

II.C Fossil-Based

II.C.1 Production of Hydrogen by Superadiabatic Decomposition of Hydrogen Sulfide

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Objectives

- Demonstrate the feasibility of the superadiabatic partial oxidation concept as a basis for developing an innovative process for production of economically viable quantities of hydrogen through the thermal, noncatalytic decomposition of hydrogen sulfide (H₂S) in H₂S-rich waste streams into hydrogen and elemental sulfur, without the input of additional energy (and no additional carbon dioxide [CO₂] emissions).
- Outline a research and development strategy leading to the demonstration of an integrated process at an industrial site.

Approach

- Develop a numerical model for the superadiabatic H₂S decomposition reactor.
- Design, construct, and operate a bench-scale reactor system to demonstrate technical feasibility of the superadiabatic partial oxidation concept.
- Evaluate process economics and markets.
- Conduct thermodynamic and kinetic modeling studies to evaluate agreement between modeling predictions and experimental data, and to extend model applicability to conditions not tested experimentally.

Accomplishments

- Identified key process variables and optimum operating conditions, and developed reactor design guidelines.
- Prepared a design package for a bench-scale testing system.
- Performed preliminary confirmation of technical viability of the concept.
- Designed and constructed a state-of-the-art superadiabatic H₂S decomposition reactor system to carry out a rigorous demonstration of the technical feasibility of the superadiabatic decomposition approach.

Future Directions

- Determine the fate of feed gas impurities (i.e., CO₂, methane [CH₄], etc.) in the product gas, and their effect on reactor performance, especially with respect to hydrogen yield.
- Evaluate several product/byproduct separation schemes to separate the unreacted H₂S for recycle (to maximize the overall H₂S conversion), the hydrogen product for purification, and the tail gas for cleanup.
- Construct and operate a pilot-scale superadiabatic reactor system to provide for a more practical evaluation of the process and to develop large-scale plant data permitting more realistic engineering and economic analysis.
- Construct an integrated superadiabatic H₂S decomposition system for field-testing at an industrial site (e.g., refinery).

Introduction

In recent years, H₂S has come to be regarded as a mineral from which two valuable products (hydrogen and sulfur) can be extracted.¹ Technology is well established for the recovery of the sulfur component, with the Claus process being the most prominent. Although this technology also produces a low-quality steam, it does not fully utilize the potential of H₂S as a resource for hydrogen. Because of the significant amounts of H₂S available worldwide, efforts have been made in recent years for the production of hydrogen, in addition to sulfur, from H₂S through a number of approaches. It is widely recognized that the most direct process of converting H₂S into hydrogen (H₂) and sulfur is through thermal decomposition (catalytic or noncatalytic). However, because of energy considerations, this approach has been considered impractical at temperatures exceeding about 927°C (1200K). In addition to being endothermic, the equilibrium of the thermal decomposition of H₂S at these temperatures is relatively low, and the reaction does not proceed to an industrially important extent.² For example, based on thermodynamic equilibria, conversion of H₂S into H₂ is only about 20% at 1000°C and 38% at 1200°C. Temperatures exceeding 1375°C are needed to drive the H₂S decomposition reaction to conversions > 50%.

Because of these limitations and other considerations, such as strict environmental regulations on sulfur emissions, any process for the recovery of hydrogen, in addition to sulfur, from H₂S based on thermal decomposition or dissociation has

to overcome a number of technical (and economical) hurdles. These include:

- Low yields even at high temperature (equilibrium limited)
- To maximize H₂ production, it is necessary to recycle unreacted H₂S
- Need to separate product gases
- Large recycle streams, unless conversion is reasonably high
- Rapid quenching of product gas may be necessary to block any recombination of H₂ and S₂ (decomposition reaction is reversible)
- Fate of impurities in feed gas has implications on emissions, tail-gas cleanup, and purity of the H₂ product.

Due to the high energy demands for thermal dissociation, other approaches were evaluated where attempts were made to carry out the decomposition reaction with equilibrium shift, such as by preferential removal of reaction products by membranes and thermal diffusion columns. Despite the advances made in these areas, no method of hydrogen sulfide decomposition can be considered commercially feasible today.

Approach

Working with the University of Illinois at Chicago (UIC) and other industrial partners, including Universal Oil Products and BP Amoco, the Gas Technology Institute (GTI) has been developing an innovative process that promises to overcome the limitations of the noncatalytic thermal decomposition approach. In this process, operation at significantly

high temperatures is made possible and economical by oxidation of part of the H_2S to provide the energy required for the decomposition reaction to proceed to a significant extent. Partial oxidation of H_2S in the H_2S -containing fuel gas is carried out in the presence of an inert, porous, high-capacity medium, and the intense heat exchange results in flame temperatures that significantly exceed the adiabatic flame temperature of the gas mixture. By coupling the partial oxidation of H_2S in the porous medium with the H_2S decomposition, temperatures as high as 1400°C (1673K) can be achieved economically within a reaction zone without the input of external energy, and therefore, no additional CO_2 emissions. In this reaction zone, the self-sustaining conditions are very favorable for the decomposition reaction to proceed to an industrially significant extent, within a slowly propagating thermal wave (Figure 1). The superadiabatic partial oxidation concept is depicted in Figure 2 for a given set of operating conditions (i.e., 20% H_2S in the feed gas, 12 cm/s gas velocity, etc.).³ It is clearly seen that in this case, for equivalence ratios > 1.5 , the temperature achieved greatly exceeds the adiabatic temperature of the gas mixture. (Equivalence ratio is defined as the molar ratio of oxygen gas (O_2) supplied to the O_2 that is stoichiometrically required to burn all the H_2S .) It is conceivable that higher temperatures than shown in Figure 2 can be achieved by manipulating the operating conditions.

GTI has envisioned a process (Figure 3) comprising the superadiabatic H_2S decomposition reactor, product/byproduct separation schemes, hydrogen purification, and tail gas cleanup. Work has so far concentrated mainly on the superadiabatic reactor, and has comprised computational modeling and experimental studies to demonstrate the technical and economical feasibility of the superadiabatic H_2S decomposition concept, using H_2S -nitrogen (N_2)- O_2 gas mixtures.

Groundwork numerical modeling of the superadiabatic decomposition reactor has been performed, identifying key process parameters. These parameters include fuel gas composition (i.e., H_2S -rich and H_2S -lean), oxidant composition (air/enriched air/oxygen), equivalence ratio, superficial gas velocity, feed gas temperature (pre-heating effect), and product gas quenching (to avoid

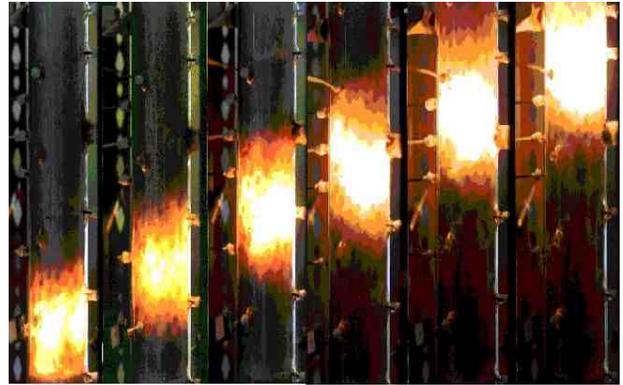


Figure 1. Propagating Superadiabatic Partial Oxidation Wave

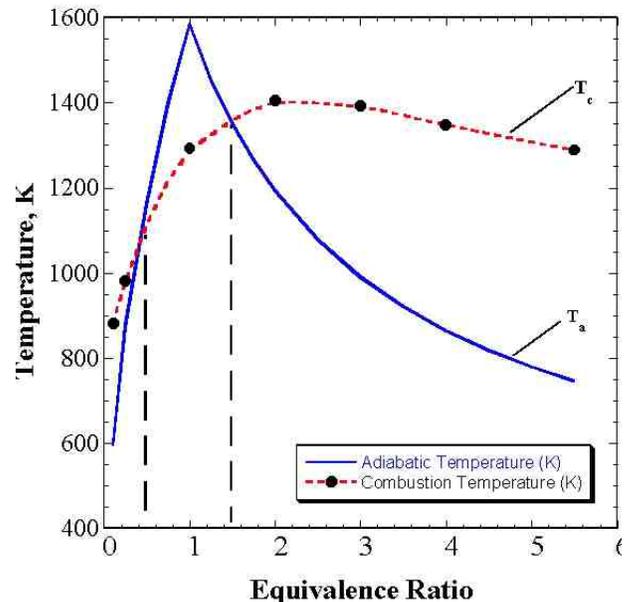


Figure 2. Partial Oxidation Temperature of H_2S (Gas Velocity= 12 cm/s)

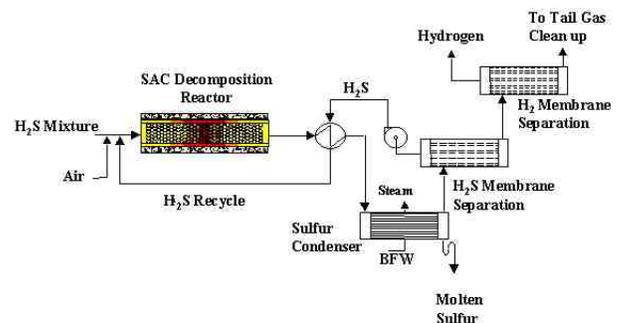


Figure 3. Conceptual Process Design for Hydrogen Production Based on the Superadiabatic Decomposition Concept

recombination of H_2 and S_2). Qualitative and quantitative determinations were made of the effects of these parameters, individually and in combination, on the performance of the superadiabatic decomposition reactor for production of hydrogen and elemental sulfur.^{4,5}

Collaborative experimental investigations by GTI and UIC researchers on the generation of hydrogen-rich gases from hydrocarbons via superadiabatic partial oxidation have shown the high potential and practicality of this approach. To carry out a rigorous process evaluation, GTI designed and constructed a state-of-the-art superadiabatic H_2S decomposition reactor system (Figure 4). This reactor is currently being operated to demonstrate the technical feasibility of the superadiabatic decomposition process, to evaluate the agreement between modeling predictions and experimental results, and to reassess the economic potential of the process.

Results

The major findings from the numerical modeling work appear to indicate that by optimizing the porous body reactor configuration, equivalence ratio, and gas velocity, the overall H_2S decomposition in a single pass can be as high as 50%, with a conversion of H_2S to the desirable product hydrogen (H_2) reaching a level of 30%. It is estimated that the overall process performance can be substantially improved with respect to hydrogen production by membrane separation of product gases and recirculation of unreacted H_2S . It is estimated that in 4 to 5 passes nearly total H_2S decomposition into sulfur can be realized, with recovery of 30-40% of the hydrogen component.

The optimum numerical modeling scenario indicates that, with feed gases entering the reactor at ambient temperature, a maximum temperature of 1631 K (1394°C or 2541°F) can be achieved in the superadiabatic reactor, resulting in an overall H_2S conversion of 50%, with a hydrogen (H_2)/water (H_2O) selectivity of 57/43 and an elemental sulfur (S_2)/sulfur dioxide (SO_2) selectivity of 99/1.

Preliminary experimental testing has shown that stable self-sustained flames could be generated using



Figure 4. Overall Arrangement of GTI's Newly-Constructed Lab-scale H_2S Superadiabatic Decomposition Reactor

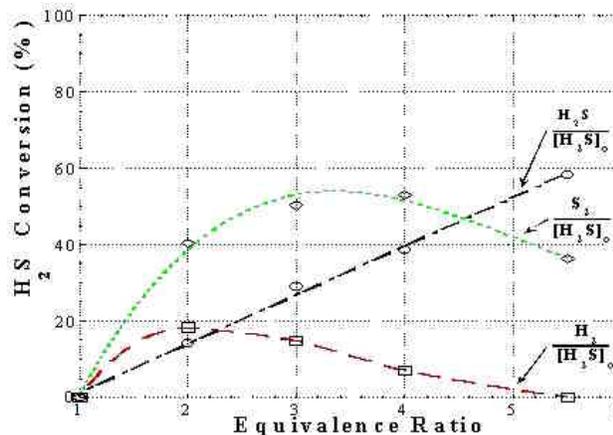


Figure 5. Hydrogen Sulfide Conversions ($V_g = 12$ cm/s)

H_2S -containing gases as a feedstock in the range of equivalence ratios from 2 to 5 with a hydrogen output at about 20%⁶, as shown in Figure 5. The agreement between the groundwork experimental data developed to-date and modeling predictions is quite reasonable.



Figure 6. Sulfur Produced Through the Superadiabatic Decomposition of H_2S

The newly constructed superadiabatic H_2S decomposition reactor system is currently being operated to develop a data package to provide evidence of the technical feasibility of the superadiabatic partial oxidation concept for the production of hydrogen (and elemental sulfur) from H_2S . Successful tests have been made; a photo of the sulfur product, collected at the end of a typical test, is shown in Figure 6.

Conclusions

The superadiabatic partial oxidation concept appears to hold significant promise as a basis for developing a novel process for the production of low-cost hydrogen (and sulfur) by enhanced thermal decomposition of H_2S in H_2S -containing waste streams, without the input of external energy, and therefore, no additional CO_2 emissions. The process has potential to utilize significant quantities of hydrogen that are currently being wasted as water vapor by conventional sulfur recovery processes (e.g., Claus).

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2. Slimane, R.B., Lau, F.S., Dihu, R., Bingue, J.P., Saveliev, A.V., Fridman, A.A., and Kennedy, L.A., "Production of Hydrogen by Superadiabatic Decomposition of Hydrogen Sulfide," Paper presented and published in the 14th World Hydrogen Energy Conference, June 9-14, 2002, Montreal, Quebec, Canada.
3. Slimane, R.B., Lau, F.S., Dihu, R., "An Economical Process for the Utilization of H_2S from Natural Gas Upgrading Operations," Paper to be presented at the Natural Gas Technologies - What's New and What's Next Conference, Sept. 29 - Oct. 2, 2002, Lake Buena Vista, Florida.
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II.C.2 Thermal Dissociation of Methane Using a Solar-Coupled Aerosol Flow Reactor

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Objectives

- Demonstrate a pilot scale solar-thermal transport tube reactor process to thermally dissociate methane to hydrogen (H₂) and carbon black.
- Develop a fundamental understanding of the reaction kinetics and transport heat and mass transfer processes to allow plant design of a scaled-up process for economic evaluation.
- Carry out an economic and environmental evaluation of the process in order to assess viability and to identify fruitful research areas where success would significantly impact the economics.
- Involve as many students and interested companies as possible in the project, nurture their interaction, and facilitate communication among all parties (students, NREL, and nine companies) to provide a framework for successful project completion and learning.

Approach

- A pilot reactor system was designed, constructed, and interfaced to the NREL High-Flux-Solar Furnace (HFSF).
- The process was successfully started up and has been operating for six months; a matrix of statistically designed experiments has been carried out to obtain data for fundamental understanding and process plant design scale-up.
- The produced carbon black has been evaluated internally and by Chevron-Phillips, the industry liaison interested in potentially marketing the carbon black.
- Four teams of senior chemical engineering students supervised by teams of the industry liaisons carried out plant designs and economic evaluations for four process scenarios - centralized hydrogen plant, distributed hydrogen plant, co-generation (H₂ and electricity) utility plant, and industrial semiconductor hydrogen plant.

Accomplishments

- Demonstrated rapid methane dissociation exceeding 60% for residence times of 0.01 second at a temperature of 1900°K (Kelvin) and without co-feeding carbon black.
- Demonstrated production of an amorphous (not graphitic), ash-free, fine sized (20 to 40 nanometer) carbon black powder suitable for tire production or conversion in a high-efficiency carbon conversion fuel cell [1] with no wall deposition in reactor.
- Demonstrated suitable materials of construction for a high-temperature solar-thermal process - reactor assembly constructed of exterior quartz and interior porous and solid graphite.

- Demonstrated a highly efficient process that requires ~ 40 times less heliostat (sun capture surface) area than photovoltaic cells powering electrolyzers to produce H₂.
- Carried out an economic assessment of the process indicating a 15% internal rate of return (IRR) for an out-the-gate hydrogen plant selling hydrogen at < \$15/GJ (Giga-Joule).
- Over a three-year period, the project involved 26 undergraduate students, one Ph.D. student, one postdoctoral researcher, nine companies, and NREL.

Future Directions

- This is the final year of a three-year project and no future research is planned. However, DOE is currently considering a process extension proposal to support a solar-thermal process to rapidly dry reform waste landfill gas to hydrogen and carbon black. Independent of the outcome of that proposal, the following issues need to be addressed:
- The produced carbon black needs to be supplied in a large enough quantity for testing by tire manufacturers. The Goodyear Tire & Rubber Company has agreed to evaluate the carbon black. Extended reactor operations should be carried out to supply the carbon black powder to Goodyear for testing.
- Efforts should be directed to study the impact of transient effects (clouds passing over, etc.) on the process, and process control systems for operating the reactor under such transient conditions should be developed.
- An economic evaluation should be carried out for a one-step solar-thermal process to supply hydrogen-enriched natural gas (HCNG) for fleet vehicle fueling. In such a process, 35% H₂ in natural gas (NG) can be achieved at only 21% conversion by stripping some carbon out of the NG. The alternative steam-reforming process (oxygen added in the form of water) requires complete processing (many steps) to pure H₂ which is then blended with NG to obtain the desired composition.
- Methods should be evaluated for operating the solar-thermal process continuously to produce H₂. Two such methods are (1) design and construction of a reactor capable of operating with an electrically heated supplementary source of power and (2) development of and integration of the solar-thermal process with a high efficiency carbon conversion fuel cell to supply electricity to an electrolyzer for splitting water. In both instances, H₂ could be supplied off-sun. Development of a carbon conversion fuel cell would also provide a significant outlet (in addition to tire sales) for all of the carbon black that is produced while on-sun. The carbon black that is produced is a perfect feed for a carbon conversion fuel cell - fine sized, amorphous, and ash-free.
- Alternative H₂ production processes using concentrated sunlight to drive rapid reactions should be investigated. These reactions include the reforming of high CO₂ containing NG wells (i.e. "contaminated wells") that may be capped and not used, and waste landfill biogas that is currently being flared or simply burned to generate electricity.

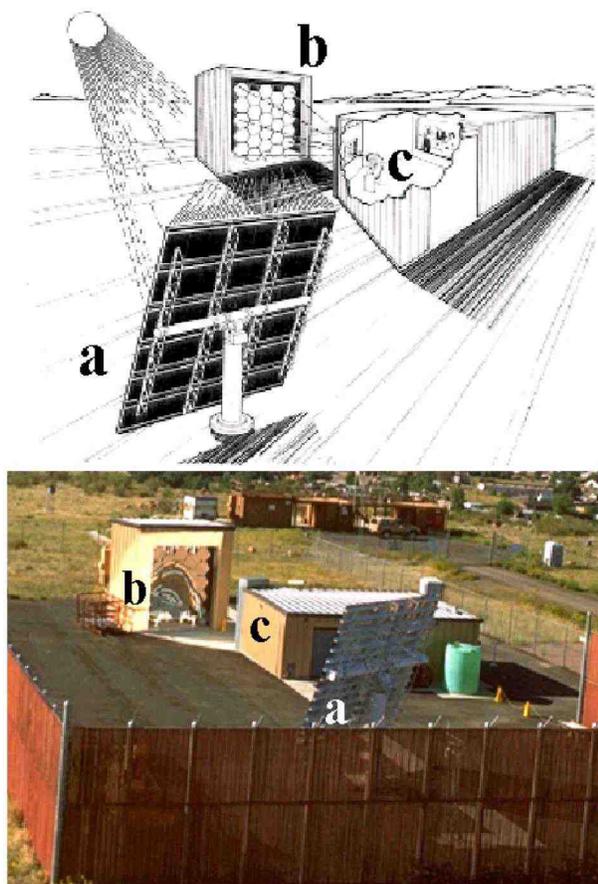
Introduction

Sunlight can be concentrated with mirrors and used to achieve ultra-high temperatures that are otherwise only achievable using electricity or nuclear power. The use of such renewable solar-thermal processing has significant potential in the desert southwest United States (AZ, CA, CO, NM, NV, and UT) for heating specialized chemical reactors to produce H₂ from NG, biogas, or waste landfill gas.

Since there is no energy conversion processing required (i.e. no efficiency losses to convert steam generated by combustion into electricity via a turbine or to convert sunlight to electricity via a photovoltaic cell and then use the electricity to split water by electrolysis), the sunlight is directly used to drive high temperature "brute force" chemical reactions - such as dissociation reactions - at high efficiency. Overall solar-thermal efficiencies approach 50%.

With the ultra-high temperatures ($\sim 2000^{\circ}\text{K}$) achieved in the process, the chemical reaction rates are enormous and approximately 1000 times faster than rates achieved when operating at more conventional ($\sim 1000^{\circ}\text{K}$) temperatures. The primary technical challenges for solar-thermal NG dissociation are related to (1) the ability to operate on an on/off mode with the sun, (2) the selection of suitable materials of construction and reactor design to achieve the ultra-high temperatures, (3) the ability to prevent carbon deposition on the inside wall of the reaction vessel, (4) the ability to heat and dissociate a gas that is transparent to radiation, and (5) the ability to operate continuously using supplementary energy or stored energy that is produced while on-sun.

In this project, a pilot scale solar-thermal reactor was constructed at the University of Colorado (Boulder, CO) and interfaced to the HFSF at NREL in nearby Golden, CO (see Figure 1). After experiments were done, the reactor was optimized. This was followed by significant experimentation to develop an understanding of the rate of reaction at ultra-high solar-thermal temperatures. Produced carbon black was evaluated for product quality (i.e. market price). A study was conducted to design a scaled-up plant for commercial processing (four scenarios), and profitability studies were carried out. Nine companies (BP, Chevron-Phillips, Chevron-Texaco, Electric Power Research Institute, General Motors, Harper International, Pinnacle West, PlugPower, and Siemens) are involved in the process and attended at least one of the two team meetings that were held during the year. Eight of the companies attended the final project review. The companies have been instrumental in guiding the research. One Ph.D. student is responsible for the fundamental understanding of the process. One chemical engineering postdoctoral researcher has been responsible for the applied aspects of the process. Ten undergraduate chemical engineering students ($\sim 50\%$ female and/or under-represented minorities) were involved in the 2002 process design and profitability analysis as part of the senior chemical engineering plant design and economics course. The process appears feasible and potentially economical.



a) Heliostat b) Primary Concentrator c) Reactor

Figure 1. Schematic of Photo and HFSF at NREL, (Golden CO)

Approach

A vertical aerosol flow reactor was constructed and interfaced to the HFSF at NREL [2]. Argon flows in the annular region between the two tubes and provides an inert atmosphere that prevents oxidation of the graphite tube while preventing any decomposition products from depositing on the inner quartz wall. Feed methane gas flows downward through the graphite tube. The reactor was placed at the focal point of the primary concentrator that can deliver up to 10 kW (kilowatt) of power on-sun. A secondary concentrator enveloping the reactor allows temperatures greater than 2000°K to be achieved.

The reactor is operated as a cold wall process because the beam is delivered directly on target.

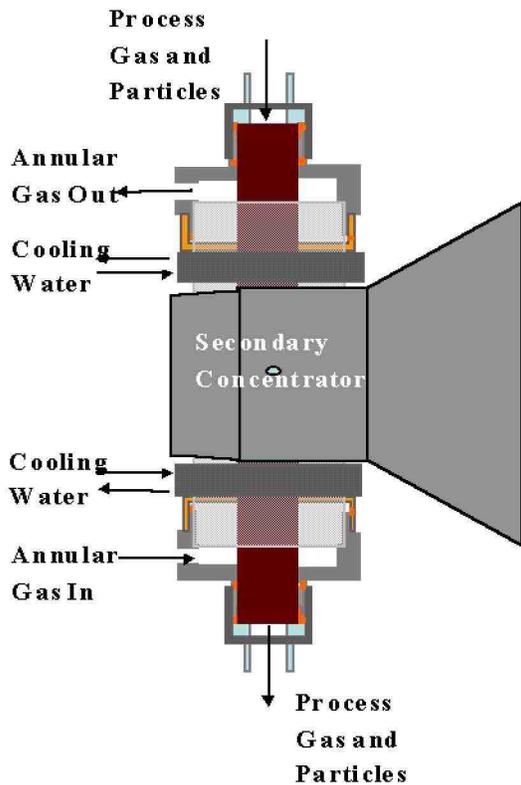


Figure 2. Solar-Thermal Aerosol Reactor (Top) Schematic, (Bottom) Installed

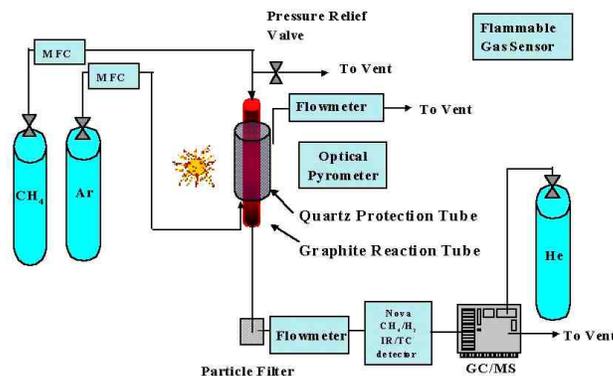


Figure 3. Schematic of Solar-Thermal Pilot Facility Interfaced to HFSF at NREL (Golden, CO)

The graphite and quartz design allows for on/off processing without thermal expansion or stress difficulties. The graphite reaction tube can be heated to reaction temperatures in a matter of seconds. A schematic of the reactor system and a photograph of the reactor that was taken after the system had been heated are shown in Figure 2. An overall pilot system schematic is shown in Figure 3.

Four process scenarios were considered for plant design/profitability studies and environmental impact: (1) a large scale plant where H₂ is being sent to a pipeline and carbon black is being sold, (2) a distributed industrial plant to supply H₂ to a semiconductor processing facility in AZ, (3) a medium sized distributed plant where H₂ is used to fill fuel cell vehicles, and (4) a large scale utility co-generation facility where H₂ is being supplied to a pipeline and carbon black is being fed to a carbon conversion fuel cell to supply electricity to the grid.

Results

The process has been operated at temperatures as high as 2100°K for high power levels (8.5 kW) and gas flows of 5 standard liters per minute (slpm). However, typical operating temperatures are in the range of 1700 to 1900°K. The effect of varying the annular flow rate was examined during experiments. It was found that an increase in the argon flow rate between the quartz and solid graphite tube of from 7 to 10 slpm at high power levels had little effect on the gas phase temperature. A greater effect is seen at lower power levels, such as 2.5 kW. In general, the

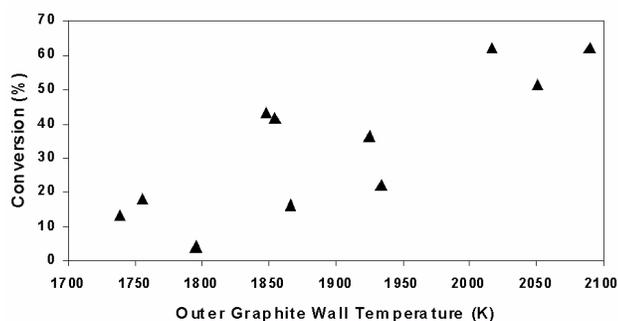


Figure 4. Experimental Dissociation Results ($t = 0.01$ to 0.02 sec)

amount of gas flowed between the quartz tube and the outer solid graphite tube will be very small and only enough to prevent deposition of any volatiles along the inside quartz wall.

Various experiments were run to determine the effect of temperature and residence time on conversion. In all cases, pure methane was fed to the reactor. As can be seen in Figure 4, conversions exceeding 60% have been obtained at 2000°K for residence times on the order of 0.01 second and with no co-fed carbon black to improve reactor heating. It should be noted that complete dissociation is expected at these temperatures and that the conversion was limited by heat transfer. Future experiments will include the co-feeding of fine carbon black particles to act as radiation absorbers for heating the gas. Math modeling has indicated that the co-feeding of carbon black particles has a substantial effect on the overall process throughput and reactor performance.

The quality of the carbon black powder (Figure 6) product was evaluated as it impacts the overall economics of the process. A transmission electron photomicrograph (TEM) of a carbon black powder produced at a power level of 8.5 kW ($\sim 2000^{\circ}\text{K}$) indicates a primary particle size of between 20 and 40 nanometers. In addition, the solar-thermally produced carbon black is compared to ShawiniganTM carbon black (tradename of Chevron-Phillips Corp.), the high quality world standard specialty carbon black. A comparative TEM image indicates that the carbon particles being formed have a similar chain-like structure as compared to the ShawiniganTM black. An X-ray diffraction pattern of the carbon

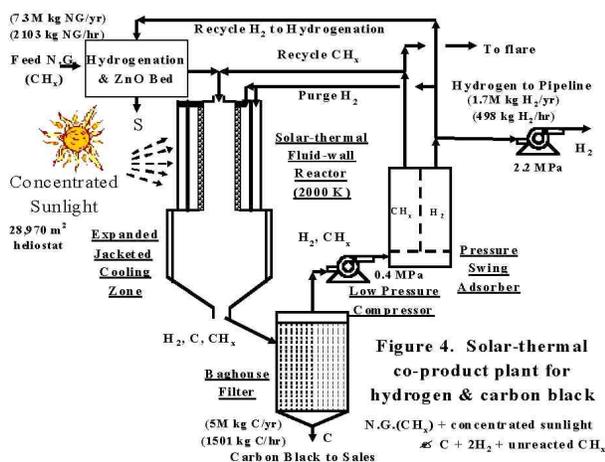


Figure 5. Solar-Thermal Co-product Plant for Hydrogen and Carbon Black

black and the TEM indicate that the solar-thermally produced carbon black is amorphous and has similar or reduced crystallinity compared to the ShawiniganTM black..

The solar-thermal process (Figure 5) for co-producing hydrogen (1670 t/yr [tonnes/year]) and carbon black (5000 t/yr) has been conceptualized and costed ($\pm 30\%$; percentage of delivered equipment cost). The 16.6 Mega-Watt thermal plant has been designed for the Phoenix, AZ (USA) area (0.38 solar capacity factor). Produced carbon black will be sold into the carbon black market (world market is 7.9 M metric tonnes (t)/yr), and produced hydrogen will be supplied to a hydrogen pipeline at a pressure of 2.2 MPa. The plant will dissociate 7300 t/yr of natural gas (NG). The reactor is sized from the kinetics rate expression developed by Dahl et al [4].

The process has been simulated and priced using base cases from Spath and Amos [3] and appropriate scale factors. The selling price of H_2 is determined to be $\$13.80/\text{GJ}$ to achieve a 15% IRR when carbon black is sold at $\$0.66/\text{kg}$. For a carbon black selling price of $\$0.80/\text{kg}$, the price of H_2 to achieve the 15% IRR drops to $\$10/\text{GJ}$. For a carbon black selling price of $\$1.10/\text{kg}$, the price of the H_2 to achieve the 15% IRR drops to $\$5/\text{GJ}$. It is important to note that most specialty carbon blacks sell for between $\$2$ and $\$3.50/\text{kg}$. The world market for these specialty blacks is 0.6 mega-t/yr. Hence, the 5000 t carbon black/yr co-product plant described here is 0.8% of

Shawinigan™ Acetylene Black

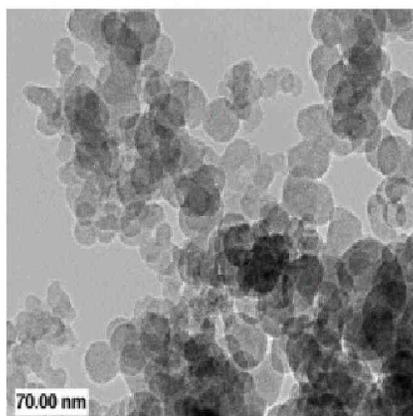
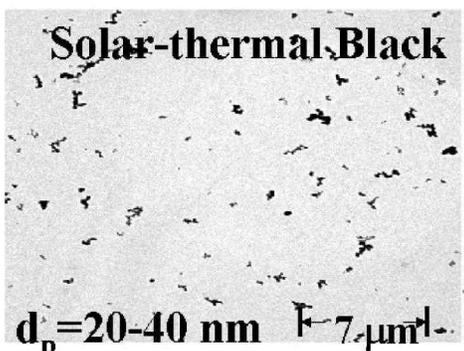
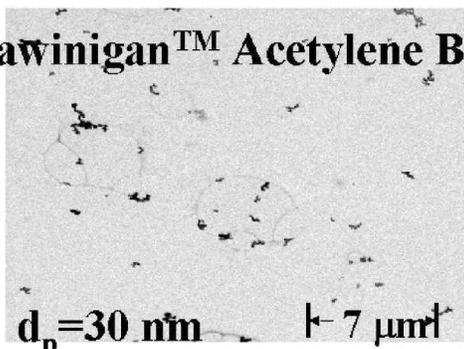


Figure 6. Comparison of Solar-Thermal Carbon Black with Commercial High Quality Standard (Chevron-Phillips Shawinigan Black™)

the world market for specialty blacks. The process has a 3rd year return on investment of 16% and a payback period of 6 years.

For the process scenario discussed, the solar-thermal process avoids 277 MJ fossil fuel and 13.9 kg-equivalent CO₂/kg H₂ produced as compared to conventional steam-methane reforming and furnace black processing.

Conclusions

The solar-thermal process is feasible: there are no technical show stoppers and there are no materials concerns. The fluid-wall reactor design allows continuous operation without inside wall deposition of carbon black. Reaction rates at the demonstrated ultra-high temperatures are enormous.

The solar-thermal process is environmentally friendly. The most environmentally friendly option is when selling carbon black into the tire carbon black market as the energy and pollution associated with normal carbon black production are avoided. If carbon is fed to a carbon conversion fuel cell, the total green house gas emissions are still ~ 60% of those of a steam reformer and the bulk of the released CO₂ is in a pure form so it can be easily sequestered.

The process is potentially economical in the desert southwest United States. However, an outlet for the carbon black is an integral part of the overall economics. Compared to photovoltaic conversion and electrolysis of water to produce H₂, the solar-thermal process requires ~ 40 times less heliostat surface, and the heliostats are lower cost mirrors rather than expensive photovoltaic cells. The solar-thermal process can produce HCNG at high rates in one step by efficiently and cleanly removing carbon from fed NG.

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1. Dahl, JK, Barocas, VH, Clough, DE, Weimer, AW, "Intrinsic kinetics for rapid decomposition of methane in an aerosol flow reactor," *International Journal of Hydrogen Energy* 2002; 27: 377-386.
2. Dahl, JK, Tamburini, J, Weimer, AW, Lewandowski, A, Pitts, R, and Bingham, C, "Solar-thermal Processing of Methane to Produce Hydrogen and Syngas," *Energy and Fuels*, 15, 1227-1232 (2001).
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4. Weimer, AW, "Ushering in the Hydrogen Economy," paper presented at the Center of the American West Program "Energy in the West: What Every Westerner Should Know", June 22, 2002 (Boulder).
5. Dahl, JK, "Solar-thermal Dissociation of Methane in an Aerosol Flow Reactor," paper presented at the Fourth World Congress on Particle Technology," Sydney, Australia, July 25, 2002 (Boulder).
6. Weimer, AW, "Solar-thermal Process for Rapid Natural Gas Dissociation," presented to the Department of Chemical Engineering - Graduate Seminar, University of Maryland (October, 2001).
7. Weimer, AW, "Rapid Process for the Benign Synthesis of Hydrogen," presented to the Department of Chemical Engineering - Graduate Seminar, Colorado School of Mines and Technology (November, 2001).

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9. Weimer, AW, "Distributed Hydrogen by Rapid Solar-thermal Dissociation of Methane," paper to be presented at the 224th American Chemical Society Meeting, Boston, MA (August 21, 2002).
10. Weimer, AW, "Rapid Solar-thermal Dissociation of Natural Gas," paper to be presented at the 11th International Symposium on Concentrated Solar Power and Chemical Energy Technologies, Zurich, Switzerland (September 5, 2002).
11. Dahl, JK, "Production of Hydrogen Using a Solar-thermal Fluid-wall Reactor," paper to be presented at the 2002 Annual Meeting of the American Institute of Chemical Engineers," Indianapolis, IN (November, 2002).
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FY 2002 Patent Applications

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2. "Solar-thermal Fluid-wall Reaction Processing," Provisional Patent Application filed March 7, 2002.

II.C.3 Thermocatalytic CO₂-Free Production of Hydrogen From Hydrocarbon Fuels

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Objectives

- Develop an economically viable thermocatalytic process for production of hydrogen (H₂) and value-added carbon products from hydrocarbon fuels
- Obviate the concurrent production of carbon monoxide/carbon dioxide (CO/CO₂) byproducts and drastically reduce (preferably, eliminate) greenhouse gas emissions from the process
- Improve the process efficiency and reduce the cost of hydrogen production

Approach

- Investigate CO/CO₂-free production of hydrogen and carbon products via efficient thermocatalytic decomposition of hydrocarbon feedstocks over carbon-based catalysts in an air/water-free environment
- Improve the process efficiency and sustainability via in-situ generation of catalytically active carbon particulates
- Design, fabricate and test a bench-scale thermocatalytic reactor for CO/CO₂-free production of hydrogen-rich gas and carbon products
- Determine the effect of heavy hydrocarbons, moisture and sulfur compounds present in commercial hydrocarbon fuels on the process efficiency and the catalyst activity/stability
- Characterize carbon products of the process and evaluate their application areas and market value

Accomplishments

- Developed new approaches to improving the catalyst long-term stability and process sustainability
- Determined the effect of heavy hydrocarbons, moisture and H₂S present in commercial hydrocarbon feedstocks on the process efficiency and the catalyst activity and stability
- Designed, fabricated and operated a bench scale thermocatalytic reactor (TCR); demonstrated CO/CO₂-free production of hydrogen-rich gas with H₂ concentration up to 80 v.%
- Tested TCR in combination with a proton exchange membrane (PEM) fuel cell
- Analyzed carbon products of the process using a number of material characterization methods; assessed potential markets for carbon products (in collaboration with industry)
- Conducted techno-economic analysis of thermocatalytic decomposition of natural gas (in cooperation with the National Renewable Energy Laboratory [NREL])

Future Directions

- Fabricate and operate the scaled-up (up to 5 kW) multi-fuel thermocatalytic reactor coupled with a gas clean-up system using commercial hydrocarbon fuels.
- Reduce the amount of greenhouse gas emissions via optimization of the thermocatalytic process and utilization of carbon materials produced in the process
- Increase the yield of high-value carbon products and reduce the cost of hydrogen production
- Address safety and reliability issues related to the operation of the thermocatalytic reactor
- Evaluate new application areas for carbon products (with industrial partners)

Introduction

Thermocatalytic decomposition (TCD) of methane (CH₄) results in the formation of hydrogen (H₂) and elemental carbon:



The energy input requirements for TCD are significantly less than that of steam methane reforming (37.8 and 63.3 kJ/mol H₂, respectively). Due to the absence of oxidants (e.g., H₂O and/or O₂), no carbon oxides are formed in the reaction. The choice of an efficient and durable methane decomposition catalyst is vital for the development of a TCD process. Two major problems associated with existing catalysts relate to their rapid deactivation (due to carbon deposition) and co-production of large amounts of CO₂ during the catalyst regeneration step. The successful development of efficient and stable carbon-based catalysts for a methane decomposition process can solve both the catalyst deactivation and CO₂ emission problems.

Approach

The approach is based on thermocatalytic decomposition of hydrocarbon fuels over carbon-based catalysts in an air/water-free environment. The important feature of the process is that the reaction is catalyzed by carbon particulates produced in the process, so no external catalyst is required (except for the start-up operation). This results in the following advantages: (1) no CO/CO₂ byproducts are generated during the hydrocarbon decomposition stage, (2) no catalyst regeneration is required, (3) the catalyst is resistant to sulfur poisoning, (4) several valuable forms of carbon can be produced in the process, (5) overall CO₂ emissions could be

drastically reduced (compared to conventional processes).

Results

Improvement in Catalyst Stability and Process Sustainability. The following new approaches to improving the catalyst long-term stability and the process sustainability have been developed: (i) the in-situ generation of catalytically active carbon species produced by co-decomposition of hydrocarbons, and (ii) activation of carbon catalysts via surface treatment with activating agents. The treatment of carbon particles with steam and CO₂ (outside the pyrolysis zone) resulted in a significant increase in methane decomposition rate (Figure 1).

Effect of Moisture and Sulfur on Methane Decomposition Rate. The presence of small amounts of moisture and H₂S (<3 v.%) in the hydrocarbon feedstock is not detrimental to the process efficiency. However, these impurities result in contamination of hydrogen with carbon oxides and H₂S, which could be removed from the product gas using methanation and H₂S scrubbing steps, respectively. Figure 2 demonstrates the removal of carbon oxides from hydrogen-rich gas via methanation reactions using Ru-catalyst.

Fabrication and Testing of Thermocatalytic Reactor. A bench-scale thermocatalytic reactor (TCR) for CO/CO₂-free production of hydrogen-rich gases was designed, fabricated and operated using methane or propane as feedstocks (Figure 3). The concentration of hydrogen in the hydrogen-containing gas reached up to 80 v.% (the balance methane). Since no carbon oxides were detected in the hydrogen gas, it was directly fed to a PEM fuel cell.

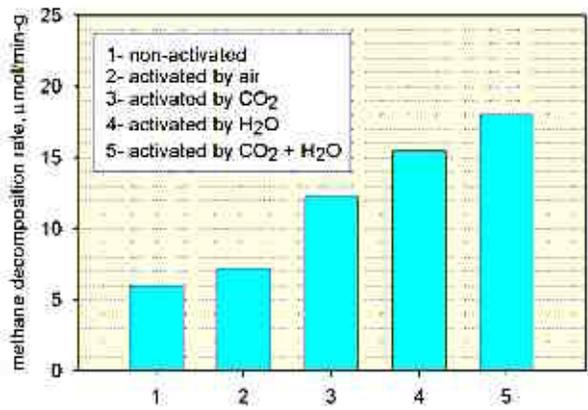


Figure 1. Effect of Carbon Catalyst Activation on Methane Decomposition Rate at 850°

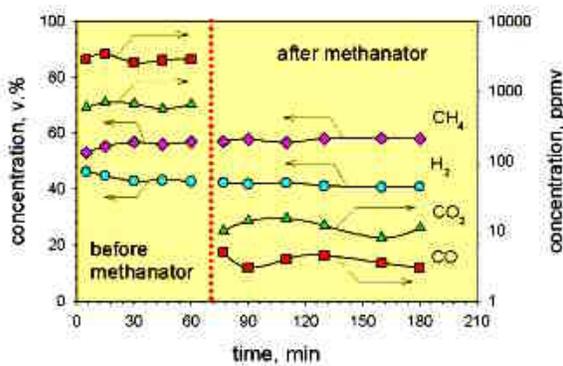


Figure 2. Removal of CO and CO₂ from H₂-CH₄ Stream via Methanation Reaction at 350°C

Structural and Surface Characterization of Carbon Products. Carbon products of the process were analyzed by a number of material characterization techniques, including x-ray diffraction, scanning electron microscopy, Auger electron spectroscopy, x-ray photoelectron spectroscopy, and others. X-ray diffraction studies revealed an ordered graphite-like (or turbostratic) structure of carbon products (Figure 4).

Techno-economic Evaluation of Hydrogen Production by Thermocatalytic Decomposition of Natural Gas. Techno-economic analysis of hydrogen production by thermocatalytic decomposition of natural gas was conducted in cooperation with



Figure 3. Experimental Set-Up with TCR, PEM Fuel Cell, Fuel Tank, and Testing Equipment

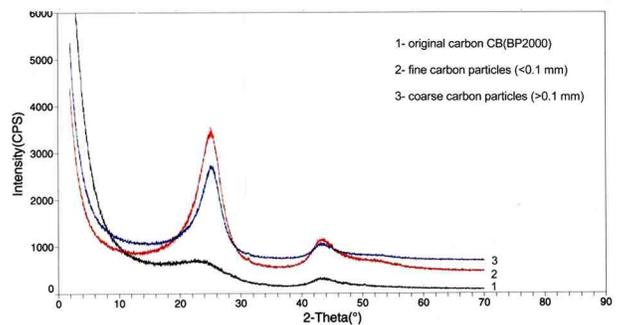


Figure 4. X-ray Diffraction Spectra of Carbon Particles Produced by C₃H₈ Decomposition Over CB(BP2000)

NREL. The hydrogen selling price varied in the range of \$7-21/GJ (giga-Joule) depending on the cost of natural gas and carbon selling price.

Conclusions

New methods for improving the sustainability of the methane thermocatalytic decomposition process have been developed. Studies indicate that the presence of small amounts of moisture and H₂S (<3 v.%) in the hydrocarbon feedstock is not detrimental for the catalyst activity and process efficiency. This implies that commercial hydrocarbon fuels could potentially be employed as feedstocks for the process. A bench-scale thermocatalytic reactor was designed, fabricated and operated using methane and propane as feedstocks. The TCR produced hydrogen-rich gas free of CO/CO₂ impurities; the gas was directly fed to PEM fuel cell. Material characterization studies indicated that depending on operational conditions, carbon could be produced in several valuable forms including turbostratic carbon, pyrolytic graphite, spherical carbon particles, or filamentous carbon.

FY 2002 Publications/Presentations

1. Muradov, N. "Low-emission Fuel Reformers for Fuel Cell Applications", 14th World Hydrogen Energy Conference, Montreal, Canada, 2002.
2. Muradov, N. "Thermocatalytic CO₂-free Production of Hydrogen from Hydrocarbon Fuels", DOE Annual Hydrogen Program Review Meeting, Golden, CO, 2002.
3. Muradov, N. and Schwitter, A. "Formation of Conical Carbon Structures on Vapor-grown Carbon Filaments", Nano Letters, v.2, 673 (2002).
4. Muradov, N. "Emission-free Fuel Reformers for Fuel Cell Applications", Fuel Cells, Science and Technology 2002, Amsterdam, Netherlands, 2002.
5. Muradov, N. "Hydrogen via Methane Decomposition: an Application for Decarbonization of Fossil Fuels", Intern. Journal Hydrogen Energy, v.26, 1165 (2001).
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Special Recognitions & Awards/Patents Issued

1. Muradov, N. U.S. Patent Application No. 60/194,828 (2001) "Thermocatalytic Process for CO₂-free Production of Hydrogen and Carbon from Hydrocarbons".
2. Muradov, N. U.S. Patent Application No. 60/203,370 (2001) "Portable Hydrogen Generator".
3. Muradov, N. U.S. Patent Application No. 60/346,548 (2002) "A Method and Apparatus for Production of 3D Carbon Fibers".

II.C.4 Novel Catalytic Fuel Processing Using Micro-Channel Steam Reforming and Advanced Separations Technology

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Objectives

The goal of this project is to produce pure hydrogen from infrastructure fuels using cost-competitive, highly efficient catalytic steam reforming and membrane separation technology. The following objectives are identified to achieve this goal.

- Optimize InnovaTek's proprietary steam reforming catalyst composition and evaluate reforming conditions for diesel fuel and natural gas.
- Optimize the hydrogen-permeable membrane composition and operating procedures, and compare to water gas shift approach for CO clean-up.
- Develop efficient thermal management using microchannel heat exchangers and an internal burner.
- Integrate processes and components to achieve smallest size and most efficient thermal management.

Approach

- Conduct system analysis and design specification.
- Design and develop components.
- Test components.
- Design process configurations.
- Evaluate configurations with model simulation.
- Predict component and operational requirements with model simulation.
- Conduct iterative testing of integrated system.

Accomplishments

- Developed process model and used output to help size system components and select range for operating conditions.
- Developed sulfur-tolerant steam reforming catalyst that reforms current hydrocarbon fuels without the need for prior sulfur removal.
- Designed and tested advanced membrane technology that separates pure hydrogen from reformate, thereby enabling higher fuel cell power densities and eliminating potential for electrode poisoning.
- Utilized micro technology for reactor, heat exchanger, and fuel vaporizer to improve system efficiency through optimized thermal management and fluid dynamics.
- Completed a successful 500-hour demonstration of natural gas steam reforming and an 80-hour test of diesel fuel reforming.

Future Directions

- Scale up to at least 60 LPM hydrogen output – enough for a 5 kWe fuel cell.
 - Complete micro-channel implementation.
 - Automate start-up, operation, shut-down.
 - Achieve more complete thermal integration.
 - Focus on manufacturability, cost-reduction and high-volume production.
 - Achieve full integration with at least one fuel cell model.
 - Conduct thorough reliability testing.
 - Incorporate enhanced controls – off-site monitoring, data mining, self-diagnostics.
 - Complete documentation – drawings, bills of material, manufacturing routers.
 - Prepare tooling – dies, molds, computer aided machining (CAM) programming etc.
 - Obtain agency approval – Underwriters Laboratory, Canadian Standards Association, Consumer Electronics, etc.
-

Introduction

To be marketable now, fuel cells need to use primary fuel sources from existing production and distribution networks – i.e. natural gas, gasoline, diesel or jet fuels.

Fossil fuel-powered fuel cells or refueling stations can form the bridge to a future when renewable resources power fuel cells. When compared to compressed hydrogen, reformed hydrocarbon fuels offer a significant cost advantage in the delivery of power. The high energy density of these fuels will also contribute to increased run times per unit of fuel consumed, and size and weight reductions associated with fuel storage.

To meet this need, InnovaTek is integrating microreactor technology with advanced sulfur-tolerant catalysts and hydrogen membrane technology to create a fuel processor for hydrogen generation from hydrocarbons. The ultimate goal of this 4-year cooperative project is the development of a catalytic reactor heated by the combustion of membrane by-products (raffinate) for production of clean hydrogen by steam reforming hydrocarbon fuels, including fuels that contain sulfur. Advanced membrane technology is being used to remove CO and CO₂ from the reformat. The fuel processor being developed will provide a pure output stream of hydrogen that can be used without further purification for electrical generation by a PEM fuel cell.

Approach

Process simulation and analysis was performed for all possible system configurations to obtain an optimal system design and a complete mass and energy balance for every individual component of the system. These include flow rates, flow compositions, and temperatures for every stream in the system. The information provided a solid foundation for the design, fabrication, and testing of the reactor, heat exchangers, and combustor. The information will also guide us during the integration and demonstration of the complete system throughout the entire project period.

Proprietary components were designed and developed to achieve a technically superior fuel processor by solving specific problems related to several of the fundamental processes associated with fuel processing. These components will comprise a more efficient system that is sulfur tolerant and produces pure hydrogen while remaining compact and lightweight.

The individual components have been tested, and results of key tests are summarized below. The components are now being integrated into a bench-top system that will undergo additional testing, culminating in a prototype demonstration in late 2002 that produces 12 LPM of pure hydrogen, enough to power a 1 kWe fuel cell.

Results

The design and optimization of a fuel processing system is complex because of the number of required components and functions (Figure 1). The first step in developing an optimal system design is evaluating different process configurations using process simulation. Another objective is to develop the specifications for the design of the components used in the system. Special attention is paid to thermal management and water management, two of the most technically challenging issues of effective system operation and integration.

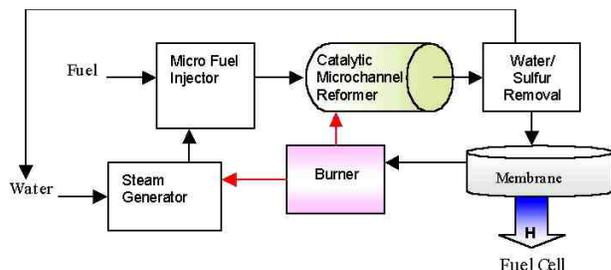


Figure 1. Flow Diagram of Major Fuel Processor System Components

A system process model was developed and used to track mass and enthalpy flows. Estimates of molar flows of reforming products were determined by solving for equilibrium concentrations at given temperatures and pressures. Thermodynamic properties were used to determine heat transfer, water removal, and air and heat required to achieve energy balance in the reforming reactor. A non-linear differential equation was used to determine membrane area for the desired hydrogen output at various temperatures and pressures. Model output helped determine the size of system components and select the range for operating conditions.

System components were designed, fabricated, tested, and optimized in an iterative process. Primary system components and their functions are listed in Table 1. Each component was tested, redesigned, and tested again until optimum geometries and formulations were determined. Then the components were integrated step by step and tested again. Complete system testing is now underway.

Component	Function	Product
catalytic reactor	catalytically reforms fossil fuels	Reformate (H, CO ₂ , CO)
catalyst	catalyzes the reforming reaction	reformate
combustor	burns raffinate to provide heat for the reforming reaction	Heat, CO ₂ , H ₂ O
fuel injector	injects and mixes fuel and steam into the reactor	Vaporized steam/fuel mixture
heat exchangers	provides the proper temperature for each component	Warmer or cooler gas streams
H-permeable membrane	converts reformate to pure hydrogen and produces raffinate (membrane reject stream) for combustor	Pure hydrogen, raffinate (H, CO ₂ , CO)

Table 1. Primary Components of InnovaTek's Fuel Processor

Initial tests were conducted to investigate the effect of reaction temperature on conversion and product gas composition using our proprietary catalyst ITC-3. Additional testing was conducted to optimize the catalyst for specific fuel types. After catalyst optimization, long-term tests for reforming natural gas were successfully conducted using InnovaTek's proprietary catalyst ITC #1148 (Figure 2). The hydrogen concentration in the reformate product was over 74% on a dry basis. CO and CO₂ concentrations were about 19% and 6%, respectively. No methane was detected, indicating 100% conversion during the entire testing period. The test was continuously conducted for 341 hours at the same conditions with the catalyst showing very high and stable activity. The reactor temperature was then set to 800°C and the tests were continued for another 100 hours with very stable performance. These results indicate that our catalyst composition has great potential for stable hydrogen generation from natural gas.

An 80-hour test with ultra-low sulfur (~5 ppm) diesel, a developmental product obtained from Chevron Phillips Chemical, was also successfully completed (Figure 3). The use of this product permits

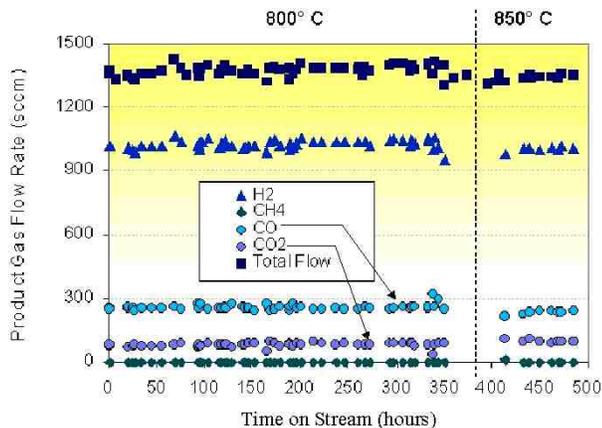


Figure 2. Steam Reforming of Natural Gas Using InnovaTek’s Proprietary Catalyst, ITC-1145

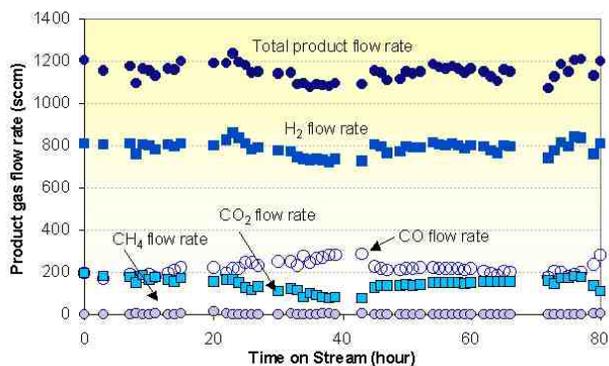


Figure 3. Steam Reforming of Low-Sulfur Diesel Fuel Using InnovaTek’s Proprietary Catalyst

us to add controlled amounts of sulfur for testing sulfur tolerance. In an 8-hour test using this fuel with 100 ppm sulfur added, the catalyst had a 100% conversion rate. These test results indicate that our ITC catalyst #1145 has very high catalytic activity and selectivity to hydrogen production and tolerates the presence of sulfur in the fuel.

A radial concept is used for the integration of the combustor and catalytic reactor where concentric functional chambers build outward from a central core (Figure 4). The innermost sections comprise the combustor unit, where air is carried to the interior and raffinate gas from the membrane penetrates through the wall to form a combustion flame along the inner wall of the reaction chamber. Preheated and mixed steam and fuel enter the reaction chamber and are catalytically converted to reformat. Reformat exits the reactor and is then sent to the



Figure 4. Photo of InnovaTek’s Steam Reformer with Integrated Raffinate Combustor



Figure 5. Photo of InnovaTek’s Hydrogen-Permeable Membrane Component

membrane, where pure hydrogen is separated. Exhaust gas from the combustion chamber is carried back so that the hot gas passes over the outside of the reaction chamber, thereby providing uniform thermal conditions. This reactor, which is about 12 inches long, has a capacity for producing enough hydrogen for a 1 kWe fuel cell. It is currently being used for integrated system testing.

For purification of the reformat, hydrogen-permeable membranes were constructed using a flat-plate design that encased ultra-thin metal foils that are permeable only to hydrogen (Figure 5). InnovaTek is investigating several formulations of metal for these membranes, including sulfur-tolerant membranes. We were successful in producing several membrane prototypes for a range of hydrogen production rates. Work on membrane optimization is continuing as we examine variables such as pressure, temperature, and sulfur content of the reformat. One important finding is that hydrogen permeation

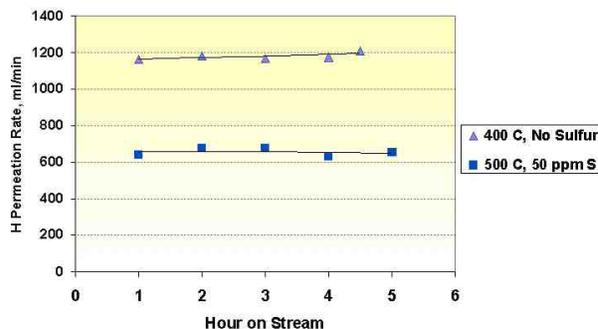


Figure 6. Hydrogen Permeation Rate through InnovaTek's S-Tolerant Membrane as a Function of Temperature and Sulfur Content

rate is reduced and higher membrane temperatures are required for processing sulfur-containing fuels (Figure 6). The membrane component has been integrated with the catalytic reactor component and testing is underway.

Conclusions

- A proprietary sulfur-tolerant catalyst developed by InnovaTek can reform natural gas, gasoline, and diesel fuels without need for prior sulfur removal, thereby greatly improving the prospects for commercialization of fuel cell technology.
- Advanced membrane technology for hydrogen separation produces nearly pure hydrogen output from reformat gas, enabling higher fuel cell power densities and eliminating potential for electrode poisoning.
- The use of micro technology for reactor, heat exchanger, and fuel vaporizer components improves system efficiency through optimized thermal management and fluid dynamics.
- The use of steam reforming and membrane purification combined with tight thermal integration can result in a highly efficient fuel processor that, when combined with a fuel cell, will produce at least twice the energy of a combustion engine for a given amount of fuel.

FY 2002 Publications/Presentations

1. Ming, Q., Healey, T., Allen, L., and Irving, P., "Steam Reforming of Hydrocarbon Fuels". *Catalysis Today*, in press, 2002.
2. Irving, P., Allen, L., Herron, T., and Stephens, R., "Diesel Fuel Reforming with Advanced Separations Technology for the Production of Pure Hydrogen". Proceedings of the 3rd Department of Defense Logistic Fuel Reforming Conference. Panama City Beach, FL, August 27-28, 2002.
3. Irving, P. "Fuel Processor for Generating Pure Hydrogen for Fuel Cells from Sulfur-Containing Fuels". Proceedings of the 4th Annual Knowledge Foundation's International Symposium, Small Fuel Cells 2002. Washington D.C., April 21-23, 2002.

Special Recognitions & Awards/Patents Issued

1. Hydrocarbon Fuel Reforming Catalyst and Use Thereof. U.S Non-Provisional Patent Application, Q. Ming, T. Healey, and P. Irving, pending.

II.C.5 ITM Syngas and ITM H₂: Engineering Development of Ceramic Membrane Reactor Systems for Converting Natural Gas to Hydrogen and Synthesis Gas for Liquid Transportation Fuels

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Main Subcontractor: Air Products and Chemicals, Inc., Allentown, PA; Ceramatec, Inc. Salt Lake City, UT; ChevronTexaco, Richmond, CA; Eltron Research Inc., Boulder, CO; McDermott Technology Inc., Alliance, OH; Norsk Hydro, Oslo, Norway; Pacific Northwest National Laboratory, Richland, WA; Pennsylvania State University, University Park, PA; University of Alaska Fairbanks, Fairbanks, AK; University of Pennsylvania, Philadelphia, PA

Objectives

- Research, develop and demonstrate ion transport membrane (ITM) Syngas/ITM H₂ ceramic membrane reactor system for the low-cost conversion of natural gas to hydrogen and synthesis gas
- Scale-up the ITM Syngas/ITM H₂ reactor technology through three levels of pilot-scale testing and precommercial demonstration
- Obtain the technical, engineering, operating and economic data necessary for the final step to full commercialization of the ITM Syngas/ITM H₂ technologies

Approach

- This project is in Phase 2 of three phases. The approach in Phase 2 includes:
- Task 2.1 Commercial Plant Economic Evaluation
- Task 2.2 Materials and Seals Development and Evaluation
- Task 2.3 ITM Syngas/ITM H₂ Membrane and Module Design and Fabrication
- Task 2.4 Nominal 24 thousand standard cubic feet per day gas flowrate (MSCFD) ITM Syngas/ITM H₂ Process Development Unit (PDU)
- Task 2.5 Nominal 330 MSCFD ITM Syngas/ITM H₂ Subscale Engineering Prototype

Accomplishments

- Process design and economic evaluation of a 760 million standard cubic feet per day gas flowrate (MMSCFD) H₂ plant with CO₂ separation to provide a carbon-free "clean fuel" showed the potential for over 30% capital cost savings in the syngas production step
- Multiple tests of lab-scale tubular membranes and seals each operated continuously for over 6 months at 250 psig and 825°C with good performance stability
- A number of sub-scale thin film membranes were tested for over 1200 hours; oxygen fluxes of over 10 sccm/cm² were recorded

- PDU module seals demonstrated good performance at 425 psig and 900°C under static conditions and pressure/thermal cycling conditions
- Pilot-scale membrane modules were fabricated for PDU tests
- The PDU reactor system was commissioned at high temperature and pressure with synthesis gas
- Initial scope definition of SEP project was completed with vendor quotes
- Design of full-scale membranes for SEP was completed
- SEP membrane fabrication development commenced with the fabrication of SEP membrane components

Future Directions

- Evaluate the ITM Syngas/ITM H₂ processes using PDU data
- Conduct long-term stability tests of tubular membranes and seals at high pressure
- Demonstrate performance of pilot-scale membrane modules in PDU
- Complete membrane module design and select catalysts for the SEP
- Commission the ceramic Production Development Facility and fabricate SEP membranes
- Design and fabricate the SEP reactor

Introduction

Ion Transport Membranes (ITMs) are a revolutionary platform technology for producing hydrogen and synthesis gas for applications in power generation, transportation fuels, and chemicals. The ITM Syngas and ITM H₂ processes provide a lower-cost method for converting natural gas to hydrogen and synthesis gas by combining air separation and natural gas partial oxidation in a single-step ceramic membrane reactor, with the potential for capital cost savings of over 30%. If successful, this technology could be important to emerging hydrogen markets, such as hydrogen-based fuel cells for transportation and large-scale centralized hydrogen production facilities with CO₂ capture.

The new technology utilizes non-porous ceramic ITM membranes, fabricated from multi-component metallic oxides that have both high electronic and oxygen ion conductivity at high temperatures (greater than approximately 700°C). In operation, oxygen from a hot air stream is reduced at one surface of the ITM membrane to oxygen ions, which diffuse through the membrane under a chemical potential gradient. At the opposite surface of the membrane, the oxygen partially oxidizes a pre-reformed mixture of hot natural gas and steam to form syngas, a mixture of hydrogen and carbon

monoxide. The ratio of hydrogen to carbon monoxide is in part dependent upon the amount of steam. The membrane material must show long-term stability in reducing and oxidizing atmospheres, and long-term compatibility with any oxygen reduction and reforming catalysts that are in contact with its surface.

Approach

The objective of this project is to research, develop and demonstrate a novel ceramic membrane reactor system for the low-cost conversion of natural gas to hydrogen and synthesis gas: the ITM Syngas/ITM H₂ processes. Through a 9½ year, three-phase program, the ITM Syngas/ITM H₂ technology will be developed and scaled up to obtain the technical, engineering, operating and economic data necessary for the final step to full commercialization of the hydrogen and syngas generation technologies. Phase 2 of the program was initiated in FY2000 and will extend for 4½ years. Process concepts and performance will be validated in two stages of scale-up in Phase 2: the Process Development Unit (PDU), which began operation in 2002, and the Subscale Engineering Prototype (SEP), which will begin operation in 2004.

In Task 2.1, "Commercial Plant Economic Evaluation," advanced ITM Syngas/ITM H₂ processes will be developed, and the economics of operation at the commercial plant scale will be evaluated based on the results of the Phase 2 program. In Task 2.2, "Materials and Seals Development and Evaluation," membrane materials and seals will be tested at the laboratory scale under ITM Syngas/ITM H₂ process conditions to obtain statistical performance and lifetime data. In Task 2.3, "ITM Syngas Membrane and Module Design and Fabrication," membrane reactors will be designed for the ITM Syngas/ITM H₂ processes at the PDU, SEP and commercial scales. Pilot-scale membrane modules will be fabricated for testing in the PDU. Fabrication of the membrane reactor modules will be scaled up in a Production Development Facility to supply the requirements of the SEP.

In Task 2.4, "Nominal 24 MSCFD ITM Syngas/ITM H₂ PDU," the components of the ITM Syngas/ITM H₂ technology will be demonstrated in a laboratory Process Development Unit (PDU). The PDU will operate at an equivalent of 24 MSCFD of syngas capacity, and will performance test pilot-scale planar membranes under commercial process conditions. In Task 2.5, "Nominal 330 MSCFD ITM Syngas/ITM H₂ SEP," a Sub-Scale Engineering Prototype (SEP) unit will be built to demonstrate the ITM Syngas/ITM H₂ technology using full-size membranes in sub-scale modules. The SEP will demonstrate the operation of the ITM Syngas/ITM H₂ processes at up to an equivalent of 330 MSCFD of syngas capacity.

Results

As reported previously, preliminary process design and economic evaluation for ITM H₂ in the "Distributed H₂" target range of 0.1 to 1.0 MMSCFD H₂ indicated the potential for up to 27% savings in production costs compared with trucked-in liquid hydrogen for 5000 psig fuel cell vehicle refueling applications. In addition, economic evaluation of the ITM Syngas process producing about 150 MMSCFD of a 2:1 mixture of hydrogen and carbon monoxide confirmed the potential for >33% capital cost savings compared with conventional technology based on an autothermal reformer and cryogenic oxygen supply.

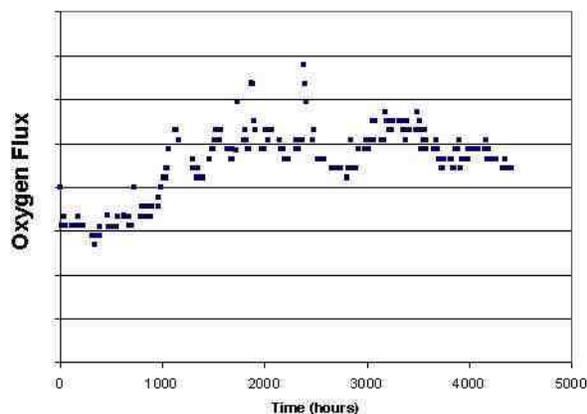


Figure 1. Six Month High Pressure Test of a Tubular Membrane

In an evaluation of advanced process concepts, the ITM H₂ process was developed for a large hydrogen production plant with CO₂ removal, producing 760 MMSCFD of fuel-grade hydrogen at 100 bar and 14,000 tonne/day of CO₂ at 80 bar for sequestration. For this application, the ITM H₂ process was compared to a conventional oxygen-blown Autothermal Reformer (ATR) with a cryogenic air separation unit to supply oxygen. Economic evaluation of the ITM H₂ process showed the potential for over 30% capital cost savings in the syngas generation process area and over 20% capital cost savings for the overall syngas/H₂/CO₂ production process. The ITM H₂ process also has a higher thermal efficiency of 74% compared to 71% for the oxygen-blown ATR process. The hydrogen product is a "clean" fuel suitable for centralized power generation (approximately 1300 MW) and for distribution to local stationary or mobile applications, including fuel cells.

Tubular membranes and seal assemblies were tested in high-pressure, high-temperature lab-scale units under ITM Syngas and ITM H₂ process conditions. In these tests, pre-reformed natural gas mixtures at process pressure were passed over the outer surface of the tubular membrane, while air at atmospheric pressure was fed to the inner surface of the tube. Multiple tests under ITM H₂ conditions each operated continuously for over 6 months at 250 psig and 825°C with good performance stability. The results of one of these six-month continuous tests are shown in Figure 1.

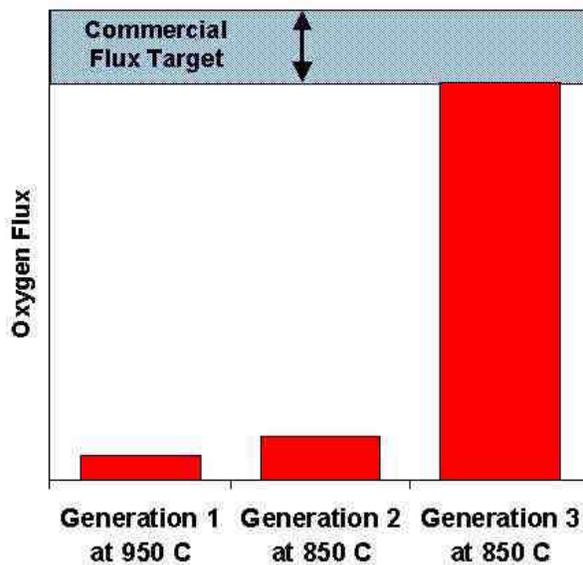


Figure 2. Advanced Catalyzed Membranes Approach Commercial Flux Target

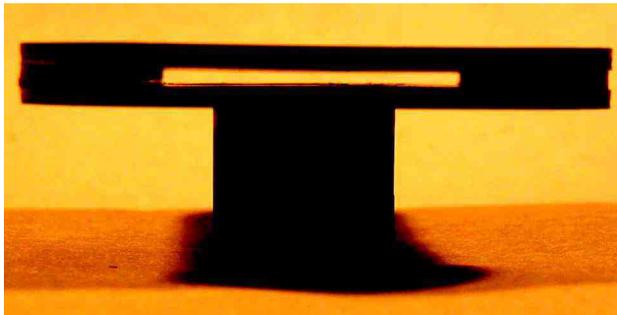


Figure 3. Process Development Unit Membrane Module

Sub-scale thin film membranes were also tested at atmospheric pressure for periods of over 1200 hours. Tests of advanced catalyzed membranes demonstrated oxygen fluxes that approach the commercial flux target range, as shown in Figure 2.

Pilot-scale PDU planar membrane modules were fabricated, an example is shown in Figure 3. Air at low pressure is passed through the inner support passages (not shown) constructed within the planar membrane, while the pre-reformed methane mixture is passed at high pressure over the surfaces of the membrane module, where partial oxidation takes place to produce syngas.



Figure 4. The ITM Syngas/ITM H₂ Process Development Unit

Installation of the PDU system was completed, and the PDU reactor system and PDU membrane modules were commissioned at high temperature and pressure with a syngas mixture. The PDU integrates the various components of the ITM Syngas/ITM H₂ reactor design and will be used to confirm the performance of the planar membrane modules and seals under commercial process conditions. The PDU reactor is shown in Figure 4.

The design of the full-scale membrane for the SEP was completed. SEP membrane fabrication development commenced with the fabrication of SEP membrane components. The rapid scale-up in ceramic membranes is shown in Figure 5. Lab-scale membranes were developed in 1999-2000 in conjunction with initial materials development and were used to demonstrate oxygen separation performance. Pilot-scale membranes were developed in 2000-2001 and have a 40-fold increase in membrane area over the lab-scale membranes. The pilot-scale membranes are being used to demonstrate membrane performance at commercial process conditions in the PDU. Fabrication methods that were developed at the pilot scale are being scaled-up for full-size membranes. Full-size membranes are currently under development and have a 180-fold increase in membrane area over the lab-scale membranes.

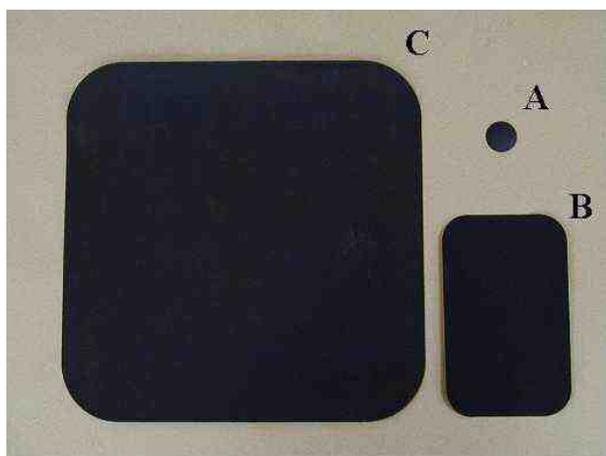


Figure 5. Scale-up of ITM Syngas/ITM H₂ Ceramic Membranes. (a) Lab-scale (b) Pilot-scale (c) Full-size

Initial scope definition of the SEP project was completed. Preliminary process flow diagrams were developed, and vendor quotes were received for major equipment items. In addition, preliminary design of the ITM Syngas/ITM H₂ SEP reactor was completed.

Conclusions

Significant progress has been made to develop the ITM Syngas/ITM H₂ technology. A database is being built up of performance data from several six-month long membrane tests. Membrane modules and seal assemblies have also been fabricated for testing in the PDU and ceramic fabrication scale-up is continuing the progression from lab-scale to full-size membranes. The PDU has been commissioned at high temperature and pressure. We continue to make excellent progress against the remaining technical challenges in the demonstration and scale-up of the ITM Syngas and ITM H₂ technology.

FY 2002 Publications/Presentations

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2. C.M. Chen, US DOE H₂ Program Review, Golden CO, May 2002, "Engineering Development of Ceramic Membrane Reactor Systems for Converting Natural Gas to Hydrogen and Synthesis Gas for Liquid Transportation Fuels."

Patents Issued

1. US Patent 6214066, S. Nataraj, S.L. Russek, "Synthesis Gas Production by Ion Transport Membranes," April 2001.
2. US Patent 6302402, S.W. Rynders, E. Minford, R.E. Tressler, D.M. Taylor, "Compliant High Temperature Seals for Dissimilar Materials," October 2001.

II.C.6 Integrated Ceramic Membrane System for Hydrogen Production

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Objectives

- Perform technoeconomic feasibility analysis of the integrated ceramic membrane system for hydrogen production.
- Define the development needed to prepare the concept for pilot testing and demonstration.

Approach

- Identify process options with potential for lower product costs.
- Evaluate performance of various process options by simulations.
- Carry out experiments to assess the performance of ceramic proton conducting membranes.
- Estimate capital and product costs.
- Select the process option that is most likely to be commercially viable.
- Identify development issues for the selected process option and prepare a development program for Phase II.

Accomplishments

- Two process options were identified: 1) Integrated oxygen transport membrane (OTM)-hydrogen transport membrane (HTM) reactor process that uses proton conducting ceramic membrane for hydrogen separation and 2) sequential OTM and HTM reactors process that uses a palladium (Pd) alloy based membranes for hydrogen separation. The efficiency hydrogen/methane (H_2/CH_4) of the sequential OTM and HTM reactor was higher at 79% (on higher heating value [HHV] basis) as compared to 76% for the integrated OTM-HTM reactor process.
- The hydrogen flux through the proton conducting membrane was much lower than for the flux required for commercial viability.
- The capital and product costs for the sequential reactor process were 10 - 12% lower than for the integrated reactor process.
- A process with sequential OTM and HTM reactors was selected for further development, and Pd alloy based membrane was identified as a major development item for Phase II efforts.

Future Directions

- Develop a composite membrane with a thin film of Pd alloy deposited on a porous support.
- Develop a suitable porous support with desired pore architecture for supporting a thin film of membrane and with necessary mechanical strength.

- Screen Pd alloy compositions for resistance to syngas and thermal cycling.
- Prepare tubes of composite membranes.
- Test a bench-scale membrane reactor for carrying out shift conversion and hydrogen separation.

Introduction

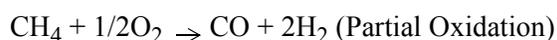
Hydrogen is expected to play a vital role in the transportation sector for the fuel cell vehicles (FCVs). One of the crucial factors for the successful introduction of FCVs on the U.S. roadways is a low-cost supply of hydrogen. The demand for hydrogen at fueling stations for FCVs is projected to be less than 10,000 standard cubic feet per hour (scfh). To be competitive with gasoline, the cost of hydrogen delivered to a vehicle must be below \$20/MMBtu. A key challenge in achieving this hydrogen price is to reduce the capital costs of an on-site plant. The approach taken in this project is to reduce capital costs by reducing the complexity of the process and thus reducing the equipment needed to generate hydrogen.

Approach

Two process options were evaluated. In the first process option, both the OTM and the HTM were integrated into a single unit such that various processing steps (syngas generation, shift conversion and hydrogen purification) necessary for hydrogen production occur in a single reactor [1]. Since the OTM reactor operates at high temperatures (800 to 1100°C), it is necessary to have the HTM operating at high temperatures. The ceramic proton conducting membranes can operate at temperatures up to 900°C and they were considered as HTMs for this process option. (The Pd alloys are not suitable for high temperature operation.) In the second process option, OTM and HTM are placed in two separate reactors (Figure 1). By de-coupling these two membranes, the temperature constraint for the HTM is removed, and the HTM reactor can be operated at much lower temperatures (e.g. 300 to 600°C) than the OTM reactor. The Pd alloy membranes were considered for this process option.

Air at low pressure (~25 pounds per square inch absolute [psia]) is passed to the retentate side of the OTM, and compressed natural gas (200 - 300 psia)

and steam are passed to the permeate side of the OTM. Oxygen is transported across the OTM to the permeate side, where it reacts with natural gas to form syngas. A portion of natural gas also reacts with steam to form syngas. Additional hydrogen is formed by the water-gas shift reaction. The basic reactions involved in the process are:



A catalyst is incorporated in the reactors to promote the reactions. The syngas from the OTM reactor is cooled and then fed to the retentate side of the HTM reactor. In the HTM reactor, the shift reaction and the hydrogen separation through the HTM take place. Hydrogen is transported to the permeate side of the HTM by the partial pressure difference driving force. Due to removal of hydrogen from the reaction zone, more hydrogen is formed by the shift reaction. As much hydrogen as possible is recovered from the reaction zone by transport through the HTM to the permeate side. Eventually, a partial pressure pinch between the reaction zone and the permeate side is reached, limiting the amount of hydrogen that can be recovered. A process model was developed for the process with sequential OTM and HTM reactors. The Hysys simulation was used to evaluate the performance of the process.

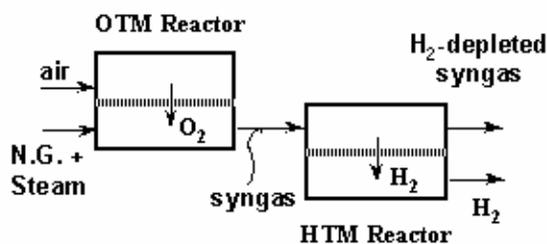


Figure 1. Sequential OTM and HTM Reactor System

Results

The overall efficiency of the plant is defined as follows:

$$\text{H}_2 \text{ efficiency} = (\text{energy recovered in H}_2 \text{ (HHV)} \times 100) / (\text{energy input in natural gas (HHV)}).$$

Table 1 Summarizes utility consumption and the H₂ efficiency for the sequential reactor process.

Table 1. Performance Summary of the Sequential Reactor Process

Hydrogen Capacity, scfh	1,000
Natural Gas, scfh	404
Power, kW	4.6
Water, gpm	1.1
H ₂ Efficiency, %(HHV)	79%

The H₂ efficiency of the process with sequential reactors was estimated to be 79% (HHV). This compares with ~76% efficiency (HHV) for the process with the integrated OTM-HTM reactor. The higher efficiency for the process with sequential OTM and HTM reactors was due to lower temperature, which is favorable for shift reaction equilibrium.

The cost estimate developed for the process based on the integrated OTM-HTM reactor was used as a baseline cost, and the cost estimate for the process with the sequential reactors was developed by extrapolation. The hydrogen plant capacity was fixed at 1,000 scfh for the cost estimation. The capital costs for 2,000 and 5,000 scfh were estimated by using appropriate scale-up factors. For each capacity, costs were estimated for 10, 100, and 1,000 plants built/year. After reviewing the results, it was clear that the plants with capacities of 1,000 and 2,000 scfh will not be economically viable, because the cost of hydrogen from such plants is either comparable to or higher than the cost of liquid hydrogen. Therefore, the results for only 5,000 scfh plants are presented here.

The cost estimate presented last year for the integrated reactor process was reviewed and revised. The cost components with significant revisions were costs of reactor, instrumentation, natural gas and capital recovery. In addition, the costs related to contingency and safety were added. To estimate

capital recovery costs, the method described in the Hydrogen Infrastructure Report [2] was used. The financial parameters listed in Table 2 were used.

Table 2. Financial Parameters

15% after-tax rate of return
38% corporate tax rate
15-year plant life
0% inflation rate

These parameters lead to capital-related charges of 23.5% of capital investment/year. In addition, the assumptions listed in Table 3 were made.

Table 3. Cost Estimation Assumptions

Natural Gas	\$4/MMBtu (HHV)
Power	\$0.05/kWh
Water	\$0.01/1000 gal.
Maintenance and Replacement	3% of capital investment/yr
Capacity Utilization	80%

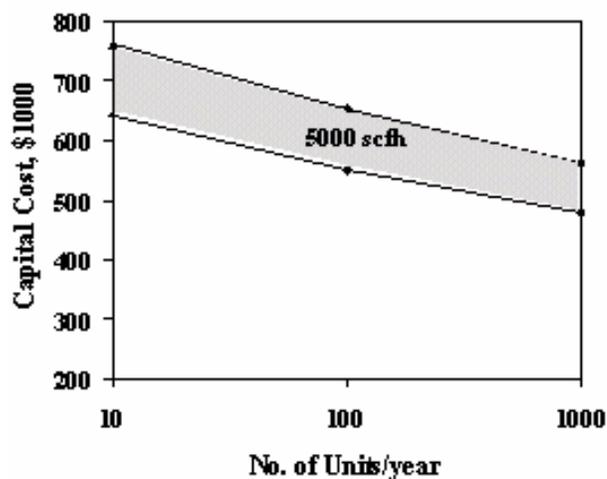


Figure 2. Capital Costs for the Integrated OTM-HTM Reactor Process

Figures 2 and 3 show the revised capital and product costs for the process with the integrated reactor. Figures 4 and 5 show capital and product costs for the process with the sequential reactors. The range in capital costs for any given point is due to the level of uncertainty in the cost estimate, especially in the costs of membrane reactors.

Comparing the costs for the two process options, the capital costs for the sequential reactor process are ~12% lower than the costs for the integrated reactor

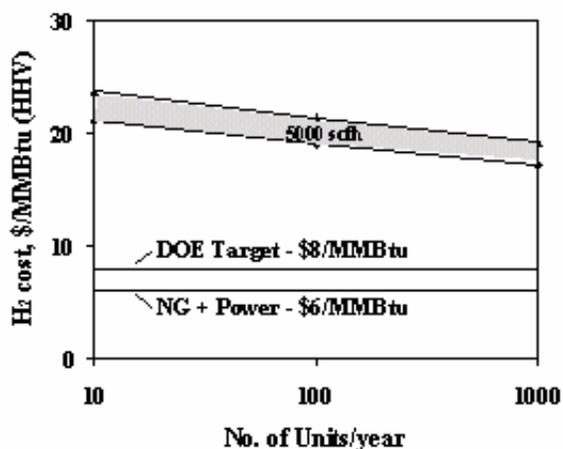


Figure 3. Product Costs for the Integrated OTM-HTM Reactor Process

process. Several factors contributed to lower costs for the sequential reactor process. The complexity of the reactor design is significantly reduced when there are two separate membrane reactors. Operation of the HTM reactor at lower temperature makes it possible to use less expensive materials of construction. The OTM reactor still operates at a high temperature; however, its size is significantly smaller than the size of the integrated OTM-HTM reactor. Finally, the hydrogen flux through a Pd alloy membrane (which is used in the sequential reactor process) is much higher than the flux through a proton conducting ceramic membrane (which is used in the integrated reactor process). As a result, less membrane area is required, which in turn reduces the size and cost of the HTM reactor.

The product hydrogen costs for the sequential reactor process were ~10% lower than the integrated reactor process. The cost of hydrogen production (at 15 psia) ranged from \$15 to \$21/MMBtu (HHV) depending on the number of plants built per year. These numbers do not include the costs of compression, storage and dispensing. At low production volume (10 units/year), the cost of hydrogen will be \$19 to \$21/MMBtu (HHV). With mass production (1000 units/year), the cost of hydrogen will drop down to \$15 to \$17/MMBtu (HHV). The capital cost reduction at higher production volume results from the volume discounts for the equipment purchases and reduction in

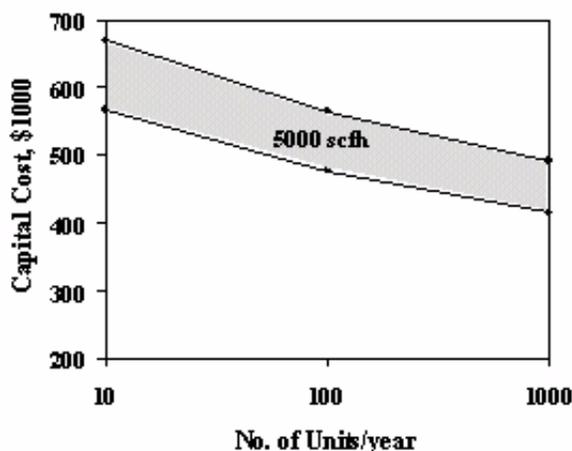


Figure 4. Capital Costs for the Sequential OTM and HTM Reactors Process

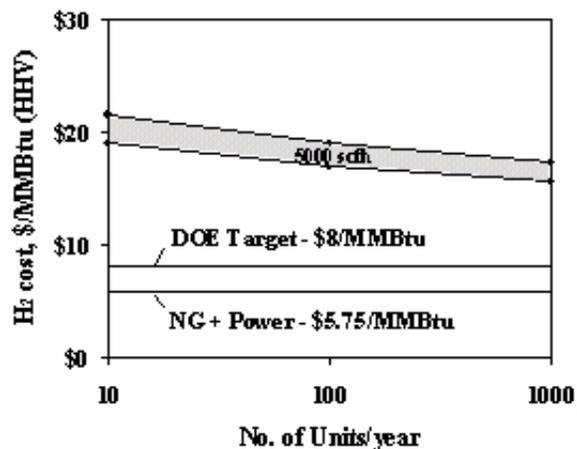


Figure 5. Product Costs for the Sequential OTM and HTM Reactors Process

assembly costs due to experience in building multiple identical plants.

Phase I indicated that the two-step reactor system with OTM reactor followed by integrated HTM shift reactor is the preferred approach for an economical hydrogen production system. Significant efforts are required in two areas for successful commercialization: development of cost-effective HTM and development of mass production approach to reduce capital costs. We are proposing a program with the emphasis on advancing the hydrogen separation technology. Any effort related to mass

production will be undertaken when the market for FCVs is more clearly visible.

The experimental work on the proton conducting materials based HTMs indicate that the hydrogen flux is not sufficient for commercial viability in the foreseeable future. Therefore, we have decided to focus on the Pd alloy based HTMs for further development efforts. The basis for the future work is the technology established by Research Triangle Institute to deposit thin, uniform, defect-free, Pd alloy membrane layer on the ceramic substrate and Praxair's ceramic membrane manufacturing technology.

Phase II of the program is expected to last three years, and it will be divided into two parts. The first part of Phase II will focus on developing a commercially viable HTM and will last two years. We expect to develop HTM and its sub-components during the first year and test a bench-scale membrane reactor (containing multiple membrane elements) with shift conversion in the subsequent year. The second part of Phase II will involve testing of critical balance of plant components such as OTM reactor, steam generator and high temperature heat exchangers.

Conclusions

The efficiency of the sequential reactor process is estimated to be 79% (HHV). The sequential OTM and HTM reactors process with the HTM reactor operating at lower temperature will result in lower hydrogen costs compared to the integrated OTM-HTM reactor process. The cost of hydrogen is estimated to range from \$15 to \$21/MMBtu (HHV) depending on the number of hydrogen plants built per year. The projected hydrogen costs from the proposed system are lower than the competing supply options, such as electrolysis and liquid hydrogen.

A Phase II plan has been defined. The sequential reactor process has been selected as a preferred process option. The first objective of Phase II is to develop a low-cost HTM (based on Pd alloy) with high hydrogen flux and tolerance for syngas components and thermal cycling. The next task will be to design and test a bench-scale membrane reactor

to carry out shift conversion and hydrogen separation. Finally, other critical components such as OTM reactor, steam generator and high temperature heat exchangers will be tested.

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II.C.7 Low Cost Hydrogen Production Platform

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Main Subcontractors: Praxair, Inc., Tonawanda, NY; Boothroyd Dewhurst Inc., Wakefield, RI;

Diversified Manufacturing Inc., Lockport, NY

Objectives

- Define process/equipment concepts and develop preliminary design suitable for mass production of a small on-site hydrogen systems.
- Perform a technoeconomic study for an on-site hydrogen production system for the transportation and industrial market (1,000 to 5,000 standard cubic feet per hour [scfh]).
- Develop business cases regarding the viability of the development project.
- Define the system in sufficient detail to develop a Phase II plan for the prototyping and system detail modeling of the major components.

Approach

- Use existing steam methane reformer (SMR) and purification process technologies as the base for the system.
- Develop design parameters for the system including natural gas, water and product specifications and pressures as well as setting goals for the mechanical details such as system footprint, shipping parameters and system setup time.
- Investigate current on-site hydrogen plant designs and develop component and overall cost breakdowns of the systems.
- Use design for manufacturing and assembly (DFMA) principles from the early stages of the design effort.
- Design the system with high volume manufacturing as an up-front design parameter.
- Select the system option that is most likely to be commercially viable when produced in high quantity production runs.
- Identify development issues for the selected design option and prepare a development plan for Phase II.

Accomplishments

- Design parameters for the system have been determined.
- A detailed review of current on-site options was completed, and a cost percentage breakdown of individual plant components has been developed. This information was then used to set goals for the overall system and component cost and design.

- Multiple process models of various reformer and purification options have been developed. These models served as a baseline to create the mechanical designs of the system.
- Three high potential conceptual designs were selected for further development. The selection process included design evaluations by the subcontractors.

Future Directions

- Complete the evaluation of the three current design concepts. Select highest potential concept(s) or combination of concepts for further development.
- Refine and optimize the selected concept(s) using DFMA techniques.
- Develop scale of economy analysis for the selected system design(s).
- Complete the techno-economic study for the system, including business model and competitive assessment.
- Develop plan for Phase II of project. Determine components requiring prototyping and/or advanced modeling/simulation in Phase II.

Introduction

Hydrogen is expected to play a vital role in the transportation sector with fuel cell vehicles (FCVs). A source of low cost hydrogen will be vital to the successful transition to a hydrogen based transportation economy and a key challenge to this goal is to reduce the overall cost for the small scale on-site generation of hydrogen. Praxair is an industry leader in the design, development and operation of hydrogen production facilities and is applying this extensive knowledge base, as well as advanced mass production, design and tooling experience provided by the subcontractors, to this development effort.

The overall goal of the Low Cost Hydrogen Production Platform (LCHPP) cooperative agreement is to develop an on-site hydrogen generation system, based on existing steam methane reformer technology, which will significantly lower the overall cost to produce hydrogen at low volumes. Praxair has, as partners in this project, Boothroyd-Dewhurst Inc. (BDI) and Diversified Manufacturing Inc. (DMI). BDI has expertise in the area of DFMA, and they have worked extensively with the automotive industry to lower the overall cost of production for mass produced systems. DMI is a design and fabrication facility with extensive experience in the areas of high temperature component design for both new designs and refurbishments, tooling design and manufacturing processes.

Approach

The requirement for industrial on-site hydrogen plants has typically been larger volumes than that of the LCHPP project. Achieving a competitive, lower volume plant offering has dictated the need to modularize plant components and streamline the installation and start-up process. The cost target of the LCHPP project is significantly lower than any previous goal set for the industrial market and to approach this goal, further integration, scale of economies and design optimization will need to be implemented. Rather than designing a system from a block flow process engineering approach, the system will be designed from the ground floor using DFMA techniques as well as a very high level of system integration. The system will also be designed for mass production and will therefore require the development of tooling and fixtures to aid in the assembly process. It will not be possible to build 0 - 10 of these units and approach the DOE cost goal. The economic viability of the system will only be achieved in large volume production runs.

The LCHPP project is structured in 3 distinct phases. Phase I is the engineering study and feasibility phase, which is scheduled to be completed in October 2002. A business plan and economic model will be developed as part of Phase I and will be updated as required during Phases II and III. Phase II is the system detail design, tooling development and prototype phase and is currently scheduled to begin in December 2002. Phase III is

the final phase where a demonstration unit will be developed and tested. The tooling required for the mass production of the system will also be developed in Phase III. Phase III is currently scheduled to begin in September 2004 and last for 1.5 years.

The process used for this project will be a SMR with a pressure swing adsorption (PSA) or membrane based purification system. The project does not include the hydrogen compression, storage or distribution system required for the high-pressure filling of FCVs. A process diagram of the system is shown in Figure 1.

Results

Praxair previously developed what was then considered to be a small on-site hydrogen plant for the industrial market in the mid 1990s. The system capacity ranges from 12,000 to 30,000 scfh (340 to 850 Nm³/hr) and generates hydrogen using a SMR with a PSA purification system. The system, although it has multiple skids requiring field assembly, demonstrates some of the potential positive effects of packaging all components on skids and limiting the field installed items to a few miscellaneous components. The installation cost percentage of the overall capital was less than one half of that of the larger systems, and the system was installed in less than 4 weeks. This is a significant improvement over the large plant approach, but the goals for the LCHPP will require additional installation and start-up cost reductions. The Praxair on-site hydrogen generating system (HGS) is shown in Figures 2 and 3.

Although the HGS system has been a success in the industrial market, with the system being over 97% reliable, the goals for the LCHPP project require a step change. The LCHPP will be approximately one-sixth the capacity, about one-fifth the footprint, and will lower the hydrogen product to about one-half that of the HGS system.

A detailed analysis of existing SMR based on-site hydrogen plants, including the HGS system detailed above, has been completed. The object of this analysis was to evaluate the current design methodology related to industrial on-site hydrogen plants. A cost matrix detailing the individual

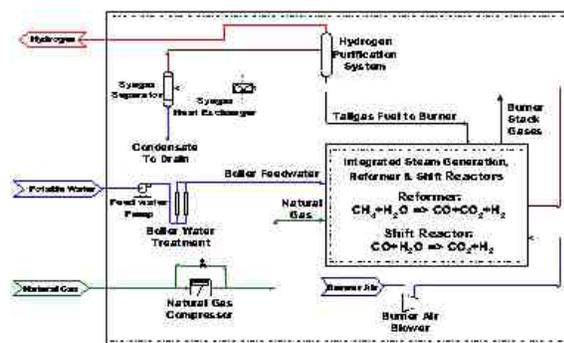


Figure 1. Low Cost Hydrogen Production Platform (LCHPP) Process Diagram

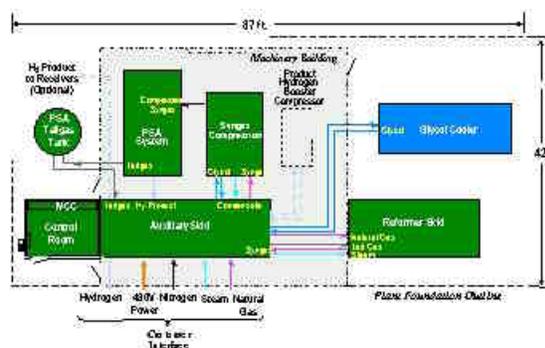


Figure 2. Praxair HGS On-Site Supply System



Figure 3. Praxair HGS On-Site Supply System (Seymour, Indiana)

component costs as well as the project and operating costs associated with the plants was created. The data was collected from over 15 on-site hydrogen supply systems currently operated by Praxair. The

systems analyzed ranged from 10 to 100 times the capacity required in accordance with this project. Data from the analysis indicates that SMR hydrogen plants are typically custom designed with very low levels of integration. A significant percentage of the capital is required for the installation of the plant. The analysis also confirmed that typically over 50% of the installed capital cost is related to the reformer and shift components. With the cost matrix component breakdown, the areas of highest potential cost savings were clearly identified.

Results to date also include the development of detailed process models of SMR and purification systems. These models served as the baseline for the development of the mechanical design concepts. Options such as high/low pressure reforming, natural gas/syngas compression, PSA/membrane purification and various levels of thermal/process integration were modeled.

After the initial development of the process flow models, the mechanical design phase of the project began. As a result of the existing technology assessment discussed above, significant initial effort was placed in the cost reduction of the reformer and shift portion of the system. Initially, 6 mechanical design concepts were developed and evaluated. After discussions with the subcontractors, the six initial concepts were narrowed down to the three highest potential concepts. The three conceptual design options are currently being evaluated from the following three perspectives: 1) Praxair is developing 3D mechanical models as well as detailed process models of the various options, 2) DMI is reviewing the designs regarding manufacturability, single unit cost and higher quantity manufacturing costs, and 3) BDI is reviewing the options from a part count and system mechanical design optimization approach. Both a preliminary manufacturing cost summary of each concept for a single unit and the potential for cost savings in a mass production operation are being developed. At the conclusion of the preliminary analysis, the concepts will be narrowed down to the one (or possibly two) highest potential concept(s).

The purification system is also currently being evaluated. A PSA-based purification system appears to be the clear overall economic choice. Praxair has extensive experience in the area of PSA development

and has developed advanced PSA cycles and system designs that will lower the overall cost of this component.

Conclusions

Development of a cost effective hydrogen supply infrastructure is a major issue facing the use of hydrogen in FCVs. Design-optimized, integrated small scale systems are likely to play an important role in the development of that infrastructure. The low cost hydrogen production platform project should lead to a cost effective SMR based system that can be an economical source of hydrogen for retail fueling stations. A report summarizing the findings of Phase I, as well as recommendations for Phase II will be developed at the end of Phase I of the agreement.

FY 2002 Publications/Presentations

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II.C.8 Effects of Fuel Constituents on Fuel Processor Catalysts

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Objectives

- Identify the effects of major constituents, additives, and impurities in petroleum-based fuels on reformer performance
- Evaluate the effects of fuel constituents and impurities on catalyst stability
- Collaborate with major oil companies for development of future fuels for fuel cells

Approach

- Investigate autothermal reforming of fuels and fuel constituents in microreactor
- Rate performance based on byproduct formation, catalyst deactivation, and dependence of hydrogen yield and conversion
- Test blends of fuel components to establish a composition/performance relationship matrix; compare results with those for pure components
- Use long-term (>1000 h) tests to determine effects on catalyst stability, poisoning and long-term degradation

Accomplishments

- Completed short-term testing of refinery blends from three oil companies and determined that fuels low in aromatic and naphthenic components can be reformed over a wider range of operating conditions.
- Completed short-term testing of paraffinic-aromatic and paraffinic-naphthenic blends and determined that aromatic and naphthenic components decrease the rate at which paraffinic species are reformed
- Determined effects of amine additives on reforming behavior
- Studied effect of composition on water requirements and water balance issues in fuel reformer-fuel cell systems
- Completed long-term tests on monolithic catalysts

Future Directions

- Investigate long-term effects of additives (e.g., detergents, antioxidants) and impurities
- Continue investigating reforming of blended fuels; determine composition/performance relationships from results
- Investigate differences in fuel reforming with different catalysts
- Make recommendations for fuel cell fuels

Introduction

On-board reforming of petroleum-based fuels, such as gasoline, may help ease the introduction of fuel cell vehicles to the marketplace. Although gasoline can be reformed, some constituents and impurities may have detrimental effects on the fuel processing catalysts, which may lead to compromised performance and decreased fuel conversion efficiency. In order to identify which constituents are beneficial and which are detrimental to the reformer, we have begun to test various components of gasoline and blends of gasoline streams under autothermal reforming conditions.

Prior work focused on the autothermal reforming of some of the major components of gasoline. We investigated the autothermal reforming of iso-octane, n-octane, octane, trimethylbenzene, toluene, methylcyclohexane, and methylcyclopentane. These chemicals represent the branched paraffins, straight chain paraffins, olefins, aromatics, and cyclic paraffins present in gasoline. We observed that trimethylbenzene required more severe reforming conditions than the other components.¹ The current work focuses on the effects of blends of components and on the effects of additives. Blends are being investigated to determine if the presence of some components can affect the reforming of others.

Approach

Fuel blends were obtained from three major oil companies. The blends were formulated to provide fuels with compositions of interest to the refineries. Reforming of the fuel blends was performed under constant $O_2:C$ and $H_2O:C$ ratios (0.42 and 1.4) on identical catalysts to allow for comparisons of the different fuels. Short-term (<20 h) tests were performed in a reactor containing ~2 g of catalyst. The fuel and water were vaporized, then mixed and sent to the reactor where oxygen was added. Four sampling ports allowed for testing at various positions (and space velocities) in the catalyst bed. A small portion (<1%) of the gas stream was diverted through one of these ports to the residual gas analyzer for analysis. The remainder of the gas stream continued through the reactor bed to the exit stream. Batch sampling was performed at the reactor exit.

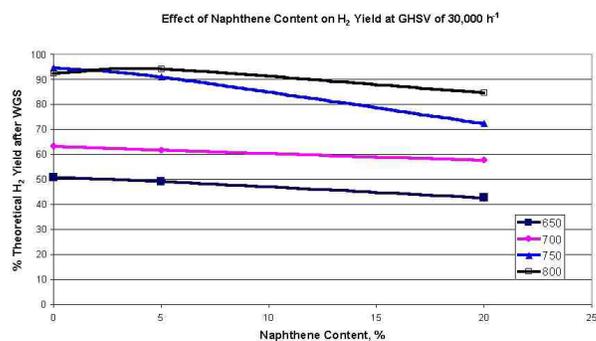


Figure 1. Effect of naphthene content on the hydrogen yield from reforming refinery blends.

Long-term (>1000 h) tests were performed in a separate reactor equipped with a solid-state on-line hydrogen sensor and infrared carbon monoxide and carbon dioxide detectors. Batch sampling was performed at the exit stream. This system allowed us to determine the durability of the autothermal reforming catalyst and to determine if there are any long-term problems (poisoning, coking) caused by the fuel components.

Results

Tests on the fuel blends indicate that fuels that are high in naphthenic components have a narrow window of operating conditions in which they provide good hydrogen yields. Figure 1 shows the dependence of hydrogen yield on naphthenic content for reforming at a GHSV of $30,000h^{-1}$ at 650, 700, 750 and 800°C. Increasing the naphthene content from 0 to 5% has very little effect; however, when the naphthene content is increased to 20%, hydrogen yield drops off substantially. To better understand the effects of naphthenes, we investigated the reforming of a binary mixture of isooctane and 20% methylcyclohexane. The partial pressures of cyclohexane, methylcyclohexane, and benzene, normalized to the partial pressure of a helium internal standard, are plotted as a function of the inverse of the space velocity in Figure 2. The inverse of the GHSV is proportional to the residence time in the reactor. At short residence times methylcyclohexane and cyclohexane (formed by removing a methyl group from methylcyclohexane) dehydrogenated to form aromatics. The aromatics then behaved as they did in the refinery blends with high aromatic content and the isooctane-xylene mixtures,² and decreased

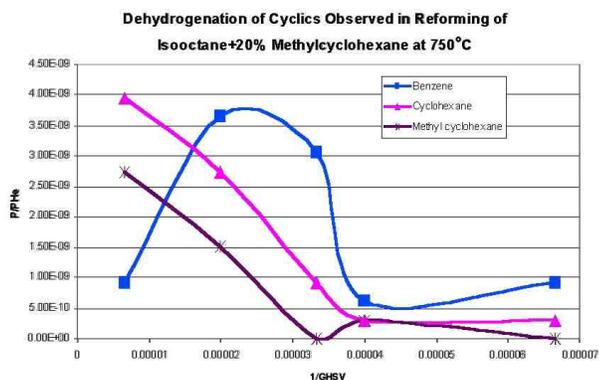


Figure 2. Methylcyclohexane, cyclohexane, and benzene content in the product gas from reforming isooctane+20%methylcyclohexane, showing conversion of cyclohexanes to benzene.

the rate of reforming of the paraffin. In addition, the dehydrogenation reaction is endothermic. This reduces the temperature at the front of the reactor and further decreases the reaction kinetics relative to those for pure isooctane.

Experiments were performed on solutions of isooctane with n-secbutylamine, a surrogate for isobutyleneamine detergents. The addition of n-secbutylamine decreased the hydrogen yield at temperatures below 750°C (see Figure 3). A closer investigation of the product gas revealed that, similar to the case for aromatics, the amine additive decreased the rate at which isooctane is reformed (Figure 4). However, with n-secbutylamine the effect is seen at much lower concentrations. A concern with amine additives is that they may form ammonia, which is a poison for PEM fuel cells at sub ppm levels. No ammonia was observed in the reforming of isooctane-n-secbutylamine solutions of 50 ppm n-secbutylamine. For solutions with 500 wppm n-secbutylamine, no ammonia was observed when the reforming was performed at 800°C; however, trace amounts (<250 ppb) were observed when the reformer was operated at 650°C. When the amine concentration was 1000 wppm, ammonia was observed in the product gas at levels of 1 ppm when the reactor was at 800°C and 1.5 ppm when the reactor was at 650°C.

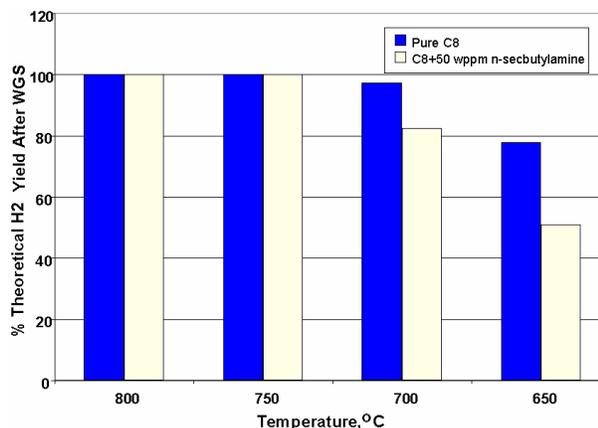


Figure 3. Effect of n-secbutyl amine on the hydrogen yield from reforming isooctane.

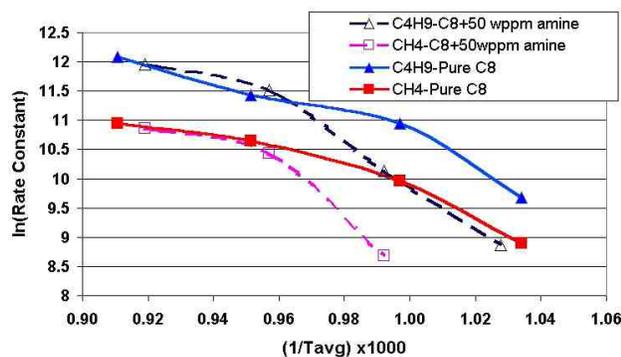


Figure 4. Effect of n-secbutylamine on the rate of disappearance of paraffinic species during isooctane reforming.

These results indicate that species that adsorb more strongly to the metal centers in the catalyst tend to decrease the rate at which the paraffinic species in the fuel are reformed. This is similar to results reported in combustion literature, where species such as aromatics have been observed to decrease the combustion of paraffins in a mixed stream.^{3,4} It also suggests that other additives and impurities that have strong adsorption to platinum will decrease the rate of reforming.

Water Balance Issues

Where fuel cell systems use on-board fuel processing of available fuels, the fuel processor requires high-purity water. For transportation applications, the process water must be recovered from the fuel cell system exhaust gas. For such

applications, it is critically important that the fuel cell system be a net water-producing device. A variety of environmental conditions (e.g., temperature, pressure), fuel cell system design, and operating conditions determine whether the fuel cell system is water-producing or water-consuming. The fuel composition can also have a significant effect. We have performed calculations determining the water balance for an ambient pressure system with on-board reforming and water recovery, assuming fuel feed rates of 1 gmol/min. In the reformer the steam-to-carbon ratio is 1.5, and oxygen flow rates are adjusted to provide a temperature rise in the reactor of 200°C. For the condenser, we have assumed a design ambient temperature of 35°C (95°F) and an approach temperature of 11.1°C (20°F), leading to an exhaust gas temperature of 46.1°C (115°F). In the fuel cell we are assuming 80% fuel utilization and 40% oxygen utilization. Calculations for several different fuels are shown in Table 1. Methane is a net water producer under these conditions, while trimethylbenzene leads to a water deficit of 81 ml/min. In order to achieve water balance for trimethylbenzene under these conditions, the exhaust gas temperature would need to be lowered to 36.6°C (97°F), just 1.6°C above the ambient design temperature. Alternatively, the pressure can be increased. For trimethylbenzene, a pressure of 1.7 atm is needed to achieve water balance, while for isooctane a pressure of 1.2 atm is sufficient.

Fuel	Net water produced, ml/min	Exhaust temperature for water balance, °C (°F)
Gasoline	-38	42.0 (107)
Isooctane	-33	43.2 (109)
Trimethylbenzene	-81	36.6 (97)
Methane	+5	49.2 (120)

Table 1. Fuel Calculations

Conclusions

These tests indicate that the fuel composition can have a large impact on reformer performance. Some fuel components can affect how other components are reformed. Species that adsorb more strongly to the metal centers in the catalyst, such as aromatics,

tend to decrease the rate at which paraffinic species in the fuel reform. This is similar to results reported in combustion literature, where species such as aromatics have been observed to decrease the combustion of paraffins in a mixed stream.^{3,4} This work also indicates that the fuel composition will have an impact on the water balance issues for the system. Fuels high in aromatics will need more aggressive conditions to be able to maintain a water balance. Future work will be directed towards understanding the interactions between the different types of components in multicomponent fuels.

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3. J. J. Spivey, Ind. Eng. Chem. Res. 1987, 26,2165-2180.
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1. Reforming Petroleum Based Fuels for Fuel Cell Vehicles: Composition-Performance Relationships, J. P. Kopasz, L. E. Miller, S. Ahmed, P. Devlin, and M. Pacheco, presented at 2002 Future Car Congress, Arlington, VA, June 3-5, 2002. SAE Technical Paper Series, 2002-01-1885, 2002.
2. Water Balance in Fuel Cells Systems, J. P. Kopasz, S. Ahmed, R. Kumar, M. Krumpelt, presented at 10th AIChE Spring National Meeting, New Orleans, LA, March 10-14, 2002.
3. Autothermal Reforming of New Gasoline for Fuel Cell Applications, J. P. Kopasz, M.A. Pacheco, S. Ahmed, X. Wang, M.A. Marquez, presented at the

7th Grove Fuel Cell Symposium, Westminster,
London, UK, Sept. 11-13, 2001.

4. Reformability of Fuels and Fuel Constituents, J. P. Kopasz, presented at the IEA Annex XV Advanced Fuel Cell Meeting, Lucerne, Switzerland, July 1-2, 2001.

II.C.9 Separation Membrane Development

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Objectives

- Produce a sol-gel encapsulated metal hydride packing material that will absorb hydrogen selectively, not break down to fines, and tolerate reactive impurities.
- Evaluate selected packing material for hydrogen separation in a small-scale column.

Approach

- Develop formulations and procedures to make silica encapsulated metal hydride composite material.
- Test selected samples in a laboratory scale separation column for hydrogen separation from feed streams of different compositions.

Accomplishments

- Produced hundred-gram size samples with three different procedures.
- Designed and installed an apparatus for gas separation tests.
- Conducted hydrogen separation from a nitrogen stream on two samples.

Future Directions

- Modify procedure to produce improved composite material to achieve required performance and reduce cost.
- Conduct hydrogen separation tests with feeds containing reactive impurities such as CO.
- Conduct cost analysis.

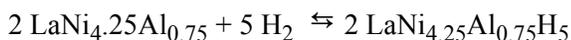
Introduction

For a hydrogen economy to become a reality, hydrogen production will have to be greatly increased from what it is today. According to U.S. DOE 1994 fuel use numbers, U.S. household transportation fuel use is a hydrogen equivalent of 0.55 billion lb/day. This is about 6 times the total U.S. hydrogen use of 0.1 billion lb/day today. Where will all the hydrogen come from? A definitive answer to this question is not yet known. One probable answer may be that hydrogen must come from multiple sources. These sources will include renewable (solar, wind, hydro, biomass, etc.) and

non-renewable (fossil, nuclear, etc.) feedstocks. One sure thing is that hydrogen will have to be recovered from all kinds of gas streams. Many of the gas streams will contain low levels of hydrogen and undesirable impurities. Today's hydrogen recovery processes include the most commonly used pressure swing adsorption process, the cryogenic process, and the membrane process. Their use with low concentration feeds and high recovery are not efficient. A new hydrogen recovery process is still needed. This work is targeted at a new hydrogen recovery process that will be suited for hydrogen recovery from low hydrogen concentration gas streams.

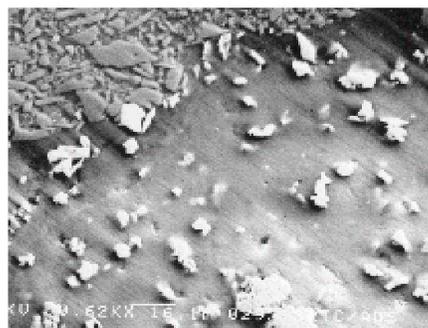
Approach

When hydrogen content in a feed stream is high (more than about 50%), it is efficient to purify the hydrogen by adsorbing the impurities. This is the principle of the pressure swing adsorption process. When the hydrogen concentration is low (less than about 50%), it is more efficient to absorb the hydrogen from the feed stream. However, a practical absorbent for hydrogen is not yet available. Metal hydrides are a promising candidate because they absorb hydrogen reversibly at moderate conditions. One example is $\text{LaNi}_{4.25}\text{Al}_{0.75}$:



Each bulk liter of this material can absorb up to 18 moles of hydrogen reversibly. The hydrogen can be absorbed and desorbed by changing the hydrogen pressure, the temperature or both. This group of materials would have been well suited for hydrogen recovery from low concentration streams if not for two practical problems. Metal hydrides in general break down to fines after repeated hydrogen absorption and desorption. The fines are in the micron range that makes them very difficult to use in separation columns. Metal hydrides are sensitive to reactive impurities like oxygen and carbon monoxide. Levels at hundredths of a fraction can render them inactive toward hydrogen. Past efforts to deal with these problems can be represented by the works of Sandrock et al [1] and Suda et al [2].

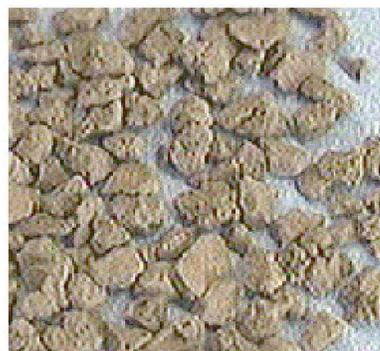
In this work metal hydride particles are encapsulated in a porous silica matrix to form a composite material. The composite is then broken into granules of desired size for packing separation columns. Each granule is a matrix of porous silica with metal hydride particles uniformly distributed in it. The porous matrix is strong so that hydrogen absorption and desorption of the metal hydride particles does not cause breakage. The porosity of the matrix permits hydrogen to reach the metal hydride particles but prevents the larger size impurity molecules from penetrating. The composite granules can therefore withstand hydrogen absorption/desorption without generating fines and can tolerate reactive impurities.



Polished surface, 620x



Polished surface, 125x
(bright spots are metal hydride)



Silica encapsulated

Figure 1. Silica Encapsulated Metal Hydride

Results

The fabrication of encapsulated metal hydride involves 3 main steps: 1) break the metal hydride to fine particles and stabilize the fines for handling in open air; 2) encapsulate the metal hydride particles in silica with the sol-gel method; 3) treat the composite with heat to obtain desired strength and porosity. Micrographs of a typical encapsulated sample are shown in Figure 1.

Samples of encapsulated $\text{LaNi}_{4.25}\text{Al}_{0.75}$ were tested for hydrogen absorption in a gas manifold with hydrogen from a known volume. The results showed that the encapsulated sample was easier to activate than the non-encapsulated metal hydride. The hydrogen absorption capacity of the encapsulated metal hydride did not change significantly. The encapsulated sample also retained its activity better than the non-encapsulated sample after exposure to air. After repeated absorption/desorption cycles, the granules did not generate fines as metal hydride did.

A laboratory scale separation apparatus was set up for testing the hydrogen separation properties of encapsulated metal hydride samples. The apparatus consists of a gas manifold, a packed column and a thermal conductivity detector (TCD). The gas manifold comprises supplies of hydrogen, nitrogen, methane, carbon dioxide and carbon monoxide. Mass flow controllers are used to generate gaseous mixtures to feed the separation column. The column is a U-shape $\frac{3}{4}$ -inch diameter, 6-inch long stainless steel tube, packed with encapsulated metal hydride granules. On the outlet side of the column, a pressure-regulating valve keeps the pressure in the column constant. A side stream is directed to the TCD for measuring the hydrogen concentration. A top-open furnace and a water bath are used to heat or cool the column when needed.

A typical test involves a hydrogen absorption step and a regeneration step. In the absorption step, hydrogen and carrier gases at target rates are joined to form a feed stream to enter the column. The hydrogen is absorbed and the carrier gas is left passing through the column. As the absorption capacity of the packing material at the inlet end is saturated gradually, an absorption front is developed in the column. The absorption front is an inverse-S shaped concentration profile of hydrogen in the gas phase. This absorption front exits the column when the packing material is completely saturated. The hydrogen concentration measured by the TCD will show the absorption front to be an S-shaped curve of hydrogen concentration versus time. This curve is often called the breakthrough curve. The actual shape of the breakthrough curve is an indication of the kinetics of hydrogen absorption of the packing material. A steep rise of the curve indicates favorable kinetics for hydrogen separation. Hydrogen

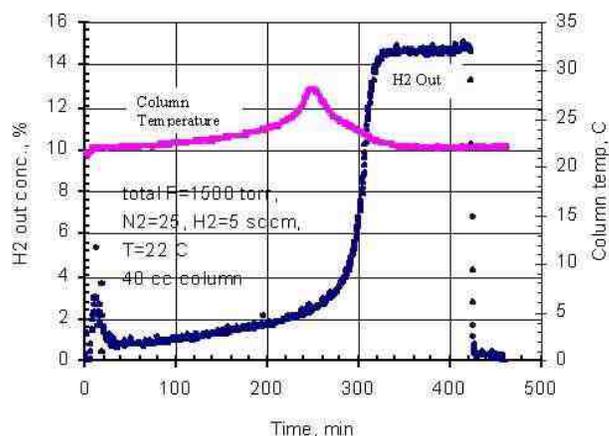


Figure 2. Breakthrough Curve of Hydrogen Absorption by Encapsulated Metal Hydride Packed

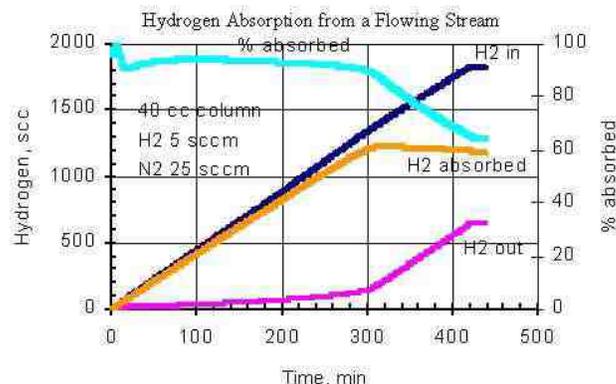


Figure 3. Hydrogen Removal from a Flowing Stream is about 95%.

absorption by metal hydride is an exothermic reaction. A thermocouple located in the column can measure the temperature peak indicating the location of the absorption front at a given time. A typical breakthrough curve and temperature peak is shown in Figure 2. This kind of data may be used to compare separation efficiencies and to design separation columns.

The efficiency of hydrogen removal can be shown by the difference in the amounts of hydrogen entering the column and the amounts of hydrogen leaving the column as a function of time. For a typical run, the results show that about 95% of the hydrogen entering the column is absorbed continuously until the column is saturated, see Figure 3.

For typical regeneration, the column is purged with nitrogen and is heated up to about 100°C at the same time. The hydrogen concentration at the exit stream is measured by the TCD. From this concentration data the partial pressure of the hydrogen can be calculated. The data in Figure 4 show that about half of the hydrogen can be recovered at 800 torr, and more than 95% can be recovered at 100 torr.

Conclusions

Metal hydride powders can be encapsulated in a porous silica matrix using a sol-gel method. The encapsulated metal hydride retains its hydrogen absorption property with increased resistance to reactive impurities. Granules of encapsulated composite can withstand hydrogen absorption/desorption cycles without producing fines. This makes them applicable in packed separation columns. Hydrogen recovery from a nitrogen stream has been demonstrated in a laboratory column with the encapsulated metal hydride. Hydrogen recovery from other gas streams such as methane, carbon dioxide and that containing carbon monoxide has been planned and will be tested. Encapsulated metal hydride is suited for hydrogen recovery from low concentration streams which will be needed in a hydrogen economy.

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1. J. J. Sheridan III et al, Journal of the Less-Common Metals, 89 (1983) 447-455.
2. X.-L. Wang et al, Journal of Alloys and Compounds, 231 (1995) 860-864.

FY 2002 Publications/Presentations

1. Paper titled "Hydrogen Separation Using Encapsulated Metal Hydride" presented in 14th World Hydrogen Energy Conference, June 9th-13th, 2002.

Special Recognitions & Awards/Patents Issued

1. US patent number 6,262,328 issued.

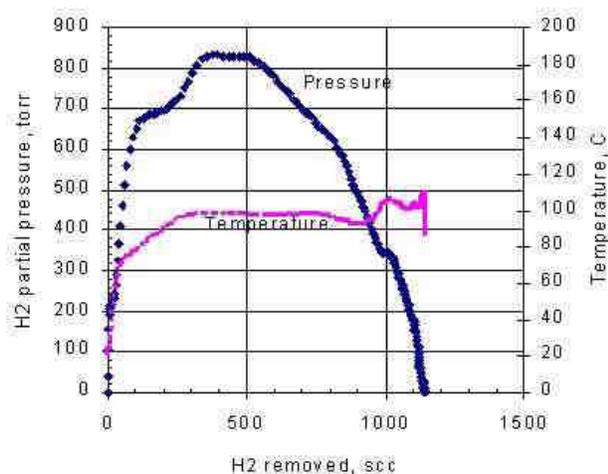


Figure 4. Hydrogen Recovery from the Column

II.C.10 Defect-Free Thin Film Membranes For H₂ Separation and Isolation

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Objectives

- Synthesize defect-free thin film zeolite membranes for H₂ isolation and purification, and use as water management membranes in proton exchange membranes (PEMs).
- Replace existing expensive and fragile Pt catalysts.
- Test the separations of light gases (pure and mixtures) through the membranes.
- Demonstrate effective light gas separations and commercialization potential of zeolite membranes.

Approach

- Synthesize defect-free thin film zeolite membranes and microporous bulk phases for future membrane applications.
- Model/simulate permeation of light gases through various frameworks/pores for optimized performance.
- Analyze flux and permeation of gases through membranes on unique in-house permeation unit.
- Validate modeling/simulation with actual permeation data to optimize membranes synthesized.

Accomplishments

- Synthesized defect-free zeolite membranes with different selectivities for various gas molecules; selectivity based upon a combination of molecular sieving through the pores and adsorption of the various composition frameworks.
- Designed and built a unique in-house permeation unit that can test both disk and tube membranes, with multiple pure or mixed gases, in a temperature range of 25-500°C.
- Analyzed selectivities of pure gases through various membranes; aluminosilicate (Al/Si) membranes are highly selective for hydrogen (H₂); all silica membranes are selective for carbon dioxide (CO₂).
- The Sandia aluminosilicate zeolite membranes have fluxes on the order of 10⁻⁶ mole/mole per meter squared Pascal second (flux unit) (m²Pa sec) and pure gas separations of H₂/N₂ ≥ 61, H₂/CO₂ ≥ 80, H₂/CH₄ = 7, CH₄/CO₂ ≥ 11. H₂ (hydrogen), N₂ (diatomic nitrogen), CO₂ (carbon dioxide), CH₄ (methane).

Future Directions

- Synthesize and characterize of thin films and bulk novel microporous phases including of Al/Si zeolite thin films doped and/or ion exchanged with other elements, unsupported aluminosilicate zeolite membranes, and silicotitanate phases.
- Synthesize membranes on (commercially viable) oxide-coated porous stainless steel supports.
- Model separation values by molecular dynamics calculations for pure and mixed light gases interacting with differing zeolite type membranes (ie., comparing ZSM-5 to ZSM-22).

- Perform permeation and flux studies of pure and mixed gases through membranes (H_2 , CO, CO_2 , CH_4 , N_2 , and sulfur hexafluoride [SF_6]).
- Build a partnership with a membrane company. Initiate an agreement for product development with an industrial partner.

Introduction

There is a great need for robust, defect-free, highly selective molecular sieve (zeolite) thin film membranes for light gas molecule separation ratios in hydrogen fuel production from CH_4 or H_2O sources. In particular, we are interested in (1) separating and isolating H_2 from H_2O and CH_4 , CO, CO_2 , diatomic oxygen (O_2), and N_2 gases; (2) water management in PEMs, and (3) as replacing for expensive Pt catalysts needed for PEMs. Current hydrogen separation membranes are based on Pd alloys or on chemically and mechanically unstable organic polymer membranes. The use of molecular sieves brings a chemically and mechanically stable inorganic matrix to the membrane. The crystalline frameworks have "tunable" pores that are capable of size exclusion separations. The frameworks are made of inorganic oxides (e.g., silicates, aluminosilicates, phosphates) that bring different charge and electrostatic attraction forces to the separation media. The result is materials with high separation abilities plus inherent thermal stability over $600^\circ C$ and chemical stability. Furthermore, the pore sizes and shapes are defined crystallographically ($<1\text{\AA}$ deviation) which allows for size exclusion of very similarly sized molecules. In comparison, organic polymer membranes are successful based on diffusion separations, not size exclusion. We envision positive results from this project in the near term with hydrocarbon fuels, and long term with biomass fuels.

Approach

The approach for this program is the development of defect-free thin film zeolite membranes and new bulk microporous phases for the selective separation of light gases. The development of these membranes includes synthesis, modeling/simulation, permeation studies and validation for separation and isolation of H_2 . The permeation of pure and mixed gases through membranes is studied at room temperature and $80^\circ C$. The modeling and

simulation work helps determine improved pore size and composition for sieving. The validation involves comparing modeling/simulation data with actual permeation values to determine needed improve upon the membranes synthesized.

Previous work at Sandia has successfully shown the ability to grow defect-free aluminosilicate and phosphate-based molecular sieve membranes. The focus now is on the enhancement and optimization of the type of molecular sieve for separation, the methodology of film growth, and the type of supports upon which to grow membranes (and remain commercially viable). We are studying aluminosilicate frameworks and metal doped frameworks to better determine the relationship between adsorption, sieving and then permeation. To study the effect and preferability of support types, we are studying and comparing unsupported film growth versus film growth on ceramic supports. We are also beginning studies on newly available ceramic coated stainless steel supports (allowing for phase match on the ceramic, with the durability of stainless steel). With all materials synthesized, we perform characterization in-house to better understand structure-permeability relationships. These include X-ray diffraction, thermal analyses, elemental analysis and permeation studies. Our in-house permeation unit is capable of fitting both disk and tubular membrane supports, either of ceramic oxide or stainless steel materials. This unique unit can be run from room temperature to elevated temperatures ($\leq 500^\circ C$), though we only plan to run as high as $80^\circ C$. The unit also contains a residual gas analyzer, enabling us to monitor and identify ratios of the permeate mixtures. We also are able to leverage end sealant technology patented through Sandia. The gases we plan to test for this project include H_2 , helium (He), CH_4 , CO, CO_2 , CH_4 , O_2 , N_2 , and SF_6 , plus mixtures of these gases.

Results

In the area of thin film membranes we have successfully synthesized micron thick aluminosilicate zeolite membranes on alumina disks (see Figure 1). Our permeation testing (see Figure 2) of the material shows that these membranes are defect-free. Defect free is denoted by permeation selectivity due to size exclusion by molecular sieving through the zeolite pores, and not through crystalline defect sites, pin holes, or crystallite mismatches (pores of this zeolite are 5.5 Å). Molecules used for this test are He (kinetic diameter = 2.6 Å) and SF₆ (kinetic diameter = 5.5 Å). Pure gas studies are run at room temperature. The only consistent problem has been that membranes have grown on both sides of the disk support, even when seeding occurs on one side. As a result, flux through the membrane/support is slightly diminished from what it would be with only one side membranes.

Once the membrane is determined to be defect-free, testing on pure gases vital to the steam reforming cycle for natural gas to hydrogen fuels can begin. Pure gas data presented in Table 1 show the results achieved by our membranes, and compares them to literature values [1,2]. Most importantly, the Sandia aluminosilicate zeolite membranes have flux values superior to those observed elsewhere. In particular, the Sandia membranes have fluxes on the order of 10⁻⁶ mole/(m²Pa sec) and separations of H₂/N₂ ≥ 61, H₂/CO₂ ≥ 80, H₂/CH₄ = 7, CH₄/CO₂ ≥ 11 (see Table 1) [3]. Also, the all-silica zeolite membranes have superior CO₂ separation from smaller light gases (such as H₂) [3,4]. Though not completely understood, these results indicate that we can tune the membrane materials to have selectivity for various light gases. This is even more valuable as it is with crystalline inorganic zeolite membranes that are chemically, thermally and mechanically robust and stable. In comparison to Pd alloy films, the zeolite membranes perform well. According to the literature [5], Pd on alumina had relative ratios of light gas separations of H₂/N₂ = 110 at elevated temperature of 350°C. The flux was also low (2 x 10⁻⁷ mole/m²Pa sec). Furthermore, we have synthesized defect-free aluminosilicate zeolite thin films supported on commercially available oxide coated stainless-steel supports (SS316); industry

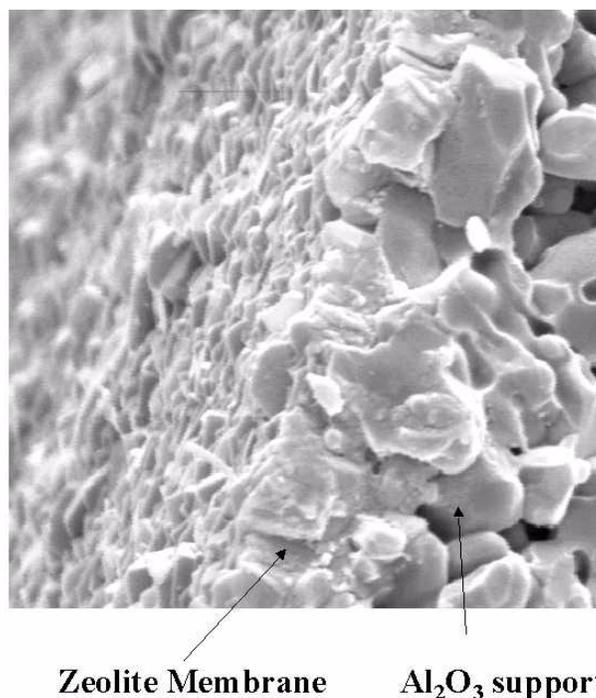


Figure 1. Cross Section View by Scanning Electron Microscope of the Micron Thick Zeolite Membrane on Gamma-Alumina Substrate

SNL All Silica (2-sided), 10 ⁻⁶ - 10 ⁻⁷ mole/(m ² Pa sec)		
H ₂ /N ₂ = 1.4		
H ₂ /CH ₄ = 0.625	CO ₂ /N ₂ = 4.2	
He/N ₂ = 1.1	CO ₂ /O ₂ = 4.9	
CH ₄ /N ₂ = 2.28	CO ₂ /H ₂ = 3.0	
H ₂ /CO ₂ ≥ 0.34	CO ₂ /CO = 4.2	
H ₂ /O ₂ = 1.7	CO ₂ /CH ₄ = 1.8	
CH ₄ /CO ₂ = 0.54		
H ₂ /CO = 1.43		
SNL Na/Al/Si (2-sided) 10 ⁻⁶ mole/(m ² Pa sec)	Knudsen Selectivity	Lit. (values for Al/Si) [1,2] 10 ⁻⁷ -10 ⁻¹⁰ mole/(m ² Pa s)
H ₂ /N ₂ ≥ 61	H ₂ /N ₂ = 3.73	H ₂ /N ₂ = 3.91
H ₂ /CH ₄ = 7	N ₂ /CO ₂ = 1.00	N ₂ /CO ₂ = 0.625
He/N ₂ ≥ 7	He/N ₂ = 2.64	H ₂ /N ₂ = 100, 150°C 10 ⁻¹⁰ perm.
CH ₄ /N ₂ ≥ 1.4	CH ₄ /N ₂ = 1.32	
H ₂ /CO ₂ ≥ 80		
H ₂ /O ₂ ≥ 11		
CH ₄ /CO ₂ ≥ 11		

Table 1. Permeation Values for Pure Gases at Room Temperature

needs stainless steel to make membranes an economically viable technology.

Another avenue of research is bulk novel molecular sieve materials, with the goal of "tuning" pore sizes to molecular sieving needs. In this arena, we have successfully synthesized many new phases,

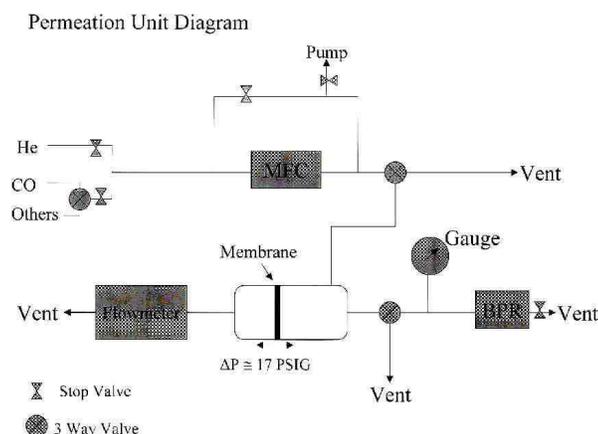


Figure 2. Sandia Permeation Unit for Light Gases (including CO), Pure and Mixed (the equipment diagram)

a number of which are promising for light gas separations. In particular, we have a novel crystalline 12-ring microporous fluorogallophosphate material. [6] Its pore sizes are in the range for light gas separations, as shown in Figure 3. We are now attempting to synthesize this as a thin film membrane.

Conclusions

There is a great need for robust, defect-free, highly selective molecular sieve (zeolite) thin film membranes for light gas molecule separations in hydrogen fuel production from CH_4 or H_2O sources. They contain an inherent chemical, thermal and mechanical stability not found in conventional membrane materials. Our goal is to utilize those zeolitic qualities in membranes for the separation of light gases, and to eventually partner with industry to commercialize the membranes. To date, we have successfully:

- Demonstrated (through synthesis, characterization and permeation testing) both the ability to synthesize defect-free zeolitic membranes and use them as size selective gas separation membranes;
- Built and operated our in-house light gas permeation unit;

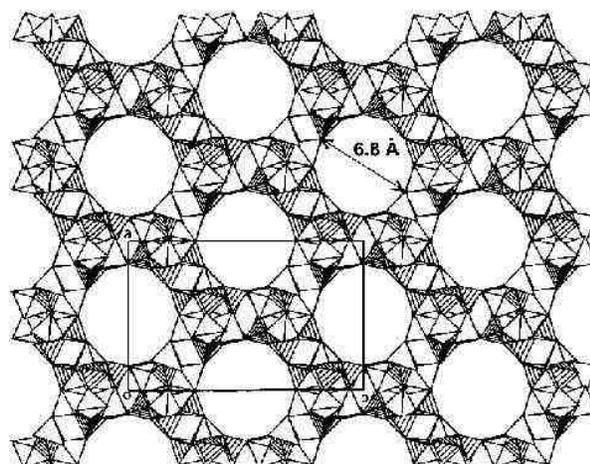


Figure 3. 3D Framework of 12-ring Gallo Fluorophosphate Microporous Phase

- Synthesized membranes on commercially available disks (this is in addition to successes we have had in synthesizing zeolitic membranes to tubular supports [7]);
- Synthesized a number of new microporous bulk phases, including the novel 12-ring fluorogallophosphate; and
- Work continues in the synthesis of these novel materials as thin film membranes.

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Special Recognitions & Awards/Patents Issued

- T.M. Nenoff; F. Bonhomme; "Zeolite Membranes with High CO₂ Selectivity". US Patent submitted to Sandia National Laboratories, August 2002.

II.C.11 DFMA Cost Estimates of Fuel-Cell/Reformer Systems at Low/Medium/High Production Rates

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Objectives

- Develop realistic and internally consistent detailed designs for automotive gasoline fuel processors and direct hydrogen PEM fuel cell systems based on current-year technology.
- Apply Design for Manufacture and Assembly (DFMA) design and costing techniques to compare system designs at low, medium, and high annual production rates.

Approach

- Update design and cost estimate for baseline 0.7 V/cell peak-power reformer/fuel cell system.
- Develop detailed designs for three additional 50 kW_{net} PEM fuel cell systems: 0.6 V/cell reformer system, 0.7 V/cell direct hydrogen system, 0.6 V/cell direct hydrogen system.
- Apply DFMA techniques to assess manufacturing methods and costs for each system for comparison to baseline.

Accomplishments

- Completed detailed baseline design and thermodynamic modeling.
- Performed annual update to cost estimates of baseline system with more detailed estimates of peripheral components.
- Completed cost estimates of additional reformer and direct hydrogen systems for comparison to baseline.

Future Directions

- Update baseline reformer and fuel cell cost estimates to reflect advances in technology and additional manufacturing and design improvements. Conduct a series of in-depth trade studies on selected issues to assess pathways to lower cost systems.

Introduction

Directed Technologies Inc. (DTI) has performed a DFMA-style cost estimation for an onboard gasoline reformer and fuel cell system at several

annual production volumes. The DFMA technique is a rigorous design/redesign and cost estimation methodology developed by Boothroyd and Dewhurst¹ and adapted by DTI. In a previous report², DTI analyzed the cost of a 50 kW_{net} baseline

system. The current report presents refined costs for the baseline system as well as comparisons to an alternate reformer/fuel cell system and two direct hydrogen fuel cell systems.

Approach

The contract statement of work defines four tasks to be completed by DTI. Having completed and reported the results for Task 1 and Task 2, our efforts are currently focused on Tasks 3 and 4. In Task 1, DTI specified the basic layout of the system and operating conditions. In Task 2, DFMA was used to identify the low-cost design and production methods and provide estimated material, manufacturing, and assembly costs. These results were reported in the “Fuel Cells for Transportation 2001 Annual Progress Report”. Task 3 consists of annual updates and refinements of the system cost to reflect changing technology and new information. In Task 4, a variety of trade-off studies will be used to elaborate on basic system architecture and operating modes.

For this report, the DFMA methodology was applied to refine costs for the baseline 0.7 V/cell reformer/fuel cell system at production rates of 500, 10,000, 30,000, and 500,000 units per year. Additionally, three other systems were analyzed for comparison to the baseline: a gasoline reformer/fuel cell system operating at 0.6 V/cell (at peak power), a direct hydrogen system operating at 0.7 V/cell, and a direct hydrogen system operating at 0.6 V/cell. Each system is designed to provide 50 kW of net electrical power. The bills of materials for reformer/fuel cell systems and direct hydrogen systems are shown in Table 1. Items specifically not included in this analysis are the Traction Inverter Module, the main automotive electric motor, and any peak-power or load-leveling battery system.

Results

Reformer/fuel cell system definition

Figure 1 shows the system schematic for a gasoline reformer/fuel cell system. The drawing applies to both the 0.7 V/cell and 0.6 V/cell systems, which only differ dimensionally. In these systems, California reformulated gasoline is pumped from the fuel tank and injected into the integrated autothermal

Subsystem	Reformer/FC	Direct hydrogen
Fuel Loop	Fuel tank assembly High-pressure fuel pump High-pressure fuel injector	Compressed H ₂ tank H ₂ recirculation ejector H ₂ intank solenoid & PRD
Fuel Cell Stacks	MEA and bipolar plate Endplates and brackets	MEA and bipolar plate Endplates and brackets
Air Loop	Air compressor/ expander Air mass flow sensors Air throttle body Air humidifier	Air compressor/ expander Air mass flow sensor Air humidifier
Water Loop	Water pump & reservoir Knock-out drum, condensers High-pressure rail system Water deionization filter	Water pump & reservoir Knock-out drum, condensers High-pressure rail system Water deionization filter
Coolant Loop	Pump, motor, controller Radiator assembly Thermostat, bypass valve	Pump, motor, controller Radiator assembly Thermostat, bypass valve
Controls	Electronic engine controller CO sensors	Electronic engine controllers
Misc./ Balance of Plant	Start-up battery Electrical System mounting Misc.	Start-up battery Electrical System mounting Misc.
Integrated ATR Assembly	Autothermal reactor Water gas shift reactors Sulfur removal Water boiler	N/A
Reformate Loop	PrOx unit Air control solenoid Catalytic burner Condenser	N/A

Table 1. Bill of Materials for Gasoline Reformer and Direct Hydrogen Fuel Cell Systems

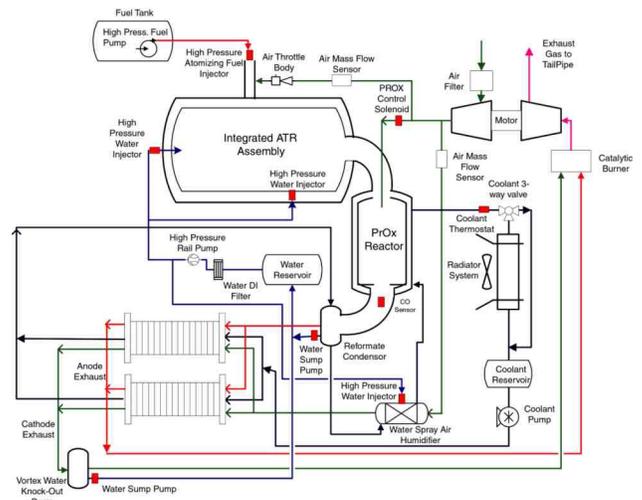


Figure 1. Gasoline Reformer/Fuel Cell System Schematic

reformer (ATR) assembly (which includes an ATR section, high and low temperature water-gas shift sections, and sulfur removal bed) where it is mixed with air and steam to generate a hydrogen-rich reformat stream. This gas stream is then sent to the preferential oxidation reactor (PrOx) to convert water and carbon monoxide to additional hydrogen and carbon dioxide. After the remaining water is condensed for removal, the reformat enters the PEM fuel cell where the hydrogen reacts with oxygen from air to generate electricity and heat. The unreacted fuel and air streams are mixed and burned in a catalytic burner and expanded in an exhaust gas expander to derive power for the air compressor.

The fuel cell system has four stacks containing 110 cells each. Table 2 provides details of each stack and its parameters. Because the reformat contains

small amounts of carbon monoxide (<50 ppm) which can poison the platinum membrane catalyst, the catalyst loadings are significantly higher than for direct hydrogen systems (0.7 g/cm² versus 0.15 g/cm²). The fuel cell performance is further hindered by the dilution of hydrogen due to the CO₂ and N₂ in the reformat stream, resulting in lower power densities (higher membrane areas).

Direct Hydrogen system definition

Figure 2 shows the system schematic for a direct hydrogen reformer/fuel cell system. Compressed hydrogen is stored in a carbon-fiber wrapped composite vessel at pressures up to 340 atm. It is fed through a control valve to the fuel cell at 2 atm, where it reacts with oxygen from air to generate electricity and heat. Unreacted hydrogen is

Peak Power Conditions	0.7 V/cell ATR (baseline)	0.6 V/cell ATR	0.7 V/cell Direct H ₂	0.6 V/cell Direct H ₂
Gross Power (kW)	55	56	56	57
Net Power (kW)	50	50	50	50
Cell Voltage (V)	0.7	0.6	0.7	0.6
Current Density (mA/cm ²)	400	650	600	1076
Nom. Operating Pressure (atm)	2.2	2.2	2.2	2.2
Power Density (mW/cm ²)	280	390	420	646
No. of strands	1	1	1	1
No. of stacks/strand	4	4	4	4
No. of cells/stack	110	110	110	110
Total active membrane area (m ²)	19.64	14.36	13.33	8.83
Active area/cell (cm ²)	446	326	303	201
Peak voltage (@ 0.92 V/cell) (V)	405	405	405	405
Min. voltage (@ peak power) (V)	308	264	308	264
Max current (@ peak power) (A)	178.6	212.1	181.8	215.9
Catalyst loading				
Cathode (mg/cm ²)	0.3 Pt	0.3 Pt	0.10 Pt	0.10 Pt
Anode (mg/cm ²)	0.4 Pt 0.2 Ru	0.4 Pt 0.2 Ru	0.05 Pt	0.05 Pt
Stack efficiency*	41.5%	35.1%	51.1%	43.1%
Onboard System efficiency*	33.4%	28.2%	51.1%	43.1%
* Stack efficiency is the electrical power output of the fuel cell stack divided by the lower heating value (LHV) per unit time of hydrogen entering the stack. System efficiency is the net electrical power of the system divided by the LHV per unit time of the fuel feed (gasoline for reformer system, hydrogen for direct hydrogen system).				

Table 2. Operating Parameters for ATR and Direct H₂ Fuel Cell Systems

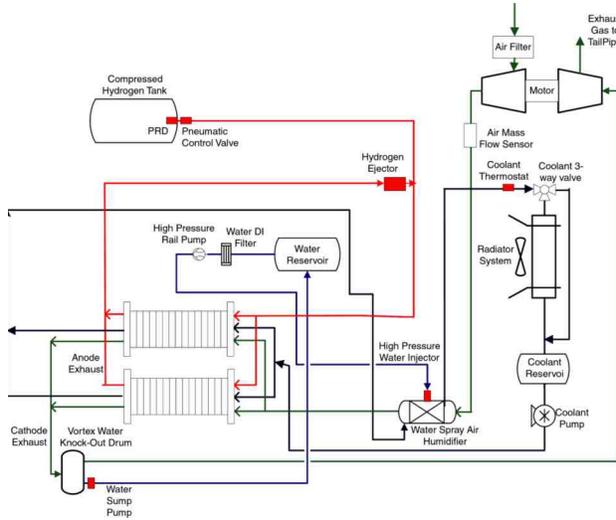


Figure 2. Direct Hydrogen Fuel Cell System Schematic

recirculated to prevent loss of hydrogen from the system, while the oxygen-depleted air stream is exhausted.

Like the reformer systems, four PEM fuel cell stacks of 110 cells each are used. These stacks are smaller and have lower catalyst loading than those for the reformer systems because the hydrogen is 99.99% pure, containing less than 10 ppm carbon monoxide. Stack parameters for the direct hydrogen systems are compared to those for the reformer systems in Table 2.

Cost estimates

Cost estimates for each system at each of the four production levels are the sum of materials, manufacturing, and assembly costs, as well as a manufacturer’s markup and a 10% cost contingency (as is standard automotive cost estimation practice). As might be expected, cost of the finished system decreases with increasing production volume.

Figure 3 shows the cost of each of the four systems at four different production volumes. The reformer/fuel cell system designed for peak power at 0.6 V/cell offers some cost reductions compared to the baseline, but both direct hydrogen fuel cell systems are significantly less expensive than either of the reformer/fuel cell systems. This cost reduction is primarily due to the decreased size and cost of the fuel cell stack, as can be seen in Figure 4. The

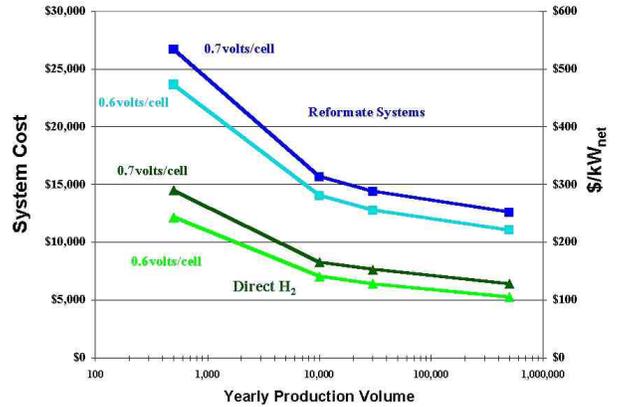


Figure 3. Power System Cost vs. Production Rate for ATR and Direct Hydrogen Systems (50 kW)

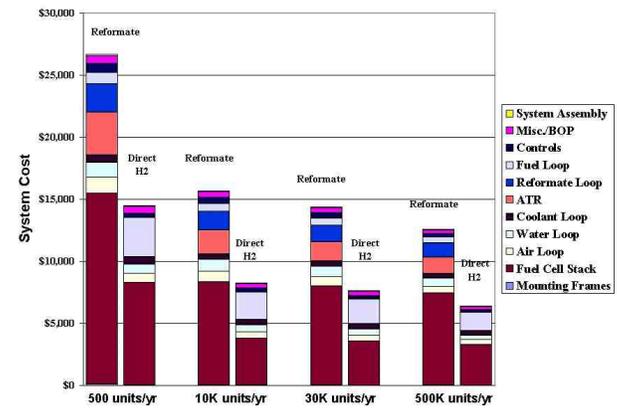


Figure 4. Comparison of 0.7 V/cell ATR and Direct H₂ System Costs (50 kW)

reformat loop and ATR are also eliminated in the direct hydrogen systems, but the fuel loop bears the cost of the fiber-wrapped composite tank for compressed hydrogen.

In all four systems studied and at all production rates, the fuel cell stack accounts for more than half of the total system cost. The cost of the stack is dominated by the membrane electrode assembly (MEA), as shown in Figure 5 for the 0.7 V/cell reformat fuel cell. The membrane material and catalyst account for roughly 85% of the MEA cost in the reformat systems and 62-76% in the direct hydrogen systems (low-high production volumes).

Differences in cost between the updated baseline system reflected in this report and preliminary costs

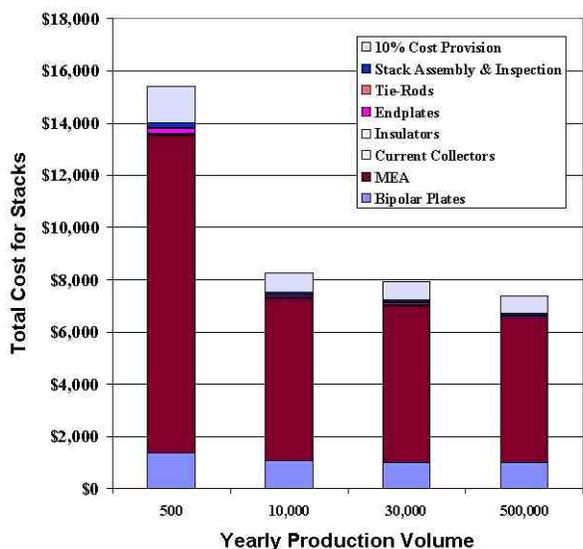


Figure 5. Cost Breakdown for Fuel Cell Stacks in 0.7 V/cell ATR System (50 kW)

from the previous report are the result of the more rigorous and thorough cost methodology performed in the past year. The updated costs, however, result in only a 3-4% change in total system cost for all production rates.

Conclusions

Capital costs for fuel cell power systems vary with production rates, peak power voltage conditions, and hydrogen source (reformate vs. direct). As with most manufactured products, the cost of materials, manufacturing, and assembly decrease with increasing annual production volumes. Designing the fuel cell stack to operate at lower voltages at peak power (0.6 V/cell vs. 0.7 V/cell) offers capital cost savings at the expense of system efficiency.

Power systems for hydrogen fuel cell vehicles are costly, with approximately half the cost coming from the fuel cell stacks. Because the MEA accounts for sixty to ninety percent of the stack cost, the cost of the entire power system is highly dependent on the total membrane area of the system. Due to the low hydrogen quality of the fuel stream in reformate/fuel cell systems, the membrane area and catalyst loadings in such systems significantly exceed those in direct hydrogen systems, driving up the cost of the power system. This cost difference is true at all

production levels, from initial introduction of fuel cell vehicles through full public acceptance. Overall system costs range from \$105/kW to \$243/kW for the 0.6 V/cell direct hydrogen system and \$221/kW to \$472/kW for the 0.6 V/cell reformate system. Comparable systems operating at 0.7 V/cell cost approximately 12% to 22% more than the 0.6 V/cell versions.

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Presentations

1. This work was presented by Brian D. James at the SAE Future Car Congress in Washington, D.C. on June 7, 2002.