

Recovery of Carbon Dioxide in Advanced Fossil Energy Conversion Processes Using a Membrane Reactor

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Abstract

Increased awareness of the global warming trend has led to worldwide concerns regarding “greenhouse gas” emissions, with CO₂ being the single greatest contributor to global warming. Fossil fuels (i.e., coal, oil, and natural gas) currently supply over 85% of the world’s energy needs, and their utilization is the major source of the anthropogenic greenhouse gas emissions of CO₂. Advanced coal gasification power plants offer many new opportunities for integrating CO₂ capture. Converting the fuel values to hydrogen by fuel reforming reactions allows CO₂ capture prior to combustion increasing overall power generation efficiency and reducing the cost of CO₂ capture. By conducting fuel reforming with simultaneous hydrogen separation in a catalytic membrane reactor unit, equilibrium-limited reforming reaction is driven to completion with conversion of the fossil fuel energy values to the equivalent of hydrogen fuel. The fuel carbon content is recovered in a compressed, sequestration-ready CO₂ form.

This paper describes development of a membrane reactor process for hydrogen generation by fuel reforming based on palladium-silver alloy/ceramic composite membrane. By utilizing a thin yet structurally stable palladium/ceramic composite membrane hydrogen flux is increased while reducing costs. Electroless plating technique is used to prepare palladium-silver alloy films of about 2 to 3 micron thickness on commercially available tubular alumina substrates. The observed hydrogen flux rates are of the order of 1 gmole/m²-sec at 500-600 °C temperature and 40 psi pressure differential. The membrane reactor concept may be used to produce hydrogen by fuel reforming for stationary power generation as well as transportation applications. Adjustment of H₂:CO ratio involved in production of liquid fuels/chemicals from synthesis gas is also possible with this concept. This paper presents the results of experimental evaluation and model simulations of the composite membrane performance both as a hydrogen separation unit and as a membrane reactor for fuel reforming.

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Introduction

Increased awareness of the global warming trend has led to worldwide concerns regarding “greenhouse gas” emissions, as evidenced by the recent signing of Framework Convention in Climate Change treaty. Greenhouse gases include CO₂, CH₄, and N₂O and are mostly associated with the production and utilization of fossil fuels, with CO₂ being the single greatest contributor to global warming. Fossil fuels (i.e., coal, oil, and natural gas) currently supply over 85% of the world’s energy needs, and their utilization is the major source of the anthropogenic greenhouse gas emissions of CO₂ (Herzog et al., 1997). Primary alternatives to fossil fuels, such as nuclear power and renewable solar energy, must overcome obstacles of public acceptance and exorbitant costs. Near-term approaches based on improving energy efficiency and switching from coal to oil or natural gas have limited impact potential. For sustained fossil fuel utilization to meet the world’s energy demands while addressing long-term mitigation of concerns over global climate change, it is necessary to develop cost-effective means to capture and sequester the resulting CO₂. The conventional technology for CO₂ recovery from dilute flue gas after fossil fuel combustion incurs substantial energy penalty. For coal-based power plants, the energy penalty is as much as 27% to 37%, depending on the CO₂ removal process and operating conditions (Herzog and Drake, 1993.) For natural gas-based power plants, the 15% to 24% penalty is lower due to lower fuel carbon content (Herzog and Drake, 1993).

Advanced coal gasification power plants offer many new opportunities for integrating CO₂ capture, for example in an integrated gasification combined cycle (IGCC) power plant (Doctor et al., 1994, 1996). An additional advantage of an IGCC power plant is that its energy conversion is more efficient than coal-fired power plants. IGCC plants first gasify the fuel to produce a pressurized synthesis gas (mainly CO and H₂). After particulate and sulfur contaminants are removed, the synthesis gas is burned in a gas turbine to produce electricity. Additional power is produced using the steam generated during heat recovery from the gas turbine exhaust.

If CO₂ were captured prior to combustion it would require treatment of substantially smaller gas volumes and thus could be less expensive than capture after combustion. CO₂ can be recovered before fuel combustion by reacting the synthesis gas (clean coal gas) with steam in a water gas shift (WGS) reactor to produce CO₂ and additional H₂ by WGS reaction: $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$. The CO₂ and H₂ are then separated, the hydrogen is combusted to produce power, and the CO₂ stream is available for disposal. The overall schematic of an IGCC process with CO₂ recovery before combustion is shown in Figure 1. The energy penalty associated with CO₂ capture in such advanced coal power plants, however, is still high at 13% to 17% (Herzog and Drake, 1993).

Available technologies for CO₂ removal from synthesis gas streams include low temperature absorption by amines, glycol, and chilled methanol; hot potassium carbonate process; reaction with calcium oxide; and separation by low temperature polymeric membranes (Doctor et al., 1994). All low temperature processes require gas cooling and heat recovery leading to energy losses. In addition, significant energy is also required (lost) for regeneration in solvent- and reagent-based systems. The major challenge regarding CO₂ capture technology is to reduce the overall costs by lowering both the energy penalty and the capital cost requirements.

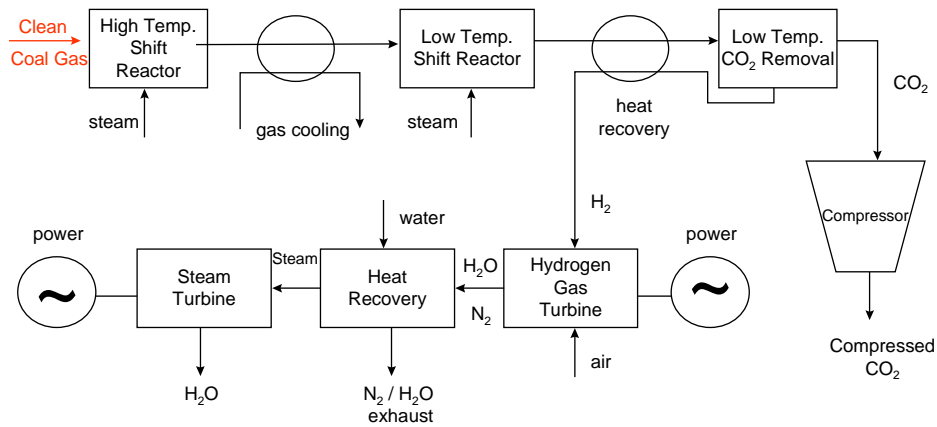


Figure 1. IGCC Process with Conventional CO₂ Recovery before Fuel Combustion

Project Concept

CO₂ capture in an advanced coal power plant, as shown in Figure 1, involves an equilibrium-limited and kinetically inhibited WGS reaction that typically requires two stages with inter-stage cooling. It also requires a separate CO₂ removal step. Additional improvements and cost reductions are possible by combining the WGS reaction and gas separation steps in one high-temperature unit and eliminating the parasitic CO₂ removal step. By continually removing a reaction product in a membrane reactor, thermodynamic and kinetic limitations to the WGS reaction are removed, leading to complete conversion of CO to H₂ (without lowering the gas temperature) as well as simultaneous separation of products. Separation of hydrogen in a membrane reactor will essentially replace the two-step shift reaction units as well as the separate CO₂ removal process by a single unit. Generation of a high purity hydrogen fuel stream will allow utilization of highly efficient alternative power generation technologies, such as PEM fuel cells. A possible schematic for PEM fuel cell power generation coupled with early heat recovery steam generation and steam turbine power generation is shown in Figure 2.

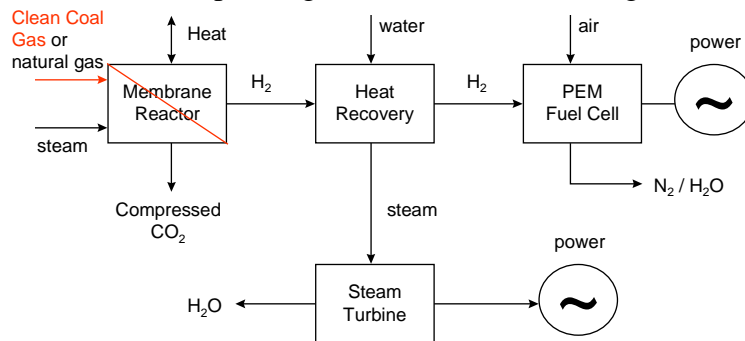


Figure 2. Schematic of Membrane Reactor Process with PEM Fuel Cell

The membrane reactor concept can also be used for power generation from other fossil fuels, such as oil and natural gas. Hydrocarbon liquid fuels, such as diesel oil or gasoline are first vaporized and then reformed with steam to produce synthesis gas containing CO and H₂ similar to coal gas. The CO in synthesis gas is then converted to H₂ by the membrane reactor. In case of

natural gas, the membrane reactor may allow one-step steam reforming with hydrogen separation leaving behind a compressed CO₂-rich stream.

For the membrane reactor concept, a hydrogen- (or CO₂) selective membrane capable of operating in a high-temperature, high-pressure environment is needed. Micro-porous inorganic membranes based upon Knudsen diffusion separation exhibit low separation factors (e.g., H₂:CO₂ separation factor of 4.7). Moreover, the separation ability of the commercially available 4 nm pore size gamma-alumina membranes depends upon the stability of the membrane pore size, which is adversely affected by the action of steam (Damle et al, 1995). The dense ceramic membranes based on inorganic perovskite oxides need considerably high temperatures, greater than 800 °C, to achieve practical hydrogen flux rates. Palladium-based dense membranes are known for their high hydrogen selectivity and permeability over other gases. Although palladium alloy tubes have been available for several decades, they are expensive for commercial applications due to the thickness needed for structural stability. The tubular membranes also exhibit low hydrogen flux rates due to their thickness. In order to be suitable for the target application, a hydrogen separation membrane must have adequate selectivity and flux rate and must be stable in the reducing coal gas or fuel reforming environment containing steam and hydrogen sulfide. The membrane module must also be economically competitive.

Project Objectives

The overall objective of the U.S. DOE sponsored program at RTI is to develop an inorganic composite palladium-based membrane reactor module that is structurally stable under the fuel reforming WGS reaction conditions with a high selectivity and flux rate for hydrogen permeation through the membrane. For membrane structural stability, the emphasis is on developing sulfur resistant palladium-silver alloy composite membranes. To maximize flux rates and to minimize cost, thin yet durable composite membranes with commercially available substrates are desirable. Another objective of this program is to demonstrate simultaneous WGS reaction with CO₂/H₂ separation using the membrane reactor at a bench scale in Phase II efforts and at a pilot scale at a host site in Phase III efforts. A membrane reactor must be able to carry out the WGS or fuel-reforming reaction to its desired conversion level while permeating all of the hydrogen produced in the reactor. Thus, the development of this technology must take into account reaction kinetics and reforming operating conditions in addition to the membrane permeation characteristics. Requirements for successful development and demonstration of the membrane reactor process through Phase III program are: (1) hydrogen-selective membrane reactor unit, (2) synthesis gas reforming with CO₂/hydrogen separation, (3) power generation unit (PEM fuel cell or hydrogen turbine), and (4) integration of all components.

Technical Approach

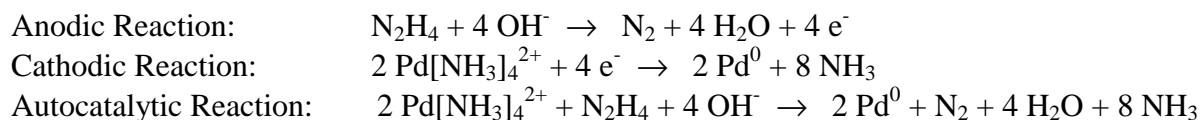
A number of recent studies have been directed toward synthesizing palladium-ceramic composite membranes to reduce the palladium-layer thickness while providing the structural integrity. Several approaches have been used to produce the thin-film membranes: physical vapor deposition (PVD), chemical vapor deposition (CVD), electroplating, compression cladding, sputtering, spray pyrolysis, and electroless plating. Of these methods, CVD and electroless

deposition methods have been considered as most promising. In our efforts, the electroless plating method is preferred over CVD for several reasons. Electroless deposition provides thin metal and metal-alloy films that have excellent adhesion properties; the deposition rate is high, and it can be easily controlled. Further, this is an auto-catalytic process that does not require any expensive setup. On the other hand, the CVD process requires appropriate stable organo-metallic precursors which may be expensive. The CVD process does provide film that has fair adhesion properties, and the deposition rate is high, but the rate cannot be controlled. It would also be difficult to deposit two species simultaneously for fabrication of palladium alloy membranes. Furthermore, CVD requires expensive and elaborate setup. The challenge in synthesizing composite membranes is to obtain uniform, defect-free coating, as even small pinholes would be detrimental to the hydrogen selectivity.

Pure palladium metal becomes brittle in presence of hydrogen and is prone to distortions during thermal cycling due to the dimensional changes caused by transformations between the α -phase palladium, which is stable at low temperatures, and the β -phase palladium, which is stable at high temperatures. Alloying elements such as Ag stabilizes the β -phase against the α -phase, substantially reducing metal embrittlement. Pd-Ag alloy also exhibits greater permeability for hydrogen than pure palladium at similar conditions. An alloy with 23% Ag and 77% Pd has been shown to have the maximum permeability as well as dimensional stability (Shu et al., 1993; Uemiya et al., 1991). Although, theoretically palladium is stable in reducing hydrogen environment at low levels of H₂S below 100 ppm (Krishnan et al., 1993), it must be protected against system upsets in the upstream desulfurization process. Platinum has been shown to be highly resistant to H₂S attack with a surface penetration of only 30 nm in the presence of 1.2% H₂S at 600 °C (Damle, 1995).

The focus in these efforts has therefore been on developing thin palladium-silver alloy composite membranes with a thin protective noble metal coating. Commercially available ceramic (alumina) micro- and ultra-filtration membranes are used as substrates for deposition of hydrogen-selective layers. By reducing the thickness of the palladium membrane, the hydrogen flux rate is increased while decreasing the cost of the membrane.

The electroless plating technique for palladium has been well known and involves pretreatment of the substrate, sensitization and activation of the substrate surface, and electroless plating with palladium deposition which is a combination of cathodic deposition of metal and the anodic oxidation of reductant:



Each of the three steps is critical for uniform deposition of the palladium metal film. The sensitization and activation process, involving adsorption of Sn²⁺ ions on the substrate followed by substitution by Pd, produces finely divided palladium metal nuclei on the substrate that initiate the autocatalytic plating process. A similar reaction scheme can also be used for depositing other metals, such as silver, which is also of interest here.

The WGS reaction ($\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$) is well known and is usually carried out in two stages: a high temperature (up to 550 °C) stage e.g. over Fe or sulfur tolerant Co-Mo based catalysts and a low temperature (175 - 205 °C) stage over copper based catalysts (Newsome, 1980). The reaction is mildly exothermic and lower temperature favors conversion of CO. Since the equilibrium limitation is removed in a membrane reactor, the reaction can be carried out at a single high/intermediate temperature. The palladium composite membrane module can be used as a reactor/separator by packing appropriate catalyst pellets on the reactant side of the module. The key issue in such membrane reactor design is matching the hydrogen flux rates with the rate of the reaction. The reactant space velocity in the membrane module is dictated by the reaction kinetics and needed conversion. The hydrogen flux rate is determined by the hydrogen partial pressure gradient across the membrane and the membrane surface area.

The natural gas reforming reaction ($\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2$) is also well studied, especially for hydrogen production, and is typically carried out over Ni-based catalyst at 400 psig and 750 °C. This reaction is endothermic and is also yield limited. WGS reaction is subsequently carried out to increase hydrogen yield. The use of membrane reactor may allow one-step reforming to produce hydrogen. In this program only commercially available catalysts will be utilized.

Results

In this program, the efforts to-date have been focussed on establishing procedures for depositing thin, uniform, defect-free palladium-silver alloy films on porous substrates. Bulk of the work so far has been conducted with commercially available porous alumina micro- and ultra-filtration membrane substrates. Techniques were developed to deposit metal alloy films on porous substrates by electroless plating process assuring uniform defect-free dense metal alloy films. A technique has also been demonstrated for deposition of a uniform ultrathin (~20 nm) platinum layer on the membrane to provide resistance to low levels of H₂S typically present in syngas following desulfurization. The overall membrane synthesis process is amenable for easy scale up and process automation and for plating longer tubes and multi-channel monolithic elements.

Membrane characterization studies have been conducted with short 2" long tubular sections as well as with 10" long tubular elements of 10 mm OD and 7 mm ID. Composite membranes were analyzed by scanning electron microscopy (SEM) and energy dispersive X-ray elemental analysis (EDAX) techniques to determine membrane thickness, structure, integrity, and elemental composition. The plating technique allows varying film thickness and composition by depositing multiple metal layer films and alloy films from 1 to 5 micron thickness have been synthesized. The metal films are annealed in flowing inert gas atmosphere (nitrogen or argon) to homogenize the film to assure uniform composition throughout the film cross-section. Figure 3 shows an example of a three-layer 1.5 μm metal composite film, prior to annealing, whereas, Figure 4

shows an example of an annealed homogenized metal/ceramic composite film. Both figures show excellent adhesion of the metal films to the porous ceramic substrates.

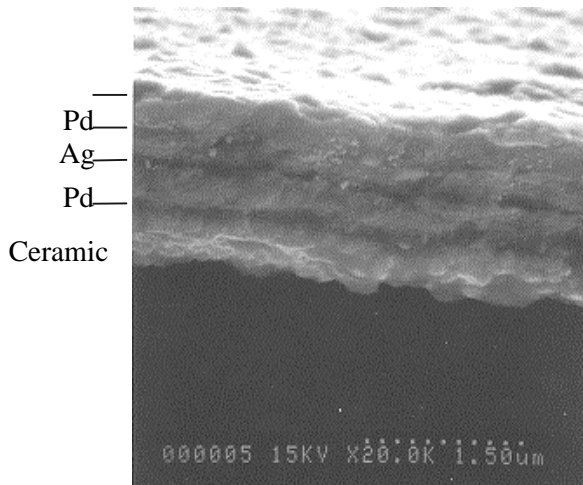


Figure 3. Metal Film Before Annealing

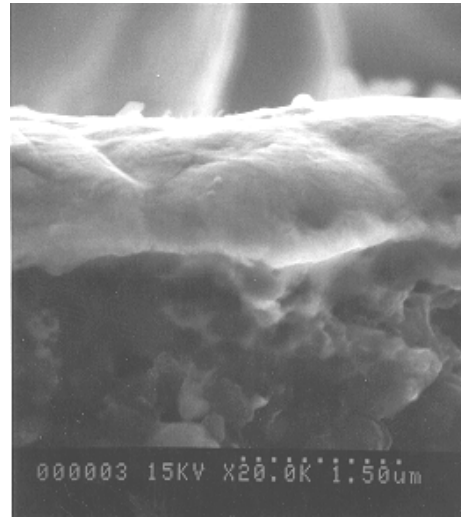


Figure 4. Metal Film After Annealing

The permeation characteristics of the composite membranes were determined by single pure component permeation as well as mixed gas permeation testing at various temperatures and trans-membrane pressure differentials. Figure 5 schematically shows the tubular membrane test apparatus used for permeation testing.

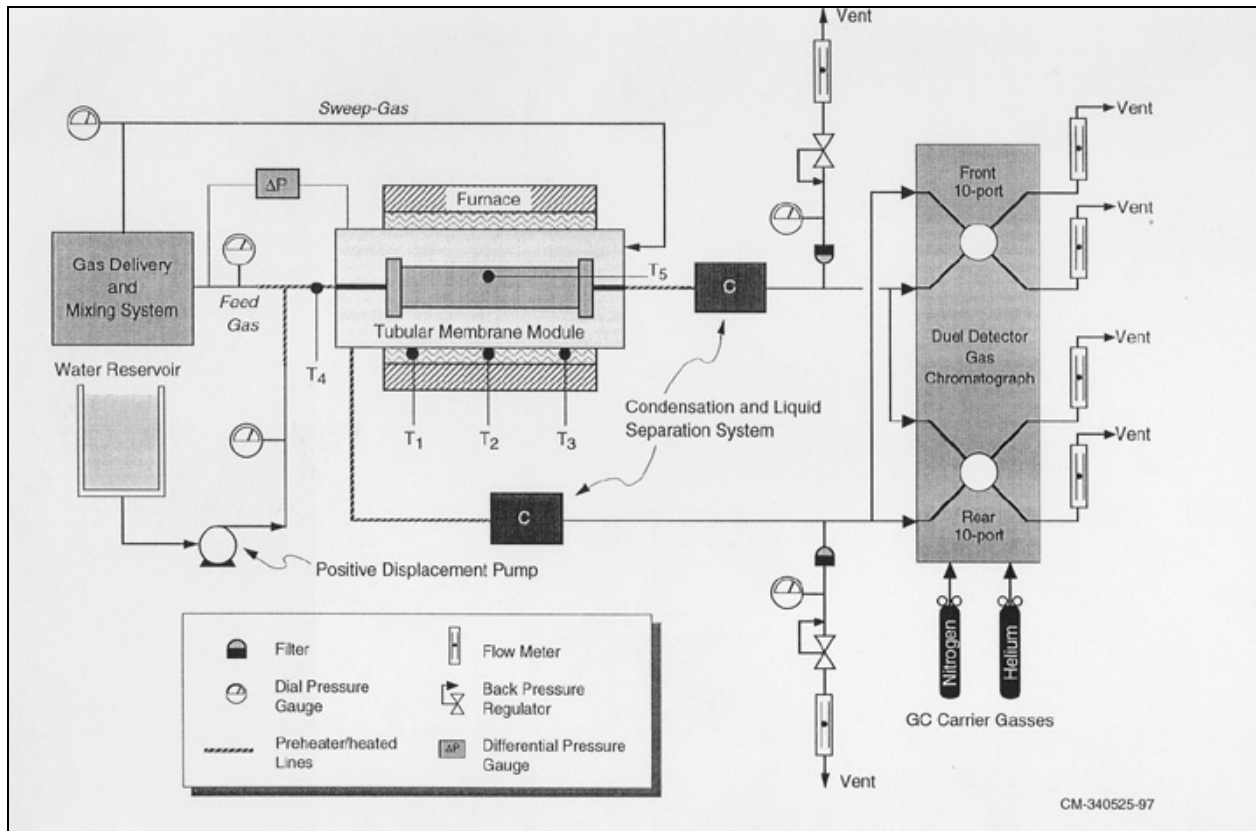


Figure 5. Schematic of Tubular Membrane Test Apparatus

The permeation test system consists of a gas mixing and delivery manifold, a controlled temperature furnace, a gas chromatograph (GC) equipped with gas sampling valves, and an integrator to analyze the GC data. The gas delivery system allows multi-component feed gases for mixed permeation and selectivity testing. The tubular furnace comprises of cylindrical heating elements capable of controlling temperature up to 800 °C. Back-pressure regulators (BPRs) control the feed and permeate side pressures independently at the desired levels. GC samples can be drawn from both the feed exhaust and sweep lines.

For sealing the ceramic tubes, in-situ-formed graphite ferrules were used with Swagelok metal reducing unions bored to allow close fitting with the 10 mm OD ceramic tubes. The leak rate at the graphite seals was found to be variable and was found to permit nitrogen leak rate from 0 to 10 cc/min. The leak rate was found to decrease with temperature as expected due to increasing gas viscosity with temperature. Although, this leak rate was more than two to three orders of magnitude smaller compared to the observed hydrogen permeation rates, it contributed to 100% of the observed nitrogen permeation rate thus affecting the mixed gas selectivity measurements.

The observed hydrogen permeation rate depends upon the film thickness, the substrate pore size, alloy composition, and the operating conditions of temperature and hydrogen partial pressure differential. Figure 6 shows typical observed annealed membrane flux rates.

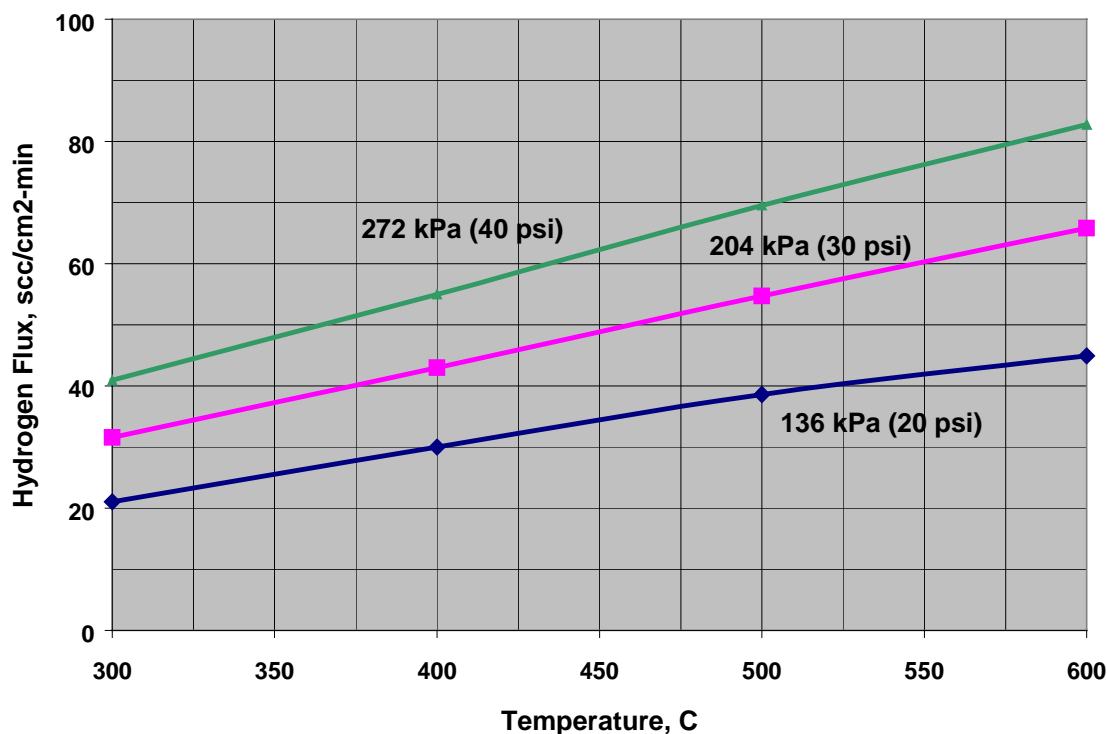


Figure 6. Hydrogen Flux with Temperature, Membrane L21

The observed hydrogen permeances range from 16 to 80 gmol/m²-min at 500-600 °C temperature and 40 psi hydrogen partial pressure differential. The observed hydrogen to nitrogen

selectivity of these membranes range from 150 to 10,000 in mixed gas experiments, primarily influenced by leak rate at the seals .

Recently, porous stainless steel substrates in both flat and tubular geometry were evaluated for depositing metal films. SEM scan of the composite membrane cross-section (Figure 7) shows excellent adhesion and complete surface coverage by the metal film as well as cohesion between different layers in spite of the surface roughness of the steel substrate. Tubular sintered metal composite membrane samples are currently being prepared for hydrogen permeation evaluation. Metal substrates have an obvious structural advantage over ceramic substrates. For using ceramic substrates for gas separation application, effective sealing technique is essential. The ongoing program, in collaboration with ORNL scientists, has indicated feasibility of a brazing technique to join ceramic tubes to metal tubes allowing metal fittings to house ceramic elements.



Figure 7. 3-Layer Plating on Porous Stainless Steel Substrate

Simple, one-dimensional model simulations of the membrane reactor concept were conducted to determine the effect of simultaneous hydrogen separation on CO conversion in the WGS reaction. Figure 8 schematically shows the one-dimensional membrane reactor.

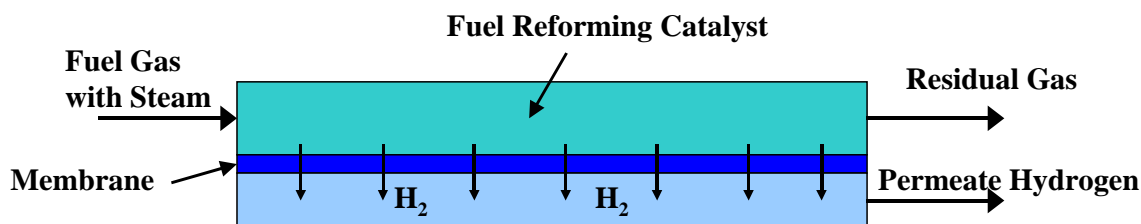


Figure 8. Schematic of a One-Dimensional Membrane Reactor Model

The basic assumptions of this simple model are: 1) temperature and total pressure are constant on both permeate and feed sides; 2) reaction kinetics is faster than the hydrogen permeation flux rates allowing the feed side to be in dynamic equilibrium; and 3) hydrogen flux is determined by the local driving force. One target application of the membrane reactor concept is to convert synthesis gas derived from coal gasification to hydrogen for power generation by PEM fuel cells. Gas composition typical of a coal gas generated by an oxygen blown gasifier was used as the dry feed gas composition in the model simulations ($H_2 - 36\%$, $CO - 47\%$, and $CO_2 - 17\%$.) Model simulations were conducted at steam to CO mole ratios of 1:1, 1.5:1, and 2:1 to determine the effect of steam to CO ratio on CO conversion and the membrane area requirements. A feed gas pressure of 20 atm and the permeate hydrogen pressure of 1 atm was assumed with an effective pressure ratio of 20. Predicted CO conversions and total hydrogen recovery are shown in Figure 9 as a function of stage cut fraction for steam to CO ratio of 1:1. As seen from this figure, CO conversion continues to increase as more and more hydrogen is withdrawn from the membrane

reactor. The eventual CO conversion and hydrogen recovery are essentially limited only by the hydrogen partial pressure in the residual gas which must be greater than the permeate pressure for hydrogen permeation. Typical target overall hydrogen recovery would be about 80% with the residual gas heating value used for the reactor. The model simulations also indicate the feasibility of using low steam to CO ratio provided carbon formation is avoided by utilization of appropriate catalysts.

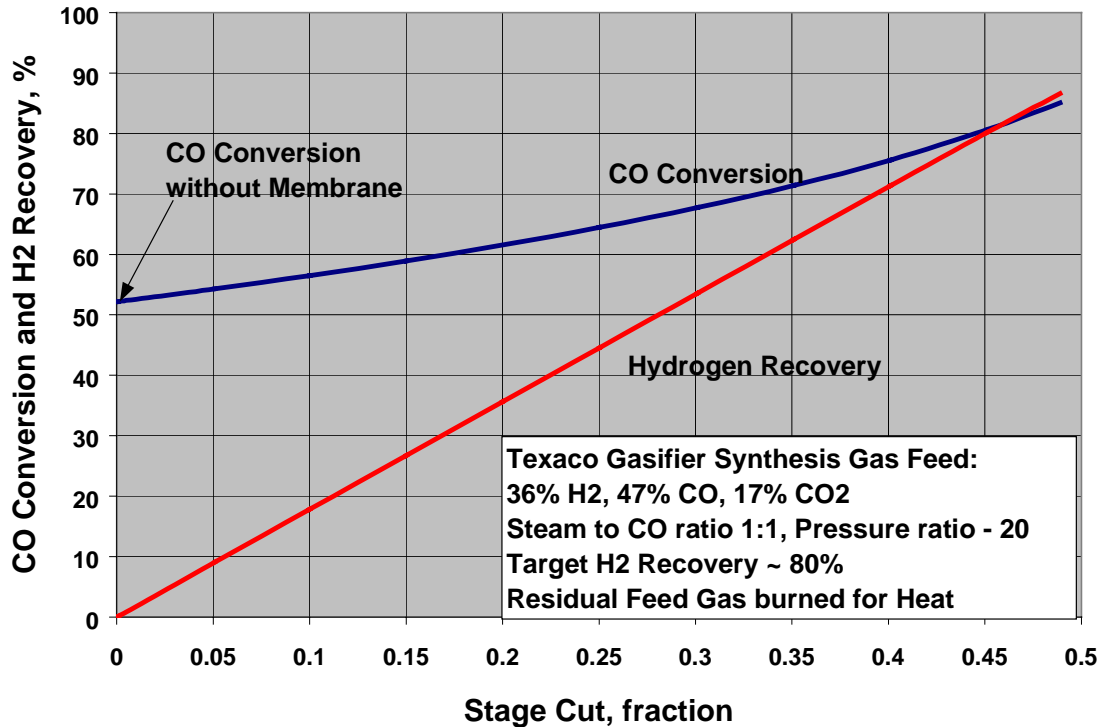


Figure 9. Increase in Equilibrium Conversion with Hydrogen Separation

Based on the observed hydrogen permeation rates the membrane area required was estimated at about 100 cm²/kW equivalent hydrogen generation (1 g/min). For a 100 kW equivalent unit the estimated module area is about 1 m². Due to the thin metal film in the composite membrane, the cost of the ceramic substrate is expected to constitute bulk of the composite membrane cost. Inexpensive ceramic substrates are therefore being investigated.

Based on a preliminary techno-economic analysis four possible applications have been identified for the membrane reactor concept:

- Distributed power generation – Reforming of fuel gas to hydrogen with power generation by PEM fuel cells (~ 50-500 kW)
- On-board fuel reforming for automobiles (~50 kW)
- Hydrogen separation and H₂:CO ratio adjustment for liquid transportation fuels production – Vision 21 Energyplex
- Portable power generation – Micro-channel reactor/PEM fuel cells (~ 20-200 W)

Potential Benefits

The membrane reactor technology will have a substantial impact on the new generation of advanced fossil fuel power plants and has the potential to capture all of the carbon content before combustion cost effectively. This technology would also fit very well in the Vision 21 energyplex concept. An important application of the proposed membrane reactor concept is in “distributed power generation” complexes for large facilities such as shopping centers or apartment complexes. Power generation systems such as PEM fuel cells are attractive for distributed power generation. The palladium-based membrane reactor concept is especially well-suited for these applications since it can provide the high-purity hydrogen needed for PEM fuel cells while capturing all carbon as compressed CO₂. Stationary power applications in the <50 kWe range are a good fit with steam reforming of natural gas coupled with palladium membranes for hydrogen separation and PEM fuel cells power generation. Table 1 summarizes the total market potential for fuel cell distributed power systems (EPRI Report TR-1006645, August 1996). The potential for CO₂ capture by a membrane reactor process is approximately 270 tons CO₂/year in a 50 kW plant. About 4800 small-scale generators with a cumulative power of 9512 MW were operating in 1996-97 with an approximate capacity growth of 250 MW. For the new capacity growth alone, the potential impact of the proposed technology is estimated to be 1.6x10⁶ tons of CO₂ /yr.

Table 1. Potential Applications of Fuel Cell Distributed Power Systems

Size Range	# of Potential Applications
<15kW	935,000
15-20kW	99,000
20-30kW	131,000
30-40kW	67,000
40-60kW	64,000
60-100kW	62,000
100-500kW	85,000
500-1000kW	8,000
>1000kW	5,000

In spite of energy conservation measures, the demand for energy continues to rise. In U.S. alone, energy consumption is estimated to increase from 91 quads in 1995 to 111 quads in 2015 or almost 1 quad/year (Winslow, 1997) with a corresponding increase in CO₂ emissions of almost 200 million tons/year. Coal based energy use is expected to increase from 20 quads in 1995 to 24 quads in 2015 or about 0.2 quad/year. About a third of the total energy increase and almost all of the coal energy increase is expected for power generation. Utilization of advanced power generation with CO₂ recovery prior to combustion using the proposed membrane reactor process will reduce the increase in CO₂ emissions as well as costs of CO₂ capture significantly.

The demand for transportation fuels is expected to increase from 17 million bbls/day in 1995 to 21 million bbls/day in 2015 (Winslow, 1997) or about 0.44 quads/year resulting in about 90 million tons/yr. increase in CO₂ emission. Due to declining oil production, it will be necessary to develop advanced Pioneer plants for producing transportation fuels from coal. The proposed

membrane reactor can be effectively used to process part of the synthesis gas to adjust the H₂:CO ratio, simultaneously capturing carbon content of the processed gas as compressed CO₂.

Hydrogen is an important high-volume feedstock in the chemical industry, e.g. in ammonia synthesis in fertilizer industry, and for hydro-cracking and hydrogenation processes in petrochemical industry. Commercial production of hydrogen by steam reforming of hydrocarbons, most commonly natural gas, is a significant contributor to CO₂ greenhouse gas emissions. Thus, the membrane reactor concept will be directly applicable for commercial hydrogen production.

Future Activities

The planned future activities in the current DOE Phase II program include experimental demonstration of the membrane reactor process with a single tube element of 50 cm² surface area using simulated coal gas composition as feed gas. The experiments will determine the effect of steam to CO ratio and stage cut fraction on the CO conversion and hydrogen recovery and will compare the results to the model simulations similar to those shown in Figure 9. Tubular sintered porous metal substrates will also be evaluated for hydrogen permeation characteristics.

Acknowledgement

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