonaceous deposition mechanisms. Deactivation of catalysts at high temperatures are not often reported since 100% ethanol conversion can be maintained, particularly at a short time on stream (<100 hours) typically reported in the literature. In addition, since the C-H bond in methane is very difficult to activate, high temperatures such as those required for natural gas steam reforming may be employed, resulting in the requirement of high temperature (i.e. high cost) alloys and an unfavorable WGS equilibrium. Similar to natural gas steam reforming, highly endothermic ethanol steam reforming is potentially a mass and heat transfer-limited process. Our approach is to identify catalyst compositions and reaction conditions to address the activity and catalyst stability issues.

Results

Based on recent literature reports that addition of Re to Pt may increase the reactivity of Pt for C-C bond cleavage, we developed a new bimetallic catalyst, 3%Pt3-%Re/C, on a hydrothermally stable carbon support. The Pt-Re/C catalyst exhibited superior hydrogen productivity and selectivity over one of the most active bimetallic catalysts previously developed at PNNL, Pt-Ru/C. As shown in Figure 1, using a 10% ethylene glycol feed, we demonstrated that hydrogen productivity increased from ~500 to ~2,000 STD L H_2/L-cat/hr. On the Pt-Re/C catalyst, it was found that hydrogen productivity typically increases with the decrease of carbon number in monohydroxyl alcohols, polyols, and carbohydrates. For the feedstocks with identical carbon numbers, carbohydrates exhibit higher hydrogen selectivity than polyols and monohydroxyl alcohols. In general, dehydrogenation-decarbonylation of carbohydrates such as sorbitol, xylitol, glycerol and ethylene glycol are the preferred reaction pathways for selective hydrogen production. However, alkane products were formed which were most likely due to the dehydration reaction pathway catalyzed by acidic sites. Our preliminary results showed that addition of KOH can significantly suppress the alkane formation. The tradeoff is that KOH also increases acid formation likely

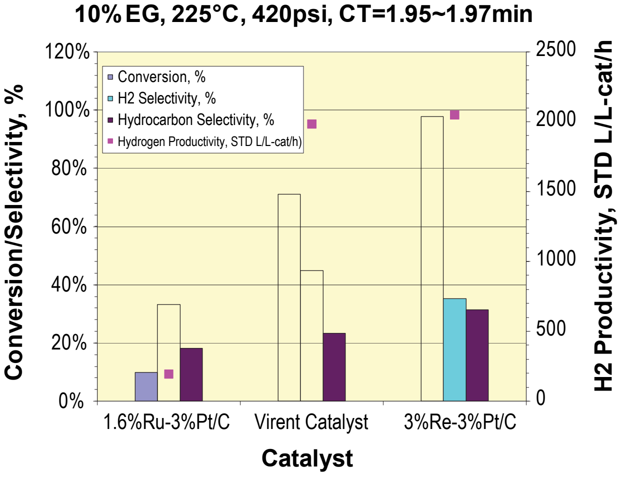


FIGURE 1. Catalyst Activity Comparison

due to the Cannizarro reaction catalyzed by hydroxyl anions. We will optimize the reaction conditions to minimize both alkane and acid formations to increase the hydrogen productivity and selectivity.

Ethanol thermal degradation products include acetaldehyde from ethanol dehydrogenation, ethylene from ethanol dehydration, and acetone from aldol condensation of acetaldehyde which are the potential coke precursors. It was found that these degradation products are insignificant at temperatures <600°C and our future studies should limit to temperatures <600°C to avoid the catalyst deactivation induced by ethanol thermal degradation. The stability of Rh/CeO_2-ZrO_2 catalyst was studied at temperatures from 350 to 550°C. Although the deactivation rate decreases with a increase in reaction temperature, there is still potential catalyst deactivation at temperatures as high as 550°C as confirmed by a slight change in gas production distributions as well as the temperature programmed oxidation and Fourier transform infrared characterization of the spent catalyst. Alternatively, we have studied the Pt-Re/C catalyst which shows improved stability and superior activity over the Rh/CeO_2-ZrO_2 catalyst (2Rh/CZ) under the identical reaction conditions (Figure 2), due to its favored ethanol dehydrogenation-decarbonylation reaction pathways at low temperatures such as 350°C. The major disadvantage with the Pt-Re/C catalyst is that a significant level of methane is formed at low temperatures and an additional methane steam reforming step is required at high temperatures followed by a separate WGS conversion step. We will continue the development of catalyst compositions and reaction conditions to further improve the catalyst stability and overall performance.

Conclusions and Future Directions

- Bimetallic catalysts exhibit improved hydrogen productivity from aqueous phase reforming of carbohydrates. Future optimization of catalyst compositions will be conducted to enhance catalyst activity and stability.
- Addition of KOH significantly enhances the hydrogen productivity by suppressing undesired alkane formation. KOH also increases acid formation likely due to the Cannizarro reaction catalyzed by hydroxyl anions. We will optimize the reaction conditions to minimize both alkane and acid formations to further increase the hydrogen productivity and selectivity.
- Deactivation of the Rh/CeO_2-ZrO_2 catalyst cannot be avoided over the range of temperature studied. Catalyst composition can be tailored to facilitate the ethanol dehydrogenation-decarbonylation reaction pathways with mitigated catalyst deactivation. However, a significant level of methane formed by this approach requires an additional methane steam reforming step at a high temperature followed by a separate WGS, leading to increased capital and operation costs. We will develop an innovative reaction engineering approach to take advantage of the high selectivity and activity of the Rh/CeO_2-ZrO_2 catalyst while overcoming its deactivation problem.

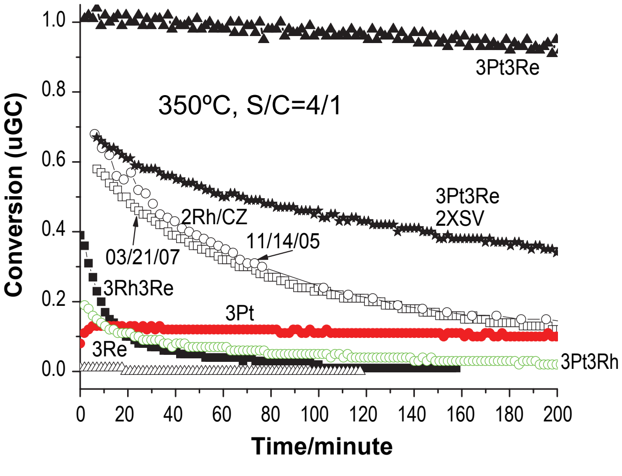


FIGURE 2. Improved Catalyst Activity and Stability

FY 2007 Publications/Presentations

1. *Selective Production of H_2 from Bio-Ethanol at Low Temperatures over Rh/CeO_2-ZrO_2 Catalyst,* H.Roh, Y.Wang, D.L.King, accepted for publication in *Topics in Catalysis*.

2. *Deactivation studies of ethanol steam reforming catalysts,* A.Platon, H.Roh, D.L.King, Y.Wang, accepted for publication in *Topics in Catalysis*.

3. *Rh/CeO_2-ZrO_2 catalyst deactivation patterns during ethanol-steam reforming (ESR) at low temperatures,* X. Wang, A.Platon, H.Roh, G.Xia, D.King, Y.Wang, oral presentation in the 20th North American Catalysis Society Meeting, June 17–22, 2007, Houston.

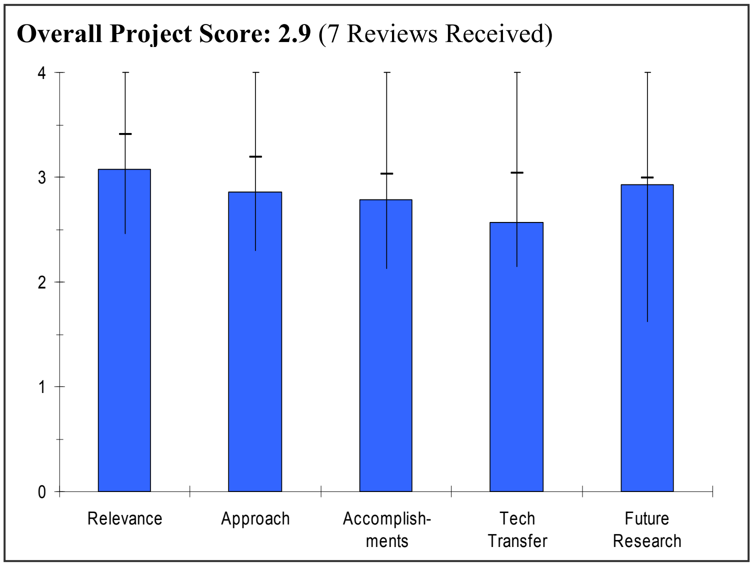
4. *Hydrogen Production from Aqueous Phase Reforming of Sorbitol and Related Oxygenated Hydrocarbons*, G.Xia, X.Wang, J.Cao, A.Platon, C.Yang, T.Peterson, D.King, Y.Wang, oral presentation in the 20th North American Catalysis Society Meeting, June 17–22, 2007, Houston.

5. *Hydrogen Production via Bio-derived Liquids Reforming* by Yong Wang, U.S. Department of Energy Bio-Derived Liquids to Hydrogen Distributed Reforming Workshop, October 24, 2006, Baltimore, Maryland.

6. *Catalytic processes for biomass conversion to fuels and chemicals: an overview*, Plenary lecture by Y.Wang in 2007 symposium on biomass conversion and environmental catalysis organized by Japan Science and Technology, Catalysis Research Center, Hokkaido University, July 13–14, Sapporo, Japan.

Project # PD-04: Bio-Derived Liquids Reforming

Yong Wang; PNNL



Brief Summary of Project

The objective of this project is to assist DOE in evaluating and developing alternatives to gasification and pyrolysis of biomass for hydrogen production that can meet the DOE 2017 cost target of <$3.00/gge. The objectives for FY 2007 were to develop stable and selective catalysts for vapor phase reforming of ethanol to produce hydrogen and to understand the reactivity and selectivity of aqueous phase reforming intermediates to enhance hydrogen productivity. An isothermal aqueous phase reforming reactor has been developed to screen catalysts and understand reaction mechanisms for improved hydrogen productivity.

Question 1: Relevance to overall DOE objectives

This project earned a score of **3.1** for its relevance to DOE objectives.

- Early evaluation of catalyst performance for reforming of bio-derived fuels, important topic as research moves beyond natural gas fuel processing.
- Project directly addresses Program goal of hydrogen production from renewable biomass resource.
- Potential long term solution to distributed reforming system with very low well to wheel CO_2 emissions
- Meets the DOE Hydrogen Program goal of cost effective H_2 production from bio-liquids.
- Presentation went into excessive detail on liquid phase reforming; needed to be balanced with how this technology has the potential to meet DOE H_2 production targets.
- Project is critical to the realization of renewable sources for hydrogen at the DOE targeted production cost of $3.00/gge by 2017. However, looks complimentary or redundant to Virent efforts in catalyst optimization.
- Critical to evaluate bioliquids as a feedstock for hydrogen.
- Capital cost reduction is critical for any hydrogen system.
- It is not clear whether any of the biofuels to hydrogen pathways shown make sense from a cost or efficiency perspective (i.e., there are probably more efficient ways to use biomass/biofuels).
- Ethanol is not competitive with gasoline without needing significant subsidies.

Question 2: Approach to performing the research and development

This project was rated **2.9** on its approach.

- Gas phase system approach not clearly presented.
- APR approach is well defined and effective.
- Need better definition of goals; minimal information provided on reactor rig and test plan; clear direction not presented.
- Very strong science focus on understanding catalytic fundamentals in this relatively unexplored system, including assessment of heat/mass transfer, identification of chemical intermediates, and exploration of potential reaction network.
- Concentrating on vapor phase ethanol because it is a current infrastructure fuel; will need to be extended to other bioliquids.
- Makes sense to explore liquid phase reforming; has obvious potential cost advantages.

- Good summary on current state of catalyst development. It appears that both PNNL and Virent are working on improving hydrogen selectivity for the Virent catalyst. So far the Virent catalyst has the best performance.
- Good that PNNL (and Virent) are working on processing low cost sugars with their catalyst.
- Fundamental mechanistic studies are well planned.
- Plan was not well explained.
- Unclear how team members were selected and how is each performing.
- Management review was unclear.
- Project doesn't seem focused on any of the barriers except identifying better catalysts.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **2.8** based on accomplishments.

- Hard to assess progress since specific goals not well defined.
- Very early in evaluation process; catalyst showed comparable performance.
- Tremendous amount of work done including:
    - Development of isothermal reactor (need this for mechanistic and kinetic studies).
    - Identification of stable and selective catalysts.
    - Complete product identification.
    - Mechanistic studies and influence of added KOH on overall reaction network.
- Demonstration of liquid phase reforming is a significant accomplishment; however, seems that the reactor productivity is very low (1-4 g feed/g catalyst/hr). Exploratory research notwithstanding, it is unclear how these levels of production will be commercially viable.
- Liquid phase reforming needs to be put in perspective with what catalyst advances would be required to meet DOE H_2 cost targets.
- Appears that a significant amount of work has been done to understand liquid phase reforming and many leads were generated on how this technology can be improved.
- The findings that microchannels, higher space velocity, and pH control can improve hydrogen conversion for the RePt catalyst may be important information to industry.
- Unclear if the project was reviewed for safety.
- No progress has been made on cost or efficiency – which were identified as barriers addressed.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **2.6** for technology transfer and collaboration.

- Minimal to date, but attempting to bring in more partners.
- Claim collaboration with Virent, but wasn't clear from the presentation what that partnership involves.
- Same goes for claimed collaboration with Ohio State research group...not clear what the nature of the collaboration is.
- Good collaboration with ANL and Ohio State.
- This seems to be limited in terms of collaborative influence. They are still not sure of likelihood that oil and ethanol producers will find value in project.
- Catalyst issues still a problem.
- Unclear whose responsible for carbon monoxide and other emissions.
- While numerous presentations appear to have been given, it is not clear if significant interactions occurred.

Question 5: Approach to and relevance of proposed future research

This project was rated **2.9** for proposed future work.

- Future work for 2008 lacks specific targets for each planned task.
- Typical catalyst testing of selectivity, stability, etc.; planning to evaluate impurities. Evaluation of potential system performance would be helpful.

- Plans include minimizing acid formation, developing kinetic models, improving catalyst activity, selectivity, stability and developing process economics.
- The first two represent valuable and sensible science development at a national lab. Skeptical about the latter two activities and if these reflect appropriate activities for a national lab, when industrial labs are now pursuing these same targets. If PNNL is successful in developing promising new catalysts, it is unclear who will develop them.
- Mentioned performing a comparison with DOE cost targets; needs to be done sooner rather than later.
- Because the benefits of liquid phase reforming are great, work should continue to advance this technology.
- Future research to focus on larger reactor is sound if catalyst life and selectivity can be improved.
- Needs more clarification on go/no go decisions for different approaches.
- There doesn't appear to be appropriate off-ramps if the project results are not promising.

Strengths and weaknesses

Strengths

- Initial effort to evaluate vapor versus aqueous reforming of bio-derived fuels.
- Building basis of strong catalyst fundamentals in this new catalysis area.
- PNNL has good experience with small scale reformer R&D.

Weaknesses

- Very academic presentation: lots of information without much analysis of its significance. Made it hard to deduce true worth of work.
- Require better definition of goals and projected performance.
- Appears to be on a path to try and optimize catalyst life, activity, and selectivity, which would put it in competition with research going on in industry.
- Not sure of the differentiating benefit of this project here unless the Virent catalyst is just used as a baseline comparator.
- Market evaluation.
- Risk assessment.
- Commercialization.
- Very difficult to follow and understand the presentation.

Specific recommendations and additions or deletions to the work scope

- No comment as no clear path forward presented.
- The project needs to perform preliminary cost and "well to farm to wheel" efficiency assessments to compare to other options (like using ethanol efficiently in an ICE) in order to establish performance targets for go/no-go decision points.

II.B.4 Hydrogen Generation from Biomass-Derived Carbohydrates via the Aqueous-Phase Reforming (APR) Process

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DOE Project Officer: Jill Gruber
Phone: (303) 275-4961; Fax: (303) 275-4753
E-mail: Jill.Gruber@go.doe.gov

Contract Number: DE-FG36-05G15046

Subcontractors:
- University of Wisconsin, Madison, WI
- Archer Daniels Midland (ADM) Company, Decatur, IL

Project Start Date: September 1, 2005
Project End Date: August 30, 2008

Objectives

The objectives of the first year of this project are as follows:

- Identify candidate sugar streams (glucose), document plant integration requirements and associated economic factors.
- Develop catalyst and reactor based on the aqueous phase reforming (APR) process suitable for converting candidate sugar streams to hydrogen.
- Design a baseline hydrogen generation system utilizing the APR process.
- Calculate the thermal efficiency and economics of the baseline APR system.
- Assess the baseline APR system with respect to Hydrogen Program goals and make a go/no-go decision to proceed with further development of a demonstration system.

The objectives of the second and third years of this project are as follows:

- Continue to investigate catalyst, reaction conditions and reactor suitable for converting low cost sugars to hydrogen.
- Calculate the thermal efficiency and economics of the APR system utilizing different feedstocks (low-cost sugars, glucose, sugar alcohols).
- Compare results of techno-economic analysis with DOE Hydrogen Program goals.
- Make a go/no-go decision on moving forward to the design and construction of a 10 kg H_2/day demonstration system with the preferred feedstock.
- Develop the detail design of the demonstration APR hydrogen generator system (10 kg/day).
- Fabrication of the integrated hydrogen generator system.
- Install and operate the APR hydrogen generator system.
- Assess APR hydrogen generator system performance with respect to Hydrogen Program goals.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section (3.1.4) 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
(E) Greenhouse Gas Emissions

Technical Targets

It is believed that using corn as a feedstock, converting this corn to glucose with cost-effective and established technologies and developing the APR process will provide a cost-effective and energy-efficient method to generate hydrogen from biomass. The project objective is to achieve the DOE 2012 cost target for distributed production of hydrogen from bio-derived renewable liquids of:

- H_2 Cost: $3.80/gge
- Feedstock Cost Contribution: $2.10/gge

Accomplishments

- Established baseline performance with sorbitol feed.
- Established operating conditions for conversion of glucose to hydrogen.

- Devised a reactor configuration that allows the conversion of high concentrations of glucose and sorbitol.
- Reported a preliminary cost model using DOE's H2A spreadsheet.
- Virent funded project to convert glycerol to hydrogen.
  - Proved catalyst lifetime of greater than a year.
  - Tested first generation reactor system.
  - Designed and constructed second generation reactor system.

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Introduction

The conversion of corn to glucose via either wet or dry milling is a well known and optimized technology. ADM is the leading producer of sweeteners from corn utilizing such processes. Virent's APR process reacts water with carbohydrate-type compounds (glycerol, sugars, and sugar alcohols) and has the following advantages over conventional vapor-phase steam reforming processes: (1) generates hydrogen and/or alkanes without the need to volatilize water, which represents a major energy saving; (2) occurs at temperatures and pressures where the water-gas shift reaction is favorable, making it possible to generate hydrogen with low amounts of CO in a single chemical reactor; and (3) takes place at low temperatures that minimize undesirable decomposition reactions typically encountered when carbohydrates are heated to elevated temperatures.

While proven in the laboratory, the APR technology must be shown viable on a larger scale. This project will result in the design, construction, and operation of a 10 kg H_2/day prototype reactor system. Such a system will provide the necessary scale-up information for the generation of hydrogen from glucose derived from corn.

Approach

This project combines the expertise of Virent Energy Systems (Virent), Archer Daniels Midland Company (ADM), and the University of Wisconsin (UW) to demonstrate the feasibility of generating high yields of hydrogen from corn-derived glucose. This proposed concept takes advantage of the fact that corn contains large amounts of starch which can be extracted and converted to glucose. The resulting aqueous solutions of glucose can be fed to the Virent's novel APR process that generates hydrogen in a single reactor. The effluent gas from the APR process can then be efficiently purified to produce high purity hydrogen utilizing pressure swing adsorption.

Results

Virent is investigating proprietary reactor configurations that allow the conversion of high concentrations of glucose derived from corn. The biomass to hydrogen route via the APR process is detailed in Figure 1. Energy balances on the APR system indicate that significant energy losses can occur because of vaporization of water in the reactor system to maintain the partial pressure of water in the hydrogen gas bubbles formed in the reactor. Figure 2 shows that the thermal efficiency of the system can be improved by operating it with higher concentrations of feedstock. This figure shows that as the feed concentration is increased from 10 wt% to 60 wt%, the efficiency of the system increases from less that 10% to greater than 80% at a 100% conversion of glucose. This analysis assumed that a portion of the product hydrogen will be combusted to provide the process heat for the generation of hydrogen via the APR process. Accordingly, Figure 2 shows that it is desirable to operate at feed concentrations of 30 wt% or greater to achieve the desired thermal efficiency for the system.

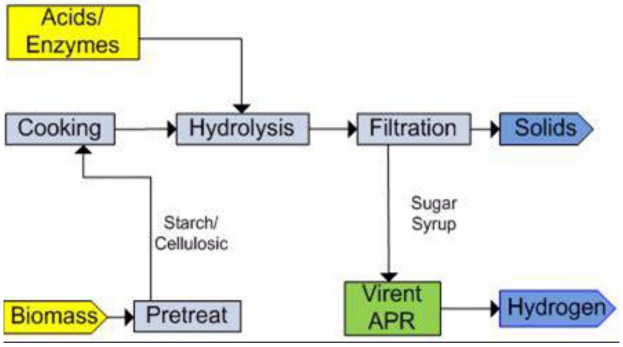


FIGURE 1. Biomass to Hydrogen via the APR Process

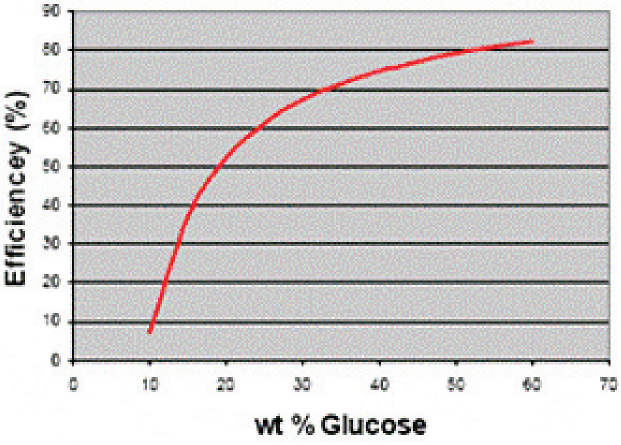


FIGURE 2. Efficiency of APR with Increasing Feed Concentration of Glucose

Catalyst lifetime at the desired feed concentration levels is a variable of importance in the overall economic feasibility of the APR process. Virent funded extended catalyst lifetime testing has been performed on glycerol feedstocks at 50 wt% concentration. Figure 3 details the extended lifetime run. The extended lifetime run was performed with a first generation catalyst. The reactor operates in a one pass system in which the reaction temperature can be raised to keep conversion high while exhibiting very stable H_2 production. The data gained from glycerol testing should correspond with future glucose catalyst information.

An initial cost estimate was made for the generation of hydrogen from glucose for fueling station applications which included the cost of feedstock, capital equipment (including catalyst costs), and operation and maintenance. DOE's H2A spreadsheet was used for this analysis. This cost estimate was for a reformer that generates 1,500 kg of H_2 per day. This analysis includes the capital cost of the reformer, pressure swing absorption (PSA) separator, compressor, storage, and dispensing equipment. Figure 4 shows the results of this analysis utilizing the following assumptions:

- Capital cost of reformer, APR, compression, storage, and dispensing: $1,960,000
- Conversion of low purity sorbitol (15 cents/lb of sorbitol)
- Conversion of high purity glucose (10 cents/lb of glucose)
- Conversion of lower grade glucose (8 cents/lb of glucose)
- Conversion of sugars derived from lignocellulosic biomass (5 cents/lb)
- Conversion of lignocellulosic biomass (5 cents/lb) at a capital cost of $980,000
- A 70% yield of hydrogen, the other 30% needs to be combusted to provide process heat

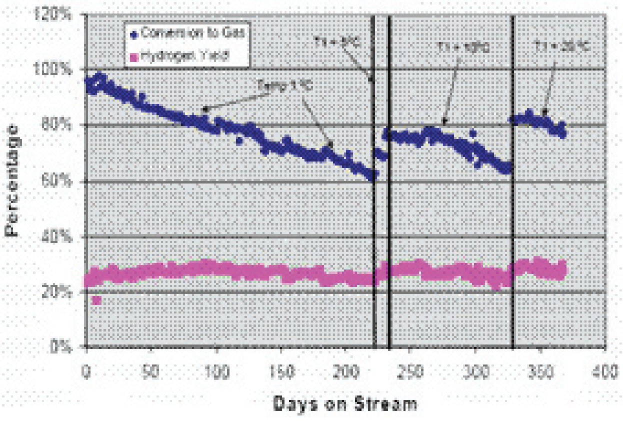


FIGURE 3. APR Catalyst Lifetime Testing

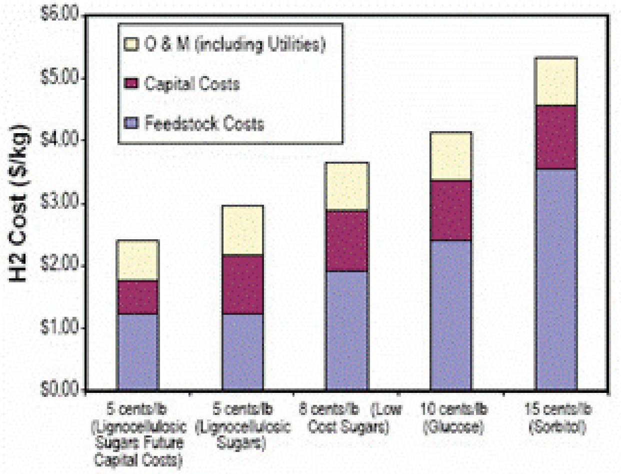


FIGURE 4. Preliminary Cost Analysis Utilizing H2A

- The above translates into a thermal efficiency of 81% based on the lower heating value (LHV) of glucose
- Catalyst contains precious metal (catalyst cost of $1,700 per kg of catalyst)
- Purification of the hydrogen with a PSA unit

Results from this cost analyses show that the 2012 DOE Target of $3.80/gge could be achieved utilizing low-cost sugars (less than 8 cents/lb). The 2017 DOE Target of <$3.00/gge could be achieved with sugars derived from lignocellulosic biomass and lower capital costs for the system. More extensive cost estimations will be performed to validate these initial model results.

Conclusions and Future Directions

Virent has identified a reactor system that allows the aqueous phase reforming of glucose. While initial results showed low selectivity to hydrogen, subsequent developments have shown improvement in generation of hydrogen with appropriate catalyst, reactor configuration, and reaction conditions.

Future Directions

- Continue development of APR catalyst and reactor that converts glucose and sugar alcohols to hydrogen.
- Investigate hydrogenation technologies that convert both monosaccharides and polysaccharides to sugar alcohols.
- Investigate the integrations of the hydrogenation technology with the APR technology.
- Calculate the thermal efficiency and economics of the baseline APR system utilizing sugars or sugar alcohols as the feedstock.

- Evaluate the baseline APR system against U.S. Hydrogen Program goals and determine whether to proceed to development of the demonstration system.

FY 2007 Publications/Presentations

1. Presentation – NHA Annual Hydrogen Conference, March 20–22, 2007.

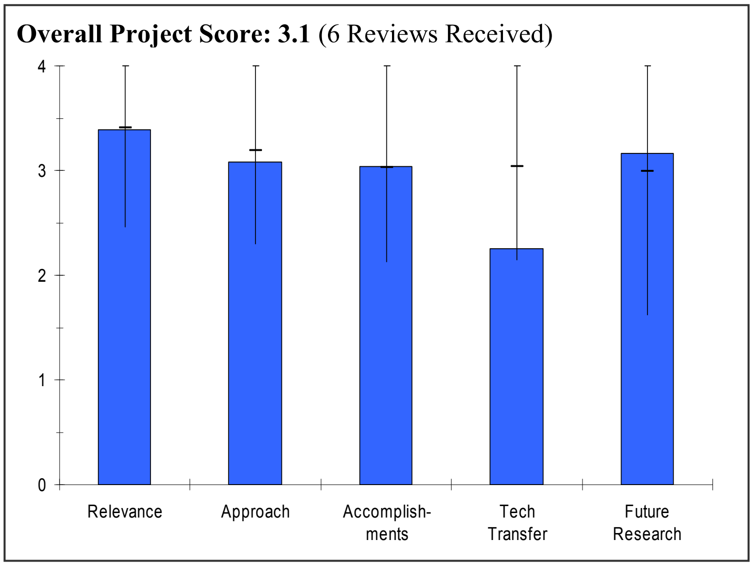
2. Presentation – Gordon Research Conference, January 10, 2007.

3. Poster – Hydrogen Program Review Meeting, May 15, 2007.

Project # PDP-08: Hydrogen Generation from Biomass-Derived Carbohydrates via Aqueous-Phase Reforming Process

Randy Cortright; Virent Energy Sys.

Brief Summary of Project



The overall objectives of this project are to design a generating system that uses low-cost sugars or sugar alcohols that can meet the DOE H_2 cost target for distributed reforming of bio-derived liquids of less than \$3.00 / gge by 2017, and to fabricate and operate an integrated 10 kg H_2/day generating system. The objective for 2006 was to develop aqueous-phase reforming (APR) catalyst, reaction conditions, and a reactor suitable for converting glucose to hydrogen. Objectives for 2007 are to 1) continue to investigate catalyst, reaction conditions, and reactor suitable for converting low-cost sugars to hydrogen; 2) calculate the thermal efficiency and economics of the APR system utilizing different feedstocks (low-cost sugars, glucose, sugar alcohols); 3) compare the results of techno-economic analysis with DOE Hydrogen Program goals; 4) reach a go/no-go decision on whether to proceed with the design and construction of a 10 kg H_2/day demonstration system with the preferred feedstock; and 5) design a 10 kg H_2/day demonstration system.

Question 1: Relevance to overall DOE objectives

This project earned a score of **3.4** for its relevance to DOE objectives.

- Simple, single-step conversion of H_2 is a major step toward achieving DOE H_2 cost goals.
- Able to use renewable feedstocks.
- Strong focus on biomass conversion to hydrogen production; important pathway.
- Addresses DOE program goal of hydrogen production from renewable resources.
- Targets cost reductions in feedstocks, capital, operations, and GHG emissions.
- Small scale could provide significant advancement for renewables H_2 production.
- The objective of this project is to design and build a 10 Kg/day H_2 generating system by aqueous phase reforming (APR) bio-mass derived carbohydrates (sugar or sugar alcohols). This project is relevant to DOE's overall objectives.

Question 2: Approach to performing the research and development

This project was rated **3.1** on its approach.

- Specific approaches are proprietary. Little on which to base a score.
- Very early in the study, much of what was presented not directly linked to project.
- Continues to build on the novel concept of aqueous phase reforming as the front end of a number of biomass to fuels processes, including hydrogen.
- Work is expanding to include ever more complex sugar and sugar alcohol feeds.
- Already demonstrated that the APR can produce H_2 from glycerol and sorbitol now needs to optimize for glucose.
- Use of sorbitol or other alcohols only make sense if you are trying to maximize conversion efficiency.

- Feedstock cost, reformer capital cost, O&M, and GHG emissions are barriers addressed by this project. Due to budget cutbacks this project is focusing efforts on development of catalysts for APR.
- If feedstock costs decrease from $2.10/gge in 2012 to $1.55/gge in 2017, and hydrogen production cost are $3.80/gge by 2012 and less than $3/gge by 2017, then the approach will reach DOE's projected cost targets for hydrogen from bio-derived liquids.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.0** based on accomplishments.

- Claimed efficiency of ~78% is impressive.
- Not clear how long term testing can show steady H_2 production while gas conversion % declines significantly.
- Limited as project is early in development.
- Much work on catalyst and process development. Impressive progress for a small startup company.
- Gained a lot of knowledge from processing glycerol and sorbitol that is transferable to glucose and other polysaccharides. Still need to optimize hydrogen production efficiency and reduce Alkane by-products.
- Not much has been accomplished.
- Performance is still behind conventional reforming technology.
- Continuing to investigate catalysts for APR of glucose provided by ADM.
- Has shown catalyst lifetime of greater than a year and tested a first generation reactor system (Green Energy Machine).
- Studied effect of feed concentration. Generated hydrogen was burned for internal process use.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **2.3** for technology transfer and collaboration.

- Not clear on partner roles in development or milestones.
- Not clear what role partners ADM and U Wisconsin have played in the work to date.
- As this is a commercial venture they are very careful about IP protection so there appears to be limited sharing around catalyst technology and plans for generator design modifications.
- Poor communication.
- ADM is the only company interested, potentially to use a thermochemical route for corn sugar.
- Teamed with ADM and University of Wisconsin. APR process was developed at University of Wisconsin and therefore Virent is closely tied with University of Wisconsin. ADM is providing biomass derived liquids.

Question 5: Approach to and relevance of proposed future research

This project was rated **3.2** for proposed future work.

- Good plan to include go/no-go decision point; need to include overall energy analysis and quantify benefits.
- Program on a clear path to a go/no-go decision for construction of 10 kW pilot demonstration system in 2007.
- Focus on low cost sugars and PSA development seems to be on target.
- Not clear what the R&D objectives are.
- Economics are marginal.
- Needs an independent assessment or risk assessment review.
- Future work in 2007 is focused on developing catalysts that converts glucose and sugar alcohols to hydrogen.
- Virent will also investigate hydrogenation technologies to convert both monosaccharides and polysaccharides to sugar alcohols.
- Go/no-go decision will be made for the APR technology.
- The PI has responded well to previous year reviewers' comments.

Strengths and weaknesses

Strengths

- Converter is simple and low temperature: no WGS, steam boiler, hydrodesulfurizer.
- Has clear commercialization potential if successful.
- Mentioned a commercial manufacturer, but didn't indicate who it was or if they had a market plan.
- Novel technology (APR).
- With limited funding, Virent has already built and operated a 6 NM3/hr alpha unit utilizing glycerol as feed stock.

Weaknesses

- Catalyst performance degrades significantly in <1 year.
- Strategy of raising temperature to higher catalytic activity helps only slightly.
- Substantial methane production: limits H_2 yield.
- Process economics is not addressed. Should be favorable since simple, low temperature reactor, but should be quantified.
- Project is built on assumption that sugar alcohols will be available as low cost feedstocks at fuels scale The emphasis of the Virent approach should shift to a focus on low cost biomass feedstocks that might be available in significant volumes at costs under $60 per ton rather than on sugar alcohols as the US is not a major sugar producer.
- No information on commercial availability of catalyst.
- Not having a clear focus on any one particular feedstock.

Specific recommendations and additions or deletions to the work scope

- Include overall energy analysis.

II.B.6 Hydrogen Production by NG and Renewable Liquids Reforming using Dense Ceramic Membranes

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Project Start Date: May, 2005
Project End Date: Project continuation and direction determined annually by DOE

Objectives

- Measure H_2 production rate using oxygen transport membranes (OTMs).
- Optimize OTM performance by doping and controlling OTM's microstructure.
- Fabricate thinner OTMs to enhance their H_2 production rate.

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)
(N) Hydrogen Selectivity
(R) Cost

Technical Targets

This project is developing compact dense ceramic membranes that transport pure oxygen to efficiently and cost-effectively produce hydrogen by reforming natural gas (NG) and renewable liquid fuels such as ethanol and bio-oil. Cost-effective small-scale reformer technology will be developed to integrate process steps, thereby minimizing unit size, capital cost, energy use, and operating cost and helping to meet DOE targets:

- Production Unit Efficiency:
  - 75.0% lower heating value (LHV) by 2015 for NG
  - 72.0% (LHV) by 2012 for bio-derived liquids
- Production Unit Capital Cost (un-installed): $580K by 2015 for NG
  - $1.0M by 2012 for bio-derived liquids
- Total Hydrogen Cost:
  - $2.00/gge by 2015 for NG
  - $3.80/gge by 2012 for bio-derived liquids
  - <$3.00/gge by 2017 for bio-derived liquids

Accomplishments

- Hydrogen production rates were measured using two types of OTM: $SrFeCo_{0.5}O_x$(SFC2) and SFT (Sr-Fe-Ti oxide).
- Confirmed that decreasing OTM thickness increases hydrogen production rate if OTM surfaces are modified to overcome limitations from surface reaction kinetics.
- Thin (0.25-0.50 mm) SFC2 membranes were coated with porous SFC2 layers to obtain the highest hydrogen production rate yet obtained at Argonne, 11 $cm^3/min\text{-}cm^2$.
- SFC2 thin (<0.10 mm) films were fabricated on porous substrates.

* * * * *

Introduction

The dissociation of water, shown by reaction (1), generates very low concentrations of hydrogen and oxygen even at relatively high temperatures (e.g., 0.1% hydrogen and 0.042% oxygen at 1600°C), because the equilibrium constant for dissociation is small.

$$H_2O(g) \Leftrightarrow H_2 + \frac{1}{2}O_2 \tag{1}$$

However, significant amounts of hydrogen and oxygen can be generated at moderate temperatures if a mixed-conducting (i.e., electron- and ion-conducting) membrane is used to separate oxygen and hydrogen. For example, if an OTM is used to remove oxygen from the water-splitting zone, the steam becomes richer in hydrogen while oxygen is transported to the other side of the membrane, where it can be used to reform NG and/or renewable liquid fuels. Because the OTM is a mixed conductor, the oxygen transport requires neither electrodes nor external power circuitry, i.e., the process is nongalvanic. The hydrogen production rate depends directly on the rate at which oxygen is removed from the water dissociation zone, which depends on the oxygen permeation rate through the membrane. The oxygen permeation rate is a function of the membrane's electron and oxygen-ion conductivities, its surface oxygen exchange kinetics, and the oxygen partial pressure (pO_2) gradient across the membrane.

We measured significant hydrogen production rates using an OTM composed of an oxygen ion conductor (Gd-doped CeO_2 [CGO]) and an electronic conductor (Ni). The hydrogen production rate increased with increases in temperature, water partial pressure on the hydrogen-production side of the membrane, and oxygen chemical potential gradient across the membrane. It also increased as the OTM thickness decreased, but surface reaction kinetics began to limit hydrogen production for thin (<0.5 mm) OTMs. To enhance the surface reaction kinetics of thin OTMs, we increased their active area by coating them with porous layers, and we made their microstructures finer to increase their triple-phase-boundary area, i.e., the region where ionic conductor, electronic conductor, and gas phase meet. Without any microstructural modifications, high hydrogen production rates were achieved using thick (>0.5 mm) OTMs made of SFC2, developed by our group to separate oxygen from air. To increase SFC2's hydrogen production rate, we developed techniques for fabricating thin films with microstructural modifications that enhance surface reaction kinetics. To increase hydrogen production during methane reforming, steam was added to methane in the presence of a steam-reforming catalyst. We began developing and utilizing a model to assess the economic potential of using an OTM to produce hydrogen during the reforming of NG and bio-derived liquids.

Approach

A system analysis will be done to determine the requirements for a reactor that would use an OTM to cost-effectively produce hydrogen during the reforming of NG and renewable liquids. For cost-effective hydrogen production, the OTM must efficiently transport the oxygen needed for reforming. To do so, the OTM needs an appropriate combination of electronic and ionic conductivity, which we will assess by measuring the conductivity of promising membrane materials. We will measure the hydrogen production rate of materials that have sufficient conductivity ($>10^{-1}$ ohm^{-1}-cm^{-1}), and will drive the removal of oxygen by using a reactive gas to establish an oxygen partial pressure (pO_2) gradient across the membrane. In order to increase the oxygen flux, and hence the hydrogen production rate, we will decrease the membrane thickness and modify selected membranes in two ways. Catalysts will be used to promote reactions, and/or the microstructure will be manipulated to enhance reaction kinetics at the surface of the membrane. If steam is used as the source of oxygen, the water-splitting equilibrium shifts away from dissociation as the steam becomes enriched in hydrogen; therefore, less water dissociates, and overall hydrogen production is less efficient than it could be. To overcome this limitation, we will remove hydrogen from the steam using a hydrogen transport membrane (HTM) in parallel with the OTM. In order for OTMs to cost-effectively produce hydrogen, they must have good chemical and mechanical stability; therefore, we will evaluate the stability of OTMs during hydrogen-production by reforming of NG and renewable liquid fuels.

Results

Both flat surfaces of thin (0.25-0.50 mm) SFC2 membranes were coated with porous SFC2 layers to increase the membranes' hydrogen production rate. Figure 1 compares the hydrogen production rates of surface-modified and unmodified SFC2 membranes, measured at 900°C using wet N_2 (pH_2O=0.49 atm) on the membranes' hydrogen-generation side and dry H_2 (pH_2=0.8 atm) on the oxygen permeate side. Porous SFC2 layers increased the surface area of coated membranes and significantly increased their hydrogen production rate relative to unmodified membranes. A 0.25-mm-thick membrane had a rate of 11 cm^3/min-cm^2, the highest hydrogen production rate yet obtained at Argonne. The effect of porous layers becomes more pronounced as the membrane thickness decreases, because surface oxygen exchange kinetics become more dominant. Ni/CGO cermet membranes showed a similar effect in previous studies. Although the porous layers clearly enhanced the hydrogen production rate, they did not eliminate limitations from surface reaction kinetics, as shown by the fact that the data for membranes with porous layers do not fall on the extrapolation for samples limited by bulk diffusion. Modifying the microstructure of the porous layers might further enhance the surface reaction kinetics and hydrogen production rate.

Figure 1 indicates that decreasing the membrane thickness can further increase the hydrogen production rate if limitations from surface reaction kinetics are overcome by coating the membranes with porous layers. To prepare thin membranes with sufficient mechanical integrity for routine handling, we are developing methods to fabricate SFC2 films on porous substrates. SFC2 thin (≈40-µm) films have been prepared on substrates consisting of porous Ni/CGO or porous SFC2. An SFC2 film on porous Ni/CGO gave a hydrogen production rate that was much lower than expected, possibly due to reaction between SFC2 and Ni. In addition, a bond layer for improving adhesion between the SFC2 film and Ni/CGO substrate contains

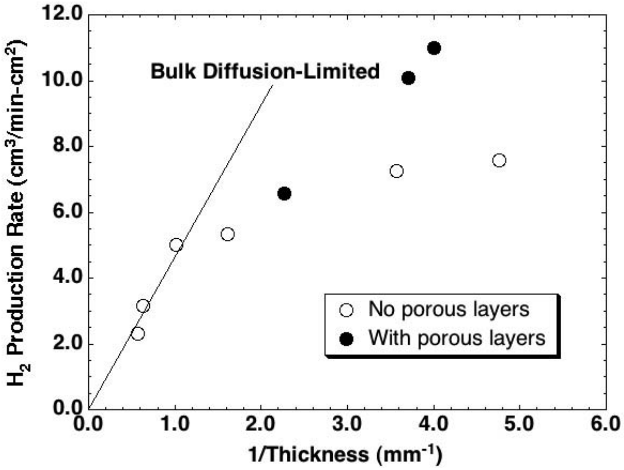

FIGURE 1. H_2 production rate at 900°C vs. inverse of thickness for SFC2 membranes with and without porous SFC2 layers, measured with wet N_2 ($pH_2O=0.49$ atm) on the hydrogen-generation side and dry H_2 ($pH_2=0.8$ atm) on the oxygen permeate side. Line indicating bulk diffusion-limited regime is drawn only to aid the eye.

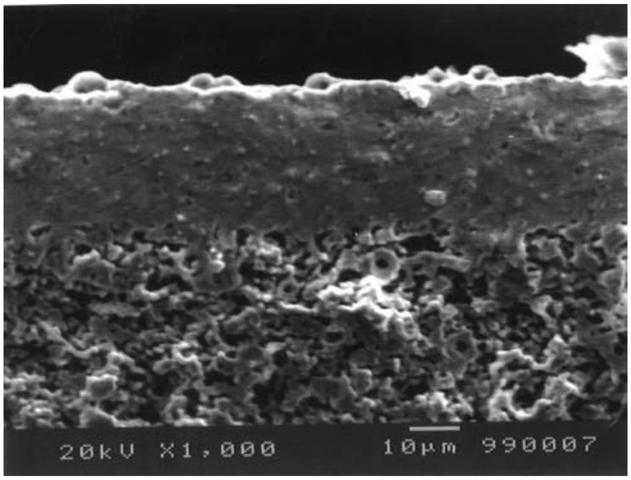

FIGURE 2. Fracture Surface of SFC2 Thin Film on Porous SFC2 Substrate

a low volume fraction (≈50%) of SFC2, which might restrict oxygen permeation. To avoid these problems with Ni/CGO substrates, SFC2 thin films were fabricated on porous SFC2 substrates. The hydrogen production rate of such a film has not been measured yet, but a cross-sectional view (Figure 2) suggests that the film is dense, the substrate has sufficient porosity, and there appears to be good bonding between the film and substrate.

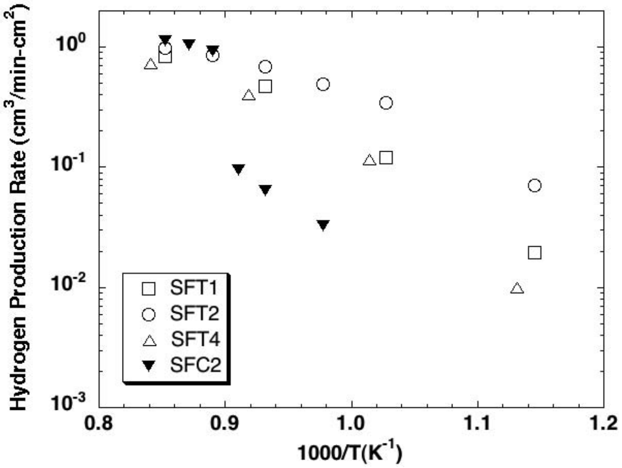

FIGURE 3. H_2 Production Rate of SFT and SFC2 Membranes (Thickness ≈1 mm) using Wet N_2 ($pH_2O=0.03$ atm) on the Hydrogen-Production Side and 4% H_2/Balance He on the Oxygen-Permeate Side

SFC2 is a promising material for OTMs due to its high hydrogen production rate at high temperatures (>850°C); however, a phase transition at 825-850°C dramatically reduces its hydrogen production rate at lower temperatures. For applications at <850°C, we are investigating Sr-Fe-Ti oxide (SFT) membranes that do not experience a phase transition like that of SFC2. Figure 3 compares the hydrogen production rates of SFT and SFC2 membranes with similar thickness (≈1 mm). The hydrogen production rate for SFC2 is the highest above 850°C, but it is much smaller below 850°C due to its phase transition. Among the SFT membranes tested, SFT2 gives the highest hydrogen production rate. To better understand the effect of Ti-doping on the hydrogen production rate, detailed studies of the electrical conductivity of SFT membranes are necessary.

Conclusions and Future Directions

Reducing the thickness of OTMs can significantly increase their hydrogen production rate if they are coated with porous layers that minimize limitations from surface reaction kinetics. To fully exploit the potential of SFC2 membranes, porous surface layers must be added to membranes with thickness <0.05 mm. We will further investigate SFC2 thin films on Ni/CGO porous substrates to better understand why their hydrogen production rates have been lower than expected to this point. We will measure the hydrogen production rate of SFC2 thin films on porous SFC2 substrates. We will continue studying alternative mixed oxygen ion/electron conductors (e.g., various SFT compositions) that do not experience a phase transition like that of SFC2. We will study the effect of SFT's titanium content on its transport properties and will test the performance of SFT cermet membranes. After the OTM's hydrogen production rate has been optimized, we will test its performance in the reforming of renewable liquid fuels such as ethanol and bio-oil and other carbon-containing fuels.

Special Recognitions & Awards/Patents Issued

1. Hydrogen Production by High-Temperature Water Splitting Using Electron-Conducting Membranes, U.S. Patent 7,087,211, Aug. 8, 2006.

FY 2007 Publications/Presentations

1. Hydrogen Production by Water Dissociation Using Mixed Conducting Dense Ceramic Membranes, Intl. J. of Hydrogen Energy, 32, 451 (2007).

2. Reforming of Natural Gas via Water Splitting using Dense Ceramic Membranes, presented at Natl. Hydrogen Assoc. Meeting, March 19–22, 2007, San Antonio, TX.

II.A.3 Integrated Hydrogen Production, Purification and Compression System

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Contract Number: DE-FG36-05GO15017

Subcontractors:
[1] Membrane Reactor Technologies (MRT) Ltd., Vancouver, BC, Canada
[2] HERA USA, Inc., Ringwood, NJ

Start Date: April 1, 2005
Projected End Date: December 31, 2008

Objectives

- To demonstrate a low-cost option for producing fuel cell vehicle (FCV) quality hydrogen to meet DOE cost and efficiency targets for distributed hydrogen production.
- To develop a hydrocarbon fuel processor system that directly produces high pressure, high-purity hydrogen from a single integrated unit by combining a fluidized bed membrane reactor (FBMR) and a metal hydride-based compressor (MHC).

Technical Barriers

This project addresses the following technical barriers listed in the Hydrogen Production section (3.1.4) of the updated version (April 27, 2007) 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)
(K) Durability
(L) Impurities
(M) Membrane Defects
(N) Hydrogen Selectivity
(O) Operating Temperature
(P) Flux
(R) Cost

In addition, the project addresses the following technical barrier from the Hydrogen Delivery section (3.2.4):

(B) Reliability and Costs of Hydrogen Compression

Technical Targets

Technical Targets and the current progress made towards achieving the 2010 milestones are presented in Table 1.

Accomplishments

- Detailed process flow diagram (PFD) and process and instrumentation drawings (P&ID), including control strategy, were developed for an integrated reformer/compressor system, designed to produce 1.35 kg/hr fuel cell grade hydrogen at 100 bar.
- Detailed hazard and operability (HAZOP) as well as risk assessment reviews were conducted. The PFD and P&ID were revised and finalized based on the recommendations developed during these reviews.
- Specifications were developed and equipment, instruments, parts and supplies were procured accordingly.
- Assembly of the natural gas and utility supply skid as well as the main reformer skid has been completed and these skids have been installed at the National Research Council's Institute for Fuel Cell Innovation (NRC-IFCI) site in Vancouver, Canada.
- The MHC skid design was completed and parts and supplies procured. The skid assembly is in progress.
- The reformer operations and testing began in June.

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Introduction

The DOE has determined that the delivered cost of hydrogen must be in the $2 to $3/gge range for hydrogen to be competitive with gasoline as a fuel for vehicles. For small, on-site hydrogen plants being evaluated for refueling stations (the "forecourt"), capital cost is the

TABLE 1. Progress Towards Technical Targets

Technical Targets: Distributed Production of Hydrogen from Natural Gas[1, 2]			
Characteristics	**Units**	**2010 Target[3]**	**Current FBMR-MHC Projection[4]**
Production Unit Energy Efficiency	%(LHV)	72.0	73.3
Production Unit Capital Cost (Uninstalled)	US$	900K	1,029K[5]
Forecourt Compressor Energy Efficiency	%	94[6] (CR=19.8)	72[7] (CR=895)
Compressor Installed Capital Cost (Basis:1,500 kg/day @6250 psi)	K$/(kg/hr)	4.0	4.43[8]
Total Hydrogen Cost	\$/gge H_2	2.50	2.81

LHV – lower heating value
CR – compression ratio

[1] The H2A Production tool (http://www.hydrogen.energy.gov/systems_analysis.html) was used for the cost modeling. Economic parameters used were for a production design capacity of 1,500 kg/day of hydrogen: 20 year analysis period, 10% internal rate of return (IRR) after taxes, 100% equity financing, 1.9% inflation, 38.9% total tax rate, and Modified Accelerated Cost Recovery System (MACRS) 7-year depreciation for 2005, 2010, and 2015. A 70% capacity factor was used for 2005, and 2010. A 75% capacity factor was used for 2015. The results for 2005, 2010, and 2015 are in 2005 dollars.

[2] The natural gas cost and electricity cost used for 2005, 2010, and 2015 were \$5.00/MMBTU (LHV) and \$0.08/kWhr respectively based on the Energy Information Administration (EIA) 2005 Annual Energy Outlook High A case projection for 2015 in 2005\$. The natural gas cost assumes industrial gas cost is available for distributed production of hydrogen.

[3] For the 2005, 2010, and 2015 analysis it was assumed that Design for Manufacture and Assembly (DFMA) would be employed and that on the order of 500 units per year would be produced.

[4] The FBMR-MHC cost projections are based on prior DOE targets and use somewhat different assumptions from those stated in footnotes 1 & 2. A direct comparison using identical assumptions to the April 27, 2007 RD&D plan will be prepared using actual performance measurements from the proof of concept (POC) unit. The figures presented in this table are based on the Advanced Prototype design, 1,500 kg/d, 6,515 psia H_2 pressure, 10% IRR after taxes, 2.5% inflation, 38% total tax rate, 83% capacity factor, \$6.00/MSCF natural gas cost, \$0.075/kWh electricity cost.

[5] Detailed estimates for an annual production quantity of 200 units yielded a capital cost of \$1,285K. Increasing production quantities to 500 units per year is anticipated to reduce costs from 15 to 25%. A reduction of 20% results in the \$1,029K figure.

[6] The 2010 target of 94% assumes a CR of 19.8 (300 psi inlet, 6,250 psi outlet) and does not include the efficiency losses from the production of electricity. If electricity efficiency of 35% is used, compressor primary energy efficiency for these conditions decreases to 65%.

[7] Compression efficiency of 72% is based upon a compression ratio of 895 and a primary energy source of natural gas, not electricity. This compares to the 2010 target forecourt compressor operating with a compression ratio of 895 at 89% (electric) and 47% if the electricity efficiency is factored in.

[8] Detailed estimates for an annual production quantity of 200 units yielded a capital cost of \$5.54K/(kg/h). Increasing production quantities to 500 units per year is anticipated to reduce costs from 15 to 25%. A reduction of 20% results in the \$4.43K/(kg/h) figure.

main contributor to delivered hydrogen cost. This project is based on achieving the target hydrogen cost by combining unit operations for the entire generation, purification, and compression system. It uses a membrane reformer developed by MRT which has H_2 selective, Pd-alloy membrane modules immersed in the reformer vessel, thereby directly producing high purity hydrogen in a single step. The continuous removal of pure hydrogen from the reformer pushes the equilibrium "forward" thereby maximizing reactor productivity with an associated reduction in the cost of product hydrogen. Additional gains are envisaged by the integration of the novel hydride compressor developed by HERA, whereby H_2 is compressed from 0.5 bar (7 psia) to 350 bar or higher in a single unit using thermal energy. Excess energy from the reformer provides over 25% of the power used for driving the hydride compressor so that system integration can improve efficiency. Hydrogen from the membrane reformer is of very high, FCV quality (purity over 99.99%), eliminating the need for a separate purification step. The hydride compressor maintains hydrogen purity because it does not have dynamic seals or lubricating oil.

Following the techno-economic analysis presented last year, the work this year was focused on designing and building the first proof-of-concept (POC) unit to demonstrate the technology and to verify the assumptions in our analysis. The POC unit is designed to produce 1.35 kg/hr high purity, high pressure (100 bar) hydrogen.

Approach

The project team will integrate the membrane reformer developed by MRT and the hydride compression system developed by HERA in a single package. This is expected to result in lower cost and higher efficiency compared to conventional hydrogen production technologies, as follows:

Lower cost compared to conventional fuel processors will be realized by:

- Reduced component count and sub-system complexity.
- Tight thermal integration of all reactions/processes in a single package.
- Thermal metal hydride compression without rotating machinery, which should result in high reliability, low maintenance and low electricity usage.

High efficiency will be achieved by:

- Using H_2 selective membranes within the reformer vessel to directly produce high-purity hydrogen, eliminating losses associated with a separate purifier.
- Using a fluidized catalyst bed to improve heat and mass transfer.
- Using the compressor suction to lower the partial pressure of hydrogen in the reaction zone, which shifts equilibrium to enhance hydrogen production.

- Thermally integrating the hydride compressor with the membrane reactor to reduce compression energy consumption.

Results

- POC prototype system designed, fabricated and installed:
  - Novel reformer mechanical design with good membrane access.
  - Prototype, large area membrane modules (6”x11”) with lower cost substrate successfully tested at operating temperature and pressure.
- Novel MHC powered by hot air designed and under construction.
- Appropriate safety reviews completed:
  - HAZOP completed in June 2006.
  - Updated safety plan submitted to DOE.
  - Technical risk assessment for POC installation and operation completed.
  - Pre-start safety inspection of the reformer skid completed.

Conclusions and Future Directions

- Cost and efficiency targets unchanged since last year, pending assessment and revision based on POC test results.
- Complete POC performance tests, and report results and economic assessment by September 2007.
- Review POC test results and the revised economic assessment with DOE for decision to proceed to the next step, which is an advanced prototype incorporating lessons learned and employing a higher degree of integration, with an associated reduction in the number of components to reduce capital cost.

FY 2007 Publications/Presentations

1. US DOE Annual Review, May 15, 2007.

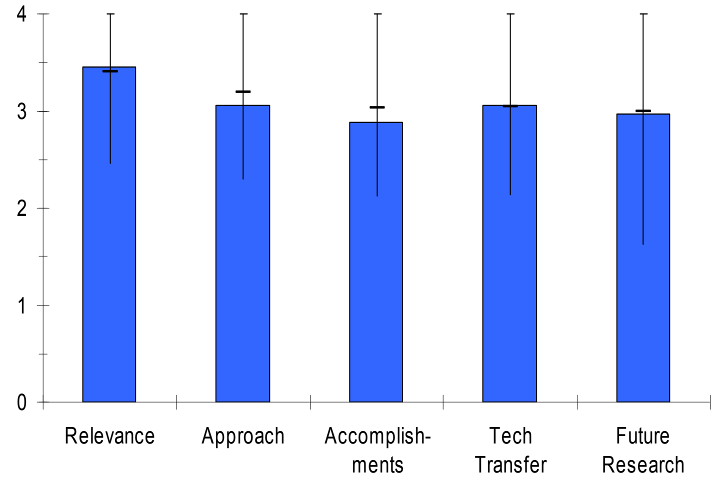
Project # PD-03: Integrated Hydrogen Production, Purification & Compression System

Satish Tamhankar; Linde

Brief Summary of Project

The goal of this project is to demonstrate a low-cost option for producing fuel cell quality hydrogen that can be adopted to meet the ultimate DOE cost and efficiency targets for distributed production of hydrogen. The project team will develop a fuel processor system that directly produces high-pressure, high-purity hydrogen from a single integrated unit. This will be accomplished by combining a membrane reformer developed by Membrane Reactor Technology and a metal hydride compression system developed by HERA USA in a single package. In 2006/2007 the objective was to build and experimentally test a proof-of-concept integrated reformer/metal hydride compressor system.

Overall Project Score: 3.1 (6 Reviews Received)



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.5** for its relevance to DOE objectives.

- Success in the project would have significant positive effect on hydrogen cost.
- Novel approach; potential to simplify overall system; probable high risk.
- Project clearly meets the objectives of the DOE Hydrogen Program.
- Good to simplify process and reduce components.
- Capital cost reduction.
- Good solid state design compressor.
- Existing industry is important to DOE success if they will commercialize and service units.
- Addresses DOE identified technical barrier.
- Project is appropriate for near-term refueling centers.
- This project's objective is to develop a fuel processor system that directly produces high pressure, high-purity hydrogen from a single integrated unit and therefore has good relevance to overall DOE objectives.

Question 2: Approach to performing the research and development

This project was rated **3.0** on its approach.

- Not clear how waste heat of compressor is used to aid reformer.
- Minimal test data presented; only benchtop component testing to date.
- Novel approach to addressing the problem of H_2 production from CH_4.
- Well conceived plan to build an initial proof-of-concept prototype and then an advanced prototype based on learnings.
- A novel approach is only beneficial if there are clear advantages over conventional technology; need a head-to-head comparison with conventional technology.
- Good plan for hazmat and resulting improvement to safety.
- Higher costs due to design modification for hydride compressor.
- 10 week setback was unplanned? How did management deal with impact instead of sitting on their hands?
- Good progress on technical barriers.
- How much has been completed on market penetration studies?

- Novel approach offers opportunity for new technologies.
- H_2 removal membranes have not been demonstrated with high flux.
- H_2 permeating membranes yield low pressure hydrogen.
- Reforming at pressure with H_2 permeation can lead to carbon formation in the reformer unless operated at high steam to carbon ratio. The latter penalizes system efficiency.
- Metal hydride compressor is novel.
- Addresses fuel processor capital costs, O&M, and reliability and costs of hydrogen compression barriers by building an integrated fluidized bed reformer and metal hydride compressor system. Process intensification will bring the cost down to DOE target levels.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **2.9** based on accomplishments.

- Substantial achievement in completing mechanical design and fabricating system.
- Longevity/membrane attrition testing mentioned during the question period but details not available.
- Minimal accomplishments to date (based on presentation); lifetime questionable; path towards high pressure output (10,000 psi) unknown; more information of performance versus goals necessary, especially efficiency.
- Significant accomplishment to construct the proof-of-concept prototype.
- MHC performance needs to be directly compared to conventional compression costs (operating and capital cost).
- Benefits of fluid bed reformer need to be clearly compared to conventional reforming technology.
- Behind schedule at go/no go decision, and management planning for schedule recovery is unclear.
- Revised safety plan was good.
- Only one data plot, and without the unit for flux.
- The projected efficiency and other performance parameters should be listed. Q&A revealed efficiencies in the "mid-70s" at a steam to carbon ratio of 3, and it is unclear how this is defined. Unclear what is included in the efficiency calculations.
- Unclear if energy losses are associated with the hydride compression technology.
- Pros and cons of reformer skid assembly addressed.
- Auto-thermal fluidized bed membrane reformer assembly has been fabricated and installed.
- Pd-membrane has been tested at operating temperature and pressures but not using reformer product streams.
- Completed appropriate safety reviews.
- Review comments from last year's review were addressed.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.0** for technology transfer and collaboration.

- Good collaboration between partners; good use of capabilities.
- Appears to have close collaboration, however seemingly limited to industry.
- Unclear about the cause of delays and how it was communicated to team members.
- Unclear how catalyst life is (still a problem) is being addressed.
- Unclear who is responsible for market plans and commercialization.
- The presentation time is better utilized with one speaker with others participating in Q&A.

Question 5: Approach to and relevance of proposed future research

This project was rated **3.0** for proposed future work.

- Minimal testing of integrated system; integration of components could be challenging.
- Future work is properly dependent on success with POC prototype.
- Project should proceed only if clear benefits for novel approach are established and communicated.
- Accelerated reliability should be considered to determine impact on cost.

- Unclear what technology life cycle costs are.
- The project end date is June 2008. By the end of May 2007 this team plans to complete site installation of reformer.
- MHC will be commissioned for one month of integrated testing. Unclear if one month of testing is sufficient to gather all relevant data needed to move forward.
- It would be helpful to provide future plans after the completion of this project.

Strengths and weaknesses

Strengths
- >200 compression ratio, release at 1500psi is very good.
- Able to operate at lower temperature due to hydrogen removal.
- No coke formation.
- Good technical team, teaming arrangement and strong management group.
- The combination of membrane and hydride compression is novel.
- The cartridge system for membrane is nice. Unclear if these can be hot swapped.
- Lower capital cost possible compared to conventional fuel processors by reducing component count and sub-system complexity.

Weaknesses
- Need to elaborate on the benefit and cost (energy, efficiency).
- Not clear how Pd membrane separator will ever be cost effective.
- Contaminants getting through the membrane will contaminate the hydride reactor. Unclear if there is an option for a guard bed.
- Should have shown membrane long term tests results.
- Where is capital cost estimate? What about substrate cost?
- Minimal time for integration and testing.
- Higher cost of operation.
- System efficiency appears lower than conventional.
- Not much data has been shown.
- How much sulfur can the membrane tolerate?
- No reason given for the delay in getting the MHC skid ready.
- Unclear what the "Advanced Prototype" is. And what will happen to this project after this phase of the project ends in June 2008.
- Membrane life and catalyst durability are of significant concern.

Specific recommendations and additions or deletions to the work scope

- More testing of integrated system needed.
- Independent risk assessment of concept needed.
- Flux data should not be proprietary. This is a performance parameter that has a target defined by DOE, just like parameters such as efficiency.
- Reviewers change or may not remember details from the previous year. Some information such as expected performance, if presented in past years, is worth repeating.
- Add the ability to track the effect of process conditions on contaminant levels, and ultimately on the cost of hydrogen.
- Test the membrane and catalyst under "real-world" application conditions before integrating the membrane reactor with the MHC.
- Provide commercialization plan for this system.

II.D.6 Novel Low-Temperature Proton Transport Membranes

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Project Start Date: March, 2007 (restarted after 2-year funding hiatus)
Project End Date: TBD

Objectives

- Identify optimal composition
- Development of thin electrolyte membranes
- Characterization of the electrical properties (ion transport) and chemical stability
- Evaluation of the thermomechanical properties
- Modeling and simulation of structure-property relationships
- Demonstrate laboratory-scale hydrogen separations with ability to scale-up

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) Fuel Processor Capital Costs
(G) Efficiency of Gasification, Pyrolysis, and Reforming Technology
(AB) Hydrogen Separation and Purification

Technical Targets

This project is conducting fundamental studies on new ceramic oxide proton (hydrogen) transport membranes. Insights gained from these studies will be applied toward the design and synthesis of hydrogen separation materials that meet the following DOE hydrogen separations targets:

- Flux: 200 scfh/ft^2
- Cost: <\$100/ft^2 of membrane
- Durability: >5 years
- Differential Pressure: 400-1,000 psi
- Hydrogen Recovery: 100%
- Hydrogen Purity: 99.99%

Accomplishments

- Coefficients of thermal expansion have been determined on several different lanthanum molybdenum oxide (LAMOx) compositions of proton conductor.
- Hydrogen flux measurements have been made on thick ceramic pellets.
- Thin membranes have been successfully formed via tape casting of homogeneous powders prepared by combustion synthesis.
- Tests have been carried out to determine that LaMOx is stable in CO$_2$ and sulfur containing environments.

✧ ✧ ✧ ✧ ✧

Introduction

Dense ion transport membranes provide a practical means of ensuring 100% selectivity, but to date the known materials are unable to achieve DOE requirements in terms of temperature stability, ion flux, durability and cost. This project began as a search for more robust ceramic oxides for proton conductors; it was determined that the recently discovered lanthanum molybdates, which are oxygen ion conductors at high temperature, also facilitated a significant hydrogen flux at moderate temperatures. The objective of this project is to establish whether these materials would be suitable as proton conducting ceramic membranes for hydrogen gas separation or membrane reactor applications.

Approach

To test the suitability of lanthanum molybdate based ceramics for hydrogen separation the following approach was used. First a high-temperature four-probe conductivity test compared dilute hydrogen to air to identify optimal compositions and temperature range. *In situ* X-ray diffraction (XRD) was used to verify the phase stability in environments including dilute hydrogen. A processing study was undertaken to determine the optimal conditions for synthesis of fully dense ceramic membranes via tape casting. A high-temperature single-ended fuel cell test station was constructed to measure the hydrogen flux as a function of gas partial pressure differential.

Results

Undoped lanthanum molybdate proved difficult to sinter to acceptable density, but this could be improved by doping with Nb or W on the Mo site. Even though the hydrogen fluxes recorded for W-doping at New Mexico Tech (NMT) and the National Energy Technology Laboratory (NETL) were lower than for Nb-doping, in the previous year we had determined that Nb-doping often led to undesired second phases, whereas W-doping did not. New powders with carefully controlled compositions at a 10% W-doping level were made using a modified combustion synthesis process. These powders were calcined, ball-milled, tape cast, punched, laminated, and sintered to form thin 1-inch diameter disks, suitable for sintering studies (Figure 1) and hydrogen conductivity testing.

The coefficient of thermal expansion (CTE) of the lanthanum molybdenum tungsten oxide (LMWO) calculated using high-temperature X-ray diffraction (HTXD) refined lattice parameters (Figure 2) showed that the CTE of LMWO is very large compared to a typical ceramic oxide (approximately 19E-6). Though the uncertainties in the lattice parameter calculations were high, a CTE value higher than reported in the literature was calculated which, if correct, would suggest the leading cause for the cracking of the pellet during testing is a CTE mismatch between the LMWO and the current testing set-up/materials. Validation of the CTE value using another technique (dilatometry) is planned in the next quarter.

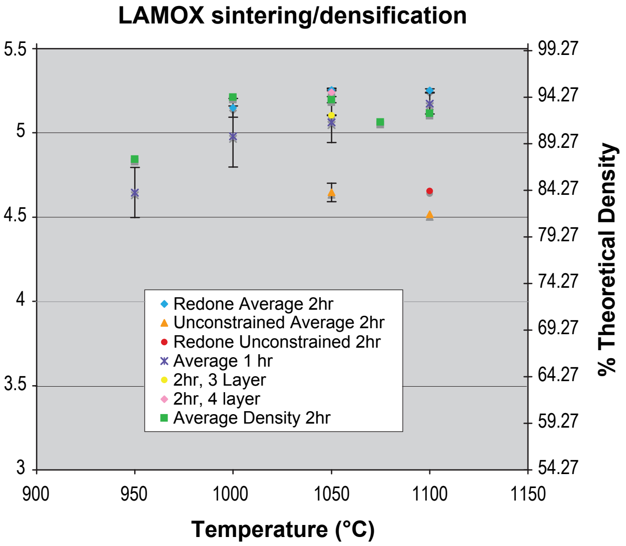

FIGURE 1. Densification data for 10% W-doped LAMOx, or LMWO, *i.e.,* $La_2Mo_{1.8}W_{0.2}O_9$, indicating T>1,000°C, t>1 hr, and use of sintering constraints yielded densities greater than 90% of theoretical, suitable for separation membranes and fuel cell electrolytes.

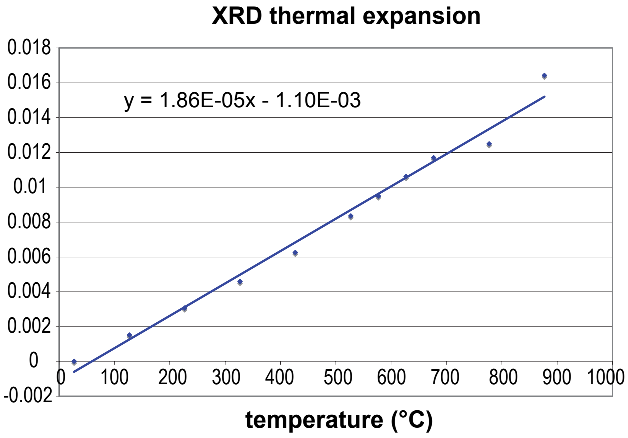

FIGURE 2. Lattice parameters (corrected for instrumental errors) determined from 25–900°C indicate a thermal expansion coefficient of 18.6x 10^{-6}.

Conclusions and Future Directions

LMWO provides an entirely new class (i.e., non-perovskite) of proton-conducting ceramic oxides for hydrogen separations. Initial hydrogen flux measurements conducted at NETL and NMT indicate that for practical application, the ceramic membrane needs to be very thin. Measured fluxes at 500°C correspond well with hydrogen fluxes measured in barium cerate at 800°C.

Special Recognitions & Awards/Patents Issued

1. T.R. Armstrong, E.A. Payzant, S.A. Speakman, M. Greenblatt, *Low Temperature Proton Conducting Oxide*, U.S. Patent Application # US 2006/0292416

II.D.4 High-Performance, Durable, Pd-Alloy Membrane for Hydrogen Separation

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Project Start Date: April 2007
Project End Date: September 2008

Objectives

- To provide advanced characterization and mechanical measurements of the palladium (Pd) alloy hydrogen gas separation membranes synthesized by Pall Corporation.
- Determine Pd alloy formation kinetics and microstructure.
- Test high temperature *in situ* mechanical properties of Pd foils and substrates.

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
(K) Durability
(P) Flux
(R) Cost

Technical Targets

This project is conducting fundamental materials support studies on metal supported Pd alloy hydrogen separation membranes, originating from Pall Corporation and the Colorado School of Mines. Insights gained from these studies will be applied toward the design and synthesis of hydrogen separation materials that meet the DOE 2010 hydrogen separations targets with respect to:

- Mechanical strength
- Cost (through optimization of the processing parameters)

✧ ✧ ✧ ✧ ✧

Approach

ORNL will provide unique capabilities in materials characterization - time-resolved high-temperature X-ray diffraction (XRD) analysis of Pd-Cu alloy membranes under controlled atmospheres, high-resolution electron microprobe analysis of the membrane microstructure, and high-temperature *in situ* mechanical testing of the tubular supports and foils. Membranes to be tested will be fabricated by Dr. Douglas Way (Colorado School of Mines), on substrates provided by Dr. Rick Kleiner of Pall Corporation. Although the project was conceived around providing unique materials development support to the Pall project, it is expected that the results will be useful across other DOE-supported research involving high-temperature supported membranes.

High temperature tensile testing of membrane/substrate tubes will be performed with a MTS 810 Material Test System utilizing hydraulic grips and a clamshell furnace. High temperature bladder collapse testing will comprise the pressurizing of a pressure vessel at temperature to create a collapsing stress on the membrane/tube assembly. Breakage of the tube will be indicated by a change in pressure of the interior of the tube and will be monitored by digital pressure transducers. High temperature tensile testing of the foils will be carried out using a foil test system consisting of a pneumatic actuator which applies a tensile stress to the foil in a controlled environment (atmosphere/temperature).

High-temperature XRD will be used to study the phase evolution of palladium alloy precursor films and lattice thermal expansion in simulated environments, including pure hydrogen gas.

Accomplishments

The project was initiated in April 2007. Experimental work is scheduled for September 2007.

II.D.7 Ultra-Thin Proton Conducting Membranes for H_2 Stream Purification with Protective Getter Coatings

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Project Start Date: May 3, 2007
Project End Date: September 30, 2010

Objectives

- Synthesize ultra-thin dense ceramic membranes on microporous supports.
- Incorporate sulfur getter technology into microporous support layer to address impurities in the feedstock.
- Demonstrate the ability of these ultra-thin membranes to separate H_2 at a high flux rate, meeting the DOE target of 250 scfh/ft^2.

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:

(K) Durability
(L) Impurities
(M) Membrane Defects
(N) Hydrogen Selectivity
(O) Operating Temperature
(P) Flux
(R) Cost

Technical Targets

As this project was funded beginning in May 2007, the following represents the targets we plan to achieve.

The thrust of this project is the investigation of the efficiency of thin dense ceramic membranes to separate H_2 at elevated temperatures via proton conduction. Insights gained from these studies will be applied toward the design and synthesis of hydrogen separation modules to meet the following DOE 2010 hydrogen separation targets:

- Flux: 250 scfh/ft^2
  - Deposition of an ultra-thin film will enhance the flux rate per square foot by minimizing the path length for protons to be conducted through the dense oxide.
- Hydrogen quality: 99.99% of total (dry) gas
  - The conduction mechanism of separation ensures high purity H_2 as only hydrogen is conducted through the membrane.
- Operating capability: 400 psi
  - The use of a microporous support structure will enhance the ability of the membrane to withstand significant pressure drops.
- Durability: 26,280 hours between membrane replacement
  - Dense ceramics are resistant to steam. The development of a “getter support” on the feed side of the stream addresses other impurities, such as sulfur, and will support a lengthened membrane lifetime.

Approach

Our approach to meeting the parameters for hydrogen separation membranes focuses on optimizing the H_2 flux through the membrane while also removing feedstock impurities. This project will address the separation of high-purity H_2 (>99%) from various feed streams using supported thin proton conducting ceramic membranes, such as $BaCeO_3$ and $LaBO_3$ [1, 2]. These dense oxide membranes exhibit 100% selectivity, resulting in extremely high-purity H_2. As thinner membranes have higher fluxes, over the course of this investigation, we will systematically synthesize and test membranes with a range of thicknesses. The effective pore size of the support material affects the minimum thickness of the membrane; i.e. support materials with smaller pore sizes can support thinner membranes.

Sulfur impurities that are typical of many feedstocks will be addressed through the deposition of a getter material, such as ZnO, onto the support structure. Both the getter and the proton conducting materials will be deposited using atomic layer deposition (ALD) thin film methodology, which is capable of producing layers on the Angstrom scale.

Accomplishments

- Successfully deposited 450 Å conformal ZnO coating on mesoporous alumina support using ALD. Powder X-ray diffraction confirmed presence of ZnO phase.
- Small loss in support surface area after deposition of ZnO (from 1.6 m^2/g to 1.2 m^2/g) was noted using BET analysis, indicating that the porosity of the support is intact.
- After surveying current proton conducting ceramics, we have decided to pursue $BaTiO_3$ and $BaCeO_3$ [3, 4]. The proton conduction in these materials is high, and the chemistry is amenable to ALD film synthesis. Development and testing of ALD deposition parameters are underway.

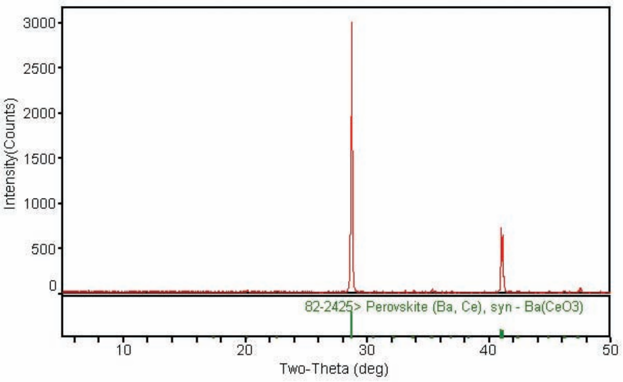

FIGURE 1. Powder X-ray Diffraction Scan of Synthesized $BaCeO_3$ (Reference peak positions from PDF # 82-2425 are shown below the scan in green.)

- $BaCeO_3$ ceramic was synthesized by solid state methods. The powder diffraction scan, shown in Figure 1, identifies the product as orthorhombic $BaCeO_3$ [5].

Planned activities for remainder of FY 2007

- Perform scanning electron microscopy to confirm the ZnO coating is conformal.
- Design and build permeation unit.
- Perform permeation measurements to confirm that acceptable levels of porosity of the support remain after ZnO coating is deposited.
- Synthesize bulk $BaTiO_3$ via solid state techniques.
- Test the H_2 permeation of both $BaTiO_3$ and $BaCeO_3$ in bulk form.
- Test sulfur impurity uptake and regenerability of ZnO getter coating.
- Deposit proton conducting oxide ($BaTiO_3$ or $BaCeO_3$) on alumina support.

References

1. Shimura, T.; Fujimoto, S.; Iwahara, H. Solid State Ionics 143 (2001) 117.

2. Alberti, G.; Casciola, M. Solid State Ionics 145 (2001) 3.

3. Kreuer, K. D.; Schonherr, E.; Maier, J. Solid State Ionics, 70/71 (1994) 278.

4. Kreuer, K. D. J. Solid State Ionics, 125 (1999) 285.

5. Powder Diffraction File reference number 82-2425.

II.D.5 Bulk Amorphous Hydrogen Purification/Separation Membranes

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Project Start Date: May 1, 2007
Project End Date: Project continuation and direction determined annually by DOE

Objectives

- Demonstrate the feasibility of using metallic glass materials in bulk form for novel advanced hydrogen purification membranes.
- Develop optimized bulk amorphous alloy compositions for hydrogen separation membranes.

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 Cost
(C) Operation and Maintenance (O&M)
(F) Control and Safety
(N) Hydrogen Selectivity
(T) Capital Cost and Efficiency of Biomass Gasification/Pyrolysis Technology

Technical Targets

DOE 2010 Separation Membrane Targets:

- Flux rate: 250 scfh/ft^2
- Cost: <\$1000/ft^2 (module cost including membrane material)
- Durability: 26,280 hours

Approach

Separation and purification membranes must have high hydrogen solubility, high diffusivity and catalytic activity on the surface of the membrane. Hydrogen separation as described in this work can be accomplished by the use of bulk amorphous materials (namely, bulk metallic glasses) permeable to hydrogen. The focal point of the SRNL effort will be on the development and optimization of a bulk amorphous material for the dense metallic-based membrane substrate.

The current generation of gas separation membranes is based on palladium/palladium alloys used either independently or in conjunction with porous ceramic supports. Pd/Pd alloys have been known to possess the ability to dissolve considerable amounts of hydrogen and to demonstrate increasing permeability with increasing pressure differential and temperature. However, the major drawbacks to their industrial use are the high cost for Pd, the relatively low flux, and that during cycling above and below a critical temperature, an irreversible change takes place in the palladium lattice structure which can result in significant damage to the membrane. SRNL has previously worked with thin section (melt–spun ribbons) of metallic glass materials for membrane applications, however, with the relatively new ability to cast fully amorphous metallic glasses in bulk sections. As a result, a new opportunity has opened for bulk metallic glasses (BMG) as hydrogen membranes. The ability to readily cast BMG alloys will allow for easier fabrication of membranes – machine thin membranes from larger BMG casting – and will also ease mass production challenges in comparison to thin section (melt spun) metallic glass ribbons. BMG alloys are traditionally processed from multi-component systems comprised of metallic species of varying atomic size. It is this vast difference in atomic sizes that results in slow diffusion/redistribution kinetics and allows for deep undercoolings to the point of freezing in the "liquid" structure to produce amorphous metallic alloys at relatively slow cooling rates (10-100 K/s). These BMG alloys have been shown to possess high permeation rates. For example, the permeation rate for a --Zr-Al-Co-Ni-Cu BMG alloy (1.13×10^{-8} mol/m s Pa$^{1/2}$) is comparable to the permeation rate measured for pure Pd metal. Furthermore, these BMG alloys have also been shown to possess high elastic toughness and excellent resistance to hydrogen degradation. Both of these properties, high permeation and high elastic toughness, potentially makes these materials attractive for gas separation membranes.

Accomplishments

Funding to support this project did not begin until May of 2007. As a result, the initial focus has been to identify commercial available metallic glass product forms for testing and to acquire these materials. To date, materials from three different alloy systems have been acquired and are as follows: 1) Zr-Cu-Ni-Al-Y bulk metallic glass plate from Howmet Research, 2) Fe-based metallic glass film from MetGlass Inc, and 3) Co-based metallic glass film from Metglass Inc. As an initial screen of these alloy systems for hydrogen permeability, high throughput electrochemical permeation testing following ASTM standard G-148 has been initiated. This test technique provides a safe, simple method for screening multiple alloy systems prior to conducting gaseous hydrogen testing. The following accomplishments have been made:

- Acquired metallic glass materials from commercial vendors.
- Set-up Devanathan-Stachurski electrochemical hydrogen permeation test cell.
- Ordered Gamry potentiostat for electrochemical testing.
- Drafted test plan and finalized testing hazards analysis package.

II.D.2 Water-Gas Shift Reaction via a Single-Stage Low-Temperature Membrane Reactor

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Project Start Date: July 1, 2005
Project End Date: June 30, 2008

Contract Number: DE-FG36-05GO15092

Objective

The water-gas shift (WGS) reaction has been considered one of the less efficient unit operations for hydrogen production via steam reforming. A highly efficient and low temperature membrane-based WGS reaction process will be developed in a bench-scale first, then tested in a pilot-scale and finally demonstrated in a field test unit. Our existing membranes will be screened and then tailored specifically for the proposed process and reactor. In parallel, hydrogen production cost will be determined and the system integration requirement will be defined for commercialization.

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:

(K) Durability
(M) Membrane Defects
(Q) Testing and Analysis

Technical Targets

Technical targets for microporous membranes are listed as follows:

- Flux Rate - 100 to 200 scfh/sq foot for 10 to 20 bar pressure, respectively
- Membrane Material and All Module Costs - \$60-80/ft^2 of membrane
- Durability - >1,100 hours
- Operating Capability - 500 psi
- Hydrogen Recovery - 80% of total gas
- Hydrogen Quality - >95% of total dry gas

Accomplishments

- We have completed the bench top experimental study and mathematical simulation to demonstrate our HiCON process to deliver 99+% CO conversion with 97-99% purity and 98-75% H_2 recovery via a simple membrane reactor (MR) process, uniquely suitable for distributed hydrogen production.
- Although membranes are not ideal to deliver 99.999% purity with trace CO contamination, our study indicates that a cost acceptable post treatment unique to our proposed process can achieve this target. This, in conjunction with our HiCON process, offers a practical and economically viable process to meet the stringent feed quality requirement for a proton exchange membrane (PEM) fuel cell.
- We have established a pilot-scale testing facility for performing a pilot-scale test to verify the optimized HiCON process using a full-scale membrane tube with synthetic feed, which is expected to be completed by the end of FY 2007.

In short, with the budget available, we anticipate to complete the minimum tasks required to take this HiCON process to the next step for field demonstration.

✧ ✧ ✧ ✧ ✧

Approach

Our overall technical approach includes three steps as follows:

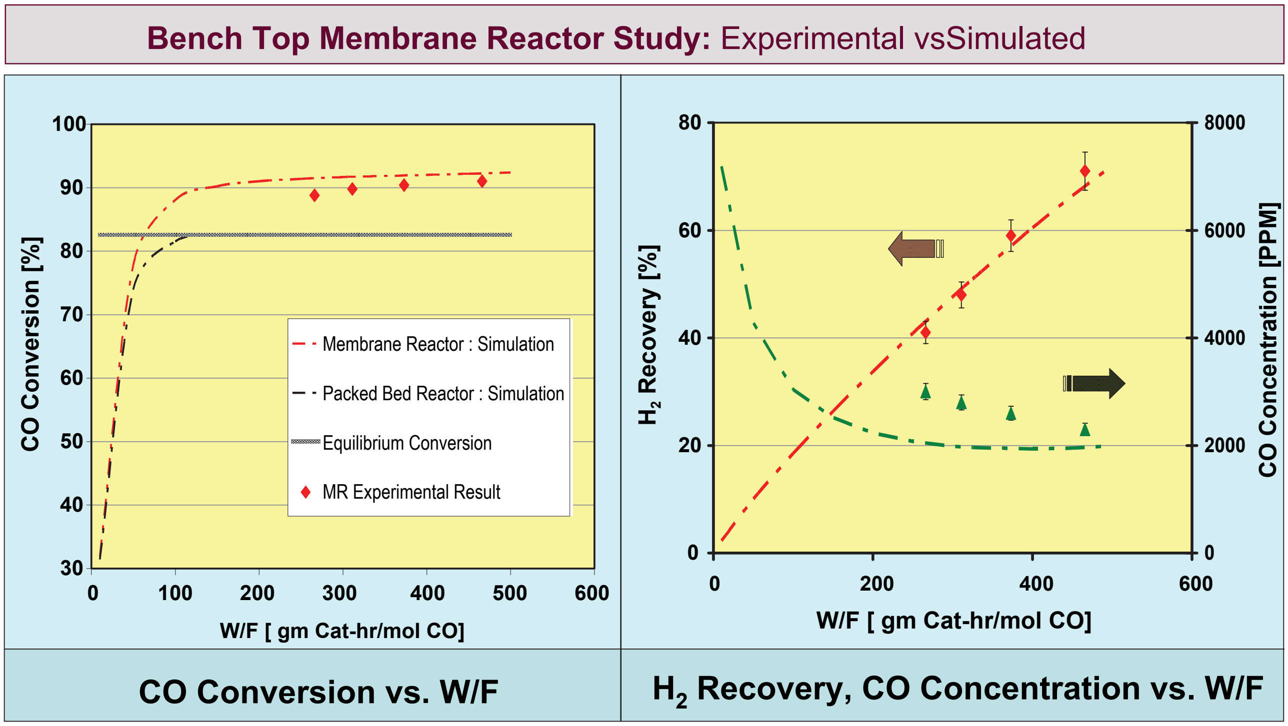
1. Bench-Scale Verification (1st to 15th month)
   - Evaluate membrane reactor: use existing membrane and catalyst via math simulation.
   - Experimental verification: use upgraded membrane and existing catalyst via bench unit.
   - Validate membrane and membrane reactor performance and economics.

2. Pilot-Scale Testing (16th to 24th month)
    - Prepare membranes, module, and housing for pilot testing.
    - Perform pilot-scale testing.
    - Perform economic analysis and technical evaluation.
    - Prepare field testing.
3. Field Demonstration (25th to 36th month)
    - Fabricate membranes and membrane reactors and prepare catalysts.
    - Prepare site and install reactor.
    - Perform field test.
    - Conduct system integration study.
    - Finalize economic analysis and refine performance simulation.

Results

In the Year 1 report, we have presented the experimental data of CO conversion in a membrane reactor to verify the performance prediction from the mathematical simulation. During this second year, we have concentrated in the evaluation of the CO impurity level, and hydrogen recovery potential. Similar to the FY 2006 result, about 8-10% enhancement of the CO conversion was accomplished by the MR over the conventional packed bed for the ratio of catalyst dosage to feed flow rate (W/F) between the range of 300-500 g-cat-hr/mol CO as shown in Figure 1. With the bench-top facility, we have a 10” long Compact Membrane Systems, Inc. (CMS) membrane; hydrogen recovery from 40-70% can be achieved experimentally as shown in Figure 2. The simulation predicts the hydrogen recovery very well. On the other hand, CO concentration at ~2,000 to 3,000 ppm is obtained under the experimental condition employed here. In comparison, ~2,000 ppm CO is predicted for this range of W/F. The simulation underestimates the CO concentration at the low range of W/F, i.e., 200-300 g-cat-hr/mol CO. This range of discrepancy in CO is considered acceptable for our purpose of obtaining an order of magnitude level of CO for the post-treatment.

Since an extremely high purity of hydrogen (i.e., 99.999%) is required for the PEM-type fuel cell application, it is not practical for our CMS membrane based upon its micro-porous structure to deliver hydrogen purity to meet the specification. We believe that a membrane reactor-based process can be developed, called HiCON, with the total hydrogen yield of near 90% through our process as described in Figure 3. Since hydrogen product requires post compression for storage at the distributed production site, the post treatment can be implemented at a pressure that is economically feasible. Presently three different levels of hydrogen purity are targeted from our HiCON process as described in Figure 3. In addition, the



W/F: Ratio of Catalyst Dosage to Feed FlowRate

FIGURE 1. Performance of Membrane Reactor: CO Conversion, Hydrogen Recovery and CO Contaminant vs. W/F

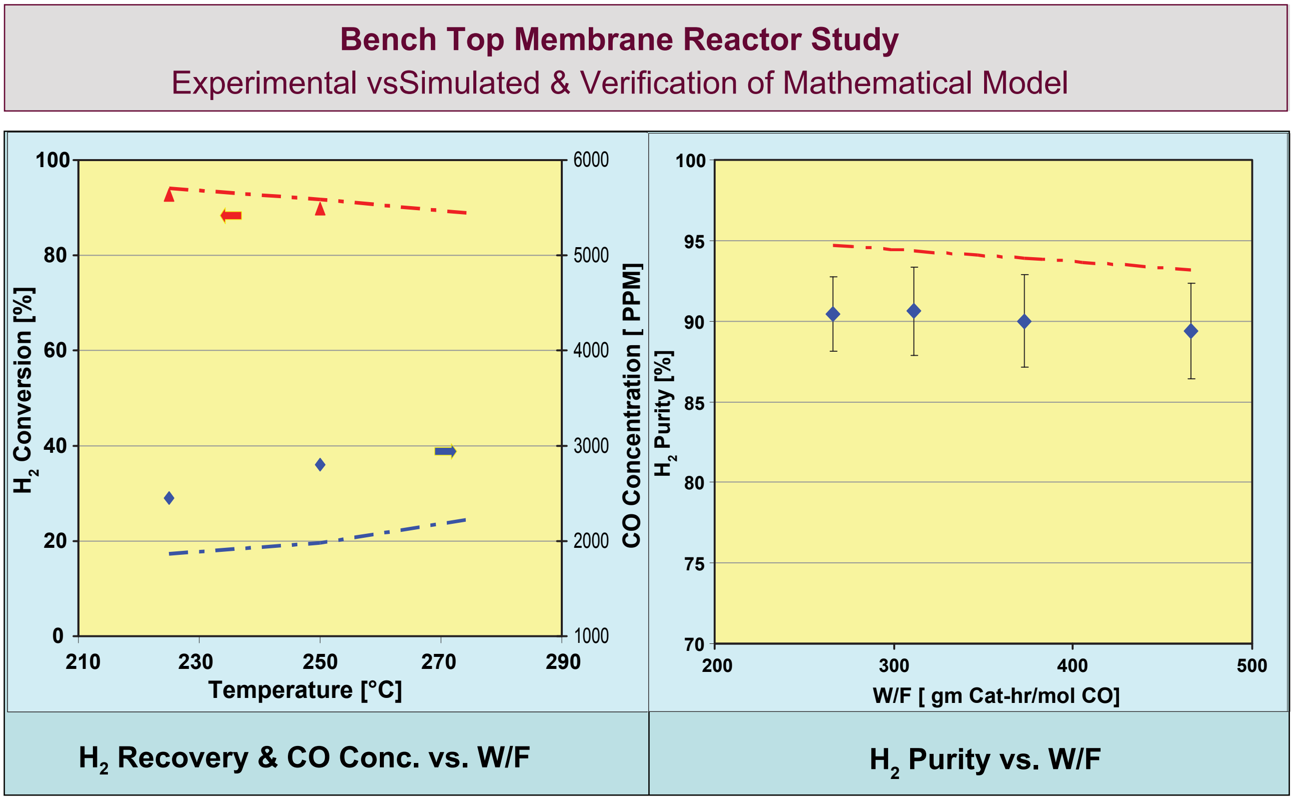
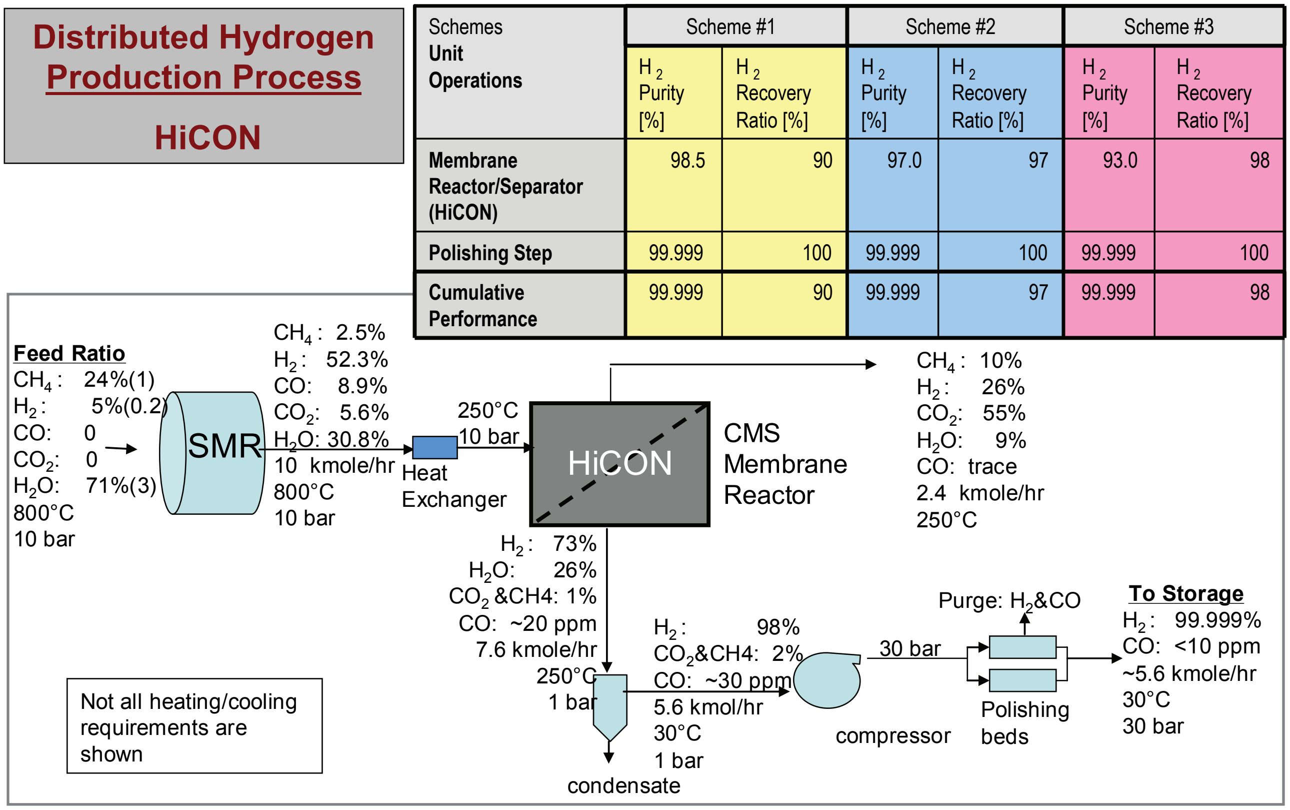


FIGURE 2. Performance of Membrane Reactor: Effect of Temperature on CO Conversion and CO Contaminant Level and Effect of W/F on Hydrogen Purity



Schemes Unit Operations	Scheme #1		Scheme #2		Scheme #3	
	H_2 Purity [%]	H_2 Recovery Ratio [%]	H_2 Purity [%]	H_2 Recovery Ratio [%]	H_2 Purity [%]	H_2 Recovery Ratio [%]
Membrane Reactor/Separator (HiCON)	98.5	90	97.0	97	93.0	98
Polishing Step	99.999	100	99.999	100	99.999	100
Cumulative Performance	99.999	90	99.999	97	99.999	98

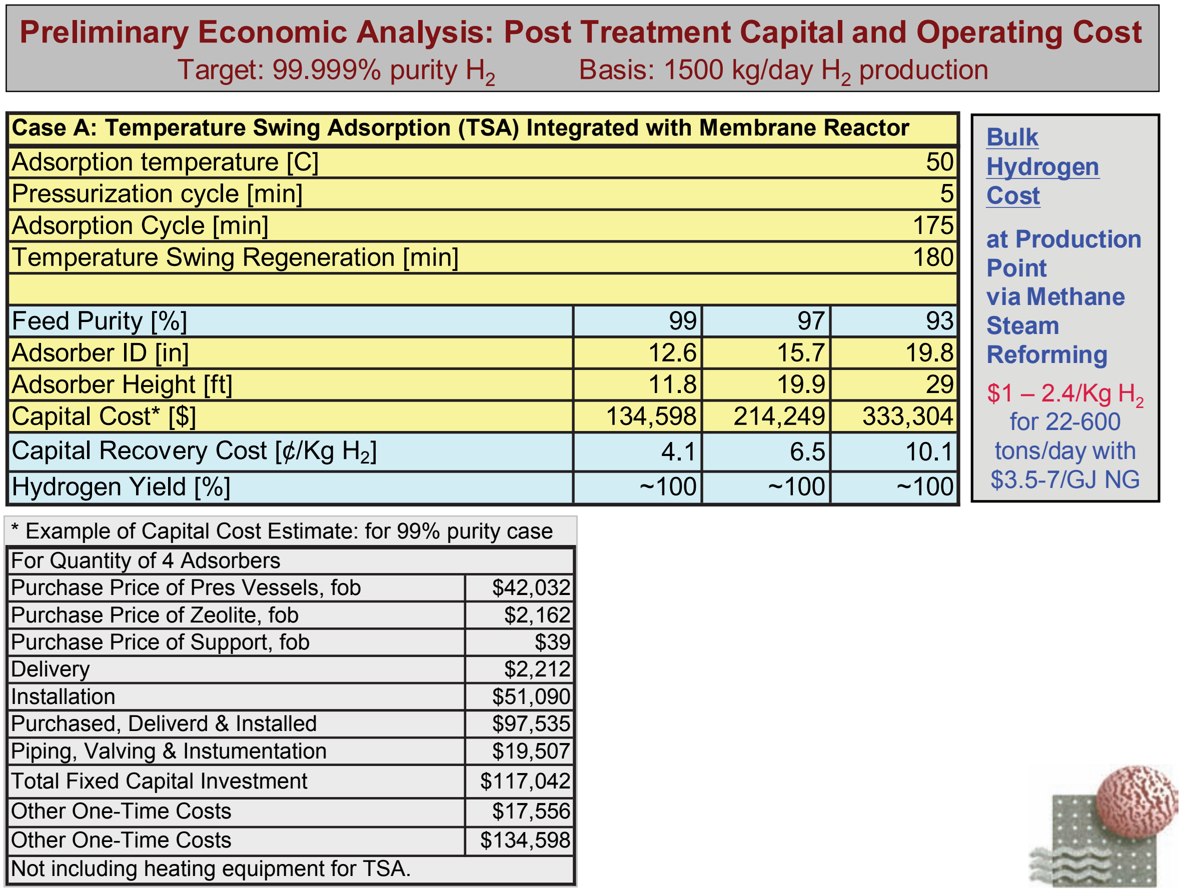
FIGURE 3. Process Diagram with Stream Composition for Steam Reforming with Our HiCON Process in Conjunction with Post Treatment

concentrations of the CO, N_2 and other contaminants in the hydrogen produced from our HiCON are much lower than that of CO_2; these trace contaminants are expected to be removed within the same absorber of our post treatment process. No separate post treatment is necessary for each contaminant.

The pressure swing adsorption (PSA) operation is conventionally practiced for hydrogen recovery from the steam reformer with a typical 70-85% hydrogen recovery. If a product stream with 99.999% purity is required, the hydrogen recovery is believed to be close to the low end of the recovery ratio. As indicated in Figure 3, the hydrogen recovery ratio is much higher if temperature swing adsorption (TSA) is employed. However, the use of our proposed TSA may require a longer bed due to the much longer cycle time, which results in the absorber bed length increase and consequent capital cost increase. A preliminary economic analysis has been performed as presented in Figure 4. Our cost analysis shows that about 5 cents/kg hydrogen produced as the capital recovery cost detailed in Figure 4. No operating cost is included. This range of cost is very insignificant in consideration of the current bulk hydrogen production cost of $1.00-2.40 per kg hydrogen. The distributed hydrogen production cost approximates toward the high end of this range. Thus, we believe that even with 100% safety factor, our post-treatment cost remains to be very acceptable. More importantly, this post-treatment offers an insurance policy for the upstream membrane reactor; the hydrogen product purity can be flexible within the range of 97-99%.

Conclusion and Future Directions

Our FY 2007 work indicates that our experimental results are very consistent with the mathematical prediction with regard to the important aspects of the membrane reactor performance, including hydrogen purity, CO contaminant level, CO conversion and effect of temperature. This model along with the reaction kinetic equation obtained here has been used to perform the process development and optimization study. Hydrogen purity of 99.999+% with the hydrogen recovery ratio of 90% can be delivered from our HiCON process based upon the simulation. For the remainder of the project, we will concentrate on the experimental



Preliminary Economic Analysis: Post Treatment Capital and Operating Cost

Target: 99.999% purity H_2 Basis: 1500 kg/day H_2 production

Case A: Temperature Swing Adsorption (TSA) Integrated with Membrane Reactor			
Adsorption temperature [C]			50
Pressurization cycle [min]			5
Adsorption Cycle [min]			175
Temperature Swing Regeneration [min]			180
Feed Purity [%]	99	97	93
Adsorber ID [in]	12.6	15.7	19.8
Adsorber Height [ft]	11.8	19.9	29
Capital Cost* [$]	134,598	214,249	333,304
Capital Recovery Cost [¢/Kg H_2]	4.1	6.5	10.1
Hydrogen Yield [%]	~100	~100	~100

Bulk Hydrogen Cost

at Production Point via Methane Steam Reforming

$1 – 2.4/Kg H_2 for 22-600 tons/day with $3.5-7/GJ NG

* Example of Capital Cost Estimate: for 99% purity case

For Quantity of 4 Adsorbers	
Purchase Price of Pres Vessels, fob	$42,032
Purchase Price of Zeolite, fob	$2,162
Purchase Price of Support, fob	$39
Delivery	$2,212
Installation	$51,090
Purchased, Deliverd & Installed	$97,535
Piping, Valving & Instumentation	$19,507
Total Fixed Capital Investment	$117,042
Other One-Time Costs	$17,556
Other One-Time Costs	$134,598
Not including heating equipment for TSA.	

FIGURE 4. Economic Analysis of Our Proposed Post Treatment Based Upon Temperature Swing Adsorption Process

verification of the above performance using a pilot-scale unit. A barricade facility has been established to perform this test. Once the test is complete, our economic analysis will be refined and finalized to incorporate the post-treatment cost performed by an outside vendor. Depending upon the budget availability, the field demonstration with a pilot-scale unit as originally planned will be pursued.

Publications and Presentations

1. Tsotsis, T.T., Sahimi, M., Fayyaz-Najafi, B., Harale, A., Park, B.G., Liu, P.K.T., "Hybrid Adsorptive Membrane Reactor," U.S. Patent Application, February 2006.

2. Harale, A., Hwang, H., Liu, P.K.T., Sahimi, M., and Tsotsis, T.T., Experimental Studies of a Hybrid Adsorbent-Membrane Reactor (HAMR) System for Hydrogen Production," In Press *Chem. Eng. Sci*.

3. Ciora, Rich J. Jr, Paul KT Liu, and Tho T. Tsotsis, "Hydrogen Separation using Carbon Molecular Sieve Membranes", Pittsburgh Coal Conference, Pittsburgh, PA, 2006.

4. Harale, A., H. Hwang , M. Sahimi , T.T. Tsotsis, "A Hybrid Adsorbent-Membrane Reactor (HAMR) for Hydrogen Production", *AIChE Annual 2006 Meeting,* San Francisco, CA, Abstract Reviewed Paper 2006-11-14.

5. Harale, A., H. Hwang, P.K.T. Liu, M. Sahimi, T. T. Tsotsis, "Experimental Studies of a Hybrid Adsorbent-Membrane Reactor (HAMR) System for Hydrogen Production", *9th International Conference on Inorganic Membranes (ICIM 9),* Lillehammer, Norway, Abstract Reviewed Paper 2006-06-25.

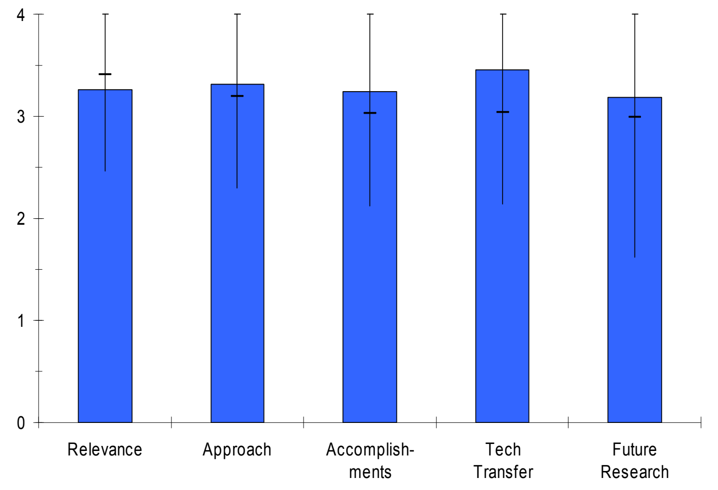
Project # PD-07: Carbon Molecular Sieve Membrane as Reactor for Water Gas Shift Reaction

Paul KT Liu; Media & Process Tech.

Brief Summary of Project

Media and Process Technologies has developed a membrane with high efficiency conversion capable of converting the CO created during on-site hydrogen production to 99+% as opposed to approximately 70% through the use of high temperature shift alone. The high conversion is a result of the new membrane configuration. A pilot test of the new membrane in a reactor will be conducted at the end of FY 07. Process simulation; hydrogen production economic analysis; design, simulation and economic analysis of the polishing step to achieve 99.999% purity will follow in preparation for conceptual design of the field test unit.

Overall Project Score: 3.3 (8 Reviews Received)



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.3** for its relevance to DOE objectives.

- Viable concepts for combining reforming/shift/separation unit processes are vital to a long term, low system cost.
- The contractor is focusing on the development of microporous membranes which are an area of interest to DOE for hydrogen separation.
- The presentation was extremely vague on the specific targets required by DOE. No cost estimates were provided. In addition, no clear flux targets were provided – just a vague comparison to metallic membranes – which appears low and in odd units.
- The work does address process intensification – which is a key area of DOE interest.
- The temperatures being considered are low – 200+ degrees. There should be consideration to get this a bit higher – maybe into the HTS range.
- Goals of this program are well aligned with the DOE Hydrogen Program.
- Interesting work, but not a critical piece of the puzzle for hydrogen success. Conventional WGS works pretty well and isn't overly expensive.
- Hydrogen purification/separation is a critical component of hydrogen production.
- Developing reactive separation membranes that do not use expensive materials (such as Pd-alloys) can have very significant payoff in overall hydrogen production costs.
- Need to address the effect of non-infinity separation factors for microporous membranes.
- A membrane within the water-gas shift reactor should benefit hydrogen production pathways that use reforming.
- Carbon molecular sieve membrane as reactor/separator for water-gas shift reaction will be developed in this project. Streamlining unit operations involving CO conversion/H_2 separation and purification is very relevant to overall DOE objectives.
- Developing a small, more cost effective (capital and operating) hydrogen clean up system is relevant to the DOE objectives.

Question 2: Approach to performing the research and development

This project was rated **3.3** on its approach.

- Well thought out and described.

- The approach is reasonably straightforward and involves general testing of existing membrane materials. There is no significant novel development, for example, no new membrane materials are being developed.
- Scale-up to a larger size unit should provide valuable information.
- Catalyst testing and membrane development appear to be occurring along two separate paths. They need to be integrated together into a single development path.
- Testing of membrane performance is comprehensive with a clear line of sight to DOE hydrogen production cost targets and reliability.
- Development of a mathematical model will be critical to ultimate process design. This is a very sound and comprehensive approach to ultimate process design.
- Nice plan for success, including scale-up, pilot testing, economic analysis, safety, and end-user tests.
- Unclear what the hydrogen pressure is exiting the membrane.
- This project is using a process development approach to determine the needed hydrogen purification and reaction kinetics to meet the performance targets.
- Using TSA-based adsorption as the final polishing step offers the potential to meet the desired hydrogen purity levels.
- The target CO value should be decreased to 1 ppm CO for distributed hydrogen production for dispersing to fuel cell vehicles.
- There will be other impurity level constraints in addition to CO, for these systems that must be met for the systems to be deployed.
- A membrane within the water-gas shift reactor will improve the CO conversion and/or reduce the size of the water-gas shift reactor.
- This process produces hydrogen at low pressure which then needs to be compressed. The ultimate measure is in the cost of hydrogen, where the hydrogen is at 300 psi.
- Unclear if the presence of H_2S and water affect the membrane.
- Team will develop a reactor/separator system capable of producing 99.999% pure H_2. To achieve this goal they will incorporate carbon molecular sieve membrane with a water-gas shift catalyst and eliminate the two separate water-gas shift reactors (low and high-temperature). By removing hydrogen using the molecular sieve membrane, they will shift reaction equilibrium.
- It is a well planned approach.
- Presenter did not mention the barriers addressed in their project. This information is missing in their slides.
- The approach to generate bench scale data, generate a model, extrapolate to pilot scale, and then validate the model is standard engineering process.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.2** based on accomplishments.

- Benchtop experiments yield useful data.
- Good comparison of simulation results and test data.
- The technical progress is difficult to judge. Although actual results are alluded to and appear to be included on some of the graphs, much of the work appears to be mathematical modeling. However, it is not clear which are results produced from this work and what is from the literature. It appears that the project has been minimally funded (30%) so it is not clear how much actual progress has been made.
- The use of microporous membranes will not likely give the most effective separations. The purity and percent recovery will remain a concern and the contractor has not done a lot to improve on the situation. The separation mechanism itself will likely limit these parameters.
- Impressive testing of membrane in real-world conditions by using a slip stream from a hydrocracker that included impurities and higher hydrocarbons.
- Very good technical accomplishments such as development of a model and demonstration of a membrane in a small scale reformer confirmed by industry end user.
- Great verification of model with experimental data.
- Excellent use of analysis during project and by end-user.
- Included polishing step which shows excellent systems understanding.
- Great pilot testing plan and results; although, membrane longevity was not discussed.

- Appropriate trade-off between lower purity and higher recovery, completed with polishing.
- They have completed modeling and some experimental verification at the component level.
- The hydrogen flux at 200 to 250 C is comparable to, or better than, that in Pd-alloy systems.
- The Pd-alloy systems typically operate at much higher temperatures, yielding 20 to 50 times hydrogen fluxes; thus, comparing the performance of the carbon molecular sieve membrane at the lower temperature is not very meaningful.
- Although the presenter indicated that the carbon molecular sieve membrane material is stable, the data show significant degradation from the 3 hour values to the 100 hour values.
- The model seemed to over-predict the observed performance indicating that the model's parameters need adjustment.
- They presented good data which indicates promising results.
- Insufficient explanations and legends lead to confusion.
- Mathematical model has been experimentally verified.
- HiCON process has been developed for the small-scale reformer by the end user of this technology.
- Process optimization study demonstrated that 97-99% H_2 purity can be accomplished. This is lower than the objective of producing 99.999% H_2 purity. The team has plans to obtain higher purity.
- This project start date was October 2003. Only modest technical accomplishments have been achieved.
- The technical accomplishments to date are somewhat confusing. The stated goal is 99.999%, but reports that 97-99% clean-up was accomplished and that a non-defined adsorbent would polish the hydrogen to 99.999% with CO apparently being the principle impurity at < 10 ppm. This must be addressed.
- The <10 ppm CO target seems out of step with fuel cell targets of < 0.2 ppm.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.5** for technology transfer and collaboration.

- Partner collaboration and contributions were not clear.
- Technology transfer and industry involvement appears minimal. There are some academic publications. The intro slides did list involvement of other partners, but their roles and contributions are not clear. It appears that the testing is primarily being conducted by MPT and the University of Southern California. The industry partners need to be more involved to ensure that the developed technology is worthwhile.
- Impressive collaboration between academia and industry; this project meets the ideal for partnership; result is the leveraging of new technology from academia (membrane) applied with an eye toward ultimate commercialization (provided by industry end user).
- Excellent inclusion of end-user!
- The project has good collaborations; academic, industry, and end-user.
- Having Chevron involved in the project is helpful to keeping a realistic check on the project's progress.
- Good combination of collaborators - include academic, manufacturer, and user.
- Good team. Team includes USC (for membranes research), Johnson Matthey (for catalyst development), and Chevron (end user).
- Seems to have good collaboration among team members.
- Working with USC, JMI and Chevron is a very good plus.
- Was consideration given to include one of the specialty gas companies (APCI, Air Liquide, BOC/Linde, Praxair)?

Question 5: Approach to and relevance of proposed future research

This project was rated **3.2** for proposed future work.

- Future direction is proceeding towards testing of a moderate scale membrane assembly. This appears to be an existing apparatus and testing should be straightforward.
- The testing needs to incorporate realistic gas feeds.
- Proposed future work is valuable; glad to see that it will include an economic analysis by industry end user; this ensures an objective, reality based analysis.

- Analysis should include a comparison with conventional, proven H_2 production technologies (e.g. steam methane reforming, water-gas-shift, pressure swing adsorption).
- Not a lot of future research proposed. Depends on funds availability?
- Researchers should present ideas for future research.
- Pilot-scale testing would help to obtain the data needed to validate the performance models.
- The proposed economic analysis is needed to substantiate the potential cost attractiveness of this process.
- In particular, the use of the polishing step needs more careful analysis, as the ultimate purification may add more to the cost than expected on the basis of a preliminary analysis.
- The pilot-scale testing and economic analysis are both needed.
- In FY2007, the team plans to complete pilot scale testing using a single, full-scale hydrogen selective membrane and synthetic feed to demonstrate the optimized HiCON process. End user will complete preliminary economic analysis.
- Field demonstration will be done in or after 2008.
- The above plans are reasonably good. The PI presented detailed path for moving forward.
- The future work proposed makes sense and fits in with the stated plan.
- Work to improve the effectiveness should be included.

Strengths and weaknesses

Strengths

- Good that a preliminary economic estimate of capital cost was made.
- Overall, a very good science and engineering effort.
- Straightforward test project that should be able to be completed in a minimum amount of time.
- The project has a good combination of modeling and experimental efforts.
- The project has a good combination of academic and industrial collaboration.
- A membrane can eliminate moving parts and switching valves of PSA based systems.
- A membrane will shrink the shift reactor.
- Good team.
- Good planning.
- The design as portrayed appears to be applicable for a number of merchant grade hydrogen applications and thus applicable.

Weaknesses

- Preliminary economic analysis capital cost estimate did not seem to properly include fabrication costs. Seems to be a materials summary only.
- The contractor needs to provide more details on the experimental conditions. Only limited data is provided to evaluate the work, and this makes it almost impossible to assess the actual state of the work.
- Although the presenter referred to 10 ppm CO as being readily achieved, during the Q&A it was stated that CO was at 20 to 30 ppm. It was not clear what caused this discrepancy.
- Compression energy is quite significant, particularly for compressing the product gas from 15 psig to 300 psig. This must be included in the process simulation; otherwise comparisons with alternative approaches will not be consistent.
- Not specifically a weakness, but it is not clear why the test feed gas had up to 31% nitrogen and only 44% hydrogen in the separation verification tests; this composition is reflective of ATR reformate rather than SMR reformate.
- If a PSA can remove the CO down to 0.1 ppm and a significant retentate is needed in the burner, then why use a membrane to convert CO, especially if the membrane will work only at low temperatures?
- Standard information about barriers addressed that was present in all other presentations is missing here.
- This project started in October 2003 and modest accomplishments were reported over the past three years — what are the reasons?
- What about long term durability of carbon molecular sieve membranes under process operating conditions?
- They missed on clean up – 99 vs. 99.999%.
- There is a lack of suggestions to determine the cause of the miss.

- There is a lack of a plan to correct the miss.
- The energy requirement for storage is not fully included. H_2 supplied at 15 psi not 300(?) psi.

Specific recommendations and additions or deletions to the work scope

- The contractor needs to finish the work as proposed and provide some solid technical data - particularly on the reaction conditions.
- DOE needs to provide the conditions to the contractor for testing.
- Appears to be an excellent research team. Suggest DOE provide additional funds to carry this project to completion and request involvement in other R&D efforts.
- The permeate from actual reformate should be analyzed in great detail to identify all species that makes it into the hydrogen. One set of data from a pilot test shows C1 and C2 species in the hydrogen.
- Very high hydrogen recoveries are not necessary since the retentate can be sent to the burner to generate heat for the reforming reaction.
- The use of a membrane is much more effective if it can operate at higher temperatures, where the CO conversion kinetics and perhaps the permeance are even faster.
- Considerable data has been shown. These should to be evaluated closely and in detail.
- No change is needed. Continue the work.
- Investigate the escape.
- Evaluate the application of a less extensive clean-up for other merchant usage (this might free up existing facilities for the higher quality demand expected in 2015-2020 time frame).

II.D.3 High Performance Palladium-Based Membrane for Hydrogen Separation and Purification

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Contract Number: DE-FG36-05GO15093

Subcontractors:
- Colorado School of Mines, Golden, CO
- Chevron Energy Technology Company, Richmond, CA
- Oak Ridge National Laboratory, Oak Ridge, TN

Project Start Date: July 1, 2005
Project End Date: June 30, 2010

Objectives

- Establish the technical and economic viability for use of a Pd alloy composite membrane in a distributed H_2 production system as per DOE targets.
- Develop a Pd alloy membrane on AccuSep® porous metal tube substrates:
  - Optimize the formation of the membrane/substrate.
  - Fabricate functional gas separation tubes and modules.
  - Test performance and durability.
  - Characterize and analyze membranes.
  - Compare results against Dense Metallic Membrane targets established in the RD&D plan.
- Design a commercial scale membrane module.
- Conduct an economic analysis:
  - Analyze economics of membrane use in a gas separation system including capital and operating costs and energy requirements.
  - Compare projected system performance to DOE target goals.
  - Compare to the pressure swing absorption (PSA) process.

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 April 27, 2007:

(A) Reformer Capital Costs
(B) Reformer Manufacturing
(C) Operation and Maintenance (O&M)
(E) Greenhouse gas emissions
(K) Durability
(L) Impurities
(M) Membrane Defects
(N) Hydrogen Selectivity
(O) Operating Temperature
(P) Flux
(Q) Testing and Analysis
(R) Cost

Technical Targets

Performance Criteria	Units	2010Target	Progress
Cost of distributed H_2	\$/gge	2.50	Note 1
H_2 quality	% of total gas	99.99	99.999*
Flux at 20 psid and 400ºC	scfh/ft^2	250	270**
H_2 recovery $95\%H_2/5\%N_2$ $95\%H_2/5\%Ar$ $95\%H_2/2.5\%CO_2/2.5\%CH_4$	%	>80	 76*** 77*** 78***
Module cost (including membrane)	\$/ft^2	\$1,000	\$1,500
Durability	hr	26,280	Note 2
Operating capability	psi	400	Note 3

* Projected H_2 quality based on H_2/N_2 ideal selectivity on membrane #102 measured at 20 psid ΔP H_2 partial pressure and 15 psia permeate side pressure at 400°C.
** H_2 flux on membrane #102 measured at 20 psid ΔP H_2 partial pressure and 15 psia permeate side pressure at 400ºC
*** Mixed gas tests on membrane #102 measured at 20 psid and 400°C

Note 1. The cost of distributed H_2 target will be demonstrated by incorporating the performance data obtained on the membranes in computer models to calculate the overall cost of this process. The computer models are operational.

Note 2. The durability goal is being addressed by procurement of a test furnace for long-term membrane testing at operating pressure and temperature conditions under mixed gas streams. Membrane #102 was tested at 400°C and 20 psid ΔP for 546 hours and six thermal cycles.

Note 3. A project was initiated to determine collapse pressures at operating temperature to create a design that meets the pressure capability and cost goals.

Accomplishments

- Achieved a flux of 270 scfh/ft^2 on a 2 micron thick Pd/Au alloy membrane using pure H_2 and N_2 gas streams, exceeding the 2010 target goal. Tests were at 20 psid and 400ºC.
- H_2 permeate quality on this membrane was 99.999%, also exceeding the 2010 target goal based on H_2/N_2 ideal selectivity.
- Achieved a H_2 recovery on this membrane of 78% on a 95%H_2/2.5%CO_2/2.5%CH_4 mixture, 77% on a 95%H_2/5%Ar mixture and 76% on a 95%H_2/5%N_2 mixture at 20 psid and 400°C.
- Validated the results for this membrane by independent testing at the three team locations.
- Further improved the diffusion barrier layer/AccuSep® substrate from a surface finish of 25-35 micro-inches to 8-12 micro-inches that enabled achievement of consistently high fluxes on Pd alloy membranes coated on the substrates.
- Improved the porous-to-dense transition stainless steel tube welding process from having zero leakage at 20 psi to having zero leakage at 40 psi.
- Continued development of the membrane module design by initiating a project to yield material collapse test data and by calculating membrane surface area requirements based on membrane performance tests.
- Membrane, energy and economic computer models were developed.
- Initiated comparisons of an in-house economic computer model to H2A model.

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Introduction

The project goal is to make significant contributions to the Hydrogen Fuel Initiative (HFI) by enabling hydrogen production that is economically competitive with conventional fuels and energy sources for application in transportation and stationary polymer electrolyte membrane (PEM) fuel cell power generation. Our plan is to develop and demonstrate pilot-scale technology to produce high purity hydrogen from reformed natural gas streams using thin, sulfur-tolerant, Pd alloy membranes on durable, cost-effective, porous stainless steel tubular supports contained in a module.

Our team has developed a smooth, high-quality, zirconia-coated, porous, stainless steel tubular substrate that has enabled the formation of high-flux Pd alloy membranes as thin as 1 micron. A new Pd/Au alloy membrane yielded high H_2 flux and quality performance test results. Mixed gas measurements were made on a Pd/Au alloy membrane and H_2 recovery measurements were obtained. Progress was made in design of a membrane module based on constraints specified for the process and the cost goal. Computer models also were developed to evaluate progress toward achieving the economic goals of the project.

Approach

The primary objective of our project is to achieve the DOE goal of producing H_2 at a cost of \$2-3/gge and at a purity of 99.99% by 2010. Achieving the other target goals of membrane flux rate, membrane durability, H_2 recovery and ΔP will assist achieving the primary cost and purity goals. To achieve the target flux and quality goals, the Pd alloy composition and process are being optimized. To maximize the H_2 recovery, it was determined that the mixed gas test conditions need to be adjusted to ensure that the total available surface area of the membrane is being utilized. Our approach to the module cost goal is to design a membrane module based on the surface area calculated from a membrane computer model using our performance test data. Information also will be obtained on collapse pressures measured at operating temperatures to design the membrane module to meet the cost and ΔP goals. Progress on the durability goal will be achieved by long-term testing of membranes on a furnace dedicated to this test. Energy and economic computer models will predict progress toward the H_2 cost goal and to compare the membrane process performance to the DOE target goals and to competing technology.

Results

The formation of high quality, thin Pd alloy membranes is highly dependent upon the quality of the membrane support or substrate. Significant emphasis was placed on improving the quality of the porous, zirconia-coated, porous stainless steel AccuSep® tubular substrate. By modifying the fabrication process, the surface finish of the barrier layer was improved from 25-35 micro-inches to 8-12 micro-inches. This improvement in the quality of the substrate resulted in our ability to achieve consistently high fluxes. It was determined that the 8-12 micro-inch finish was optimal for our membrane. Substrates with finer surface finishes resulted in membranes with inadequate adhesion, most likely due to elimination of any mechanical interlocking of the two phases.

A non-porous, stainless steel tube is used to connect the porous stainless steel substrate to a tube sheet header. A welding process was developed to seal the dense tube to the porous substrate. The process was improved from where leakage at the weld initiated at pressures of 20 psi to where leakage initiates at 40 psi. Welded stainless steel tubes are shown in Figure 1.

A flux of 270 scfh/ft^2 was achieved on Pd/Au alloy membrane #102 using pure H_2 and N_2 gas streams, exceeding the 2010 target goal as shown in Figure 2. Test conditions were 20 psid of pure H_2 and 400ºC. The membrane was 2 microns thick. The H_2 permeate quality on this membrane was 99.999% as can be determined from the data in Figure 2. This also exceeded the 2010 target goal based on H_2/N_2 ideal selectivity. The H_2 recovery curve on membrane #102 is shown in Figure 3. A H_2 recovery of 78% was measured on a 95%H_2/2.5%CO_2/2.5%CH_4 mixed gas stream, 77% on a 95%H_2/5%Ar mixed gas stream and 76% on a 95%H_2/5%N_2 mixed gas stream at 20 psid and 400°C. It was determined that the H_2 recovery values obtained may not have been maximized with test conditions used. The technical team reached a consensus conclusion that the membrane was in a "starved" condition in which the total area of the membrane was not being utilized. Test conditions will be modified and repeated.

A scanning electron microscopy/energy dispersive X-ray analysis (SEM/EDAX) was carried out on membrane #102 after a few hundred hours at 400°C and after several thermal cycles and some limited mixed gas testing. The alloy composition was determined to be $Pd_{95}Au_5$. The original composition was not able to be determined since our current method for composition analysis is based on the destructive test using SEM/EDAX. On future membranes, techniques will be developed to determine the composition before and after testing to determine if any changes occurred. A project was initiated to conduct an analytical study on the kinetics of intermetallic diffusion during the alloy formation process. Another task on this project is to determine the phase composition of the alloys as a function of temperature, time and environment. Changes in the micro/nanostructure as a function of the alloy formation process will also be investigated.

FIGURE 1. AccuSep® Substrate Tubes with Welded Dense Stainless Steel End Fittings

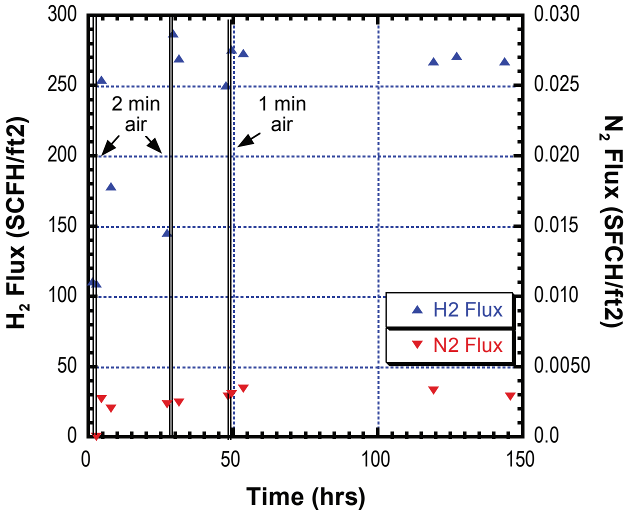


FIGURE 2. H_2 Flux and Quality of Pd/Au Alloy Membrane #102 at 20 psid and 400°C

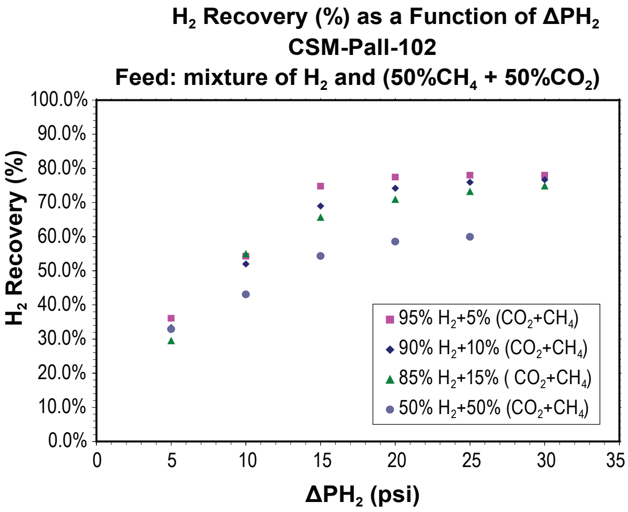


FIGURE 3. H_2 Recovery as a Function of ΔP_{H2} in H_2, CO_2 and CH_4 Mixed Gas Streams

Additionally, the phase stability of the alloy films will be examined under appropriate atmosphere and temperature combinations.

Design work was initiated on a commercial membrane module. A schematic of this concept is illustrated in Figure 4. A key factor in the design is to minimize the wall thickness of the membrane element as well as the housing to meet the 2010 process operating capability (400 psid) and module cost ($1,000 per ft^2) target goals. High-temperature tensile tests were initiated at Oak Ridge National Laboratory using the expected operating conditions on the AccuSep® tubular substrates to confirm the calculated strength. This will permit us to accurately specify the minimum wall thickness required. Mechanical properties on Pd alloy membranes at expected operating conditions will also be conducted. The membrane surface area required for the module was determined using the membrane computer model and performance data obtained with the non-optimal H_2 recovery values. These tests will be repeated using modified test conditions to maximize the performance of the membrane and a new surface area will be calculated for the module design.

Progress was made on our system economic and energy analysis task. An in-house membrane model was developed that calculates the surface area requirement from membrane performance test results. An energy model was developed to calculate the parasitic energy. An in-house system economic model will calculate H_2 production costs, net present value and internal rate of return for the membrane system based on our module cost and performance data. It will be compared to H_2 production cost using a PSA system and to the DOE target goals. All three models are currently operational. The parameters of our internal energy and economic models will be aligned with the parameters and assumptions of the H2A model so that the results can be compared.

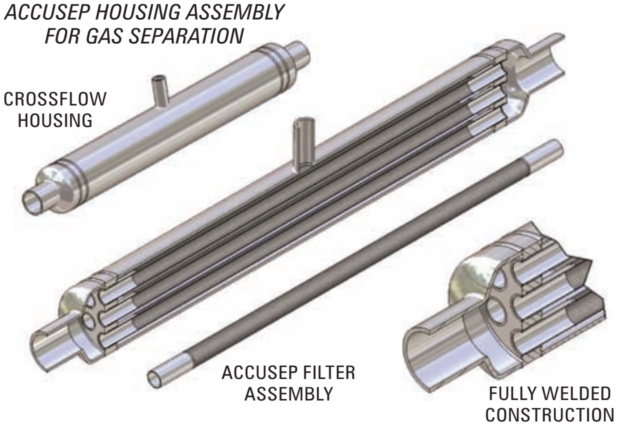


FIGURE 4. Proposed Design of Membrane Module

Conclusions and Future Directions

- In the second year of our project, it was shown that a new alloy system (Pd/Au) yielded H_2 flux and quality measurements with pure gases that exceeded the 2010 target goals.
- H_2 recovery values as high as 78% were achieved in a $95\%H_2/2.5\%CO_2/2.5\%CH_4$ mixed gas stream. The mixed gas test procedure will be modified to maximize utilization of the entire surface area of the membrane in order to maximize the H_2 recovery.
- Improvements were made to the diffusion barrier layer that increased the consistency of Pd alloy formation and increased the separation factor and flux rate.
- The process for welding the end fitting seals to the membrane was improved resulting in an increase in the integrity of the seals.
- Modifications are continuing to being made to the Pd/Au ratio to maximize the performance of this alloy system. Studies are continuing on the Pd/Cu alloy system to maximize performance of that system before down-selecting to one alloy system.
- Using new mixed gas test conditions, membrane performance test results will be measured. These test results will be used in the membrane model to calculate the surface area required. This surface area will be used to design the membrane module and to calculate the cost of the module.
- A durability furnace will be set up and long-term tests will be conducted on membranes to determine their lifetime and replacement operating costs for the economic model analysis.
- The parameters of our internal energy and economic models will be aligned with the parameters and assumptions of the H2A model so that the results can be compared.

FY 2007 Publications/Presentations

1. A presentation on the project status was given at the DOE Annual Merit Review Meeting (May 15, 2007).

2. Way, J.D., “Palladium-Gold Composite Membranes for Hydrogen Separations”, 233rd ACS National Meeting, March 25-29, 2007, Chicago, IL.

3. Way, J. D., “Composite Palladium Alloy Membranes for Hydrogen Separation,” presented at the Membranes: Materials and Processes Gordon Research Conference, New London, NH, August 2006.

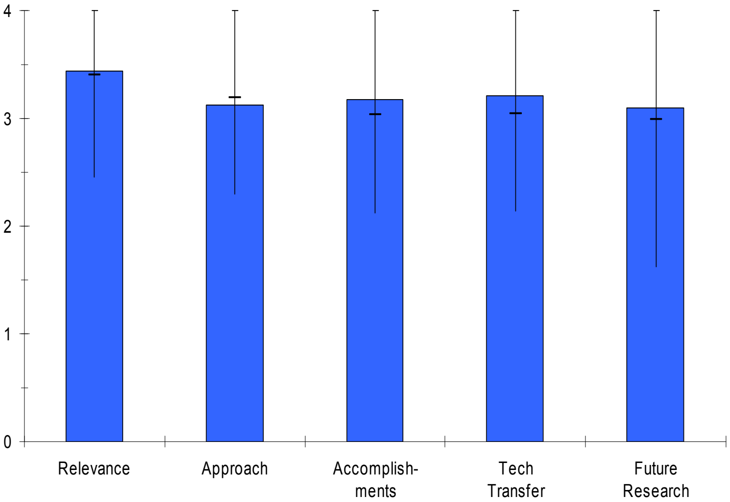
Project # PDP-11: High-Performance, Durable, Palladium-Alloy Membrane for Hydrogen Separation & Purification

Scott Hopkins; Pall Corp.

Brief Summary of Project

The overall objective of this project is to establish the technical and economic viability for use of a palladium alloy composite membrane in a distributed hydrogen production system. Objectives are to 1) develop a process that leverages the technical capabilities of a membrane for maximum economic benefit (reduced gallon of gas equivalent cost); 2) optimize membrane performance in terms of hydrogen throughput, purity and durability; and 3) minimize capital cost for the gas separation module, including pressure vessel, internal hardware, membrane, and substrate.

Overall Project Score: 3.2 (8 Reviews Received)



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.4** for its relevance to DOE objectives.

- Demonstration of process intensification is necessary to achieve DOE H_2 cost goals.
- Pall is developing supported membranes for hydrogen separation. This is a primary DOE need for the production of pure hydrogen. The researchers are well aware of the DOE targets and are making a good effort to meet or exceed these targets.
- Pall is well aware that the membranes must move beyond a research stage and have a plan for further commercial development.
- Hydrogen separation and purification is a key element of distributed hydrogen production from natural gas and renewable fuels.
- At least for small scales of production, this approach can be cost competitive with the established PSA technology.
- One aspect of this approach is the need to establish reliability and durability, even after repeated thermal cycling.
- Technology could achieve cost and performance goals for a number of technologies.
- Permeation membranes are good. Pd-based membranes are challenged by pin-holes / thickness, hydrogen flux, poisons, and cost.
- Ties directly to the Program goal of reducing the costs of distributed hydrogen production.
- This project has the potential to reduce the capital and operating costs of distributed hydrogen production (and can also contribute to process intensification goals in the DOE Fossil Energy Hydrogen-from-Coal program).
- This project's objective is to develop durable Pd-alloy membrane for hydrogen separation.
- Development of a small, more cost effective (capital and operating) hydrogen purification system (relative to PSA) is relevant to the DOE objectives.

Question 2: Approach to performing the research and development

This project was rated **3.1** on its approach.

- Relatively simple approach that appears to have very good potential. The researchers are utilizing a porous metal tube as a support that will provide mechanical integrity. They have been able to produce membranes with

a varied pore structure capable of accepting a Zr coating that will then accept the metal layer. Metal layer thickness has been minimized (5 micron) to maximize permeation.
- The experimental approach is reasonably straightforward and they are obtaining solid data that supports the fact that these membranes are capable of separating and producing high purity hydrogen.
- Pall realizes that membrane sealing is typically a major problem and have developed an approach to overcome this problem. Their data tends to indicate that seal leakage is not an issue with the current design.
- The project approach is based on a palladium-gold composite membrane that has demonstrated high hydrogen permeance with very high separation factors at 400°C.
- The high hydrogen flux implies that a greatly reduced active surface area can be used, which, in turn, lowers the cost of the noble metals required.
- There was no discussion of a duty cycle under which the durability testing will be conducted (as listed under Future Work).
- Addresses barriers, but unclear how costs and performance will be improved.
- Pd membranes are the only known materials that conduct hydrogen exclusively thus having the potential to produce very pure hydrogen.
- Attempting to reduce cost by developing manufacturing methods with porous supports.
- The porous stainless steel tubes appear to provide a good approach for membrane supports.
- Pall will deposit defect-free Pd-alloy membrane on porous stainless steel tubes. The deposition process for the diffusion barrier layer and the active membrane material is not disclosed (proprietary?) and therefore it is difficult to judge their approach.
- Developing a small more cost effective (capital and operating) hydrogen clean up system is relevant to the DOE objectives.
- The approach to develop a compact device is especially appealing.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.2** based on accomplishments.

- Achievement of flux goal is excellent.
- Achievement of weld joint Pd coverage (to avoid gas leakage) is excellent.
- Pall has produced small scale membranes that meet or exceed the DOE targets for flux and cost.
- They have been able to accomplish this with a minimal budget.
- Pall has been able to produce numerous membrane samples that all appear to be leak free.
- The larger scale membrane reactor is of a simple design and will be simple to assemble and test. In addition, it appears that membranes could be replaced with a minimal effort.
- High hydrogen permeance with high separation factors has been achieved.
- Thin membranes exceeding the hydrogen flux targets for 2005, 2010, and 2015 have been tested.
- Membrane / module fabrication techniques have been developed.
- Reproducibility of test data has been confirmed.
- Prepared tubes membrane tubes of 3/8-in diameter and 2-in long.
- Membranes as thin as 1 micron have been tested, though not at sizes above.
- Good progress on reducing the thickness of the membrane.
- High flux rates were achieved using measurements made under ideal conditions, however measurements were not made using gas streams typical of reformer gas. Effects of trace impurities on performance of membranes were not studied.
- The yield is very interesting.
- It is hoped the additional work is conducted to reduce the operating pressure down into the 100-300 psi range to relax the reformer operating cross pressures at temperature.
- It is hoped that the capital cost will be reduced or a projection thereof. The CAPEX looks to be currently ~\$2000/kg H_2.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.2** for technology transfer and collaboration.

- Good partnership including academics, industry and a national lab. Pall is a commercial developer of other membrane systems and appears to be committed to further developing this technology. Pall is very open with the data and information generated and even if this project is not successful, the data will be of significant value to future researchers.
- The project team includes Pall Corporation, Chevron, Colorado School of Mines, and Oak Ridge National Laboratory as active participants and testing is conducted at different project sites.
- Communication appears to be lacking.
- Lacks consultation with a supplier for the stainless steel support tubes regarding cost or manufacturability issues.

Question 5: Approach to and relevance of proposed future research

This project was rated **3.1** for proposed future work.

- Future plans including the development of larger scale membrane modules are based on larger scale modules that have been used commercially in the past, and there is a high probability that this approach will also be successful here.
- More realistic and variable gas feeds (reformate) are necessary and will be tested. For example, the membrane needs to be tested with a gas stream containing contaminants found in commercial natural gas. Currently, the data is being obtained from pure (or nearly pure) feeds which will provide some basic flux data. Mixed feed transport may be significantly different.
- Reformate should including trace species some of which may poison the membrane, before conducting optimization.
- Future work includes testing with synthetic reformate to establish operating conditions needed to achieve target performance.
- The economic analysis strategy outlined is comprehensive and should enable sound comparisons with alternative technologies, such as PSA.
- Material issues should be expanded to include more substrates.
- Longer term stability and performance.
- Planned long-term durability testing at temperature will be important.
- It is good that an economic analysis is planned as part of "future work" to estimate the cost of hydrogen production from this system.
- Other than durability testing and optimization of substrate and alloy properties, detailed future plans are lacking.
- Stated future research is rational and appropriate.

Strengths and weaknesses

Strengths

- A reasonable test project with well defined tasks. The work plan is logical and the work is progressing nicely. The project is constructed so it should be completed in a reasonable time frame.
- Good teamwork with active participants.
- Good progress towards developing gas separation modules.
- High purity.
- Good progress on flux and membrane dimensions.
- Maintaining focus on manufacturability.
- Fabrication capability.
- Pall's experience in membranes area.
- Pall's long-term relationship with ORNL.
- The yield values are very good.
- The foot print size appears to be suitable for distributed generation applications.

Weaknesses

- Unclear how the system is viable with only a 20-40 psi trans-membrane pressure differential.
- Hydrogen recovery data is not obvious. Unclear how high recovery is possible if only a <40 psi delta P.
- The work has only looked at ideal gas transport at this point.
- The work has not considered the effect of impurities in the feed.
- An economic analysis, even if preliminary, would have been helpful to provide a first-cut at the potential costs of the proposed technology.
- It would have been useful to demonstrate that the complete membrane-tube subassembly can undergo repeated thermal cycling without degradation or failure.
- Project proposes to use conventional manufacturing, has limited capabilities.
- No innovation on architecture.
- No tests yet on sulfur tolerance.
- Based on the process concept, it is unclear what the estimate is for the cost of hydrogen at 300 psi.
- No data on performance of Pd-alloy membrane using reformer gas stream.
- Unclear what will be the effect of moisture on the membranes.
- Operating pressures are a little high for SMR materials.
- Clean-up values based on Nitrogen. The effects on the likely composition of a Reformed Natural gas reformate are not discussed.

Specific recommendations and additions or deletions to the work scope

- The project is progressing nicely and needs no modifications.
- Risk assessment (is recommended) to achieve market goals.
- Economic analysis needed.
- Contaminant tolerance should be tested.
- Study the performance of the membranes in reformer gas streams (with trace impurities of sulfur, moisture, etc.).
- Evaluate the hardware for N_2, Ar, He and other trace materials that would be expected from reformed natural gas. Guidance on trace impurities is contained in the GRI Report 94/02432.2.
- Compare the results to the current thoughts on the quality needs for the vehicle OEMs. The current thinking is in a Technical Information Report Number J2719 published in 2005 by SAE. This report will be revised as additional data from fuel providers and OEMs becomes available.

II.D.1 Zeolite Membrane Reactor for Water-Gas-Shift Reaction for Hydrogen Production

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Contract Number: DE-PS36-03GO93007

Subcontractors:
- University of Cincinnati, Cincinnati, OH
- Arizona State University, Tempe, AZ
- Ohio State University, OH

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

Objectives

- Synthesize chemically and thermally stable silicalite membranes with hydrogen permeance >5 x 10^{-7} mol/m^2·s·Pa and and H_2/CO_2 selectivity >50.
- Fabricate tubular silicalite membranes and membrane reactor module suitable for membrane reactor applications.
- Identify experimental conditions for the water-gas-shift (WGS) reaction in the zeolite membrane reactor that will produce a hydrogen stream with at least 94% purity and a CO_2 stream with 97% purity.

Technical Barriers

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

(A) Reforming Capital Costs
(C) Operation and Maintenance
(K) Durability
(N) Hydrogen Selectivity
(P) Flux

Technical Targets

This project is conducting fundamental studies of zeolite membrane reactors to perform WGS for hydrogen production. Insights gained from these studies will be applied toward the development of low-cost, high-efficiency technology for distributed and central hydrogen production that meet the following DOE 2010 hydrogen storage targets:

- Cost: $0.4/kg
- Flux rate: 200 scfh/ft^2
- Hydrogen recovery: >80%
- Hydrogen quality: 99.5%
- Operating capability: 400 psi
- Durability: 26,280 hrs

Accomplishments

Developed and studied methods and techniques for:

- Synthesis of disk-shaped supports with intermediate zirconia and silicalite layers (improvement of thermal stability).
- Improved understanding of gas transport, permeation and separation in microporous zeolite membranes at high temperatures.
- Development of silicalite membranes modified by thermal cracking method (H_2 permeance: >1×10^{-7} mol/m^2·s·Pa, H_2/CO_2 permselectivity: 20, H_2/CO_2 separation selectivity: 13).
- Development of the cost-effective microwave method to synthesize the silicalite membranes (shorter time and less energy consumption).
- Fabrication of tubular silicalite membranes and membrane reactor module suitable for membrane reactor applications.
- Development of membrane support by colloidal casting.
- Development of catalysts for the WGS membrane reactor application.

* * * * *

Introduction

Gasification of biomass or heavy feedstock to produce hydrogen fuel gas using current technology includes partial oxidation to produce syngas, the WGS reaction to convert carbon monoxide with water to hydrogen, separation of hydrogen from the product stream, and removal of water vapor and other impurities (such as H_2S) from the CO_2 containing stream. Commercially, WGS is normally conducted in two or more reactor stages with inter-cooling to maximize conversion for a given catalyst volume. Complete conversion of WGS is possible in a single membrane reactor at high temperatures (~400°C). The membrane removes product hydrogen from the reactor, facilitating higher conversion at a given temperature.

This project is focused on experimental and theoretical studies of the synthesis of a new hydrogen permselective and thermally/chemically stable zeolite membrane and its use in the membrane reactor for the WGS reaction to produce hydrogen and CO_2 rich streams. The membrane reactor system is designed for operation with feeds containing sulfur or other biomass residual contaminants. The zeolite membrane consists of a continuous thin (1-3 µm), aluminum-free silicalite film without intercrystalline micropores on a support with macroporous zirconia and mesoporous silicalite intermediate layers. These composite silicalite membranes in disk and tubular geometries were prepared by a unique technique that combines several synthesis methods including a template-free secondary growth step. Research efforts were also directed towards development of the cost-effective microwave method to synthesize the MFI (a zeolite structure code) zeolite (silicalite and high Si/Al ratio ZSM-5) membranes in disk and tubular geometries. A new catalyst was developed for the WGS reaction under membrane reactor conditions. The final research task is to perform experimental and modeling studies on the performance of the WGS reaction in the membrane reactors with the silicalite membranes and the catalyst developed in this project. The results obtained in this project will enable development of a large-scale one step membrane reactor process for the WGS reaction for cost-effective production of hydrogen to below $0.40/kg.

Approach

The approach used in this project is to study fundamental issues related to synthesis of high quality, stable zeolite membranes and a membrane reactor for WGS reaction and hydrogen separation. The details of project are to (1) synthesize disk-shaped and tubular supports with desired intermediate layers and silicalite membranes with a template-free hydrothermal synthesis method, (2) optimize the hydrothermal synthesis condition and perform thorough permeation and separation characterization of silicalite and ZSM-5 membranes, (3) perform chemical vapor deposition (CVD) for improvement of H_2 permselectivity, (4) develop a microwave synthesis approach to more efficiently and cost-effectively synthesize high quality silicalite membranes, (5) obtain a new WGS catalyst with activity and selectivity comparable to the best available commercial catalyst with improved chemical stability for SO_2 and H_2S containing WGS reaction stream, and (6) develop methods to fabricate a tubular membrane support with desired intermediate layers and a membrane module and sealing system for a tubular membrane reactor that can be operated in WGS conditions.

Results

The work conducted during this reporting period was focused on testing the hydrogen separation performance of silicalite zeolite membranes in a wide temperature range. Decomposition CVD (or thermal cracking) was applied to modify silicalite membranes to improve the H_2 separation performance at high temperatures. The hydrothermal stability of the modified membranes was also examined. The morphology and thickness of the supported membranes were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD).

H_2 separation performance for a silicalite membrane at dry conditions can be seen in Figure 1. The permeances (H_2, CO, CO_2) that are obtained by ternary-component gas separation are quite similar to those for single gas permeation above 400°C. However, a clear difference between these permeances was observed below 300°C. The permeances of H_2 and CO for ternary-component gas separation decrease drastically with decreasing temperature, lowering the H_2 permselectivity.

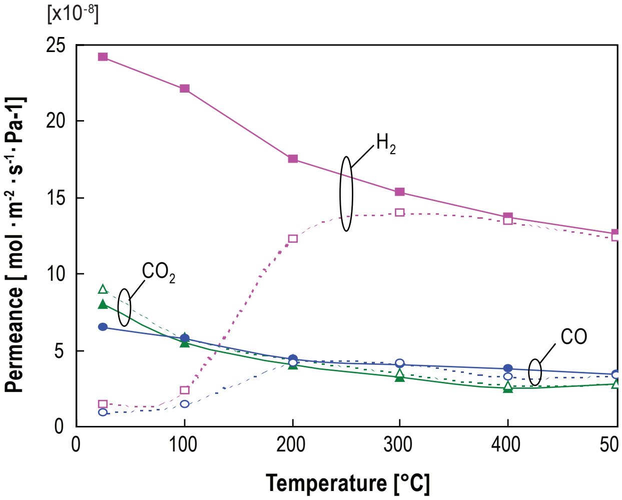


FIGURE 1. Temperature dependency of gas permeances for MFI-type zeolite membrane (closed symbols on solid line: gas permeances for single permeation, open symbols on broken line: those for multi-component gas separation), feed composition (H_2:CO:CO_2=1:1:1, P_{feed}: 0.3 MPa, $P_{permeate}$: 0.1 MPa).

On the other hand, CO_2 permeance for ternary-component gas separation is similar to that for single gas permeation. It is expected that CO_2 preferential adsorption on zeolitic pores should occur due to much stronger affinity between CO_2 and zeolitic pores than that between H_2 or CO and zeolitic pores. Since CO_2 adsorption on zeolitic pores decreases with increasing temperature, it can be considered that H_2 separation performance for ternary-component gas separation coincides well with that for single gas permeation at high temperature (>400°C). On the other hand, at low temperature, the zeolitic pores are blocked by the adsorbed CO_2 molecules that make H_2 and CO molecules unable to permeate through these pores in the membrane.

An MFI-type zeolite membrane was modified by decomposition CVD (thermal cracking of methyl-diethoxy silane, MDES) in a reducing atmosphere. The surface of the zeolite layer was exposed to MDES at 450°C. MDES appeared to diffuse into zeolite pores and decompose to cause deposition of carbon or silicon in the pores. The zeolite membrane before modification was first tested by p/o-xylene vapor separation at 300°C. The membrane exhibited p/o-xylene a vapor separation factor of ~9 before modification. After modification, the membrane became non-selective for p/o-xylene and the xylene permeance decreased by two orders of magnitude. This indicates that the zeolite pore size/structure was successfully reduced/modified, and became inaccessible to the both p- and o-xylene molecules.

The modified membrane was then tested by separation of H_2/CO_2 (50:50) gas mixtures. The results show that the zeolite pore modification by the decomposition CVD dramatically enhanced the separation of H_2/CO_2 with a moderate decrease of the H_2 permeance. Figure 2 shows the separation of a H_2/CO_2 50/50 mixture with 11% and 28% of water vapor in the feed stream. The membrane exhibits a H_2/CO_2 selectivity of 13 at 450°C. This result also indicates that the modified membrane is stable at humid operation conditions.

Continuing efforts in developing the microwave heating synthesis method, MFI-type zeolite membranes were synthesized on high quality seed layers with seed crystallite size of 60~120 nm. Template-free synthesis precursors were used for secondary growth to form continuous zeolite membranes, which were successfully obtained from precursors with and without aluminum contents by microwave heating. It was found that 3-4 hours of hydrothermal reaction were sufficient for the secondary growth process under microwave heating, while a 10 to 20-hour reaction time was necessary in conventional heating. It has been also confirmed that aluminum components in the synthesis precursor facilitate secondary growth and a high concentration of SiO_2 is needed for membrane formation in an aluminum-free precursor.

Membrane reactor modules have been assembled incorporating commercially available, custom porous tube (CoorsTek Inc., Golden, CO, USA) with dimension (O.D.×I.D.×length) of 12×10×100 mm. In this reporting period the surrounding framework for the membrane reactor has been put into place including control systems for gas handling, back pressure, temperature, and process characterization. The membrane reactor and its accompanying control systems have been assembled within a rack mount with a centralized computer, which monitors and implements the control systems on a LABView™ 7.1.1 platform.

A schematic diagram of the membrane reactors control components is shown in Figure 3. The steady-state flow rates for the H_2/CO_2 gaseous feed and N_2 sweep are maintained by mass flow controllers (Brooks Instruments, The Netherlands) with a mild back pressure preserved by combining down stream pressure flow controllers (Brooks Instruments) and precision pressure transducers (MKS, USA). The

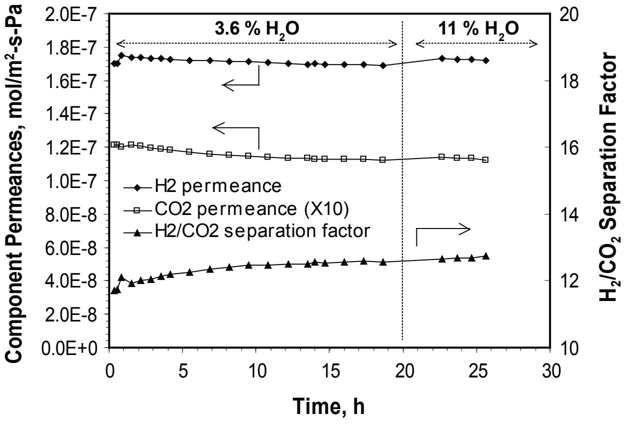


Figure 2. Separation of H_2/CO_2 (50/50) (with Steam Added) for the Modified Membrane

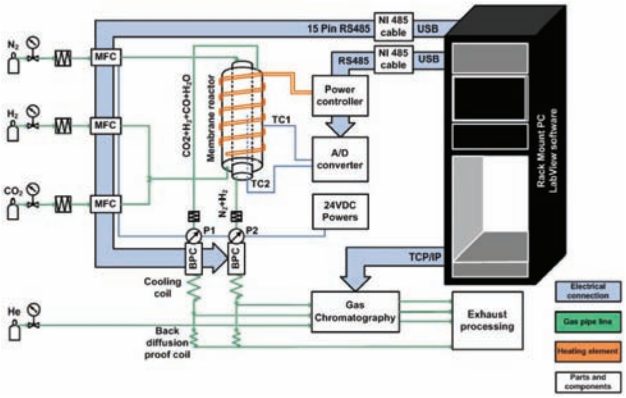


FIGURE 3. A Schematic Diagram of the Membrane Reactor Control Components

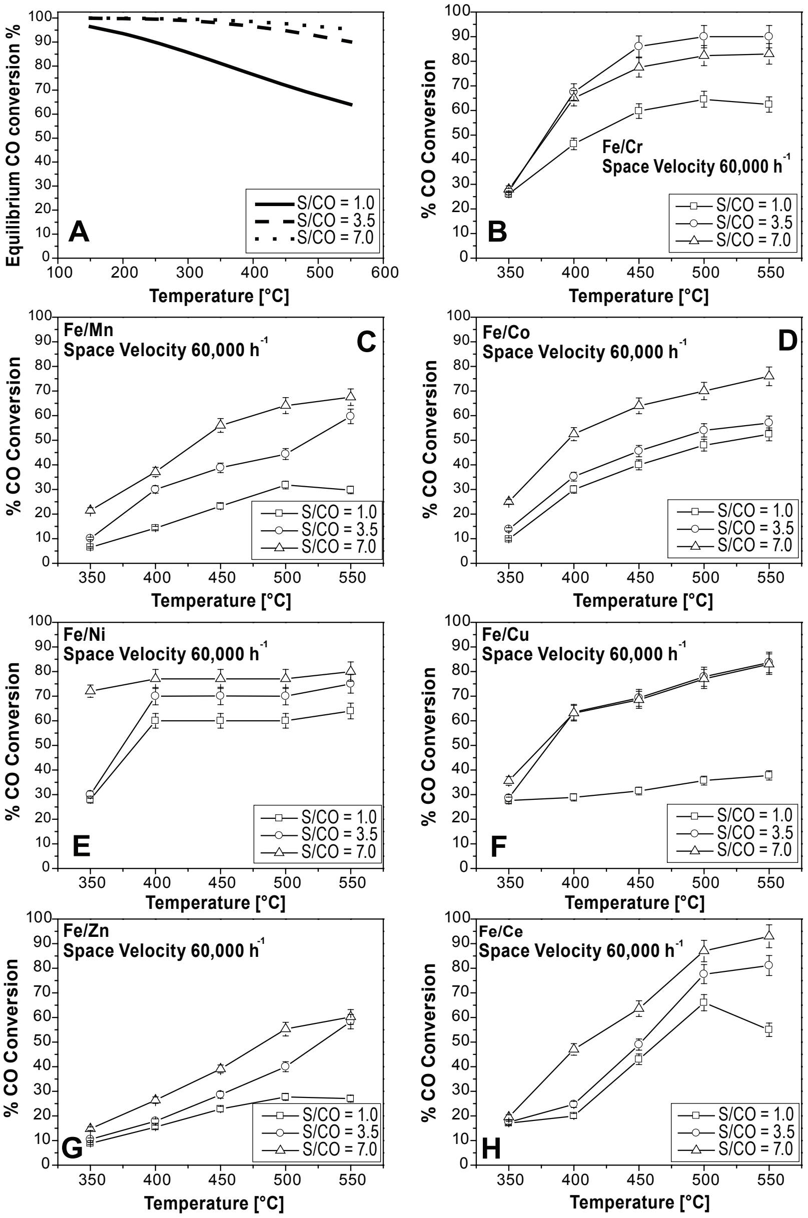


FIGURE 4. WGS Activity Performance over Various Ferrite-Based Catalysts at Different Steam-to-CO Ratios

membrane reactor is heated to temperature by a coiled resistive Kanthal heating element with the internal and element temperature monitored with dedicated type S thermocouples. The membrane reactors temperature control system is the multi-zone furnace. The composition of the membrane reactors retentate and permeate streams is examined by gas chromatography (Dual channel CP-4900 Micro-GC, Varian Inc.) where the 10 m, 5 Å molsieve and 10 m poraplot Q column allow accurate determination of CO, CO_2 and H_2.

The work on catalysis was focused on preparation of a new family of ternary spinel-based catalysts for sulfur-tolerant WGS reaction. The WGS reaction was performed at a low steam-to-CO ratio (S/CO = 1) to study the influence of a steam deficient environment on the activity of the catalysts. Figure 4 shows WGS activity performance over various ferrite-based catalysts at different steam-to-CO ratios. The WGS reaction was performed in the temperature range of 350 to 550°C using a designated amount of steam and CO. In general with increase in temperature from 350 to 550°C, the WGS activity was found to increase. Also the WGS activity was found to increase as the steam-to-CO ratio was increased, particularly from S/CO = 1 to S/CO = 3.5. However, the WGS activity went down slightly for S/CO = 7.0 when compared to S/CO = 3.5 in the case of Fe/Cr catalysts.

Conclusions and Future Directions

- Tested hydrogen separation performance for silicalite membranes in a wide temperature range (25-500°C).
- Developed modified silicalite membranes with high hydrothermal stability (H_2 permeance: $>1\times10^{-7}$ mol/ $m^2\cdot s\cdot Pa$, H_2/CO_2 permselectivity: 20, H_2/CO_2 separation selectivity: 13).
- Identified the optimum conditions of microwave synthesis for silicalite membranes.
- Designed and realized membrane reactor system.
- Developed membrane support by colloidal casting.
- Developed ternary spinel-based catalysts for sulfur-tolerant WGS reaction.

Future work will include the following tasks.

- Improve H_2 separation performance for silicalite membranes by CVD modification.
- Test hydrogen separation and chemical/hydrothermal stability of silicalite membranes under syngas conditions.
- Develop and design intermediate layer/tube leak/flow testing membrane module.

- Test the performance of sulfur-tolerant hybrid WGS catalyst developed by simulating SO_2 & H_2S in the feed stream.

FY 2007 Publications/Presentations

Journal Papers

1. H. Verweij, Y.S. Lin, and J. Dong, "Micro-porous silica and zeolite membranes for hydrogen purification", *MRS Bull.*, **31**, 756-764 (2006).

2. M. Kanezashi, J. O'Brien and Y.S. Lin, "Template-free synthesis of MFI-type zeolite membranes: Permeation characteristics and thermal stability improvement", *J. Membr. Sci*., **286** (1-2): 213-222 (2006).

3. K. Shqau, M.L. Mottern, D. Yu, and H. Verweij, "Preparation and properties of porous α-Al_2O_3 membrane supports", *J. Am. Ceram. Soc*., **89** [6] 1790–94 (2006).

4. M. Kanezashi, J. O'Brien and Y.S. Lin, "Thermal stability improvement of MFI-type zeolite membranes with doped zirconia intermediate layer", *Micropor. Mesopor. Mater*., **103**, 302–308 (2007).

5. T.A. Kuzniatsova, Y.H. Kim, K. Shqau, P.K. Dutta, and H. Verweij, "Zeta potential measurements of zeolite Y: application in homogeneous deposition of particle coatings," *Micropor. Mesopor. Mater*., **103,** 102–107 (2007).

6. M.L. Mottern, K. Shqau, J.Y. Shi, D. Yu, and H. Verweij, "Thin supported inorganic membranes for energy-related gas and water purification," *Int. J. Hydrogen Techn*., in press, (2007).

7. J. O'Brien-Abraham, M. Kanezashi and Y.S. Lin, "A comparative study on permeation and mechanical properties of random and oriented MFI-type zeolite membranes", *Micropor. Mesopor. Mater*., in press (2007).

8. A. Khan and P.G. Smirniotis, "Modified ferrite-based shift catalysts for ultra high temperature membrane reactor applications," *Journal of Catalysis*, submitted (2007).

9. X. Gu, Z. Tang, J. Dong, "On-stream modification of MFI zeolite membranes for enhancing gas separation at high temperature", *Micropor. Mesopor. Mater*., submitted (2007).

10. Z. Tang, X. Gu, J. Dong, "Microwave Synthesis of MFI-Type Zeolite Membranes by Secondary Growth Using Organic-Free Precursor Solutions," *J. Membr. Sci., Submitted (2007).*

Proceedings/Book Chapters

1. M. Kanezashi, J. O'Brien, H. Zou and Y.S. Lin, "Permeation and Separation Characteristics of Silicalite Membranes on Porous Alumina Support by Template-Free Secondary Growth Method", *Proc. 9th Internal. Conf. on Inorganic Membranes*, R. Bredesen and H. Ræder (Eds), pp. 591-594 (2006).

2. M.L. Mottern, J.Y. Shi, K. Shqau, D. Yu, and H. Verweij, "Micro-structural optimization of thin supported inorganic membranes for gas and water purification, "in Membranes: Manufacturing and Applications, Norman N. Li, Anthony G. Fane, W.S. Winston Ho, and Takeshi Matsuura, eds., John Wiley & Sons, New York, (in press) (2007).

3. J. L. O'Brien-Abraham, M. Kanezashi, Y.S. Lin, "Effect of microstructure of MFI-type zeolite membranes on separation of xylene isomers", *Proc. 15th International Zeolite Conf.*, in press (2007).

4. J.Y. Shi, K. Shqau, H. Verweij, R. Revur, S. Sengupta, and J.R. Schorr, "Preparation of well-defined thin YSZ and SSZ membranes with a narrow pore size distribution," *Proceedings 9th International Conf. on Inorganic Membranes,* R. Bredesen and H. Ræder (Eds), pp. 69-73 (2006).

5. M.L. Mottern, K. Shqau, D. Yu and H. Verweij, "A closer examination of permeation porometry," *Proceedings 9th International Conf. on Inorganic Membranes,* R. Bredesen and H. Ræder (Eds), pp. 118-123 (2006).

6. D. Yu, M.L. Mottern, K. Shqau, and H. Verweij, "Synthesis and Optimization of supported γ-alumina membranes for water purification," *Proceedings 9th International Conf. on Inorganic Membranes,* R. Bredesen and H. Ræder (Eds), pp. 691-695 (2006).

Conference Presentations

1. J. O'Brien, M. Kanezashi and Y.S. Lin, "Separation of xylene isomers by pervaporation through MFI-zeolite membranes of varying microstructure," The 17th North American Membrane Society Annual Meeting, Chicago, U.S.A. (2006).

2. H. Verweij, "Inorganic membranes for energy-related gas separation and water purification," Virginia Tech, Department of Chemical Engineering, April 3, 2006.

3. H. Verweij, "Clean Energy Research at OSU," 12th Annual Coalition for National Science Funding, Exhibition & Reception, Washington, DC, June 7, 2006.

4. Khan and P.G. Smirniotis, "Modified Ferrite Based Catalysts for Ultra-High Temperature Water Gas Shift Reaction for Membrane Reactor Applications" AIChE Annual Meeting, San Francisco, Nov. 12–17, 2006.

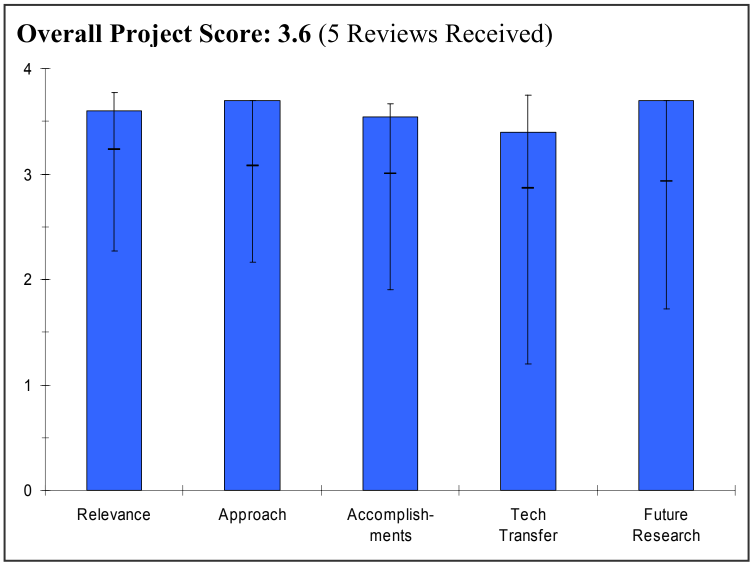
5. M. Kanezashi, J. O'Brien and Y.S. Lin, "Permeation and separation characteristics of MFI type zeolite membranes on zirconia intermediate layer by template-free secondary growth method," AIChE Annual Meeting, San Francisco, Nov. 12–17, 2006.

6. X. Gu, J. Dong, and T.M. Nenoff, "Effect of intercrystalline pores in MFI zeolite membranes on xylene separation and membrane improvement by online coking," AIChE Annual Meeting, San Francisco, CA, USA, Nov. 12–17, 2006.

7. T.A. Kuzniatsova, M.L. Mottern. M.C. Schillo, K. Shqau, D. Yu, and H. Verweij, "Application of inorganic membranes in energy conversion technology," TMS 135th Annual Meeting, Orlando, FL, March 12–16, 2007.

Project # PDP-08: Zeolite Membrane Reactor for Water-Gas-Shift Reaction for Hydrogen Production

Jerry Y.S. Lin; U of Cincinnati



Brief Summary of Project

The University of Cincinnati is studying fundamental issues related to synthesis of high quality, stable zeolite membranes and membrane reactor for water-gas-shift reaction and hydrogen separation. Activities include synthesis and characterization of chemically and thermally stable silicalite membranes, experimental and theoretical study on gas permeation and separation properties of the silicalite membranes, hydrothermal synthesis of tubular silicalite membranes and gas separation study, and experimental and modeling study of a membrane reactor for water-gas-shift reaction.

Question 1: Relevance to overall DOE objectives

This project earned a score of **3.6** for its relevance to DOE objectives.

- The technology could apply to a number of hydrogen production options. For example, it might be used in steam methane reforming, renewable liquids reforming, and gasification. Membranes likely resistance to S is an additional bonus.
- Single step high efficiency Water Gas Shift process is important to the development of low cost hydrogen production methods.
- Project addresses new processes that reduce cost and increase efficiency of hydrogen production from natural gas and renewable biomass resources.

Question 2: Approach to performing the research and development

This project was rated **3.7** on its approach.

- The program is a well integrated project addressing all key aspects of the development of the membrane reactors from materials and catalyst development to equipment construction.
- Strong combination of relevant experimental and modeling capabilities at four universities. Team clearly has the core capabilities to synthesize membranes, fabricate membrane reactors, carryout integrated reaction/separation evaluations, and compare results against engineering models of the system.
- Comprehensive approach with well balanced technical expertise.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.5** based on accomplishments.

- A bit too early to tell since no performance data has been generated yet.
- Good progress in the first year of the project.
- Progress in: synthesizing high quality silicaline layers and intermediate layers; pervaporation and gas permeation unit set up; synthesis and testing water gas shift catalysts; construction of facilities to produce tubular alumina reactors; and putting in place characterization tools for thin (membrane) layers.
- Multidisciplinary team making significant accomplishments.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.4** for technology transfer and collaboration.

Although there is outstanding collaboration among four academic institutions, should coordinate with potential industrial partners for future commercialization of the technology. An industrial collaboration may help replace outdated, inefficient, or costly purification technology used today with new separations technology under development.

Question 5: Approach to and relevance of proposed future research

This project was rated **3.7** for proposed future work.

Strengths and weaknesses

Strengths
- Innovative technology with potential for breakthrough. Sulfur tolerance of the membrane. Versatility of the approach (can be used for separation only, WGSR, or reformer).
- A diversified team among multiple institutions bringing complementary skills to bear on the project. The level of coordination among the groups is impressive.

Weaknesses
- Potential mechanical issues with the material such as the ability of the final reactor to withstand vibrations.
- Difficulty with connecting ceramic membrane with the metal piping.
- No apparent industrial contacts as yet.
- The future work should have increased emphasis on durability testing including review of all types of contaminant issues. In addition, some work on corrosion of the membranes at elevated temperatures in the water gas shift environment should be considered to demonstrate robustness of zeolite membrane and catalysts.

Specific recommendations and additions or deletions to the work scope

- Consider adding an industrial partner, particularly in the areas where industry can provide existing solutions (such as in the catalyst area) as well as to help evaluate the materials under realistic industrial conditions.
- Consider building reformer from thermally stable materials thereby combining reformer-water gas shift reaction -separation in one step.
- The motivation the water gas shift membrane reactor is reducing overall cost of the water gas shift step in hydrogen production from hydrocarbons or alcohols by reducing the number of water gas shift reactor stages. The benefit cannot be realized if the membrane reactor system costs more that the multistage reactor system. This project should include an element that addresses the impact of the membrane reactor on overall system cost as a function of transmembrane flux and selectivity and membrane reactor costs. The model should include the cost of adding heat transfer functionality to the membrane water gas shift reactor (heat is usually removed between stages of Water gas shift reaction). This analysis would help the researchers set specific flux, selectivity, and cost targets that would define project success.