**NOVEL POLYMER MEMBRANE PROCESS FOR PRE-COMBUSTION
CO₂ CAPTURE FROM COAL-FIRED SYNGAS**

Award Number DE-FE0001124

Final Report

Report Period: September 15, 2009 – September 14, 2011

by

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ABSTRACT

This final report describes work conducted for the Department of Energy (DOE NETL) on development of a novel polymer membrane process for pre-combustion CO₂ capture from coal-fired syngas (award number DE-FE0001124). The work was conducted by Membrane Technology and Research, Inc. (MTR) from September 15, 2009, through December 14, 2011. Tetramer Technologies, LLC (Tetramer) was our subcontract partner on this project. The National Carbon Capture Center (NCCC) at Wilsonville, AL, provided access to syngas gasifier test facilities.

The main objective of this project was to develop a cost-effective membrane process that could be used in the relatively near-term to capture CO₂ from shifted syngas generated by a coal-fired Integrated Gasification Combined Cycle (IGCC) power plant.

In this project, novel polymeric membranes (designated as Proteus™ membranes) with separation properties superior to conventional polymeric membranes were developed. Hydrogen permeance of up to 800 gpu and H₂/CO₂ selectivity of >12 was achieved using a simulated syngas mixture at 150°C and 50 psig, which exceeds the original project targets of 200 gpu for hydrogen permeance and 10 for H₂/CO₂ selectivity. Lab-scale Proteus membrane modules (with a membrane area of 0.13 m²) were also developed using scaled-up Proteus membranes and high temperature stable module components identified during this project. A mixed-gas hydrogen permeance of about 160 gpu and H₂/CO₂ selectivity of >12 was achieved using a simulated syngas mixture at 150°C and 100 psig. We believe that a significant improvement in the membrane and module performance is likely with additional development work.

Both Proteus membranes and lab-scale Proteus membrane modules were further evaluated using coal-derived syngas streams at the National Carbon Capture Center (NCCC). The results indicate that all module components, including the Proteus membrane, were stable under the field conditions (feed pressures: 150-175 psig and feed temperatures: 120-135°C) for over 600 hours. The field performance of both Proteus membrane stamps and Proteus membrane modules is consistent with the results obtained in the lab, suggesting that the presence of sulfur-containing compounds (up to 780 ppm hydrogen sulfide), saturated water vapor, carbon monoxide and heavy hydrocarbons in the syngas feed stream has no adverse effect on the Proteus membrane or module performance.

We also performed an economic analysis for a number of membrane process designs developed in this project (using hydrogen-selective membranes, alone or in the combination with CO₂-selective membranes). The current field performance for Proteus membranes was used in the design analysis. The study showed the current best design has the potential to reduce the increase in Levelized Cost of Electricity (LCOE) caused by 90% CO₂ capture to about 15% if co-sequestration of H₂S is viable. This value is still higher than the DOE target for increase in LCOE (10%); however, compared to the base-case Selexol process that gives a 30% increase in LCOE at 90% CO₂ capture, the membrane-based process appears promising. We believe future improvements in membrane performance have the potential to reach the DOE target.

NOVEL POLYMER MEMBRANE PROCESS FOR PRE-COMBUSTION CO₂ CAPTURE FROM COAL-FIRED SYNGAS (Final Report)

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EXECUTIVE SUMMARY

This final report describes work conducted for the Department of Energy (DOE NETL) on development of a novel polymer membrane process for pre-combustion CO₂ capture from coal-fired syngas (award number DE-FE0001124). The work was conducted by Membrane Technology and Research, Inc. (MTR) from September 15, 2009, through December 14, 2011. Tetramer Technologies, LLC (Tetramer) was our subcontract partner on this project. The National Carbon Capture Center (NCCC) in Wilsonville, AL, provided access to their syngas gasifier test facilities.

The goal of this project was to develop a membrane separation process to provide cost-effective CO₂ management in future coal-based Integrated Gasification Combined Cycle (IGCC) power plants. Current absorption technologies used for CO₂ separation are costly, energy intensive and unlikely to meet DOE CO₂ capture targets. Membrane processes have also been considered for these applications. Key membrane challenges include high membrane cost, low flux, instability in a challenging thermal and chemical environment, device reproducibility, scale-up issues, and poor membrane system design understanding. For an IGCC membrane process to be successfully implemented, innovations in the membranes and membrane process designs that address these issues are required.

During this project, newly-developed polymeric membranes (designated by MTR as Proteus™ membranes) were tested in the laboratory and in the field at NCCC with warm shifted syngas (up to 150°C). These membranes demonstrated separation performance that exceeded project targets and was stable over 500+ hours with a high sulfur feed. A process design study using field performance showed a membrane-based process has the potential to reduce the increase in Levelized Cost of Electricity (LCOE) caused by 90% CO₂ capture to about 15% if co-sequestration of H₂S is viable. This value is still higher than the DOE target for increase in LCOE (10%); however, future improvements in membrane performance have the potential to reach the DOE target.

All project milestones were met on schedule and within budget. Specific project accomplishments organized by task area are as follows:

Membrane Development

- For Proteus membranes, a hydrogen permeance up to 800 gpu and H₂/CO₂ selectivity of >10 was achieved using a simulated syngas mixture (50/50 vol% H₂/CO₂) at 150°C. These values significantly exceed the original project targets of 200 gpu for hydrogen permeance and 10 for H₂/CO₂ selectivity.
- Proteus membranes were successfully fabricated on commercial-scale production equipment at MTR, and this membrane was used to make lab-scale Proteus modules.
- Stability tests conducted at the MTR laboratory showed that the performance of Proteus membranes was stable at feed temperatures up to 150°C and at feed pressures as high as 800 psig. A more rigorous long-term thermal stability test performed at the NCCC showed Proteus membranes are stable at feed temperatures of 150°C for ~500 hours, even in the presence of syngas feeds containing saturated water vapor, heavy hydrocarbons, and >700 ppm hydrogen sulfide.

- A stable hydrogen permeance of 200-300 gpu and a H_2/CO_2 selectivity of 16-25 were achieved for Proteus membrane stamps (with an area of 30 cm^2) at the operating conditions (feed pressures: 150-175 psig and feed temperatures: 120-135°C) encountered at NCCC.

Module Development

- Module components and sealing elements were modified for high temperature operation. Thermal stability tests at MTR indicate that modules developed in this project can be used at elevated temperatures (up to 150°C) for an extended period of time (>150 hours).
- In lab tests, a mixed-gas hydrogen permeance of about 160 gpu and H_2/CO_2 selectivity of >12 at 100 psig and 150°C was achieved using current module configurations. Future optimization is likely to improve performance.
- A stable hydrogen permeance of ~150 gpu and a H_2/CO_2 selectivity of ~14 were achieved for a lab-scale Proteus membrane module (with an area of 0.13 m^2), at the operating conditions (feed pressures: 150-175 psig and feed temperatures: 120-135°C) encountered at NCCC. The results indicate that all module components were stable under the field conditions for a prolonged time period (>600 hrs), and the presence of sulfur-containing compounds (up to 780 ppm hydrogen sulfide), saturated water vapor, carbon monoxide and heavy hydrocarbons in the syngas feed stream has no adverse effect on the Proteus membrane or module performance.

Process Design and Economic Analysis

- A simple membrane process using either hydrogen-selective or CO_2 -selective membranes is capable of capturing 90% of CO_2 from syngas while causing about a 20% increase in the LCOE (when hydrogen sulfide is co-sequestered). These designs produce high-purity liquid CO_2 ready for sequestration and ~92% hydrogen at 30 bar ready for delivery to the gas turbine combustor.
- Hydrogen-selective membranes offer a number of significant advantages over CO_2 -selective membranes when treating oxygen-blown IGCC syngas. These advantages include the ability of hydrogen-selective membranes to operate warm, to use a nitrogen sweep stream to reduce energy use, and to dry the high-pressure CO_2 stream by permeating water in syngas with hydrogen.
- The current best membrane process design – using hydrogen-selective countercurrent/sweep membranes that operate warm for bulk hydrogen recovery, combined with low-temperature CO_2 -selective membranes that assist CO_2 purification and liquefaction – has the potential to reduce the increase in LCOE caused by 90% CO_2 capture to about 15%. This value is still higher than the DOE target for increase in LCOE (10%); however, compared to the base-case Selexol process that gives a 30% increase in LCOE at 90% CO_2 capture, the membrane-based performance looks promising. Even larger cost reductions might be possible if higher permeance and higher selectivity membranes can be developed.
- A sensitivity study shows that as either H_2/CO_2 selectivity or hydrogen permeance increase, the increase in LCOE is reduced. At H_2/CO_2 selectivities of less than 20, increasing the selectivity has the largest impact on reducing the increase in LCOE. At H_2/CO_2 selectivities of more than 20, increasing the permeance is more beneficial to improving the economics of CO_2 capture with membranes. To approach the DOE target of less than a 10% increase in LCOE will require very permeable membranes (~1,000 gpu) with H_2/CO_2 selectivities approaching 40.

- In the designs described above, sulfur compounds such as H₂S that are present in coal-derived syngas will be captured and co-sequestered with CO₂. If H₂S needs to be separated from the CO₂ stream, additional gas processing will be required, which will increase the cost of CO₂ capture.

We believe future work should focus on the following areas:

- Improving the performance of both MTR Proteus membranes and Proteus membrane modules. Better membrane performance is required to achieve the DOE target of less than a 10% increase in LCOE. We believe that a significant improvement in the module performance is likely with additional development work.
- Increasing the operating temperature of membrane modules. There are significant benefits to extending the operating temperature of Proteus membrane modules to the low-temperature shift reactor exit temperature (~200°C). To achieve stable operation at this temperature will require additional materials development and testing.
- Developing high-temperature *commercial-scale* membrane modules. Scale-up of modules to commercial size is an important development stage that will allow testing with larger feed streams at NCCC, and use of these modules in near-term commercial applications.
- Examining new process schemes that capture sulfur as a separate stream in a manner similar to that of conventional acid gas removal technologies. The current membrane process design co-captures H₂S with CO₂; however, this may not be possible for regulatory reasons, or it may be desirable to produce byproducts based on sulfur. Process designs that combine the membrane technology developed in this program with separate sulfur removal technology may be preferred. The techno-economic competitiveness of these hybrid process designs should be studied.
- Continuing long-term membrane module field tests at NCCC and/or at an oxygen-blown gasifier to clarify module lifetime. Field tests are invaluable for surfacing materials and operating challenges, and producing real-world solutions. Field lifetime data are critical to improve assumptions used in process economic evaluations.

1. INTRODUCTION

1.1 Background

Growing evidence indicates that man-made emissions of greenhouse gases, principally carbon dioxide (CO_2), are contributing to global climate change.^[1] The bulk of these CO_2 emissions are caused by the combustion of fossil fuels. In the United States, approximately one-third of anthropogenic CO_2 emissions come from combustion of coal or natural gas in power plants. Because of the low cost and large domestic supply of coal, power production from this feedstock is expected to increase over the next 20 years.^[2,3]

One approach to controlling CO_2 emissions to the atmosphere is carbon capture and sequestration (CCS). In this scheme, CO_2 is captured from large point sources, such as power plants, and sequestered underground in geological structures for long periods of time. A key to this approach is technology that can separate CO_2 from process gases cost effectively, allowing it to be sequestered without radically increasing energy costs. Figure 1.1 shows three pathways that are being considered by DOE for CO_2 capture from fossil fuel power production: post-combustion CO_2 capture from flue gas, pre-combustion capture from syngas, and oxy-combustion, which produces a nearly sequestration-ready CO_2 effluent.^[3] This project is directed toward improving the cost and efficiency of CO_2 capture from pre-combustion syngas.

Figure 1.1. Routes to decarbonized fossil fuel power production.

Gasification of coal produces syngas, a mixture of hydrogen and carbon monoxide that, with treatment, can be used to produce power or chemicals. For example, hydrogen in syngas can be separated and utilized for refinery hydrogenation reactions or as an energy carrier for the hydrogen economy. Alternately, in the IGCC power approach, the decarbonized syngas is sent to a combustion turbine and the waste heat from gasification is used to power steam turbines. A variety of studies have shown that when costs of carbon capture are included, IGCC power production is less costly than power generated by direct combustion of pulverized coal.^[2,4] If carbon emission penalties are implemented in the future, advanced IGCC power plants are likely to play a growing role in meeting the nation's power needs.

Figure 1.2 shows a simplified schematic of CO₂ capture from IGCC power plant syngas. Gasification of coal generates raw syngas, which is sent to particulate removal units and water-gas-shift reactors. The shifted syngas – about 55% hydrogen on a dry basis – then must be treated to remove CO₂ prior to combustion in the power plant turbines. Because the CO₂ in syngas is relatively concentrated and at high pressure, CO₂ capture is easier in the pre-combustion IGCC approach than removal of CO₂ from post-combustion flue gas.

Figure 1.2. Simplified process flow diagram for hydrogen or energy production from gasified coal.

The current leading technologies for pre-combustion CO₂ capture are physical absorption processes, such as Selexol[®] or Rectisol[®]. These processes have a number of drawbacks.^[3, 5] Most importantly, the CO₂ gas from the absorption unit is produced at low pressure. This gas must then be recompressed so that it can be transported by pipeline and injected into the ground at a sequestration site. The recompression step represents a considerable energy and capital cost. The absorption step using physical or chemical absorbents is also complex and consumes large amounts of energy in the absorber-stripper operation. For these reasons, better methods of separating CO₂ from the shift reactor product are widely sought.

Membrane processes have previously been suggested as a means to lower the cost and energy intensity of IGCC syngas cleanup. Much of this effort has focused on inorganic membranes because of the perceived desirability of operating at high temperatures.^[6-8] Over the past decade, a large research effort has been expended on palladium alloys and other metallic membranes that selectively transport hydrogen at elevated temperatures. Membranes of this type offer the potential of process intensification in syngas cleanup by combining water-gas shift reactions with hydrogen separation.^[8, 9] Despite this promise, there are significant hurdles to moving this technology beyond the laboratory. In the 1950s and 1960s, Union Carbide studied palladium alloy membranes extensively, even building a large demonstration plant for hydrogen separation. However, in the end, membrane cost and reliability issues made this technology uncompetitive with other separation techniques.^[10] These practical problems persist today. Ongoing work seeks to reduce membrane cost, improve the membrane tolerance to sulfur species and other contaminants, and address module fabrication, reliability, and scale-up challenges. Nevertheless, no commercial inorganic membrane system for industrial gas separations has yet been installed or is in sight.

Compared to inorganic membrane materials, polymeric membranes exhibit lower hydrogen permeances and lower H₂/CO₂ selectivities. However, polymeric materials are inexpensive, stable to sulfur compounds, and easily fabricated into large, defect-free membrane modules.^[10] Polymeric membranes are two orders of magnitude less costly than inorganic materials on a per-square-meter basis. For example, in the reverse osmosis industry, polymer membrane modules

are produced at costs as low as \$10/m².^[10] This compares with costs of roughly \$1,000/m² for inorganic membrane modules.^[8, 11] If polymer membranes with the necessary performance and lifetime can be developed, it seems reasonable to investigate whether this robust, cost-effective technology can be extended to syngas H₂/CO₂ separations. Such low-cost, modest-selectivity polymer membranes may be particularly suited for IGCC power applications, where high-purity hydrogen is not required for combustion.

1.2 Membrane Gas Separation Fundamentals

Membranes for gas separations are characterized by their flux and selectivity. Gas flux, N_A (cm³(STP)/s), through a nonporous polymeric membrane can be expressed as follows:^[12]

$$N_A = \frac{P_A}{l} \cdot \Delta p_A \cdot A \quad (1)$$

where P_A (cm³(STP) cm/cm²·s·cmHg) is the permeability coefficient of gas component A, l is the thickness of the membrane selective layer [cm], Δp_A is the partial pressure difference across the membrane (cmHg), and A is the required membrane area (cm²). The permeance, P_A/l (cm³(STP)/cm²·s·cmHg), is also used to characterize the pressure-normalized flux in composite membranes, in which the thickness of the selective layer cannot be measured.

If the diffusion process obeys Fick's law and the downstream pressure is much less than the upstream pressure, permeability is given by:

$$P_A = D_A \times S_A \quad (2)$$

where D_A is the average effective diffusivity, and S_A is the apparent solubility of penetrant A in the polymer. The ideal selectivity of a membrane for gas A over gas B is the ratio of their pure gas permeabilities:

$$\alpha_{A/B} = \frac{P_A}{P_B} = \left(\frac{D_A}{D_B} \right) \times \left(\frac{S_A}{S_B} \right) \quad (3)$$

where D_A/D_B is the diffusivity selectivity, which is the ratio of the diffusion coefficients of gases A and B. The ratio of the solubility of gases A and B, S_A/S_B , is the solubility selectivity.

For H₂/CO₂ separation, diffusivity selectivity favors hydrogen because hydrogen (with a kinetic diameter of 2.89Å) is smaller than CO₂ (with a kinetic diameter of 3.3Å). However; solubility selectivity favors CO₂ because CO₂ (with a critical temperature of 304K) is much more condensable than hydrogen (with a critical temperature of 33K). The favorable H₂/CO₂ diffusivity selectivity is offset by the unfavorable solubility selectivity, so most polymeric materials do not show high H₂/CO₂ selectivity.

1.3 Hydrogen-Selective Polymeric Membrane Development

Polymers that exhibit selectivity for hydrogen over CO₂ are typically rigid glassy materials. In these materials, the mobility selectivity term favoring hydrogen permeation outweighs the sorption selectivity term favoring CO₂ permeation. Figure 1.3 presents a permeability/selectivity trade-off plot for H₂/CO₂ separation in polymeric membranes at 25°C.^[13] Each point on the graph represents the separation characteristics of a specific material. The upper bound line in the figure gives a rough estimate of the highest H₂/CO₂ selectivity possible for a given permeability

in polymer-based materials.^[13, 14] A trade-off exists between gas selectivity and permeance; that is, materials with higher H₂ permeance have lower H₂/CO₂ selectivity.

Figure 1.3. H₂/CO₂ selectivity versus hydrogen permeance trade-off curve. Pure-gas performance from the literature is compared for a variety of newly developed glassy polymers^[15] at 20–35°C, polybenzimidazole (PBI)^[16] at 250°C and MTR proprietary materials at 150°C. The data points have been calculated from film permeability data at 25°C, assuming a selective layer thickness of 1 micron; the MTR proprietary material data are experimental results for composite membranes measured using a 50% H₂/50% CO₂ gas mixture at 150°C.

Development of better membranes for syngas separations is an area of active research.^[17] A variety of newly developed polymers such as crosslinked polyimides and polybenzimidazole (PBI) reportedly have separation properties superior to those of conventional polymeric materials for hydrogen and CO₂.^[16, 18–20] As shown in Figure 1.3, pure-gas performance of these advanced polymeric materials clearly exceeds the upper bound limitations.

Among the advanced polymers, PBI has received the greatest attention in the past decade due to its excellent thermal stability (up to 300°C) and superior separation performance (pure-gas H₂/CO₂ selectivity up to 40 at 250°C). Recently, as part of the DOE effort to develop new technologies for carbon capture from IGCC syngas, a group led by SRI International and Los Alamos National Laboratory has investigated high-temperature hydrogen-selective polymeric membranes based on PBI. Laboratory studies show that these PBI membranes exhibit attractive H₂/CO₂ selectivities at operating temperatures of 200–300°C. However, the chemistry of PBI makes these materials difficult to fabricate into the extremely thin, high-surface-area membranes required for an industrial system. The main challenge will be improving the permeance (throughput) of the membranes and developing ways to process the PBI materials into an industrially viable membrane module.

MTR, in collaboration with Tetramer Technologies, LLC (Tetramer) (Pendleton, SC), has recently discovered a new high-temperature hydrogen-selective polymer (referred to as the MTR proprietary material) that shows great potential in separation of hydrogen and CO₂ from IGCC shifted syngas. More importantly to commercial development, these materials are readily solution-processable and can be easily fabricated into high-flux composite membranes. As shown in Figure 1.3, a first generation of composite membranes based on this new MTR proprietary material exhibits performance that places it significantly above the upper bound line. A mixed-gas hydrogen permeance of as high as 150 gpu and a mixed-gas H₂/CO₂ selectivity of close to 14 at a feed temperature of 150°C have already been achieved.

Figure 1.4 shows mixed-gas hydrogen and CO₂ permeances as well as H₂/CO₂ selectivity as a function of operating temperature for this newly developed composite membrane. The permeances of both gases increase with increasing temperature. This behavior is typical for size-selective polymers where diffusion – an activated process – largely governs permeance. Because hydrogen permeance increases faster than that of carbon dioxide, the H₂/CO₂ selectivity of this membrane generally increases with temperature. Such a selectivity trend occurs because as temperature increases, solubility selectivity, which favors CO₂, is reduced. For this separation, useful membranes should have high gas permeances to reduce the membrane area required, and high H₂/CO₂ selectivities to reduce the required compressor power. The permeation results indicate that it is desirable to perform the H₂/CO₂ separation at the highest temperature at which the membrane can operate reliably. The selective layer polymer, that is, the MTR proprietary material in this newly developed membrane is thermally stable to at least 250°C. The factor limiting high temperature operation for these membranes will be the membrane module components and sealing materials. Our current commercial membrane modules can operate at up to 100°C. Part of this project was directed at improving other module components and sealing techniques, to extend the operating temperature to shift reactor effluent conditions.

Figure 1.4. Mixed-gas (a) H₂ and CO₂ permeance and (b) H₂/CO₂ selectivity of a newly developed composite membrane at 50 psig as a function of temperature. Feed mixture is 50 mol% H₂/50 mol% CO₂.

The preliminary results for the newly developed MTR composite membranes are encouraging. We believe a more thorough study of the effect of molecular structure on H₂/CO₂ separation performance in the newly discovered polymer will allow us to further improve the membrane performance. Based on the chemistry of the MTR proprietary polymer, we believe that the pathway to forming these membranes into durable modules of the type used in MTR's commercial high-pressure natural gas and syngas products is relatively straightforward. The proven module manufacturing capabilities of these newly developed membranes offer a lower risk, near-term alternative to inorganic membranes or other advanced polymer materials. As such, with further improvement in the membrane performance, these polymeric membranes will provide a technology for faster, lower-cost commercialization of membranes for use in IGCC syngas separations.

1.4 Project Objectives and Scope

In IGCC power plants, raw materials produced from coal gasification have to be cleaned of all contaminants to produce a convenient energy source (hydrogen) or sent to a turbine for direct power production. This project was focused on the post-shift separation of hydrogen and CO₂. The separation of hydrogen from CO₂ in future IGCC power plants has been the subject of various studies. Current absorption technologies used for this separation are costly, energy intensive and unlikely to meet DOE CO₂ capture targets. Membrane processes have also been considered for these applications. As stated earlier, key membrane challenges include high membrane cost, low flux, instability in a challenging thermal and chemical environment, device reproducibility, scale-up issues, and poor understanding of membrane system design. For an IGCC membrane process to be successfully implemented, innovations in the membranes and membrane process designs that address these issues are required.

The main objective of this project was to develop a cost-effective membrane process that could be used in the relatively near-term (5- to 10-year horizon) to capture CO₂ from shifted syngas generated by a coal-fired IGCC power plant. In this research project, novel gas separation membranes based on newly discovered low-cost polymers were developed. The initial target properties of the membrane were hydrogen permeance of >200 gpu and H₂/CO₂ selectivity of >10 at 100-200°C. As part of this project, we evaluated the economic feasibility of using our newly developed membrane-based process to meet DOE's pre-combustion goal of <10% increase in the levelized cost of electricity (LCOE) at 90% CO₂ capture. The specific objectives of the program were to:

- Investigate novel, stable high-temperature polymers identified by Tetramer for use in H₂/CO₂ selective membranes;
- Prepare composite polymer membranes and bench-scale modules with H₂/CO₂ selectivities of 10 or higher and hydrogen permeances of greater than 200 gpu at desired syngas cleanup temperatures (100-200°C);
- Optimize membrane process designs, investigate the sensitivity of different proposed processes to membrane performance, and assess the optimal integration of a membrane system into the syngas cleanup train;

- Conduct bench-scale testing of optimized membranes at MTR with simulated water-gas-shift (WGS) syngas mixtures, to evaluate membrane performance and lifetime under expected operating conditions;
- Prepare a comparative evaluation of the cost of the polymer membrane-based separation process versus current cleanup technologies (Selexol[®]).

This project was a joint effort of MTR, Tetramer and Southern Company, with MTR serving as the lead organization. The program consisted of two phases, each of 12 months duration. All project milestones were met on schedule and within budget.

The first phase of the project was focused on materials development, with an emphasis on identifying high-temperature polymers with desirable H₂/CO₂ separation properties. During this phase, Tetramer utilized their expertise to synthesize and scale up novel high-temperature polymers, and conduct preliminary screening of new materials. Promising polymers were fabricated into composite membranes and tested with simulated syngas mixtures at MTR.

The second phase of the project focused on optimizing the composite membrane performance and scaling up the production of optimized composite membranes on commercial-scale equipment. These membranes were used to fabricate lab-scale spiral-wound modules, each containing about 0.1 m² of membrane. In this phase, one of the goals was to extend the operating temperature of spiral-wound modules to shift reactor effluent conditions (our current commercial membrane modules can operate at up to 100°C); this work involved improving the thermal stability of all module components and sealing techniques. The modules were tested with simulated syngas mixtures to provide separation performance and lifetime data. The membrane performance obtained in the laboratory was used to estimate the cost of a newly developed membrane CO₂ capture process for future IGCC power plants, and that cost was compared with the costs of competitive technologies that are currently being considered for this application.

In addition, because of the early successes in the membrane development work on this project, we started field tests of the optimized membranes and lab-scale membrane modules using a coal-derived syngas available from a reformer operated by Southern Company at the National Carbon Capture Center. The main objective of the field tests was to evaluate the long-term stability of membrane or module components at elevated temperatures in the presence of water, sulfur-containing compounds and heavy hydrocarbons.

2. MEMBRANE DEVELOPMENT

2.1 Identifying the Selective-Layer Polymer Candidate

Early work on this project focused on screening candidates for selective-layer polymers. During this project, a variety of hydrogen-selective polymer materials with potential for H₂/CO₂ separations were synthesized by our subcontractor, Tetramer. Based on both gas transport performance and the potential for scale up to commercial fabrication, the three most promising polymer materials (designated as MTR proprietary materials A, B and C) were selected. All three polymer materials showed hydrogen and CO₂ separation properties superior to those of

conventional polymer materials. More importantly, we were able to fabricate composite membranes using these three polymer candidates, to further evaluate their potential for the targeted separation.

Pure-gas performance of the three types of composite membranes prepared (Types A, B and C, corresponding to the selective-layer polymers A, B and C) are shown in Table 2.1. All three composite membranes showed very promising performance for hydrogen and CO₂ separation (hydrogen permeance ~10; H₂/CO₂ selectivity >10) at 25°C. Type B and C membranes were particularly promising; H₂/CO₂ selectivities were above 15, which are significantly better than the selectivities of conventional polymers (H₂/CO₂ selectivity are typically less than 6). At 25°C, Type B and C membranes were clearly better than Type A, but there was no significant difference between Types B and C.

Table 2.1. Pure-gas Separation Properties of the Most Promising Polymer Material Candidates Screened During This Project. Test conditions: 50 psig.

Composite Membrane	Polymer Selective Layer Candidate	Performance at 25°C		Performance at 150°C	
		H ₂ Permeance (gpu)	H ₂ /CO ₂ Selectivity	H ₂ Permeance (gpu)	H ₂ /CO ₂ Selectivity
Type A	A	10	10	160	8
Type B	B	10	17	140	10
Type C	C	12	15	200	19

As discussed in the Introduction, operating such hydrogen-selective membranes at elevated temperatures is always favored, from both membrane performance and economic perspectives. As a result, it is important to look at how temperature impacts H₂/CO₂ separation performance for these three types of membranes. We evaluated their performance as a function of temperature to determine how the membranes perform at elevated temperatures. For all three membranes, the hydrogen permeances showed significant increases when temperature was increased from 25°C to 150°C (Table 2.1). At 150°C, Type A and B membranes showed very similar performance (a hydrogen permeance of ~150 gpu and a H₂/CO₂ selectivity of ~10). However, for Type C membrane, at 150°C, the hydrogen permeance reached a value of 200 gpu, combined with a H₂/CO₂ selectivity of 19. Even though Type B and C membranes showed very similar performance at 25°C, the difference between these two became quite significant at elevated temperatures. Undoubtedly, based on these results, Type C is a better membrane for the targeted separation. All three membranes were further tested with a hydrogen and CO₂ gas mixture at elevated temperatures (up to 150°C). The conclusion remained the same. Therefore, MTR proprietary polymer C was chosen as the selective layer material for fabrication of composite membranes in this project (designated as the MTR Proteus™ membrane throughout the report).

2.2. Developing the MTR Proteus Membrane

To achieve high membrane permeances, polymers must be fabricated into composite membranes with ultra-thin selective layers, even for high permeability materials. The membranes developed in this project consist of a microporous support membrane and three surface layers, including the selective layer, as shown schematically in Figure 2.1. In order to achieve the optimal membrane performance, production of an ultrathin, defect-free selective layer is the critical step, but it is also very important to engineer each individual layer in the composite membrane. In addition to identifying the most promising selective layer polymer, we devoted significant efforts to generating membranes with consistently better performance, through approaches such as optimizing each functional layer in the composite membrane, developing membrane fabrication/post-treatment protocols and investigating the effect of coating conditions on membrane performance.

Figure 2.1. Schematic diagram of a multi-layer composite membrane. The selective layer determines the membrane separation performance.

During this project, we made great progress improving the performance of MTR Proteus hydrogen membranes. Figure 2.2 shows the mixed-gas performance of Proteus membranes over the course of this project. The typical membrane performance obtained for each development stage during this project is indicated as 1st, 2nd, 3rd and 4th generation performance, respectively. Performance targets set in the proposal (hydrogen permeance = 200 gpu, H₂/CO₂ selectivity = 10) are also included for comparison.

Figure 2.2. Mixed-gas performance of MTR Proteus membranes over the course of this project. The feed gas is an H₂/CO₂ (50:50 vol%) mixture at 50 psig and 150°C. Performance targets (H₂ permeance = 200 gpu, H₂/CO₂ selectivity = 10) set in the proposal are included for comparison.

As shown in the figure, the membrane performance improved significantly during each development stage. For example, hydrogen permeance increased from 150 gpu to 250 gpu with no loss in selectivity from the first to the second generation. A significant improvement in the membrane performance was achieved from the second to the third generation membranes (hydrogen permeance increased an additional 60%, while the H₂/CO₂ selectivity remained above 10). A further improvement in the hydrogen permeance was achieved for the fourth generation (to about 800 gpu), with a slight decrease in the H₂/CO₂ selectivity (still above 10). The current best membrane shows a hydrogen permeance four times higher than the original target set in our proposal.

To achieve such improvements in the membrane performance, we devoted significant effort to minimizing the thickness of the selective layer (<0.2 μm), and we also explored other fabrication protocols to further optimize the membrane configuration. We discovered that post-treatment and the type of overcoat layer have a large impact on the performance of Proteus membranes. Detailed results are discussed in the following sections.

2.2.1. *Effect of Post-Treatment on Membrane Performance*

Two types of post-treatment methods (designated as Type I and Type II) were applied to the Proteus membranes after membrane formation. Following treatment, both membranes were tested at 50 psig with pure hydrogen and CO₂ at different feed temperatures ranging from 20 to 150°C; membrane performance is presented in Figure 2.3. For both types of membranes, the permeances of hydrogen and CO₂ increased with increasing feed temperature. This behavior is typical for size-selective polymers where diffusion, an energy-activated process, largely governs permeance. At 150°C, the Proteus membrane post-treated using the Type II method showed

much higher hydrogen permeance (~ 800 gpu) than that using the Type I method (~ 400 gpu). Pure-gas H_2/CO_2 selectivities of these two types of membranes follow the same trend, increasing with an increase in feed temperature and reaching a maximum at about 120°C . The membrane treated using the Type I method has higher H_2/CO_2 selectivity over most of the temperature range tested; however, at 150°C , the H_2/CO_2 selectivities of these two membranes are similar, at values of about 15.

Figure 2.3. a) Pure-gas hydrogen permeance and b) H_2/CO_2 selectivity of Proteus membranes post-treated using two different approaches as a function of feed temperature. Test conditions: 50 psig. Lines are added to guide the eye.

The mixed-gas performance of Proteus membranes with Type I and Type II post-treatment at different feed temperatures ranging from 21°C to 150°C is presented in Figure 2.4. The experiments were carried out at a feed pressure of 50 psig using an H_2/CO_2 (50:50) gas mixture (gas mixture ratios are in vol% for this report, unless indicated otherwise). As observed in the pure-gas measurements, the permeances of both hydrogen and CO_2 increase with increasing feed temperature. At 150°C , hydrogen permeances of both membranes are >400 gpu and H_2/CO_2 selectivities of both membranes are >10 . These results showed that different post-treatment methods after membrane formation also had a large impact on the performance of Proteus membranes, particularly on their hydrogen permeance.

Figure 2.4. a) Mixed-gas hydrogen permeance and b) H_2/CO_2 selectivity of Proteus membrane with Type I and Type II post-treatment, as a function of feed temperature. Test conditions: 50 psig using a 50/50 H_2/CO_2 gas mixture. Lines are added to guide the eye.

2.2.2. Effect of Various Overcoat Layers on Membrane Performance

The effect of different overcoats on membrane performance was also evaluated. The main purpose of overcoat layers is to seal minor membrane defects, as well as to protect the membrane from damage during handling or in actual operation. One of the major criteria of choosing the overcoat layer is that the overcoat materials should have much higher hydrogen permeance than the selective layer. Otherwise, if the hydrogen permeance of the overcoat layer is comparable to that of the selective layer, it will contribute to the overall membrane selectivity.

Four different types of overcoat layers (Overcoat 1, Overcoat 2, Overcoat 3 and Overcoat 4) were applied to Proteus membrane samples and tested. Figure 2.5 shows the mixed-gas hydrogen permeance and H_2/CO_2 selectivity of these membranes tested at different feed temperatures ranging from 21°C to 150°C. As shown, the overcoat layer affects both hydrogen permeance and H_2/CO_2 selectivity.

Figure 2.5. a) Mixed-gas H₂ permeance and b) H₂/CO₂ selectivity of Proteus membranes with different membrane overcoats as a function of feed temperature. Test conditions: 50 psig using a 50/50 H₂/CO₂ gas mixture.

The relative hydrogen permeance of these overcoat layers alone follows the order: Overcoat 1 > Overcoat 2 > Overcoat 3 > Overcoat 4. This overcoat hydrogen permeance order helps explain the Proteus membrane results presented in Figure 2.5. Over the temperature range studied, the hydrogen permeance of the Proteus membranes follows the order of the overcoat hydrogen permeances. For example, the Proteus membrane with Overcoat 1 is the most permeable, while the membrane with Overcoat 4 is the least permeable. These results indicate that the overcoat layers are contributing to the overall transport resistance in the membranes. However, this contribution is not dominant because, as shown in Figure 2.5(b), the overall membranes are H₂/CO₂-selective, whereas the overcoat layers themselves are CO₂/H₂-selective (with the exception of Overcoat 4, for which H₂/CO₂ < 2). At 150°C, the Proteus membrane with Overcoat 1 shows higher hydrogen permeance and higher H₂/CO₂ selectivity than those with other overcoats. Using Overcoat 1 as the overcoat layer shows the benefit in achieving membrane performance close to the intrinsic property of selective layer. One other potential benefit of using Overcoat 1 as an overcoat layer is that it could improve the Proteus membrane resistance to other contaminants, such as heavy hydrocarbons, that could be present in the shifted syngas effluent from IGCC power plants.

2.3. Scaled Up Production of Proteus Membranes

As we worked on scale up of Proteus membrane production to commercial scale, we systematically evaluated the effect of coating parameters on membrane performance. Both the transport properties of MTR Proteus membranes and the reproducibility of performance improved significantly. Proteus membrane rolls (40 inches wide by 100 feet length) were successfully fabricated on our commercial equipment. The membrane from the scale-up production coating runs was used to fabricate lab-scale Proteus prototype membrane modules. Detailed discussion of the Proteus membrane module work is presented in Section 3 (Module Development).

Figure 2.6 shows the schematic drawing of commercial equipment including a casting machine and a coating machine used to scale up production of Proteus membranes. The casting machine used to prepare the microporous support membrane is shown in Figure 2.6(a). The casting solution, consisting of the polymer in a water-miscible solvent, is doctored onto the moving web. The web passes into a water bath, which precipitates the polymer to form the film. The coated web is collected on a take-up roll, washed overnight to remove any remaining solvent, and dried to form the support film. The thin-film coating machine for building the additional layers of the membrane composite is illustrated in Figure 2.6(b). The support membrane from the feed roll passes into the coating tank, where a layer of polymer coating solution is deposited. After evaporation of the solvent, a 0.1-1 μ m-thick polymer film is formed on top of the support membrane. (The thickness depends on the polymer and the concentration of the solution.) The selective layer and protective layer are added by the same process.

Figure 2.6. Schematic diagrams of (a) a microporous support membrane casting machine and (b) a thin-film coating machine.

Table 2.2 shows the pure-gas results for Proteus membranes from three different scale-up production runs. All membrane rolls showed consistently good pure-gas performance at room temperature. The hydrogen permeance ranged from 15 to 24 gpu and the H₂/CO₂ selectivity was in the range of 15-19. These results are consistent with the pure-gas performance of Proteus membranes prepared in lab-scale coating trials, confirming that the production scale up was successful.

Table 2.2. Pure-gas Test Results for Proteus Membranes Prepared at Commercial Scale. Test conditions: feed pressure of 50 psig and room temperature.

Proteus Membrane	H ₂ Permeance (gpu)	CO ₂ Permeance (gpu)	H ₂ /CO ₂ Selectivity
Run 1	24	1.3	19
Run 2	15	1.0	15
Run 3	22	1.5	15

2.4. Evaluating the Stability of Proteus Membranes

Various tests were performed at the MTR laboratories to evaluate the transport properties of the Proteus membrane and characterize these membranes under conditions that are close to those of a real syngas cleanup train (higher feed pressure and higher feed temperature than used to date). The main objective of these tests was to demonstrate the feasibility of using Proteus membranes developed in this project in the targeted separation, that is, the separation of hydrogen from shifted syngas effluent in future IGCC power plants. The syngas stream exiting from the water shift reactor of such plants will be at high pressures (>600 psig) and high temperatures (>100°C). From the perspective of the economics of capturing CO₂ while separating hydrogen, it is always preferable to maintain the syngas stream entering the membrane separation unit at as high a pressure and temperature as possible, while maintaining reliable membrane performance. For the membrane process developed in this project, we were aiming to operate the Proteus membrane, a polymer-based membrane, at 100-200°C and >600 psig. To test the potential range of successful operation, it was important to investigate the impact of temperature and pressure on the membrane performance, as well as to examine the membrane stability under the same conditions. Details of the test results are described as follows.

2.4.1. Effect of Feed Temperature on Membrane Performance

The mixed-gas performance of a Proteus membrane at different feed temperatures ranging from 21°C to 150°C is presented in Figure 2.7; The experiments were carried out at a feed pressure of 50 psig using an H₂/CO₂ (50:50) gas mixture. As observed in previous measurements, the permeances of both hydrogen and CO₂ increased with increasing feed temperature. The hydrogen permeance increased from 7 gpu to 390 gpu as the temperature increased from 25°C to 150°C. At the same time, the selectivity increased from 4 to 14, reaching a maximum around 110°C, and then plateaued or dropped slightly as the temperature further increased from 110°C to 150°C. At 150°C, hydrogen permeance was close to 400 gpu and H₂/CO₂ selectivity was about 12. Overall, these results suggest that operating the Proteus membranes at higher temperature was preferred, in order to achieve better membrane performance.

Figure 2.7. a) Mixed-gas permeance and b) H₂/CO₂ selectivity of a Proteus membrane as a function of feed temperature tested at 50 psig using a 50/50 H₂/CO₂ gas mixture. Open symbols are data from the first temperature cycle and closed symbols represent data from the second temperature cycle. The same membrane stamp was tested in both cycles. Lines are added to guide the eye.

To determine whether the slight drop or plateau in H₂/CO₂ selectivity beyond 110-120°C was caused by degradation of the membrane, the same membrane stamp was tested a second time, with feed temperature cycling from 21°C to 150°C using an H₂/CO₂ (50:50) gas mixture. The time spent at each temperature was about 30-60 minutes, with a full cycle taking about 9 hours. As shown in Figures 2.7(a) and 2.7(b), hydrogen permeance and H₂/CO₂ selectivity were essentially the same on the first and second cycles. This similar performance for both cycles suggests that the decrease in H₂/CO₂ selectivity from around 110°C to 150°C is not caused by membrane degradation or physical damage to the membrane, but is more a characteristic of this type of membrane. The thermal stability of this Proteus membrane stamp was further evaluated at 135°C for a prolonged time period. As shown in Figure 2.8, the membrane performance at this temperature was relatively constant throughout a test period of eight hours. Current porous support used in Proteus membranes was susceptible to some morphology change upon thermal exposure above 150°C, therefore, we did not test Proteus membranes at >150°C in this project. Advanced support materials to be developed in the future will allow Proteus membranes to be operated above 150°C, potentially ~200°C.

The initial thermal stability test at the MTR laboratory showed that the performance of Proteus membranes was stable at high feed temperatures (up to 150°C). More rigorous long-term thermal stability tests performed at the NCCC syngas facility operated by Southern Company also indicate that Proteus membranes are stable at elevated feed temperatures (up to 150°C), even in the presence of saturated water vapor, heavy hydrocarbons, and hydrogen sulfide at concentrations of >700 ppm in the syngas feed. Detailed results are presented in the Field Testing section of the report (Section 4).

Figure 2.8 Mixed-gas H₂ permeance and H₂/CO₂ selectivity as a function of time for a Proteus membrane tested at 135°C and 50 psig using a 50/50 H₂/CO₂ gas mixture. Lines are added to guide the eye.

2.4.2. Effect of Feed Pressure on Membrane Performance

We performed mixed-gas tests at pressures up to 800 psig to determine whether these conditions (similar to those of a GE gasifier syngas) would impact membrane separation performance. A Proteus membrane was tested at feed pressures ranging from 200 to 800 psig using a standard syngas mixture (50%/50% H₂/CO₂) at 135°C. The results are shown in Figure 2.9.

Figure 2.9. (a) Mixed-gas H₂ permeance and (b) mixed-gas H₂/CO₂ permeance as a function of the feed pressure. Data points are included for a test at 50 psig performed after the test at the highest pressure, to determine any change in membrane performance after prolonged testing at high pressures. Feed temperature: 135°C.

The hydrogen permeance remained at around 310 gpu as the feed pressure increased from 200 psig to 800 psig at 135°C; at the same time, the H₂/CO₂ selectivity declined slightly from 13 to

11. The slight decline in the H_2/CO_2 selectivity resulted from the increase in the CO_2 permeance with feed pressure (the increase in CO_2 permeance may have been due to membrane plasticization at high pressure by CO_2 , a typical phenomenon seen in most polymeric membranes). Immediately after the mixed-gas measurement at 800 psig, the Proteus membrane was tested once again at 50 psig to see whether the membrane performance changed after being tested at high pressures. As shown in Figure 2.9, the mixed-gas hydrogen permeance and H_2/CO_2 selectivity at 50 psig were almost the same as the initial membrane performance obtained at 200 psig. Previous test results (not shown in the report) showed that in the feed pressure range from 50-200 psig, the membrane performance was independent of pressure. These results indicate that the feed pressure does not have a significant impact on membrane performance within the pressure range of 50-800 psig. This pressure range covers the possible conditions expected for different gasifier technologies (GE, Shell, Conoco Phillips, etc.).

2.5. Effect of a Permeate-Side Nitrogen Sweep on Membrane Performance

Since a nitrogen diluent stream is available from the IGCC air separation units (nitrogen is mixed with hydrogen at the gas turbine combustor to control flame temperature in IGCC power plants), this nitrogen can be used as a sweep gas for a hydrogen-selective membrane, to significantly reduce energy requirements for the step in which hydrogen is separated from CO_2 . The benefit of utilizing this nitrogen has been confirmed in the process design and analysis studies conducted for this project (See details in the Section 5 – Process Design and Analysis).

One open question that needs to be determined experimentally is the efficiency of the membrane countercurrent/sweep unit fitted with hydrogen-selective membranes. We have developed this type of gas-gas membrane contactor for treatment of low-pressure flue gas containing CO_2 . In that work, concentration polarization effects that might degrade the performance on the sweep side of the membrane were small, and the experimentally measured performance of the membrane modules was within 20% of the expected theoretical performance. However, the sweep process shown in Figure 5.3 (p. 57) operates at very different conditions and the effect of concentration polarization on the sweep side of the membrane may be more noticeable. In particular, the flux of hydrogen through the membrane will be relatively high because of the high syngas feed pressure. In this situation, where the volumetric flow of hydrogen through the membrane is comparable to that of the nitrogen sweep gas, concentration polarization may hinder performance. This issue will need to be addressed in future module design work to maximize the benefit of nitrogen sweep. An early laboratory test using nitrogen sweep on the permeate side of the Proteus membrane has confirmed that the presence of a nitrogen sweep stream could significantly improve the separation performance for the targeted separations.

To determine the efficiency of the membrane countercurrent/sweep unit fitted with hydrogen-selective membranes, we conducted laboratory tests by introducing a nitrogen sweep gas on the permeate side of a Proteus membrane. The experiment was performed in a high pressure cell (active area = 30.2 cm^2) modified for sweep testing. Figure 2.10 shows the effect of sweep/feed flow rate ratio on Proteus membrane performance. In these tests, the membrane was tested using a simulated syngas mixture (50%/50% H_2/CO_2) at a feed pressure of 115 psia and a feed temperature of 110°C . The sweep gas pressure was set to 57 psia, giving a fixed feed/permeate pressure ratio of 2, which is close to the actual pressure ratio used in the process design studies.

The sweep/permeate flow rate ratio was varied from 0 to 2.5 (actual design value will be close to 1) and the stage-cut was maintained at 1%.

Figure 2.10. Improvement in mixed-gas hydrogen flux as a function of the sweep/permeate flow rate ratio for a Proteus membrane. Feed pressure: 100 psig; feed temperature: 110°C; sweep pressure: 42 psig.

The introduction of a nitrogen sweep stream on the permeate side improved both hydrogen flux and H₂/CO₂ selectivity. The H₂/CO₂ selectivity without a sweep stream was about 15; in the presence of a nitrogen sweep, the selectivity slightly increased to around 17-19. As shown in Figure 2.10, the hydrogen flux increased as the sweep/permeate flow rate ratio increased from 0 to 2.5. The hydrogen flux more than doubled as the sweep/permeate flow rate ratio was increased from 0 to 0.5. With a sweep/permeate ratio of 2.5, the hydrogen flux was four times higher than that without sweep. The theoretical hydrogen flow rate was determined using ChemCad simulation software (ChemStations, Houston, TX) for an ideal countercurrent flow using mixed-gas permeances (see Figure 2.10). The experimental data points are below the theoretical line, indicating the sweep operation was not 100% effective in the membrane stamp tests. The difference between theoretical and experimental results might be partially due to the design of the permeation cell. A better design in the test cell would ensure a much more efficient sweep operation. Nevertheless, these results show that a nitrogen sweep stream could be used to enhance the separation performance of the Proteus membrane for the targeted separation.

2.6. Membrane Development Summary

In summary, during this project, we made great progress in identifying a proprietary polymer candidate, developing the Proteus membrane, optimizing Proteus membrane performance, and scaling up membrane production. The main accomplishments in the area of membrane development can be summarized as follows:

- Hydrogen permeance of >400 gpu and H₂/CO₂ selectivity of >12 was achieved using a simulated syngas mixture (50/50 vol% H₂/CO₂) at 150°C and 50 psig. By further

optimizations in the membrane fabrication protocols, such as introducing a post-treatment method, further improvements in the hydrogen permeance were achieved (to about 800 gpu) while the H_2/CO_2 selectivity was maintained above 10. Current Proteus membrane performance exceeds the original project target of 200 gpu for hydrogen permeance and 10 for H_2/CO_2 selectivity.

- Proteus membranes were successfully fabricated on commercial-scale production equipment at MTR. These membranes were used to fabricate lab-scale Proteus membrane modules in this project, and will also be used to fabricate commercial-scale Proteus membrane modules in future projects, as well as for commercial applications.
- Stability tests conducted at the MTR laboratory showed that the performance of Proteus membranes is stable at feed temperatures up to 150°C and at feed pressures as high as 800 psig. These results suggested that Proteus membranes developed in this project could be used to separate hydrogen from shifted syngas streams in future IGCC power plants. A more rigorous long-term thermal stability test performed at the NCCC syngas facility operated by Southern Company in Wilsonville, AL, also indicated that Proteus membranes are stable at elevated feed temperatures (up to 150°C), even in the presence of syngas feeds containing saturated water vapor, heavy hydrocarbons, and >700 ppm hydrogen sulfide. Detailed results are presented in the Field Demonstration section of the report (Section 4).
- A test using nitrogen as a sweep gas on the permeate side of the membrane was performed, to evaluate the potential of the sweep membrane process design to improve hydrogen separation from CO_2 . The test was conducted by varying the sweep/permeate flow rate ratio from 0 to 2.5, at a fixed feed/permeate pressure ratio of 2, which is close to the practical operating conditions in the IGCC separation process. The results showed that the presence of a nitrogen sweep stream on the Proteus membrane permeate side could increase the driving force for hydrogen separation, and thus improve the separation performance for the targeted separation.

3. MEMBRANE MODULE DEVELOPMENT

3.1. Background

Because of early success in the development of the Proteus membranes, we started the fabrication of lab-scale Proteus membrane modules at the beginning of the second year of the project. The lab-scale modules we made were spiral-wound modules 2.5 inches in diameter and 12 inches in length. Related parts that were needed for fabricating and testing the lab-scale Proteus membrane modules – such as seal carriers, module product tubes and module housings – were custom designed and manufactured. Figure 3.1(a) shows pictures of a lab-scale Proteus membrane module and a module housing. The housing was used to test the modules in both laboratory and field settings during the project. The design of a spiral-wound membrane module and the cross-flow scheme of feed and permeate flows in the module is shown schematically in Figure 3.1(b).

Figure 3.1. (a) Photo of a module housing and a lab-scale Proteus membrane module, and (b) a schematic design of a spiral-wound module and the cross-flow scheme of feed and permeate flow occurred in the module.

Spiral-wound modules are the dominant module design used at MTR for commercial gas separations in the natural gas and petrochemical industries. Depending on the process requirements for different applications, spiral-wound modules with different membrane areas or sizes can be fabricated. Typical MTR commercial spiral-wound modules are 8 inches in diameter and 40 inches in length (which corresponds to about 20-30 m² of membrane area). The design of our standard commercial modules only allows operating temperatures up to about 100°C. However, from the performance profile of Proteus membranes as a function of temperature, and also from the economic perspective of separating hydrogen from hot syngas effluent from the water shift reactor in IGCC plants, operating membranes at temperatures higher than 100°C are favored for this application. In this project, we worked to extend the operating temperatures of spiral-wound membrane modules to optimize Proteus membrane performance at temperatures as high as possible (135°C to 150°C). To achieve this end, all module components were examined individually for their thermal stability properties before use. Particularly critical materials included those used for feed and permeate spacers, and various sealing applications.

3.2. Selection of Non-Membrane Module Components

The first components tested for thermal stability were a variety of commercially available polymeric spacer materials, selected for their general thermal characteristics such as melting point, heat deflection temperature and recommended maximum temperature for continuous use. Six different materials were tested by placing them in a convection oven at 150°C for 24 hours. After thermal exposure, any physical changes (such as brittleness, shrinkage, color change or weight loss) in the spacer samples were noted. All materials experienced some shrinkage, weight loss or discoloration after treatment, but three of them were obviously better than the other commercially available materials. Taking into consideration other factors such as morphology (thickness, roughness, etc.), hydrolytic stability and chemical resistance, as well as previous MTR experience in fabricating modules for other high-temperature applications, the choices were narrowed to two. Compared to the process used to choose the right spacer material, determining which sealing material or glue component to use was fairly straightforward. A high-temperature silicone glue was used for all the modules.

A total of eight lab-scale membrane modules were fabricated, using Proteus membranes from a commercial-scale production run and high temperature module components identified as described above. Each module had an active area of about 0.13 m². In addition to being examined for thermal stability, these modules were also tested for gas separation performance. Both pure-gas and mixed-gas performance were measured in the laboratories at MTR, using pure gases or a simulated syngas mixture. Also, we evaluated the long-term thermal stability and module performance using syngas streams available at the NCCC syngas test facility operated by Southern Company in Wilsonville, AL. The MTR lab results are described in this section of the report. Results from the tests at NCCC are detailed in Section 4 (Field Demonstration).

3.3. Performance of Lab-Scale Proteus Modules

Pure-gas and mixed-gas performance of the first lab-scale Proteus membrane module (SN# 6086) at different feed temperatures is presented in Figure 3.2. The experiments were carried out at a feed pressure of 50 psig using either pure gases or a simulated syngas mixture (50% H₂/50% CO₂). As observed for Proteus membrane stamps, pure-gas and mixed-gas hydrogen permeances measured for the module increased with increasing feed temperature; H₂/CO₂ selectivity showed maximum values around 110°C. At 150°C, the pure-gas hydrogen permeance and H₂/CO₂ selectivity of this module reached 160 gpu and 20, respectively. At this temperature, the mixed-gas test showed a hydrogen permeance of about 110 gpu and a H₂/CO₂ selectivity of 14. Compared to the performance of a Proteus membrane stamp, hydrogen permeances of the membrane module were significantly lower.

Figure 3.2. (a) Pure-gas and mixed-gas H₂ permeances and (b) pure-gas and mixed-gas H₂/CO₂ selectivities of the first lab-scale Proteus membrane module (SN# 6086) as a function of feed temperature. Test conditions: 50 psig using pure gases or a 50/50 H₂/CO₂ gas mixture. Lines are added to guide the eye.

To improve the hydrogen permeance, a second module (SN# 6103) using a different configuration was fabricated. Figure 3.3 shows the pure-gas and mixed-gas performance of this module at different feed temperatures. At 150°C, the pure-gas hydrogen permeance and H₂/CO₂ selectivity of this module reached 250 gpu and 20, respectively. At this temperature, the mixed-

gas test showed a hydrogen permeance of about 160 gpu and H_2/CO_2 selectivity of 12. Compared to the first module, pure-gas and mixed-gas hydrogen permeances of this module showed some improvement; however, they were still lower than those of Proteus membrane stamps.

Figure 3.3. (a) Pure-gas and mixed-gas hydrogen permeances and (b) pure-gas and mixed-gas H_2/CO_2 selectivities of the second lab-scale membrane module (SN# 6103) as a function of feed temperature. Test conditions: 50 psig using pure gases or 100 psig using a 50/50 H_2/CO_2 gas mixture. Lines are added to guide the eye.

We hypothesized that the relatively low hydrogen permeances of the first two modules compared to Proteus membrane stamps were probably related to module configuration and effective utilization of membrane area. We investigated these possibilities and made significant progress toward achieving performance consistent with that observed in membrane stamps. Figure 3.4 shows pure-gas performance of the third lab-scale membrane module (SN# 6150) at different feed temperatures, using a new module configuration. The experiments were carried out at a feed pressure of 50 psig. At 150°C, the pure-gas hydrogen permeance and H_2/CO_2 selectivity of this module reached about 360 gpu and 18, respectively. Compared to the other modules prepared previously, hydrogen permeance of this module showed significant improvement (from 250 to 360 gpu). However, compared to the performance of a Proteus membrane stamp, the hydrogen permeance of the module was still about 25% lower; H_2/CO_2 selectivities for the module were in the same range as that measured for stamps.

Figure 3.4. (a) Pure-gas hydrogen permeances and (b) pure-gas H₂/CO₂ selectivities of the third lab-scale membrane module (SN# 6150) as a function of feed temperatures. Test pressure was 50 psig. Lines are added to guide the eye.

Table 3.1 summarizes the pure-gas and mixed-gas performance of lab-scale Proteus membrane modules fabricated and tested either in the laboratories at MTR or in the field at NCCC during this project. Various approaches to module fabrication improved the module performance significantly, but mixed-gas hydrogen permeances of these lab-scale modules were still about 25-40% lower than those observed for Proteus membrane stamps, even though mixed-gas H₂/CO₂ selectivities were within the expected range of membrane stamps.

Table 3.1. Pure-Gas and Mixed-Gas Performance of Lab-Scale Proteus Membrane Modules Fabricated During this Project.

Module SN #	Pure-Gas Properties at 50 psig, 130°C		Mixed-Gas Properties (50 psig, 130°C at lab; 175 psig, 120 or 135°C at NCCC Syngas Site)		Hydrogen Permeance Ratio of Module/Stamp (%)***	Comments
	Hydrogen Permeance (gpu)	H ₂ /CO ₂ Selectivity	Hydrogen Permeance (gpu)	H ₂ /CO ₂ Selectivity		
6086	113	19	82	17	30	Lab test
6103	220	20	112	14	35	Lab test
6150	280	20	Leakage detected after a shutdown in the field		75 (pure gas)	Lab test and field test
6283	220	20	Leakage detected after installed in the field		60 (pure gas)	Lab test and syngas feed test
6373	185	21	135 (at 120°C)	23 (at 120°C)	67	Lab test and field test
6420	-	-	150 (at 135°C)	14 (at 135°C)	60	Field test
6462	-	-	Results pending		-	Field test

*** Mixed-gas hydrogen permeance was used to calculate the ratio unless otherwise noted. Mixed-gas hydrogen permeance for a Proteus membrane stamp used in the syngas field test was 260 gpu.

The lower hydrogen permeance in a Proteus module observed both in the lab and in the field could be related to a significant morphology change in spacer materials in the module. All of the spacers for the lab-scale modules were made from the same polymer material, except for the last module (SN# 6462). For a certain type of polymer, when a higher load is applied, the heat deflection temperature decreases. Beyond this temperature, the polymer might still be used, but will experience some changes in morphology. The morphology of a spacer material is one of the key factors that can affect the flow distribution or pattern in a module, and thus affect the membrane module performance.

This hypothesis was later confirmed by a closer examination of the spacer materials used in the modules. The Forchheimer coefficients for a new spacer sample and a used spacer sample (cut from a module after being tested at elevated temperatures, up to 150°C) were determined at room temperature. Results are shown in Table 3.2. The used spacer was not only about 20% thinner than the fresh sample, but also showed a lower Forchheimer viscous coefficient and a higher Forchheimer inertial coefficient than that of the new spacer. The change in the Forchheimer coefficients indicates a morphology change of the spacer after being exposed to elevated temperatures. Both lower Forchheimer viscous coefficient and higher Forchheimer inertial coefficient values indicate higher transport resistances. These findings may also explain why, for module testing in the lab, the hydrogen permeance at elevated temperatures obtained in the very first heating cycle was always higher than those of the following heating cycles (see Figure 3.5). Interestingly, there was no appreciable change in the performance between the subsequent second and third heating cycles, suggesting that significant morphology change in the spacers only occurred during the first heating cycle.

Table 3.2. Forchheimer Coefficients and Thicknesses of Spacer Materials Before and After Testing at Elevated Temperatures (up to 150°C).

Property Measured	New Spacer	Used Spacer
Thickness (mil)	16	13
Forchheimer viscous coefficient ($k_1 \times 10^6 \text{ cm}^{-2}$)	2.6	1.9
Forchheimer inertial coefficient ($k_2 \times 10^3 \text{ cm}^{-1}$)	2.9	9.4

Figure 3.5. Pure-gas (a) hydrogen permeance and (b) H_2/CO_2 selectivity of a lab-scale Proteus membrane module (SN# 6150) as a function of the feed temperature in multiple test cycles. Test conditions: feed pressure of 50 psig.

Just recently, we received spacer materials made from the other material MTR identified as suitable for use in fabricating high-temperature membrane modules. The last module listed in Table 3.2 was fabricated using this spacer material. The goal was to achieve module performance consistent with that observed in membrane stamps by using this more thermally stable spacer material; the material could be used continuously at 150°C and had a higher heating deflection temperature than the first material. We plan to test this last Proteus membrane module in a future syngas feed run at NCCC. The results will not be available for the final report; nevertheless, when completed, the tests will allow us to continue optimizing Proteus modules for use in separating hydrogen from syngas, as well as for other commercial applications.

3.4. Thermal Stability of Lab-Scale Proteus Membrane Modules

Despite their relatively low hydrogen permeances compared to those of Proteus membrane stamps, the Proteus membrane modules showed very good thermal stability and stable performance under some rigorous lab testing conditions. Figure 3.6 shows the mixed-gas performance of module SN# 6103 as a function of time at 100 psig and 130°C (prior to the test, this module had been exposed to several temperature cycles from 20°C to 150°C). The module performance was relatively stable throughout the test. Mixed-gas hydrogen permeance and H_2/CO_2 selectivity were consistent with the performance data obtained before several temperature cycles at the same test conditions (Figure 3.3).

Figure 3.6. Mixed-gas performance of a lab-scale membrane module (SN# 6103) as a function of time. Prior to this test, the module had been exposed to several temperature cycles from 20°C to 150°C. Test conditions: 100 psig, 130°C using a 50/50 H₂/CO₂ gas mixture. Lines are added to guide the eye.

An extensive thermal stability study was also performed on a lab-scale Proteus membrane module. The goal was to examine the module integrity under aggressive heat treatment conditions. The module was heated from room temperature to 150°C, maintained at this temperature for about 20 hours, and then cooled down to room temperature; this procedure was repeated for eight cycles. All module components, including the Proteus membrane, were expected to experience thermal expansion and shrinkage during these cycles. The total time the module was kept at 150°C was about 150 hours. Pure-gas performance of this module was measured at room temperature after each cycle. Figure 3.7 shows photos of this Proteus membrane module before and after the heat treatment cycling. The module appeared to be brownish after the test; however, no gas leakage was observed at the end of the study.

a) Module after fabrication

b) Module after first thermal stability test (eight heat cycles as described in text)

Figure 3.7. Photos of a Proteus membrane module (a) before and (b) after a week of thermal treatment (being placed in a 150°C oven for 150 hrs). The tension spacer (outside layer) turned from light yellow to brown.

These results suggested that the Proteus membrane modules developed in this project could be used at elevated temperatures (up to 150°C) for an extended period of time (>150 hours). Long-

term thermal stability testing of the module was conducted using the syngas feed at NCCC; more detailed field test results including module performance data are included in Section 4.

3.5. Module Development Summary

We have shown that lab-scale Proteus membrane modules can be successfully fabricated using scaled-up Proteus membranes and module components identified during this project. The thermal stability study results suggest that the Proteus modules developed in this project can be used at elevated temperatures (up to 150°C) for an extended period of time (>150 hours), and potentially in future IGCC power plants to separate hydrogen from hot shifted syngas streams. Long-term thermal stability testing of the module was also conducted in the field at NCCC. See detailed results in the next section.

A mixed-gas hydrogen permeance of about 160 gpu and H₂/CO₂ selectivity of >12 at 100 psig and 150°C was achieved using current module configurations. The mixed-gas hydrogen permeances of the lab-scale modules are still about 30-40% lower than those observed for Proteus membrane stamps, even though H₂/CO₂ selectivities were within the expected range. This may be due to an increase in feed flow resistance as a result of the morphology change in the spacer materials used in the module at elevated temperatures (well above the heat deflection temperature of the spacer material). In the future, if advanced spacer materials are commercially available or can be custom-designed and constructed, a significant improvement in the module performance is likely, at least to a level similar to that of the Proteus membrane stamps. The major current challenge is not the lack of polymer resins with high-temperature stability, but the lack of available spacer materials made from those polymer resins. Several advanced engineered polymer materials, including glass-reinforced grades, that could be used continuously at >200°C in air are commercially available. The last module fabricated for this project used a spacer material with better thermal stability that could potentially improve the hydrogen permeance. The test results for that module, using simulated syngas mixtures in laboratory studies, as well as the syngas feed at NCCC, will not be available in time for this report, but will allow us to better understand the hydrogen permeance issue, and eventually optimize the Proteus modules for use in separating hydrogen from IGCC syngas, as well as in other commercial applications.

4. FIELD TESTING OF PROTEUS MEMBRANES AND MODULES

4.1. Introduction

In addition to a series of parametric tests performed at the MTR laboratories using both pure gases and simulated syngas mixtures, we also evaluated Proteus membranes and lab-scale Proteus membrane modules using coal-derived syngas streams at Southern Company's Power Systems Development Facility (PSDF) in Alabama. PSDF is part of the National Carbon Capture Center (NCCC) sponsored by DOE at the same location and includes a coal gasifier that can produce 12,000 lb/h syngas. Unlike other syngas production plants that produce syngas primarily as a commercial venture, PSDF's mission is to support the development of new technologies by providing syngas streams and necessary personnel assistance and/or analytical instrumentation

for real-time testing. PSDF is an ideal facility for testing our newly developed membranes and membrane modules.

The main objective of the tests conducted at NCCC was to demonstrate the feasibility of using polymeric membranes and membrane modules developed in this research project to perform the separation of hydrogen from shifted syngas. Specifically, through the field tests, we aimed to

- 1) determine separation properties and long-term stability of Proteus membranes and modules at elevated temperatures using a real coal-derived syngas,
- 2) evaluate the effect on membrane and module performance of sulfur compounds, carbon monoxide, water and other contaminants (heavy hydrocarbons and so forth) present in the coal-derived syngas stream, and
- 3) based on results from the tests, further improve the membrane performance and optimize the membrane process design.

Figure 4.1. Flow scheme of the syngas membrane test setup at NCCC. The process includes a series of treatment steps to condition the syngas prior to membrane separation.

Figure 4.1 shows a flow scheme of syngas delivery to the membrane/module test system at NCCC. The PSDF unit operates in a campaign mode for several weeks at a time. During operation, a stream of syngas from the PSDF coal gasifier is passed to a water gas shift reactor to convert carbon monoxide to CO_2 . The shifted syngas exits the reactor at around 170°C , and is cooled using a heat exchanger before being fed to a water tank for further cooling and condensate knock out. The water in the tank is circulated to a chiller and recycled back using a pump. The chiller allows the water temperature to be controlled at 40°F , so that the gas exiting the water tank maintains a temperature of around 70°F , regardless of the ambient temperature. After exiting the gas cooling section, the gas passes through a series of coalescing filters before entering the membrane skid installed by MTR. The membrane test skid includes temperature control so that the syngas can be re-heated. The test membranes separate the syngas into two

streams, and after appropriate measurements, the streams are recombined and sent back to the thermal oxidizer at the PSDF.

(a) MTR membrane test skid at NCCC

(b) MTR lab-scale test unit at NCCC

Figure 4.2. Photos of (a) the MTR test skid and (b) the MTR lab-scale test unit installed at NCCC.

Figure 4.2 shows photos of the MTR membrane test setup at NCCC. The whole setup consists of a module test skid [Figure 4.2(a)] and a lab-scale membrane test unit [Figure 4.2(b)]. The test skid (which can accommodate two 4" × 40" (diameter × length) membrane modules) was used to test MTR CO₂-selective Polaris membranes. The lab-scale test unit was used to test the MTR hydrogen-selective Proteus membranes and modules developed in this project. These two test systems are designed to operate in parallel. Parallel operation enables different membrane modules to be tested simultaneously with syngas feeds of the same composition. The feed gas is split into two streams – one of about 1 or 5 lb/h, which enters the lab-scale Proteus membrane test unit, and the remainder of 9 or 45 lb/hr (depending on the overall flow rate of syngas provided on site to the membrane units), which is sent to the Polaris membrane test skid. After testing, the residue and permeate streams from both test units are combined and sent as one stream to the flare line at NCCC.

Both test systems were installed at NCCC in September 2009 and have been used since that time for membrane testing during the gasification campaigns at PSDF. So far, MTR has conducted a total of five test runs, including the most recent one started in November 2011. General information about these five tests is summarized in Table 4.1. With the exception of the first test run (during which the syngas feed stream was unshifted and desulfurized), the syngas streams provided for all other test runs were shifted and contained ~3% carbon monoxide, >300 ppm hydrogen sulfide and about 1,000 ppm heavy hydrocarbons (benzene, naphthalene, etc.). The typical feed conditions for the shifted syngas stream provided at PSDF/NCCC as it entered the membrane test unit are shown in Table 4.2. It contained 9-15% hydrogen and 10-15% CO₂, with the remainder being primarily 60-70% nitrogen.

Table 4.1. General Descriptions of Five Proteus Membrane Tests Using the MTR Lab-Scale Membrane Unit During Syngas Campaigns at NCCC Since November 2009.

Field Run	Date	Targeted Test Duration (hrs)	Targeted Feed Flow Rate (lb/hr)	Size of Proteus Membranes or Membrane Modules Tested (surface area)	Comments
1	November 2009	500	1	Membrane stamp (30 cm ²)	Unshifted syngas desulfurized
2	April 2010	500	1	Membrane stamp (30 cm ²)	Shifted syngas containing 780 ppm sulfur compounds
3	August 2010	750	1	Membrane stamp (30 cm ²)	Shifted syngas containing 360 ppm sulfur compounds
4	August 2011	1,000	5	Membrane stamp and lab-scale module (0.13 m ² area)	Shifted syngas containing 320 ppm sulfur compounds
5	November 2011	1,000	5	Lab-scale module (0.13 m ² area)	Shifted syngas containing 320 ppm sulfur compounds

Table 4.2. Specifications of the Pretreated Shifted Syngas Stream Entering the MTR Membrane Test System at NCCC.

Feed Gas Conditions	
Pressure (psig)	150-175
Temperature (°C)	5-35
Feed Gas Composition (vol %)	
Nitrogen	60-70
Carbon dioxide	10-15
Hydrogen	9-15
Carbon monoxide	1-3
Methane	1
Hydrogen sulfide	320-780 ppm
Heavy hydrocarbons (benzene, naphthalene, etc.)	~1,000 ppm
Water content	Nearly saturated

4.2. Results for Proteus Membrane Stamps

Since the start of this project, three field tests using Proteus membrane stamps, each with an area of about 30 cm², have been conducted at NCCC. The objectives of these tests were to determine the separation properties and the long-term stability of Proteus membranes using a real syngas feed stream, as well as to evaluate whether the presence of sulfur-containing compounds such as hydrogen sulfide and carbonyl sulfide in the coal-derived syngas would have an adverse affect

on the Proteus membrane performance. The main difference between these tests was that for the second and third test runs, the syngas feed contained certain quantities of sulfur-containing components, while the syngas feed for the first test run was desulfurized. By comparing results from these tests, the impact of sulfur species on the Proteus membrane performance can be determined. Feed gas conditions for these syngas field test runs are listed below.

- During the first test, the unshifted coal-derived syngas stream was provided at 150 psig with a composition close to 69% nitrogen, 13% carbon dioxide, 10% hydrogen, 7% carbon monoxide, and 1% methane. The air-blown syngas delivered to our membrane was desulfurized, so the total sulfur content was believed to be <10 ppm.
- During the second and third tests, a shifted syngas (saturated with water) at 170-175 psig was provided with a composition close to 66-69% nitrogen, 15% carbon dioxide, 13-14% hydrogen, 2-3% carbon monoxide, 1% methane, and 360-780 ppm hydrogen sulfide.

Pictures of the lab-scale test setup (including an oven, a micro GC and other accessories for flow rate measurement) at NCCC and a test cell with a Proteus membrane stamp inside are shown in Figure 4.3. The oven was used to heat the syngas feed stream to the experimental temperatures (up to 150°C) because the syngas provided by NCCC was cooled to a temperature of below 35°C (essentially ambient temperature), as depicted in Figure 4.1. The micro GC was used to analyze the feed and permeate gas streams at the field site. Test results for each run are discussed separately below.

Figure 4.3. Photos showing (a) the MTR lab-scale field test setup and (b) an MTR membrane test cell used for testing Proteus membrane stamps at NCCC.

4.2.1. Results Using a Desulfurized Feed Syngas

The results of field run #1 are provided in Figures 4.4-4.6. Figure 4.4 shows the hydrogen concentrations in the membrane feed and the permeate streams. The hydrogen concentrations in both streams show some fluctuations throughout the test. Nevertheless, an average hydrogen concentration of ~70% in the permeate stream was achieved at 135°C and 150 psig. Figure 4.5 shows both membrane permeances and H₂/CO₂ selectivity as a function of time. At 135°C and a feed pressure of 150 psig, the membrane showed stable performance during the test period of two weeks and gave an average hydrogen permeance of 270 gpu and H₂/CO₂ selectivity of 17. This performance is consistent with the results obtained at the MTR laboratory, and exceeds the

project bench-scale performance targets (>200 gpu for hydrogen permeance and >10 for H_2/CO_2 selectivity) from the proposal.

During the first field test, we also evaluated the effect of feed temperature on Proteus membrane performance. Membrane performance was measured as the feed temperature varied from 80°C to 150°C (the data were collected within one hour after each target temperature was reached). The results are presented in Figure 4.6. The hydrogen permeance showed an increase from 60 to 300 gpu and the CO_2 permeance also showed an increase from 4 to 19 gpu as the feed temperature increased from 80°C to 150°C . As observed in the measurements conducted at MTR's laboratory, the H_2/CO_2 selectivity showed a maximum value (about 22) at feed temperatures around 120°C . As the feed temperature was further increased from 120°C to 150°C , the H_2/CO_2 selectivity dropped to around 14. Such a trend in the membrane performance with the change in the feed temperature was expected and consistent with the laboratory results obtained when only a simulated syngas mixture (50% H_2 /50% CO_2) was used. We believe that the decrease in the H_2/CO_2 selectivity at the high end of the temperature range is related to the intrinsic membrane properties (and may include transport resistance from the porous support layer or the overcoat protective layer that influences hydrogen permeance), and is not an indication of membrane degradation under field conditions.

Figure 4.4. Concentrations of H_2 in the feed and permeate streams as a function of time for a Proteus membrane. Test conditions: 135°C and 150 psig. Lines are added to guide the eye.

Figure 4.5. (a) Permeance and (b) H₂/CO₂ selectivity of a Proteus membrane as a function of time, using a syngas feed stream at NCCC. Test conditions: 135°C and 150 psig. Lines are added to guide the eye.

Figure 4.6. (a) Permeance and (b) H₂/CO₂ selectivity of a Proteus membrane as a function of feed temperature using a syngas feed stream at NCCC. Feed pressure: 150 psig. Lines are added to guide the eye.

4.2.2 Results Using a Sulfur-Containing Syngas Feed

During the second and third field test runs, the Proteus membranes were subjected to more rigorous tests in which other gas components such as hydrogen sulfide and carbonyl sulfide are present. In these tests, a Proteus membrane stamp was tested at 120°C for one week and then tested further at 135°C for another week. The results of these field tests are presented in Figure 4.7 to 4.8. As shown in Figure 4.7, the hydrogen concentrations in the permeate stream decreased slightly from ~80% to ~70% when the feed temperature increased from 120°C to 135°C. Figure 4.8 shows the hydrogen and CO₂ permeances, as well as H₂/CO₂ selectivity of a Proteus

membrane as a function of time. As the feed temperature increased from 120°C to 135°C, the H₂/CO₂ selectivity increased from 24 to 16 and the hydrogen permeance increased from 200 to 250 gpu. These results are consistent with what we observed in measurements at MTR as well as the first NCCC test. Figures 4.7 and 4.8 also demonstrate that MTR Proteus membranes showed stable performance throughout the test, providing a hydrogen permeance of 250 gpu coupled with an average H₂/CO₂ selectivity of 16 at 135°C. These results suggested that the presence of sulfur-containing compounds (up to 780 ppm hydrogen sulfide) in the syngas feed stream had no adverse effect on the Proteus membrane performance.

Figure 4.7. Concentrations of H₂ in the feed and permeate streams as a function of time for a Proteus membrane tested using a shifted syngas stream. Test conditions: 120°C or 135°C and 175 psig; see text for syngas composition. Lines are added to guide the eye.

Figure 4.8. (a) Permeance and (b) H₂/CO₂ selectivity of a Proteus membrane as a function of time, using a syngas feed stream at NCCC. Test conditions: 120°C or 135°C and 175 psig; Lines are added to guide the eye.

In addition to hydrogen and CO₂ permeances, the second and the third field tests also provided information on the permeance of Proteus membranes to carbon monoxide (CO), hydrogen sulfide (H₂S), nitrogen (N₂) and methane (CH₄). The selectivities of hydrogen over these species are presented in Table 4.3. For all the other gases, the hydrogen/gas selectivity is higher than the H₂/CO₂ selectivity.

Table 4.3. The Selectivities of Hydrogen over Other Gas Species in the Syngas Feed. Test Conditions: 135°C and 175 psig.

Gas Pair	Selectivity
H ₂ /CO ₂	16
H ₂ /CO	~100
H ₂ /N ₂	~150
H ₂ /CH ₄	~200
H ₂ /H ₂ S	25

4.3. Results for Lab-Scale Proteus Membrane Modules

Since August 2011, we have conducted two field tests of lab-scale modules (with a membrane area of 0.13 m²), fabricated using Proteus membranes from the scaled up membrane production run. The main objective of these tests was to evaluate the module performance and the long-term stability of all module components, using a real coal-derived syngas feed at elevated temperatures (up to 150°C). Our previous field testing of Proteus membrane stamps showed that the Proteus membrane itself was stable during separation of real syngas feeds at temperatures up to 150°C. However, the other module components had not been tested, and we needed to

determine if they could be a limiting factor on the performance of MTR Proteus membrane modules at temperatures up to 150°C (our current commercial membrane modules can only operate at <100°C).

Figure 4.9. Photos of (a) the Proteus module test unit installed by MTR at NCCC and (b) a module housing and one of the lab-scale Proteus membrane modules tested at NCCC.

Figure 4.9 shows photos of the module test unit at NCCC, the module housing, and one of the 2.5" × 12" (diameter × length) Proteus membrane modules that fits inside the housing. The composition of the feed stream entering the module test unit was 12-14% hydrogen, 65-70% nitrogen, 1% methane, 1-3% carbon monoxide, 13-16% carbon dioxide and 320 ppm hydrogen sulfide. Test specifications and the Proteus membrane module performance obtained in the test are presented in Table 4.4. A total of four lab-scale Proteus membrane modules have been tested. Results of each test run are detailed as follows.

Table 4.4. Specifications and Performance of Lab-Scale Proteus Membrane Modules in the Syngas Field Tests.

Module SN #	Date of Test Run	Membrane Area (m ²)	Temperature (°C)	Hydrogen Permeance (gpu)	H ₂ /CO ₂ Selectivity	Comments
6150	August 2011	0.13	135	56	7	Duration: 1 day Showed leaks after the system shutdown
6283	August 2011	0.13	135	N/A	N/A	Showed leaks immediately after installation
6373	August 2011	0.13	120	135 at 120°C	23 at 120°C	Duration: 4 days; Good performance throughout the test
6420	November 2011	0.13	135	150 at 135°C	14 at 135°C	Duration: 4 weeks Good performance throughout the test
6462	November 2011	0.13	>135	N/A	N/A	Results pending

During the August 2011 field run, originally we planned to test lab-scale Proteus membrane modules only. However, due to some technical issues that developed on site, the first two modules showed leaks either immediately after the installation (SN# 6283) or after one day of operation (SN# 6150). While waiting to resolve the problems related to the module test setup or module configuration issues, a Proteus membrane stamp from a scale-up production run was installed and tested at 135°C for 7 days. After the initial module issues were resolved, a third lab-scale Proteus membrane module (SN# 6373) was installed and tested at 120°C for about 4 days before the end of this gasification campaign. Test results for the membrane stamp and the membrane module are presented in Figure 4.10. At 135°C, the Proteus membrane stamp performance was stable for 7 days, with a hydrogen permeance of ~220 gpu and a H₂/CO₂ selectivity of ~25. The lab-scale module (SN# 6373) was only tested at 120°C for 4 days, due to an early syngas shutdown. Under such test conditions, the module exhibited stable performance, with a hydrogen permeance of 135 gpu and a H₂/CO₂ selectivity of 23. These results were in good agreement with the mixed-gas performance of Proteus membrane modules obtained in the laboratory at MTR.

Figure 4.10. Mixed-gas performance of a Proteus membrane stamp and a lab-scale Proteus membrane module (SN# 6373) as a function of testing time at NCCC. See text for test gas composition. Feed pressure: 170 psig.

During the November 2011 field test run (the test is still ongoing and will run until the end of December 2011), we are testing a fourth Proteus lab-scale membrane module (SN# 6420) for a prolonged period of time. The module has been tested in the field for about four weeks (>600 hrs) at 135°C. Field test results for this module are presented in Figures 4.11-4.12. As shown in Figure 4.11, the hydrogen concentrations in both feed and permeate streams fluctuated somewhat throughout the test. Nevertheless, an average hydrogen concentration of ~60% in the permeate stream was achieved at 135°C and 170 psig. Figure 4.12 shows both permeances and H₂/CO₂ selectivity as a function of time. This Proteus membrane module (SN# 6420) showed stable performance throughout the first three weeks of the test, with an average hydrogen permeance of 150 gpu and H₂/CO₂ selectivity of 14. These values are in good agreement with the mixed-gas

performance of Proteus membrane modules obtained in earlier laboratory studies. However, the module performance was slightly lower than what we have seen in the Proteus membrane stamps tested previously at NCCC (hydrogen permeance >250 gpu and H₂/CO₂ selectivity >17 at 135°C).

To date, lab-scale Proteus membrane modules have shown relatively lower hydrogen permeances and selectivities than those of Proteus membrane stamps in both laboratory and field settings. This could be attributed to the spacer material we used to fabricate these modules. When the modules are tested continuously at >120°C, the spacer may become soft, changing flow patterns and effective membrane area; see detailed explanations in Section 3 – Module Development. To address this issue, a fifth Proteus membrane module (SN# 6462) with a different feed spacer material having better thermal stability was fabricated. This module was originally planned to be tested at NCCC at >135°C (potentially >150°C) at the end of November 2011 test run, to determine whether the use of a feed spacer with better thermal stability will improve the Proteus membrane module performance. However, the test was cancelled due to an early syngas feed shutdown at NCCC. We will perform the test of the fifth module at the MTR laboratories and in a future NCCC campaign. The results will not be available for this report, but the continued study should help us to further optimize our Proteus membrane modules for use in future IGCC power plants, as well as in other commercial applications.

Figure 4.11. Concentrations of H₂ in the feed and permeate streams as a function of time for a Proteus membrane module (SN# 6420) tested using a shifted syngas stream. Test conditions: 135°C and 170 psig; see text for syngas composition. Lines are added to guide the eye.

Figure 4.12. Mixed-gas performance of a Proteus membrane module (SN# 6420) as a function of testing time. See text for test gas composition. Test conditions: 135°C and 170 psig. Lines are added to guide the eye.

4.4. Field Test Summary

To summarize the syngas field test results, at NCCC operating conditions (feed pressures: 150-175 psig and feed temperatures: 120-135°C):

- a stable hydrogen permeance of 200-300 gpu and a H₂/CO₂ selectivity of 16-23 were achieved for Proteus membrane stamps (with an area of 30 cm²), and
- a stable hydrogen permeance of 130-150 gpu and a H₂/CO₂ selectivity of 14-23 were achieved for a lab-scale Proteus membrane module (with an area of 0.13 m²).

The results suggest that all module components, including the Proteus membrane, were stable under the field conditions for a prolonged time period (>600 hrs). The field performance of both Proteus membrane stamps and modules is consistent with the results obtained at the MTR laboratory when a simulated syngas mixture (50% H₂/50% CO₂) is used, suggesting that the presence of sulfur-containing compounds (up to 780 ppm hydrogen sulfide), saturated water vapor, carbon monoxide and heavy hydrocarbons in the syngas feed stream has no adverse effect on the Proteus membrane or module performance.

The lab-scale membrane and module field tests have demonstrated the feasibility of using Proteus membranes and modules developed in this project to perform the separation of hydrogen from warm shifted syngas. The current module performance is still lower than we expected, but we believe that further improvement in module performance is possible if a better high-temperature spacer material becomes available. Finding or developing this spacing material, along with moving forward on development of *commercial-scale* high-temperature Proteus membrane modules will be key steps in commercializing this approach to H₂/CO₂ separations. MTR plans to test commercial-scale Proteus membrane modules at NCCC during the next gasification campaign (scheduled in April 2012), using the MTR membrane skid as shown in Figure 4.2 (a), at our own expense.

5. PROCESS DESIGN AND ECONOMIC ANALYSIS

5.1. Process Design Background

During this project, we performed process design studies to evaluate the expected performance of a pre-combustion membrane CO₂ capture process, and to identify areas where development work should be focused. For ease of comparison, we have used the DOE baseline report for fossil energy plants for all assumptions and calculation methods. The base case shifted syngas in the designs that follow has a dry gas composition of 56.5 mol% hydrogen, 40.6 mol% CO₂, 0.8 mol% carbon monoxide, and 2.1 mol% other gases (including methane, nitrogen, argon, and hydrogen sulfide). Details of the syngas process conditions are given in Table 5.1. These values are consistent with the feed to the Selexol unit in Case 2 of a recent DOE study in which CO₂ capture from a GE gasifier was analyzed.^[21]

Table 5.1. CO₂ Capture Design Parameters for GE Gasifier Syngas.

System Parameter	Unit	Value
Feed to membrane system	tons/h	565
Syngas feed pressure	bar	50
CO ₂ captured	tons/h	508
CO ₂ captured	%	90
Cleaned syngas H ₂ content	%	92
H ₂ recovery in clean syngas	%	99
Cleaned syngas pressure	bar	30

Depending on the sulfur content of the feedstock, the syngas feed to the membrane process may contain up to 1% hydrogen sulfide (For the DOE study, Illinois No. 6 coal produces a syngas feed to the Selexol unit containing 0.61% hydrogen sulfide). The bulk of this hydrogen sulfide (>95%) will end up with the liquid CO₂ in the membrane process designs studied during this project. The most straightforward and low-cost membrane capture option would be to co-sequester this hydrogen sulfide with the CO₂. Co-injection of hydrogen sulfide with CO₂ is practiced in industry for enhanced oil recovery (EOR) operations.^[22] Moreover, a recent DOE study has shown that co-injection of sulfur species with CO₂ for sequestration is possible.^[23] For these reasons, our default membrane process designs and their associated cost analyses assume hydrogen sulfide is co-sequestered with CO₂. If necessary, hydrogen sulfide removal downstream of the membrane processes by absorption is possible. Additionally, there is ongoing research to develop warm sulfur removal technologies that could be used to remove hydrogen sulfide upstream of the membrane processes. An affordable commercial version of this sulfur removal technology would be beneficial to membrane CO₂ capture processes because it would eliminate any uncertainties associated with co-sequestration or hydrogen sulfide slip into the fuel gas stream.

To make a side-by-side comparison of membranes and absorption for IGCC CO₂ capture, the cost assumptions used in a 2010 DOE report^[21] for a Selexol plant were also used as the basis for

the membrane designs, where appropriate. For example, our membrane designs apply the installation factors, and process and project contingencies used in the DOE report. These cost factors are summarized in Table 5.2 and represent values typically used by process engineers preparing preliminary budgetary estimates.

Table 5.2. Process Cost Assumptions Used in Membrane Designs.

System Parameter	Value
Process contingencies*	20%
Project contingencies	20%
Installation cost multiplier: Selexol and membrane skids	1.85
Installation cost multiplier: compression equipment	1.61
Membrane skid cost	\$500/m ²
Compression equipment cost	\$1,000/kW
Refrigeration equipment cost for -30 °C (or -55 °C)	\$1,000/kW (\$1,500/kW)

* Following the methodology of the DOE study, no process contingencies were applied to CO₂ compression equipment. All other equipment used in the membrane designs was assigned a 20% process contingency (the same value used for Selexol equipment). Project contingencies were applied to all equipment.

Table 5.2 includes a value of \$500/m² for the cost of turnkey membrane skids. The skid cost includes the cost of membrane modules, module housings, connecting valves, supporting structure, and instrumentation; it is today's cost for spiral-wound membrane module skids supplied to natural gas processing plants. These plants operate with flammable gases at high pressures, similar to those anticipated for IGCC CO₂ capture. A number of natural gas plants with membrane areas in the range of 20,000-50,000 m² have been built in the past ten years, so membrane systems of the scale required for CO₂ capture from a 500 MW_e IGCC power plant are within the scope of today's industry.^[10]

The calculations were performed with a computer process simulation program (ChemCad 6.3, ChemStations, Houston, TX). The computer package was modified with differential element subroutines written at MTR for the membrane separation steps. The membrane simulation is a non-isothermal model that assumes flow in the modules is cross-flow when no sweep is used and countercurrent when a sweep gas is present. The Soave-Redlich-Kwong equation of state was used for the thermodynamic model. For each membrane step, a feed-to-residue pressure drop of 5 psi was assumed. Similarly, if a sweep gas was used, the sweep-to-permeate pressure drop was 5 psi. For all membrane simulations, constant gas permeances without flux coupling were assumed. Compressors and turboexpanders used in the process designs operate with a polytropic efficiency of 85%.

The properties of the CO₂-selective and hydrogen-selective membranes used in the process designs are shown in Table 5.3. The performance values used are achievable with today's MTR membranes, and can be considered a baseline. Two types of membranes are used in the

calculations that follow. The first are polar rubbery membranes that selectively permeate CO₂. The CO₂/H₂ selectivity of these membranes is about 10 at room temperature, but improves at lower temperatures. In our designs, these membranes will operate at 10°C, at which a selectivity of about 12 can be expected.

The second type of membrane is the hydrogen-selective Proteus membrane developed in this project. As discussed earlier in this report, the H₂/CO₂ selectivity of Proteus membrane is about 10 at room temperature, but the hydrogen permeability and hydrogen selectivity both increase as the membrane temperature is raised. In our designs, these Proteus membranes will be operated at around 150°C, where field data indicate an H₂/CO₂ selectivity of 15 can be expected. Ultimately, it would be desirable to operate hydrogen-selective membranes at the low-temperature-shift reactor exhaust gas temperature (~200°C) to optimize thermal efficiency. Future membrane and module research is aimed at increasing the maximum operating temperature for polymer membrane modules toward this target.

Table 5.3. Permeances of Membranes Used in the Process Design Calculations.

Type of Membrane	Mixed-gas Membrane Permeances (gpu)*					
	H ₂	CO ₂	CO	H ₂ S	H ₂ O	Inerts**
Hydrogen-selective membrane at 150°C	300	20	~2	10	1,000	<1
Carbon dioxide-selective membrane at 10°C	85	1,000	20	2,000	4,000	<15

*1 gpu = 1×10^{-6} cm³ (STP)/cm²·s·cmHg.

** The trace inerts nitrogen, methane and argon are lumped together and given the average permeance shown.

5.2. Single-Stage Membrane Process Designs

Many possible membrane system designs can be considered for removing CO₂ from IGCC syngas. Two simple process designs of this type are shown in Figures 5.1 and 5.2. These designs are similar to compression-condensation-plus-membrane processes widely used in the petrochemical industry to separate condensable hydrocarbons (for example, propylene) from non-condensable gases (for example, nitrogen).^[10, 24] Both processes recover 90% of the CO₂ in a liquid CO₂ stream ready for sequestration, and a hydrogen product stream containing 99% of the hydrogen content of the feed gas.

Figure 5.1. A one-stage membrane-condensation design using CO₂-selective membranes to separate hydrogen and CO₂ mixtures. The membranes used have the permeation properties shown in Table 5.3.

Consider the design using a CO₂-selective membrane first (Figure 5.1). A feed gas (stream ①) at 50 bar is dried, cooled to -30°C, and sent to a short fractionating condenser column. About 45% of the CO₂ in the gas is condensed and removed as liquid CO₂ (stream ②). A simple condenser could be used, but a short column with three or four stages of separation produces an almost pure CO₂ bottoms liquid, and a cold overhead gas from the condenser containing about 35% CO₂. After heat exchange with the incoming feed, the overhead gas passes across the surface of the CO₂-selective membrane. The residue hydrogen fuel gas product (stream ③) leaving the membrane unit contains ~90% hydrogen, ~7% CO₂ and ~3% other inert components. This stream contains 99% of the feed hydrogen and, after expansion to recover energy and to provide cooling to the CO₂ condenser, the gas is sent to the combustion turbine. The membrane permeate gas (at 5 bar) containing 65% CO₂ is recompressed to 50 bar and recirculated to the front of the CO₂ condenser. The liquid CO₂ stream leaving this condenser contains 90% of the CO₂ in the feed stream. The liquid CO₂ can be pumped without further treatment to a pipeline for sequestration.

The benefit of using a membrane unit in this process is that the cryogenic condenser only needs to remove a fraction of the CO₂ in the feed gas to the condenser. The remaining CO₂ is separated and recycled by the membrane unit. Without the membrane unit, the condenser would have to operate at much lower temperatures (-50 to -60°C) to achieve the same CO₂ separation. This increases the energy cost of condensation, requires special low-temperature (and expensive)

materials of construction for the condensing column, and introduces potential issues with solid CO₂ formation.

Stream compositions (mol%)	Stream #			
	① Hot, shifted syngas	② Liquid CO ₂	③ Fuel gas	④ Inert purge
H ₂	56.1	0.8	94.0	68.5
CO ₂	40.6	96.5	5.8	15.4
CO	1.1	1.0	0.1	9.1
N ₂	0.7	0.4	0.03	6.9
H ₂ S	0.5	1.3	0.05	0.2
Flow rate (tons/h)	565	468	68.1	31.8
Pressure (bar)	50	140	32	49
Temperature (°C)	150	10	150	-50

Figure 5.2. A one-stage membrane-condensation design using hydrogen-selective Proteus membranes to separate hydrogen and CO₂ mixtures. The membranes used have the permeation properties shown in Table 5.3.

When hydrogen-permeable Proteus membranes are used, a process design of the type shown in Figure 5.2 can be employed. For simplicity, the shifted syngas feed in this design is the same as that for the CO₂-selective membrane except that the gas is warmed to the preferred membrane operating temperature of 150°C. In reality, one of the advantages of a hydrogen-selective membrane is that it could operate at elevated temperature immediately downstream of the low-temperature shift reactor, eliminating the need to cool the syngas and knock out a large mass of water. This process configuration will be considered later, while here we will simply compare the hydrogen- and CO₂-selective membranes as a direct replacement for Selexol.

As the feed gas (stream ①) in Figure 5.2 is passed across the surface of the hydrogen-selective membrane, a hydrogen-rich product gas (stream ③) containing about 94% hydrogen and 6% CO₂ is removed at a pressure of about 8 bar. After being recompressed to 30 bar, this gas can be sent to the combustion turbine. The residue gas leaving the hydrogen-selective membrane is enriched in CO₂. When this gas is cooled to -55 °C, most of the CO₂ is removed as liquid CO₂ (stream ②). The off-gas from the condenser is only a few pounds lower in pressure than the incoming feed, so a simple low-power recirculation compressor is all that is required to send this gas back to the membrane feed for further treatment.

The presence of 2-4% of various inert gases – carbon monoxide, methane, argon and nitrogen – is a complication in the design shown in Figure 5.2. These components are not permeable through the hydrogen-selective membrane, and so are concentrated together with the CO₂. However, the inerts are relatively non-condensable, so they are not removed with the liquid CO₂ stream and build up in the recirculation loop. An inert gas purge (stream ④) is needed to remove these components. In this simple design, the inert purge is sent to the combustion turbine with the permeate hydrogen. Methods for treating the purge gas (including using membranes) are possible, but are not used here for simplicity.

Using the cost assumptions shown in Table 5.2, the cost of CO₂ capture using the membrane designs shown in Figures 5.1 and 5.2 are compared to Selexol in Table 5.4. The process using CO₂-permeable membranes uses less membrane area, but slightly more compression power than the hydrogen-selective membrane process. Compared to the Selexol plant, both membrane processes use slightly less total energy. The real difference from Selexol is in the expected plant cost. The total costs of the membrane units including CO₂ compression are about 50% those of a Selexol plant. The cost differential is due mainly to the simple flow scheme of the membrane processes compared to the more complex Selexol system, which uses a number of large high-pressure columns. The net result is that the increase in the LCOE for 90% CO₂ capture is about 20% for the two membrane designs, compared to 30% for Selexol. It is noted that cost estimates at this conceptual stage typically have an accuracy of $\pm 30\%$.

Table 5.4. Comparison of Energy Use and Capital Costs for IGCC CO₂ Capture Using Selexol and Various CO₂-Selective and Hydrogen-Selective Proteus Membrane Processes (cost basis is 2007 US\$).

System/Cost Parameter	Units	Selexol + CO ₂ Compression	CO ₂ -Selective Membrane	H ₂ -Selective Proteus Membrane
Compression power used	MW _e	31	31	18
Refrigeration (or steam) used	MW _e	19	14	20
Total power used	MW _e	50	45	38
Membrane area used	m ²	--	16,000	25,000
Membrane or Selexol equipment cost	\$ million	74	8	12.5
Compression and/or refrigeration equipment cost	\$ million	18	45	48
Bare erected plant cost	\$ million	166	88	100
Engineering fees	\$ million	16	8	9
Contingencies	\$ million	69	21	26
Total plant cost	\$ million	252	117	135
Estimated increase in LCOE	%	31	20	21

In the Table 5.4 comparison, the Selexol process captures hydrogen sulfide separately in a stream with 35% hydrogen sulfide (in CO₂, nitrogen and water) that is sent to a Claus plant, whereas the membrane designs co-capture dilute hydrogen sulfide with CO₂. If co-capture is not desired, then an absorption or sorbent-based technology would have to be used in the membrane designs

to remove hydrogen sulfide. This would increase the cost of the membrane-based CO₂ capture approach. For example, if the small, single-stage Selexol unit used for sulfur removal in Case 1 of the DOE study is placed upstream of the condenser in the Figure 5.1 membrane design, this will increase the levelized cost of electricity (LCOE) for this process by about 5 points (increase in LCOE changes from 20% to 25%). New, warm sulfur removal technologies being developed might lower these additional costs. Nevertheless, if viable, co-capture will always be the low-cost option for a membrane-based process, because membranes tend to concentrate hydrogen sulfide with CO₂ without additional cost.

Comparing the two membrane designs, the calculation results show that both types of membranes are capable of capturing 90% of CO₂ from syngas while causing about a 20% increase in the LCOE (when hydrogen sulfide is co-sequestered). Both designs produce high-purity liquid CO₂ ready for sequestration and ~92% hydrogen at 30 bar ready for delivery to the gas turbine combustor. The hydrogen-selective membrane design uses more membrane area, but offers a number of significant benefits, as follows:

1. Because the hydrogen-selective membrane can operate at higher temperature – 150°C (and perhaps higher) versus 30°C for the CO₂ membrane – the syngas does not need to be cooled to near room temperature for CO₂ removal. This offers the potential to improve the thermal efficiency of the power plant versus a cold acid gas removal process. It also allows cost savings by requiring less heat exchange and water knockout equipment.
2. A hydrogen-selective membrane will permeate water vapor, leaving a dry CO₂-enriched residue that can be readily liquefied. The water vapor in the hydrogen-enriched permeate is beneficial for controlling flame temperature in the combustor and increases the mass flow to the turbine. In contrast, a CO₂-selective membrane will permeate water with the CO₂. The CO₂-enriched stream must then be dried using molecular sieves or glycol before it can be liquefied. This increases the cost and complexity of the process.
3. Nitrogen from the air separation unit that is mixed with hydrogen at the combustion turbine as a diluent to control flame temperature can be used as a sweep gas with a hydrogen-selective membrane.^[25, 26] Use of a nitrogen sweep on a hydrogen-selective membrane can reduce energy requirements for the hydrogen/CO₂ separation step. A CO₂-selective membrane does not benefit from a nitrogen sweep.

Based on these considerations, a hydrogen-selective membrane is preferred over a CO₂-selective membrane for IGCC power applications. As we will show in the following section, the potential to use nitrogen sweep is a particularly powerful advantage for hydrogen-selective membranes. Compared to Selexol, the single-stage membrane designs shown in Figures 5.1 and 5.2 use less energy, and cost significantly less, although they do not produce a separate H₂S stream that can be fed to a Claus unit. This suggests that current membrane designs – both hydrogen-selective and CO₂-selective – are competitive with conventional absorption processes for IGCC syngas separations, particularly if co-capture of H₂S and CO₂ is viable. Better membranes, especially those with improved selectivities that reduce energy use, will improve the competitive position of membrane-based IGCC CO₂ capture.

5.3. Membrane Designs with Sweep

A variation of the hydrogen-selective membrane design is shown in Figure 5.3. This design makes use of nitrogen available from the on-site air separation plant as a sweep gas to reduce the energy cost of recompressing permeated hydrogen going to the combustion turbine. In the conventional IGCC process, pressurized nitrogen from the air separation plant (at 30 bar) is mixed with hydrogen before the hydrogen is burned in the gas turbine combustor. The hydrogen going to the combustor typically contains 45-50% hydrogen and about 50-55% nitrogen. The nitrogen diluent controls the combustor burner temperature and reduces NO_x formation.^[27] Availability of this nitrogen stream makes membrane sweep process designs possible. In particular, the nitrogen sweep can be used with a hydrogen-selective membrane to separate hydrogen and CO₂ while maintaining both residue and permeate streams at elevated pressure (thereby reducing compression requirements). This nitrogen sweep concept has been proposed for use with inorganic membrane reactors, and was recently studied by Ciferno and Marano for polymer membrane designs.^[28, 29]

Figure 5.3. A hydrogen-selective membrane process that uses a compressed nitrogen sweep. The membranes used have the permeation properties shown in Table 5.3.

In the Figure 5.3 design, the hot shifted syngas (stream ①) is passed across the feed side of a hydrogen-permeable membrane. For this case, the syngas has not passed through a low-temperature water knockout step, so it is saturated with water at 150°C (10% water). Nitrogen from the air separation plant, at 30 bar and 150°C, is circulated countercurrently to the feed gas on the permeate side of the membrane (stream ③). The feed-to-permeate pressure ratio is only 1.7, so permeation is mostly driven by concentration rather than pressure differences across the

membrane. The partial pressure gradient created by the nitrogen sweep produces a flow of hydrogen and, to a much lesser extent CO₂, from the feed to the permeate gas, and a small flow of nitrogen from the permeate gas to the feed. The permeate gas leaving this unit (stream ④) contains about 45% hydrogen, 47% nitrogen and 2% CO₂. A key benefit of the sweep design is that the permeate gas is at a pressure of 30 bar and so can be sent directly to the combustion turbine without further compression. The hydrogen-stripped gas leaving the residue side of the membrane is heat exchanged, and then cooled in a fractionating condenser to capture liquid CO₂ (stream ②), in the same manner as in the Figure 5.2 design.

Table 5.5 compares the estimated power use and costs of the membrane process with nitrogen sweep to those of a Selexol separation plant. The installed capital cost of the hydrogen membrane process with sweep (Figure 5.3) is lower than membrane designs without sweep (see Table 5.4), and less than 50% of the Selexol unit. The power consumption for the Figure 5.3 process using a hydrogen-selective membrane with sweep is 25 MW_e compared to 40-50 MW_e for the previous membrane designs and Selexol. The combination of lower cost and reduced energy use results in an expected increase in LCOE of about 15% for the hydrogen-selective membrane with sweep. This almost halves the increase expected from the Selexol process and approaches the DOE target of <10% increase in LCOE.

Table 5.5. Comparison of Energy Use and Capital Costs for IGCC CO₂ Capture Using Selexol and Membrane Processes Using Nitrogen Sweep (cost basis is 2007 US\$).

System/Cost Parameter	Units	Selexol + CO ₂ Compression	H ₂ -Selective Membrane With Sweep (Figure 5.3)	H ₂ - And CO ₂ - Selective Membranes With Sweep (Figure 5.4)
Compression power used	MW _e	31	1.0	13
Refrigeration (or steam) used	MW _e	19	24	12
Total power used	MW _e	50	25	25
Membrane area used	m ²	--	25,000	34,000
Membrane or Selexol equipment cost	\$ million	74	12.5	17
Compression and/or refrigeration equipment cost	\$ million	18	38	25
Bare erected plant cost	\$ million	166	83	72
Engineering fees	\$ million	16	8	7
Contingencies	\$ million	69	22	22
Total plant cost	\$ million	252	114	101
Estimated increase in LCOE	%	31	17	16

One open question that needs to be determined experimentally is the efficiency of the membrane countercurrent/sweep unit fitted with hydrogen-selective membranes. We have developed this type of gas-gas membrane contactor for treatment of low-pressure flue gas containing CO₂. In that work, concentration polarization effects that might degrade the performance on the sweep side of the membrane were small, and the experimentally measured performance of the

membrane modules was within 20% of the expected theoretical performance. However, the sweep process shown in Figure 5.3 operates at very different conditions and the effect of concentration polarization on the sweep side of the membrane may be more noticeable. In particular, the flux of hydrogen through the membrane will be relatively high because of the high syngas feed pressure. In this situation, where the volumetric flow of hydrogen through the membrane is comparable to that of the nitrogen sweep gas, concentration polarization may hinder performance. Nevertheless, laboratory tests using nitrogen sweep on the permeate side of the Proteus membrane (See Section 2) have confirmed that the separation performance with sweep under expected operating conditions is consistent with values used in our design calculations. This sweep issue will need to be addressed in future module design work to maximize the benefit of nitrogen sweep.

While the Figure 5.3 membrane design looks very promising, further improvements (in addition to sweep optimization) are possible. With current hydrogen-selective membranes, because the residue gas still contains significant amounts of hydrogen, it must be cooled to $-55\text{ }^{\circ}\text{C}$ or lower to capture 90% of the CO_2 as a liquid stream. As a result, costly low-temperature materials are required for the condenser, and an expensive multi-stage refrigeration system is needed. Membranes with higher H_2/CO_2 selectivity would help by removing more of the hydrogen without losing CO_2 in the hydrogen-selective membrane step. However, if only currently-available membranes are used, a design using both hydrogen-selective and CO_2 -selective membranes in a single process, such as that shown in Figure 5.4, can be used. This design is similar to the hydrogen-selective membrane process with sweep shown in Figure 5.3, except that a CO_2 -selective membrane is used to treat the overhead gas of the CO_2 condenser. The CO_2 -selective membrane recycles CO_2 in the overhead gas to the front of the condenser and produces a residue stream containing the inert gases and residual hydrogen that can be burned.

The primary advantage of the Figure 5.4 design is that CO_2 liquefaction can be conducted at $-30\text{ }^{\circ}\text{C}$ rather than $-55\text{ }^{\circ}\text{C}$. This means lower-cost materials of construction can be used for the CO_2 condenser, and a simple propane refrigeration system can be used for cooling (minimum effective temperature of $-40\text{ }^{\circ}\text{C}$). As shown in Table 5.5, the total energy use for the Figure 5.4 design (hydrogen- and CO_2 -selective membranes) is about equal to that of the Figure 5.3 design (hydrogen-selective membranes only). The Figure 5.4 design uses less refrigeration power, but more compression power to recycle the CO_2 -enriched permeate to the condenser. However, the cost of the Figure 5.4 design is lower because it operates at a higher temperature and uses a less complex refrigeration process.

Stream compositions (mol%)	Stream #				
	① Hot, shifted syngas	② Liquid CO ₂	③ N ₂ sweep	④ Fuel gas	⑤ Inert purge
H ₂	50.9	1.1	0	43.7	80.0
CO ₂	36.8	96.9	0	3.2	4.0
CO	1.1	0.3	0	0.8	6.5
N ₂	0.7	0.3	100	43.8	9.5
H ₂ S	0.5	1.4	0	0.01	0.02
H ₂ O	10.0	0	0	8.4	0
Flow rate (tons/h)	622	468	445	595	36.3
Pressure (bar)	50	140	32	32	50
Temperature (°C)	150	10	150	150	25

Figure 5.4. A membrane process that uses both hydrogen- and CO₂-selective membranes. The membranes used have the permeation properties shown in Table 5.3.

Overall, the calculation results shown in Tables 5.4 and 5.5 suggest that simple process designs using currently available membranes look promising for IGCC CO₂ capture. Hydrogen-selective membrane designs that can take advantage of an existing nitrogen diluent stream as a sweep gas use less energy than conventional absorption processes or CO₂-selective membrane designs. For example, both the Figure 5.3 and 5.4 hydrogen-selective membrane designs with sweep use 50% less energy compared to Selexol to accomplish 90% CO₂ capture. Combination membrane designs, where CO₂-selective membranes are used on the cold end of the process to assist with CO₂ liquefaction, show potential to lower system costs. All of these design cost calculations assume that H₂S can be co-captured with CO₂. If this is not the case, another technology, such as an absorption process, will have to be added downstream of the Proteus membrane to remove H₂S. Future design work should be directed toward examining the possible sulfur removal technologies that can be used in combination with the membrane systems described in this section.

5.4. Targets for Membrane Development

The final section of this process analysis describes how development of membranes with enhanced properties could improve the economics of membrane-based CO₂ capture.

The design shown in Figure 5.4 is based on membranes with the permeation properties shown in Table 5.3. These values reflect the properties of membranes already obtained in our laboratory, as well as in the field using a real syngas. The bulk of the membrane area in the process is in the hydrogen-permeating sweep modules, and improvements in permeance and particularly selectivity would be beneficial in this unit. Figure 5.5 shows the impact of higher H_2/CO_2 selectivity on the total energy used by the Figure 5.4 process and the membrane area needed. As the selectivity of the hydrogen-permeable membrane increases, the total energy consumption decreases sharply. This is because the membrane unit is able to remove a larger fraction of the hydrogen in the feed gas into the product stream while still maintaining the CO_2 content of the permeate stream at 2-3% CO_2 . The CO_2 concentrate stream leaving this step is then smaller and has a higher concentration of CO_2 . Liquefaction of the CO_2 when this stream is cooled is easier and the size of the recycle compressors is much reduced. Higher H_2/CO_2 (and H_2/H_2S) selectivities will also help limit any slip of H_2S through the Proteus membrane to the fuel gas. However, at very high selectivities (>30), the membrane area needed for the separation increases as the membrane separation step becomes controlled by the pressure ratio.

Figure 5.5. Impact of H_2/CO_2 selectivity on total energy and membrane area requirements (in thousands of m^2) for the process design shown in Figure 5.4. For these calculations, the CO_2 capture rate is fixed at 90% and the membrane hydrogen permeance is 300 gpu.

The trade-off between compression power and membrane area produces the LCOE versus membrane selectivity relationship shown in Figure 5.6. With today's base-case membranes having the permeation properties shown in Table 5.3, the increase in LCOE is about 15%. But hydrogen-permeable membranes with better separation performance can provide even more attractive LCOE increases. If membranes with a hydrogen permeance of 900 gpu and a selectivity of about 40 could be made, the LCOE would approach the DOE target for 90% CO_2 capture. Producing membranes with higher permeances is likely in the near future; producing membranes with a H_2/CO_2 selectivity of 40 is more of a stretch.

Figure 5.6. Increase in LCOE resulting from changes in membrane properties at 90% CO₂ capture.

Overall, polymer membranes offer near-term promise as an IGCC CO₂ capture option that is substantially more efficient and lower cost than conventional absorption processes. One of the key remaining challenges will be effectively integrating a membrane CO₂ capture process into an overall syngas treatment train that includes removal of sulfur and other trace contaminants.

5.5. Process Design and Economic Analysis Summary

During this project, we completed the work on a comparative systems and economic analysis of our membrane process compared to the base-case Selexol absorption process. For this work, we used the recent DOE report, “Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity,” Revision 2, November 2010. Initially, we did some baseline design calculations to compare the performance of simple hydrogen-selective and CO₂-selective membrane processes with a Selexol unit operating on GE gasifier syngas. Then we expanded our design analysis to include processes using nitrogen sweep and both hydrogen-selective and CO₂-selective membranes. Our goal was to identify the most promising membrane process designs for CO₂ capture from pre-combustion syngas, and clarify the membrane requirements for these designs. The main findings of our analysis can be summarized as follows:

- A simple membrane process using either hydrogen-selective or CO₂-selective membranes is capable of capturing 90% of CO₂ from syngas, while causing about a 20% increase in the LCOE (when hydrogen sulfide is co-sequestered). Both designs produce high-purity liquid CO₂ ready for sequestration and ~92% hydrogen at 30 bar ready for delivery to the gas turbine combustor.
- Hydrogen-selective membranes offer the following significant advantages over CO₂-selective membranes.

- 1) Hydrogen-selective membranes can operate at higher temperatures [150°C (and perhaps higher) versus <50°C for the CO₂ membrane], and therefore, would require less syngas cooling and water knockout equipment.
 - 2) A hydrogen-selective membrane will permeate water vapor, leaving a dry CO₂-enriched residue that can be readily liquefied. The water vapor in the hydrogen-enriched permeate is beneficial for controlling flame temperature in the combustor and increases the mass flow to the turbine. In contrast, a CO₂-selective membrane will permeate water with the CO₂. The CO₂-enriched stream must then be dried using molecular sieves or glycol before it can be liquefied. This increases the cost and complexity of the process.
 - 3) Nitrogen from the air separation unit that is mixed with hydrogen at the combustion turbine as a diluent to control flame temperature can be used as a sweep gas with a hydrogen-selective membrane^{25,26}. Use of a nitrogen sweep on a hydrogen-selective membrane can reduce energy requirements for the hydrogen/CO₂ separation step. A CO₂-selective membrane does not benefit from a nitrogen sweep.
- We have evaluated a number of process designs using hydrogen-selective membranes, alone or in the combination with CO₂-selective membranes. The best process designs – using hydrogen-selective countercurrent/sweep membranes that operate warm for bulk hydrogen recovery, combined with low-temperature CO₂-selective membranes that assist CO₂ purification and liquefaction – have the potential to reduce the increase in LCOE caused by 90% CO₂ capture to about 15%. This value is still higher than the DOE target for increase in LCOE (10%) and does not include separate capture of sulfur species. However, compared to the base-case Selexol process that gives a 30% increase in LCOE at 90% CO₂ capture, the membrane-based performance looks promising. Even larger cost reductions might be possible if higher permeance and higher selectivity membranes can be developed.
 - We conducted a sensitivity study of our current best design to see how the separation performance of the hydrogen-selective membrane would impact the increase in LCOE at 90% CO₂ capture. The study shows that as either H₂/CO₂ selectivity or hydrogen permeance increase, the increase in LCOE is reduced. At H₂/CO₂ selectivities of less than 20, increasing the selectivity has the largest impact on reducing the increase in LCOE. At H₂/CO₂ selectivities of more than 20, increasing the permeance is more beneficial to improving the economics of CO₂ capture with membranes. To approach the DOE target of less than a 10% increase in LCOE will require very permeable membranes (~1,000 gpu) with H₂/CO₂ selectivities approaching 40.
 - In the designs described above, sulfur compounds such as H₂S that are present in coal-derived syngas will be captured and co-sequestered with CO₂. If H₂S needs to be separated from the CO₂ stream, additional gas processing will be required, which will increase the cost of CO₂ capture. Therefore, co-sequestering H₂S with CO₂ is more compelling economically – if such an approach is environmentally acceptable. We recommend future work that will explore technology options for sulfur removal that can be used in combination with the membrane processes studied in this program.

6. CONCLUSIONS AND FUTURE WORK

During this project, newly-developed Proteus polymeric membranes were tested in the laboratory and in the field at NCCC with warm shifted syngas (up to 150°C). These membranes demonstrated separation performance that exceeded project targets and was stable over 500+ hours with a high sulfur feed. A process design study using field performance showed a membrane-based process has the potential to reduce the increase in LCOE caused by 90% CO₂ capture to about 15% if co-sequestration of H₂S is viable. This value is still higher than the DOE target for increase in LCOE (10%); however, future improvements in membrane performance have the potential to reach the DOE target.

All project milestones were met on schedule and within budget. Specific project accomplishments organized by task area are as follows:

In the area of membrane development, we made great progress in identifying a proprietary polymer for use as the selective layer of a membrane, developing the MTR Proteus membrane for H₂/CO₂ separations, optimizing Proteus membrane performance, and scaling up membrane production. Proteus membranes were evaluated for their stability under practical operating conditions and also characterized for their gas separation performance using pure gases or a simulated syngas mixture (50%/50% H₂/CO₂) at feed temperatures ranging from 20 to 150°C. The main accomplishments in the area of membrane development can be summarized as follows:

- Hydrogen permeance of >400 gpu and H₂/CO₂ selectivity of >12 was achieved using a simulated syngas mixture (50/50 vol% H₂/CO₂) at 150°C and 50 psig. By further optimizations in the membrane fabrication protocols, such as introducing a post-treatment method, additional improvements in the hydrogen permeance were achieved (to about 800 gpu) while the H₂/CO₂ selectivity was maintained above 10. Current Proteus membrane performance significantly exceeds the original project targets of 200 gpu for hydrogen permeance and 10 for H₂/CO₂ selectivity.
- Proteus membranes were successfully fabricated on commercial-scale production equipment at MTR. These membranes were used to fabricate lab-scale Proteus membrane modules in this project, and will also be used to fabricate commercial-scale Proteus membrane modules for future commercial applications.
- Stability tests conducted at MTR showed that the performance of Proteus membranes is stable at feed temperatures up to 150°C and at feed pressures as high as 800 psig. A more rigorous long-term thermal stability test performed at the NCCC syngas facility operated by Southern Company in Wilsonville, AL, also indicated that Proteus membranes were stable at feed temperatures up to 150°C for ~500 hours, even in the presence of syngas feeds containing saturated water vapor, heavy hydrocarbons, and >700 ppm hydrogen sulfide.
- Tests using nitrogen as a sweep gas on the permeate side of the membrane were performed, to evaluate the potential of the sweep membrane process design to improve hydrogen separation from CO₂. The test was conducted by varying the sweep/permeate flow rate ratio from 0 to 2.5, at a fixed feed/permeate pressure ratio of 2, which is close to the practical operating conditions in the IGCC separation process. The results confirmed

that the presence of a nitrogen sweep stream on the Proteus membrane permeate side could increase the driving force for hydrogen separation, and thus improve the separation performance for the targeted separation.

In the area of module development, module components and sealing elements were modified for high temperature operation. Proteus membrane modules were produced and evaluated for their stability under practical operating conditions and also characterized for their gas separation performances in the MTR laboratory using pure gases or a simulated syngas mixture (50%/50% H₂/CO₂) at feed temperatures ranging from 20 to 150°C. The main accomplishments in the area of module development can be summarized as follows:

- Thermal stability study results suggest that the Proteus modules developed in this project can be used at elevated temperatures (up to 150°C) for an extended period of time (>150 hours), and potentially in future IGCC power plants to separate hydrogen from warm shifted syngas streams.
- A mixed-gas hydrogen permeance of about 160 gpu and H₂/CO₂ selectivity of >12 at 100 psig and 150°C was achieved using current module configurations. The mixed-gas hydrogen permeances of the lab-scale modules are still about 30-40% lower than those observed for Proteus membrane stamps, even though H₂/CO₂ selectivities were within the expected range. This may be due to an increase in feed flow resistance as a result of the morphology change in the spacer materials used in the module at elevated temperatures.

In the area of field tests, both Proteus membranes and lab-scale Proteus membrane modules were evaluated using coal-derived syngas streams in the field at NCCC. The field tests demonstrated the feasibility of using Proteus membranes and modules developed in this project to perform the separation of hydrogen from warm shifted syngas. The main field test accomplishments can be summarized as follows:

- A stable hydrogen permeance of >200 gpu and a H₂/CO₂ selectivity of >16 were achieved for Proteus membrane stamps (with an area of 30 cm²) and a stable hydrogen permeance of ~150 gpu and a H₂/CO₂ selectivity of ~14 were achieved for a lab-scale Proteus membrane module (with an area of 0.13 m²), at the operating conditions (feed pressures: 150-175 psig and feed temperatures: 120-135°C) encountered at NCCC. The results indicate that all module components, including the Proteus membrane, were stable under the field conditions for a prolonged time period (>600 hrs).
- The field performance of both Proteus membrane stamps and Proteus membrane modules is consistent with the results obtained at the MTR laboratory when a simulated syngas mixture (50% H₂/50% CO₂) was used, suggesting that the presence of sulfur-containing compounds (up to 780 ppm hydrogen sulfide), saturated water vapor, carbon monoxide and heavy hydrocarbons in the syngas feed stream has no adverse effect on the Proteus membrane or module performance.

In the area of process design and economic analysis, we completed an economic analysis of a number of membrane processes developed in this project. The current field performance for Proteus membranes was used in the design analysis. The processes were compared to the base-case Selexol absorption process operating on GE gasifier syngas. The main findings can be summarized as follows:

- A simple membrane process using either hydrogen-selective or CO₂-selective membranes is capable of capturing 90% of CO₂ from syngas while causing about a 20% increase in the LCOE (when hydrogen sulfide is co-sequestered). These designs produce high-purity liquid CO₂ ready for sequestration and ~92% hydrogen at 30 bar ready for delivery to the gas turbine combustor.
- Hydrogen-selective membranes offer the following significant advantages over CO₂-selective membranes when treating IGCC syngas.
 - 1) Hydrogen-selective membranes can operate at higher temperatures [150°C (and perhaps higher) versus <50°C for the CO₂ membrane], and therefore require less syngas cooling and water knockout equipment.
 - 2) A hydrogen-selective membrane will permeate water vapor, leaving a dry CO₂-enriched residue that can be readily liquefied. The water vapor in the hydrogen-enriched permeate is beneficial for controlling flame temperature in the combustor and increases the mass flow to the turbine. In contrast, a CO₂-selective membrane will permeate water with the CO₂. The CO₂-enriched stream must then be dried using molecular sieves or glycol before it can be liquefied. This increases the cost and complexity of the process.
 - 3) Nitrogen from the air separation unit that is mixed with hydrogen at the combustion turbine as a diluent to control flame temperature can be used as a sweep gas with a hydrogen-selective membrane. Use of a nitrogen sweep on a hydrogen-selective membrane can reduce energy requirements for the hydrogen/CO₂ separation step. A CO₂-selective membrane does not benefit from a nitrogen sweep.
- We evaluated a number of process designs using hydrogen-selective membranes, alone or in the combination with CO₂-selective membranes. The best process designs – using hydrogen-selective countercurrent/sweep membranes that operate warm for bulk hydrogen recovery, combined with low-temperature CO₂-selective membranes that assist CO₂ purification and liquefaction – have the potential to reduce the increase in LCOE caused by 90% CO₂ capture to about 15%. This value is still higher than the DOE target for increase in LCOE (10%) and does not include separate capture of sulfur species; however, compared to the base-case Selexol process that gives a 30% increase in LCOE at 90% CO₂ capture, the membrane-based performance looks promising. Even larger cost reductions might be possible if higher permeance and higher selectivity membranes can be developed.
- We conducted a sensitivity study of our current best design to see how the separation performance of the hydrogen-selective membrane would impact the increase in LCOE at 90% CO₂ capture. The study shows that as either H₂/CO₂ selectivity or hydrogen permeance increase, the increase in LCOE is reduced. At H₂/CO₂ selectivities of less than 20, increasing the selectivity has the largest impact on reducing the increase in LCOE. At H₂/CO₂ selectivities of more than 20, increasing the permeance is more beneficial to improving the economics of CO₂ capture with membranes. To approach the

DOE target of less than a 10% increase in LCOE will require very permeable membranes (~1,000 gpu) with H₂/CO₂ selectivities approaching 40.

- In the designs described above, sulfur compounds such as hydrogen sulfide that are present in coal-derived syngas will be captured and co-sequestered with CO₂. If hydrogen sulfide needs to be separated from the CO₂ stream, additional gas processing will be required, which will increase the cost of CO₂ capture. Therefore, co-sequestering hydrogen sulfide with CO₂ is more compelling economically – if such an approach is environmentally acceptable. We recommend that future work explore technology options for sulfur removal that can be used in combination with the membrane processes studied in this program.

Future Work and Recommendations

We believe future work should focus on the following areas:

- Improving the performance of both MTR Proteus membranes and Proteus membrane modules. As suggested by the results of the process design analysis, better membrane performance with both higher selectivity and higher permeance is required to achieve the DOE target of less than a 10% increase in LCOE. The current module performance is already encouraging, but still below the level we expected. We believe that a significant improvement in the module performance is likely – at least to a level similar to that of the Proteus membrane stamps – if advanced spacer materials become commercially available or can be custom-designed and constructed. The major current challenge is not the lack of polymer resins with high-temperature stability, but the lack of available spacer materials made from those polymer resins. Several advanced engineered polymer materials, including glass-reinforced grades, that could be used continuously at >200°C in air are commercially available.
- Increasing the operating temperature of membrane modules. There are significant benefits to extending the operating temperature of Proteus membrane modules to the low-temperature shift reactor exit temperature (~200°C). To achieve stable operation at this temperature will require additional membrane and module materials development and testing.
- Developing high-temperature *commercial-scale* membrane modules. Scale-up of modules to commercial size is an important development stage that will allow testing with larger feed streams at NCCC. It is also important to MTR so that the Proteus membrane can be used for other, potential near-term commercial applications.
- Examining new process schemes that capture sulfur as a separate stream, in a manner similar to that of conventional acid gas removal technologies. The current membrane process design co-captures H₂S with CO₂; however, this may not be possible for regulatory reasons, or it may be desirable to produce byproducts based in sulfur. For these reasons, process designs that combine the membrane technology developed in this program with

separate sulfur removal technology may be preferred. The techno-economic competitiveness of these hybrid process designs should be studied.

- Continuing long-term membrane module field tests at NCCC and/or at an oxygen-blown gasifier to clarify module lifetime. Field tests are invaluable for surfacing materials and operating challenges, and producing real-world solutions. Field lifetime data are critical to improve assumptions used in process economic calculations.

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Appendix A. Critical Path Project Milestones Schedule

Project Milestone Description	Project Duration - 24 months Start: 9/15/09 End: 9/14/11								Planned Start Date	Planned End Date	Actual Start Date	Actual End Date	Comments (notes, explanation of deviation from baseline plan)
	Project Year 1				Project Year 2								
	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4					
Confirm that composite membranes meet target performance – hydrogen permeance of 200 gpu and H ₂ /CO ₂ selectivity of 10 with mixtures.	xxx	xxx	xxx	xxX					4QFY09	3QFY10	4QFY09	1QFY10	Milestone achieved ahead of schedule.
Using actual membrane performance data, complete design studies that show the membrane process has the potential to meet DOE program targets.			xxx	xxX					1QFY10	3QFY10	1QFY10	3QFY10	Milestone achieved on schedule.
Complete fabrication of bench-scale membrane modules and demonstrate module performance/lifetime during simulated WGS mixture testing.					xxx	xxx	xxX		4QFY10	2QFY11	2QFY10	1QFY11	Milestone achieved ahead of schedule. Some field tests added to the project was completed in 4QFY11.
Finish data analysis, process optimization studies, and comparative economic evaluation.								xxX	2QFY11	3QFY11	1QFY11	4QFY11	Milestone achieved on schedule.

x=Duration of effort directed toward the milestone; X=Milestone evaluation and decision point