Carbon Molecular Sieve Membrane as a True One Box Unit for Large Scale Hydrogen Production

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EXECUTIVE SUMMARY

IGCC coal-fired power plants show promise for environmentally-benign power generation. In these plants coal is gasified to syngas then processed in a water gas-shift (WGS) reactor to maximize the hydrogen/ CO_2 content. The gas stream can then be separated into a hydrogen rich stream for power generation and/or further purified for sale as a chemical and a CO_2 rich stream for the purpose of carbon capture and storage (CCS). Today, the separation is accomplished using conventional absorption/desorption processes with post CO_2 compression. However, significant process complexity and energy penalties accrue with this approach, accounting for ~20% of the capital cost and ~27% parasitic energy consumption. Ideally, a "one-box" process is preferred in which the syngas is fed directly to the WGS reactor without gas pre-treatment, converting the CO to hydrogen in the presence of H_2S and other impurities and delivering a clean hydrogen product for power generation or other uses. The development of such a process is the primary goal of this project.

Our proposed "one-box" process includes a catalytic membrane reactor (MR) that makes use of a hydrogen-selective, carbon molecular sieve (CMS) membrane, and a sulfur-tolerant Co/Mo/ Al_2O_3 catalyst. The membrane reactor's behavior has been investigated with a bench top unit for different experimental conditions and compared with the modeling results. The model is used to further investigate the design features of the proposed process. CO conversion >99% and hydrogen recovery >90% are feasible under the operating pressures available from IGCC. More importantly, the CMS membrane has demonstrated excellent selectivity for hydrogen over H_2S (>100), and shown no flux loss in the presence of a synthetic "tar"-like material, i.e., naphthalene. In summary, the proposed "one-box" process has been successfully demonstrated with the bench-top reactor.

In parallel we have successfully designed and fabricated a full-scale CMS membrane and module for the proposed application. This full-scale membrane element is a 3" diameter with 30"L, composed of ~85 single CMS membrane tubes. The membrane tubes and bundles have demonstrated satisfactory thermal, hydrothermal, thermal cycling and chemical stabilities under an environment simulating the temperature, pressure and contaminant levels encountered in our proposed process. More importantly, the membrane module packed with the CMS bundle was tested for over 30 pressure cycles between ambient pressure and >300 - 600 psi at 200 to 300°C without mechanical degradation. Finally, internal baffles have been designed and installed to improve flow distribution within the module, which delivered $\geq 90\%$ separation efficiency in comparison with the efficiency achieved with single membrane tubes. In summary, the full-scale CMS membrane element and module have been successfully developed and tested satisfactorily for our proposed one-box application; a test quantity of elements/modules have been fabricated for field testing.

Multiple field tests have been performed under this project at National Carbon Capture Center (NCCC). The separation efficiency and performance stability of our full-scale membrane elements have been verified in testing conducted for times ranging from 100 to >250 hours of continuous exposure to coal/biomass gasifier off-gas for hydrogen enrichment with no gas pre-treatment for contaminants removal. In particular, "tar-like" contaminants were effectively

rejected by the membrane with no evidence of fouling. In addition, testing was conducted using a hybrid membrane system, i.e., the CMS membrane in conjunction with the palladium membrane, to demonstrate that 99+% H₂ purity and a high degree of CO₂ capture could be achieved. In summary, the stability and performance of the full-scale hydrogen selective CMS membrane/module has been verified in multiple field tests in the presence of coal/biomass gasifier off-gas under this project.

A promising process scheme has been developed for power generation and/or hydrogen coproduction with CCS based upon our proposed "one-box" process. Our preliminary economic analysis indicates about 10% reduction in the required electricity selling price and ~40% cost reduction in CCS on per ton CO₂ can be achieved in comparison with the base case involving conventional WGS with a two-stage Selexsol[®] for CCS. Long term field tests (e.g., >1,000 hrs) with the incorporation of the catalyst for the WGS membrane reactor and more in-depth analysis of the process scheme are recommended for the future study.

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1. Introduction

Being comparatively inexpensive and relatively plentiful coal is an attractive energy source [1]. Integrated gas combined cycle (IGCC) power plants, in particular, show promise for environmentally benign power generation and production of chemicals, such as hydrogen and liquid fuels. In such plants, coal is gasified into synthesis gas, and is then processed in a water-gas shift (WGS) reactor to further enhance its hydrogen content for clean-power generation. The current process involves, as the first step, reacting coal with steam and/or oxygen in a gasifier to produce syngas. The syngas must then be cooled down in order to remove its contaminants, especially H_2S , and then reheated to be further reacted with steam in a WGS reactor to maximize its hydrogen content. The WGS reaction is exothermic and its equilibrium conversion decreases with temperature. Therefore, typically two reactors, one operating at high temperature (HTS) and another at lower temperature (LTS) are used in order to overcome equilibrium limitations, and to increase CO conversion of the feed at practical space velocities [2]. The gas stream exiting the WGS reactors must be treated further in separation units to produce nearly pure hydrogen. The total process, as it now stands, is not very attractive. If one takes into consideration of the carbon capture and storage (CCS), its process becomes very complex and extremely energy intensive.

In order to avoid using the dual WGS reactor system, membrane reactors (MR) have been considered for this application. Through the use of the MR, and by removing H_2 in situ from the WGS reaction mixture, the equilibrium is shifted towards the products, ultimately resulting in higher conversions in a single-stage reactor. Many inorganic hydrogen selective inorganic membranes have been considered for this purpose, including palladium, silica, zeolite, and carbon membranes. Pd membranes have been studied extensively. Despite being able to attain high CO conversions and to deliver high hydrogen purity, Pd membranes have drawbacks which have limited their widespread industrial applications. CMS membranes, which have attracted recent attention for gas separation applications [19], have also found use in MR for the WGS reaction. To our knowledge, all the WGS-MR studies, so far, have been performed with pure feeds in the absence of impurities that one may typically encounter in coal-derived syngas, particularly H_2S , which has proven detrimental to both conventional WGS (HTS and LTS) catalysts [20] and Pd membranes [17,18]. In this paper, we study, instead, a WGS-MR treating a feed which contains substantial quantities of H_2S (several thousand ppm) typical of what may be encountered in the off-gas of a coal gasifier. The idea is to make this MR the “heart” of a “one-box” process in which the gasifier syngas is fed directly into the WGS reactor, which then effectively converts the CO into hydrogen in the presence of H_2S and other impurities, and delivers a substantially contaminant-free hydrogen product. For the MR we have chosen to use CMS membranes which are prepared by the deposition of polymeric precursors on tubular alumina substrates commercially available by us. (for further details about the preparation technique, see [21–23]).

The objectives of this project include:

- Demonstrated the separation of hydrogen from the coal-derived syngas at 200 to 300°C with our CMS membranes for the implementation of the proposed water gas shift membrane reactor.
- Conducted bench-top experimental study to demonstrate the enhancement of the CO conversion with the concomitant hydrogen production using the CMS membrane reactor.
- Developed and fabricated full-scale membranes and modules suitable for the proposed gas separations and membrane reactor applications.
- Performed field tests to demonstrate the technical feasibility of the use of the developed full-scale membrane module for hydrogen separation from coal-derived syngas without gas pre-treatment for contaminants removal.
- Identified promising process schemes based upon the proposed membrane reactor for hydrogen production and/or power generation with CCS for future field tests and demonstration.

In what follows, we first discuss the separation properties of the CMS membranes relevant to the proposed application. Then, the full-scale membrane module development and fabrication are presented. Then, we discuss the experimental results obtained from the bench-top membrane reactor study for a range of pressures and sweep ratios, and compare it with the simulated results obtained from a simple isothermal MR model. Then, the results from the field test we conducted at the National Carbon Capture Center (NCCC) using the full scale CMS module are presented. Finally, several promising process schemes based upon our results are described along with their operating economics.

2. Gas Separation Properties of Hydrogen Selective Membranes

Carbon molecular sieve (CMS) membranes were developed by us prior to entering this project. Instead of discussing the synthesis of the membranes, this chapter focuses on the separation performance evaluation we have performed relevant to our proposed application, including single component permeations, mixture separations, and effect of tar-like materials on gas permeation.

2.1. Single Component Permeances

Separation performance of our CMS membranes at the target operating temperature, i.e., 200 to 300°C, correlates well with the size and geometry of gas molecules. Typical hydrogen and nitrogen (representing the retaining compounds) permeances are 1 to 2 and ~0.01 m³/m²/hr/bar respectively

at 220°C as shown in Figure 2.1. The permeance was somewhat slower than hydrogen's, attributing to the geometry of molecules vs porous structure of the CMS membrane material¹. The selectivities of hydrogen against other gas molecules interested to us are presented in Table 2.1. Evidently, hydrogen and water permeances are comparable and can permeate rapidly against CO₂, CO and H₂S. Water permeance is expected to be similar to hydrogen, due to their proximity in kinetic diameters. The separation performance profile of the CMS membrane described above provides a unique property to separate hydrogen along with water from other gas molecules involved in water-gas-shift reactions and hydrogen production from coal-derived syngas, as opposed to other hydrogen selective membranes, such as palladium membranes, which permeates hydrogen only. Since gas molecules permeate through

Table 2.1 Kinetic Diameters and Selectivities of Hydrogen against Selected Light Gas Molecules

Gas Molecules	Kinetic Diameter [Å]	Selectivity over H ₂ at 220°C
NH ₃	2.6	30 to >50
H ₂ O	2.75	~1
H ₂	2.89	1
CO ₂	3.3	10 to 40
H ₂ S	3.6	>100
N ₂	3.64	60 to >100
CO	3.76	70 to >100
CH ₄	3.8	70 to >100

¹ It is generally believed that the porous structure of carbon molecular sieve materials is slit shaped.

our CMS membranes at this temperature range, i.e., 200 to 300°C, is via the molecular sieving mechanism, gas permeation rate in general is proportional to temperature except at the low temperature range, such as 50 to 100°C and lower. At this low temperature range surface diffusion mechanism may kick in in addition to molecular sieving via activated diffusion mechanism.

2.2. Mixture Separations

Synthetic gas mixtures composed of H₂, CO, CO₂, CH₄, H₂O and H₂S were prepared in the lab to evaluate the separation efficiency of our CMS membranes in mixtures. Hydrogen concentration in the range of 40%, CO concentration of 5 to 15%, and H₂S of 0.2 to 0.7% were targeted to simulate the coal-derived syngas as presented in Table 2.2.

**Table 2.2 Separation Factors obtained from Synthetic Mixtures
Simulating Water Gas Shift Reaction Conditions**

Gas mixture composition		
Gas	Permeance m ³ /(m ² h bar)	Separation Factor (S.F.)
(1) H ₂ :CO:CO ₂ :CH ₄ :H ₂ S = 39.5%:15.2%:32.4%:12.2%:0.7%		
H ₂	1.37	1.0
CO	0.02	68.5
CO ₂	0.05	27.4
CH ₄	0.01	137.0
H ₂ S	0.01	137.0
(2) H ₂ :CO:CO ₂ :CH ₄ :H ₂ S = 45.36%:4.52%:38.91%:11%:0.21%		
H ₂	1.40	1.0
CO	0.02	70.0
CO ₂	0.04	35.0
CH ₄	0.01	140.0
H ₂ S	0.01	140.0
(3) H ₂ :CO:CO ₂ :CH ₄ :H ₂ O:H ₂ S = 42.45%:4.233%:36.4%:10.29%:6.43%:0.197%		
H ₂	1.56	1.0
CO	0.02	78.0
CO ₂	0.05	31.2
CH ₄	0.01	156.0
H ₂ O	1.1	1.4
H ₂ S	0.01	156.0

In addition, water was included in one of the mixtures to simulate the water gas shift environment. Gas permeance for each component in mixtures was determined via calculation

with a mathematical model to minimize the deviation between the experimental vs the calculated. The hydrogen permeance ranging from 1.37 to 1.56 m³/m²/hr/bar was obtained at 300°C, which is very close to the typical hydrogen performance from the single components reported in Sec. 2.1. The separation factor determined from the ratio of the permeances obtained from the mixtures was also presented in Table 2.2. Our hydrogen selective membrane shows excellent rejection to H₂S and CH₄, ~140, over hydrogen, which is consistent with the order of magnitude obtained from single components. The selectivities for CO/H₂ and CO₂/H₂ are ~70 and 30 respectively, consistent with the kinetic diameter of CO > CO₂. Finally, the water permeance is in fact faster than the hydrogen permeance for this particular membrane. The above mixture separation performance profile supports the unique properties of our hydrogen selective membrane as discussed in Sec. 2.1 from single component permeance measurement. Since the separation trend obtained from the mixtures follows the prediction from single components obtained from numerous in-house measurements we performed, it is concluded that the interaction between molecules is insignificant for separation targeted in our proposed application. The surface diffusion by CO₂ was observed even at this temperature range. Thus, under this project, a correlation was used to describe the permeation of CO₂ in the mixture, while the single component permeances for the rest of the gas components were used for our modeling study involving the membrane reactor discussed in Chapter 4.

2.3. H₂S Permeation through CMS Membranes

H₂S is used as a target contaminant to be removed from syngas generated from coal gasification. Separation of H₂S in simulated coal-derived syngas by our CMS membrane was investigated comprehensively in this project. H₂S permeance was measured from 4 different synthetic mixtures at ~60 psi and 250°C as described in Figure 2.2. The 1st mixture represents the H₂S in a

Figure 2.2 H₂S Permeances obtained from Four Synthetic Mixtures Simulating Syngas (H₂S ranging from 1 to 4%)

Date	Temp [°C]	Δ P [psi]	H ₂ [%]	CO [%]	CO ₂ [%]	H ₂ S [%]	H ₂ O [%]	H ₂ /H ₂ S
311	250	68	0	96	0	4	0	-
312	250	60	33	32	33	1.3	0	84.5
313	250	61	47	25	27	1.3	0	74.4
314	250	60	25	24	25	1	25	124

binary mixture of CO and H₂S. The 2nd and 3rd mixtures represent the composition encountered in a coal gasifier without steam. The 4th mixture represents the coal gasifier off-gas with steam presence. As shown in Figure 2.2, the H₂S permeance in the neighborhood of 0.007 ± 0.001 m³/m²/hr/bar was obtained from these four mixtures. The selectivity of H₂S over H₂ ranging from 75 to 124 was obtained. Since the H₂S permeance remains relatively constant throughout these mixtures containing various components and a wide range of concentrations, we conclude that the H₂S molecule permeates through our membrane independently, i.e., no interference with other components we are interested. Moreover, H₂S permeance was found to be less than CO permeance, indicating that its permeation behavior is consistent with the trend set by the molecular size/geometry typically experienced with our CMS membrane. In summary, our membrane has shown its material stability in the presence of H₂S, and the selectivity of H₂/H₂S is about 100 ± 25 under the condition interested to us.

2.4. Thermal and Hydrothermal Stability

Our CMS membrane has shown excellent thermal and hydrothermal stability under the application condition interested to us. Its hydrothermal stability was evaluated at 220°C with the steam pressure at 22 and 55 psi for about 900 hours. As shown in Figure 2.1, no visible degradation of the membrane performance in terms of hydrogen permeance and its selectivity over nitrogen was noticed. In fact, the nitrogen permeance decreases gradually throughout the 900 hours of the testing period, most likely resulted from the trace contaminants present in water/steam, which plugged the pore size/defect responsible for nitrogen, but not the small pore size for hydrogen. Similarly the CMS membrane has demonstrated long term thermal stability at 250°C as shown in Figure 2.3 below:

During about 75 days at 250°C, the helium and nitrogen performance of this membrane remains relatively constant, in particular from day 50 to 75. The gradually increase of both He and N₂

initially was most likely resulted from the regeneration of the carbon membrane, which were previously stored in atmosphere. Finally the membrane has also demonstrated excellent thermal cycling stability as shown in Figure 2.4 below

Through 30 thermal cycles between 23 and 250°C, both He and N₂ permeances are considered stable. Similar to the initial increased phenomenon observed for the thermal stability test in Figure 2.3, during the beginning of the test, i.e., up to 10 cycles, their He and N₂ permeances increase gradually, attributed to the membrane surface regeneration. Once the surface was completely regenerated, their He and N₂ permeances remain stable for the rest of the test, i.e., from 10 to >30 cycles.

Porous carbon is known for its ability to adsorb miscellaneous contaminants in atmosphere during storage, resulting in the membrane fouling. Thermal regeneration at 250°C can effectively regenerate the porous surface of the membrane. Our test results shown in Figure 2.5 verify this, i.e., its permeance reached a nearly constant level after three cycles of heating at 250°C. In routine practice, we regenerate the membrane at 250°C for >2-3 hours as a means to completely regenerate the membrane.

As a final note, our CMS membrane exhibits a similar material stability in the presence of H₂S. Our lab experience includes (i) its material stability during a short term (8 hrs total) exposure to a high level of H₂S (~6%) and (ii) the gas separation performance remained unchanged in a mixture separation study with vs without 0.15% H₂S. In summary, the CMS membrane performance stability under our proposed application environment was experimentally verified through various tests in this project, including thermal, hydrothermal, thermal cycling, atmospheric storage and chemical stability (in the presence of H₂S as a model contaminant).

2.5. Membrane Performance in the Presence of Tar-like Species

In the early field testing conducted with single CMS membrane tubes at the NCCC, we experienced flux decay as a result of buildup of tar-like species on the membrane surface. In laboratory testing, we have demonstrated that this was a result of operating at temperatures below a critical temperature that led to condensation of the tar-like species in the module. Permeation testing with helium conducted in our laboratory with single tubes in the presence of synthetic tar and organic species, specifically, toluene and naphthalene, was conducted with the specific objective to verify that stable operation could be attained at some minimum operating temperature. Further, our goal was to verify whether a membrane fouled by these species could be regenerated. Figure 2.6 shows the effect of operating temperature on the helium permeance of a CMS membrane for a gas feed containing ca. 0.8% naphthalene as a synthetic tar species. Significant permeance decay is noted during the first 12 hours of testing and can be attributed to condensation of naphthalene on the membrane surface or in the pores. Interestingly, on heating the membrane to 250°C, essentially complete recovery of the membrane helium permeance is observed in less than one hour. Hence, although it is clear that tar-like species can yield significant flux losses, they can be readily remove from the membrane surface and no

irreversible fouling is observed.

Figure 2.6. Effect of simulated tar-like species on the permeance of helium at various operating conditions.

Following this initial study, additional work was conducted to verify stable performance could be obtained in the presence of synthetic tar under appropriate operating conditions. Figure 2.7 shows the performance of a single tube CMS membrane in the presence of toluene and naphthalene as simulated organic vapor and tar-like species obtained at an operating temperature of 250°C. As can be seen, little to no permeance or selectivity decay is observed throughout the test study. Hence, a similar temperature range was chosen for the full scale bundle test at NCCC as summarized in Chapter 5.

2.6. Conclusions

Based upon the results discussed in this chapter, several conclusions can be drawn as follows:

1. *Hydrogen and water permeances are comparable and can permeate rapidly through the CMS membrane against CO₂, CO, CH₄ and H₂S...* Since gas molecules permeating through our CMS membrane at this temperature range, i.e., 200 to 300°C, are via molecular sieving mechanism, the gas permeation rate in general is proportional to temperature except at the low temperature range, such as 50 to 100°C and lower. At this low temperature range surface diffusion mechanism may kick in in addition to molecular sieving via activated diffusion mechanism.
2. *Interaction between molecules is determined to be insignificant for the mixture separation at 200-300°C for our target applications* since the separation trend observed from the mixtures follows the prediction based upon single components obtained from numerous in-house measurements we performed,. The surface diffusion by CO₂ was observed even at this temperature range. Thus, under this project, a correlation was used to describe the permeation of CO₂ in the mixture.

3. *Our carbon molecular sieve membrane has shown excellent thermal, hydrothermal, thermal cycling and chemical stability under the application condition interested to us. In addition, no performance degradation was observed for our CMS membrane through atmospheric storage.*
4. *The selectivity of H_2S over H_2 for our current CMS membrane is 100 ± 25 ... The H_2S permeance in the neighborhood of $0.007 \pm 0.001 \text{ m}^3/\text{m}^2/\text{hr}/\text{bar}$ was observed from the four mixtures relevant to coal gasifier off-gas. H_2S molecules permeate through our membrane independently, i.e., no interaction with other components we are interested. Moreover, H_2S permeance was found to be less than CO permeance, indicating that its permeation behavior is consistent with the trend set by the molecular size/geometry typically experienced with our CMS membrane.*
5. *Although it is clear that tar-like species can yield significant flux losses, they can be controlled via operation at $\geq 250^\circ\text{C}$. Further they can be readily removed from the membrane surface at this high temperature and no irreversible fouling is observed if membrane fouling by tar-like species takes place at a lower temperature.*

3. Full-Scale Membrane Product Development

Our CMS membrane product development under this project has been concentrated in two areas: (i) bundling single tubes together into an element, which can meet the burst pressure requirement with negligible leak, and (ii) distributing flow evenly within the feed side (i.e., shell side), which can minimize flow by-pass and maximize the overall throughput of the element. Instead of discussing the details of the bundling technique and the flow distribution design, the performance of the full-scale bundle we developed under this project is discussed thoroughly in this chapter.

3.1. *Burst Pressure of Full-scale Bundles Developed under This Project*

A typical full-scale bundle is exhibited in Figure 3.1 along with the pilot scale bundles and the single tubes. Leak rate vs pressure is used to qualify the operating pressure of our CMS membrane bundles. The burst test schedule and protocol are summarized in Table 3.1.

Under this project, a pilot scale bundle (#37) was tested extensively for >30 cycles. The leak rate obtained from each cycle was well below the acceptable level, i.e., on the order of $0.0004 \text{ m}^3/\text{m}^2/\text{hr}/\text{bar}$ at 1,000 psi in comparison with a typical nitrogen permeance of our membrane on the order of $0.01 \text{ m}^3/\text{m}^2/\text{hr}/\text{bar}$ or less. The leak rate profile for each cycle is presented in Figure 3.2. Major findings are summarized below:

Table 3.1 Protocol for Extended Pressure and Temperature Cycling Test for CMS Bundles
1. Heating from room temperature to 220C at low pressure in the beginning of the day
2. 1st pressure cycling test from low pressure to 1000 psi for a period of 2 to 3 hrs. Permeate flux is recorded at each 100 psi increment.
3. Depressurization to 200 psi by opening the valve at 220C
4. 2nd pressure cycling test follow Step 2.
5. 3rd pressure cycling test following Step 2
6. Depressuization and free cooling to room temperature overnight.

Testing Schedule		
Day [-]	Date	Pressure Cycle #
1	2-Sep	37-11 to 13
2	3-Sep	37-14 to 16
3	4-Sep	37-17 to 19
4	5-Sep	37-20 to 23
5	8-Sep	37-24 to 26
6	9-Sep	37-27 to 30

- *Mechanical stability of bundle and housing through significant pressure and temperature cycling was demonstrated...* It is essential to have a housing design to match the bundle and O-ring near perfectly in order to avoid the deformation of O-ring during contraction and expansion resulted from temperature and/or pressure cycling. The ending leak permeance at 1,000 psi and 220°C in the end of the day before shut down for cooling and depressurization reached a steady state, indicating that the bundle/O-ring remained its mechanical stability/relative position/configuration through this rigorous cycling test.
- *Ending daily leak rate increase from Day 1 to Day 2 could be resulted from the increase of the maximum pressure of 800 to 1,000 psi respectively.* Initially, the module was tested up to 800 psi as the maximum pressure. Beginning the pressure/temperature cycle #37-11, a new cylinder was installed and the maximum pressure was increased to 1,000 psi. As noticed in Figure 3.2, the leak rate profiles were quite similar for the cycles #2 to 10 tested at the maximum pressure of 800 psi. However, after cooling overnight after the first day at 1,000 psi, the module was settled at a new steady state as shown from Cycles #14 to 30. We believe that the position of the O-ring and our packing material is somewhat dependent upon the maximum pressure of the operation. This nature of dependence is expected in consideration that the purpose of the O-ring/packing material is to provide the flexibility to seal the bundle against the housing. Thus, at a higher maximum pressure, the O-ring and bundle settled at a new position, which was repeatable based upon similar leak rate profile obtained from Cycles #14 to 30. We believe that “repeatability” for a given operating condition is essential for a reliable module design for this demanding application.

Our comprehensive pressure/temperature cycling test above demonstrates that the bundle leak rate is negligible and can sustain the application environment without degradation. The pilot test

bundle used in this test was later scaled up to the full-scale bundle (i.e., 3" diameter) for field test under a similar temperature and pressure range as presented in Chapter 5 Field Test.

3.2. Flow Distribution within Full Scale Module

During our testing conducted at the NCCC in Q4 2011 with full scale CMS bundles, the mixed gas H₂ permeance was found to be ca. 30 to 40% below the value expected based upon the permeance obtained from the single component. Initially, we suspected that contamination of the membrane element which resulted in fouling may account for this discrepancy. However, as discussed in Chapter 5 Field Test, the He permeance, as determined periodically during the 500 hours of bundle testing in NCCC in this particular field test, remained stable and equivalent to its starting value. Further, although the mixed gas H₂ permeance was lower than expected, it also remained stable throughout the run. Hence, by the finish of our testing at NCCC in November 2011, we had concluded that there was likely a feed flow distribution problem in the bundle that

accounted for the discrepancy between the mixed gas and pure component results. Under this project, the internal baffling of the CMS bundle was pursued to improve feed gas dispersion to the individual membrane tubes to overcome this discount in separation efficiency observed for the full-scale bundle. Two specific areas, i.e., Diagnosis of the Flow Distribution, and Improvement with Internal Baffles, were focused under this project, which are discussed below:

- Diagnosis of Flow Distribution in Full-Scale Bundles

Table 3.2. Ratio of the mixed gas to pure gas permeate flow rate from various tubes in the B3-32 bundle before and after the modified baffles were added. The “rings” correspond to the tube from different sections of the bundle as shown in the attached graphic.

Tube	"Ring"	Ratio of Mixed/Pure He		Ring Average
		Test1	Test2	
4	2	0.27	0.25	0.26
5	2	0.23	0.28	
3	3	0.17	0.16	0.17
1	4	0.14	0.15	0.15
2	4	0.16	0.15	
7	5	0.18	0.19	0.18

Post Addition of Internal Baffles

Tube	"Ring"	Ratio of Mixed/Pure He		Ring Average
		Test1b		
4	2	0.32		0.36
5	2	0.40		
3	3	0.44		0.43
8	3	0.43		
1	4	0.40		0.43
2	4	0.45		
7	5	0.37		0.37

In an effort to profile the flow distribution within the module, the flux of He from various individual tubes in the bundle were experimentally obtained in both pure component and mixed gas testing under a lower pressure. Two or more tubes from each concentric “ring” of tubes were tested (see Table 3.2 for definition of “rings”). Table 3.2 shows the results of this testing in terms of the ratio of mixed gas to pure gas permeate flow rate for He for each individual tube in the various “rings”. In general, if there is no flow distribution problem between the interior and exterior tubes, then this ratio should be constant for all of the tubes. As can be seen, the average variance between the pure and mixed gas flows increases moving from the 2nd to 5th ring of tubes (1st ring tubes could not be tested due to the module configuration). At 0.26 for “ring” #2 and <0.18 for interior rings, this represents a permeate flow reduction of nearly 30 to 40% for the

interior versus exterior tubes. Interestingly, this deviation is comparable to that observed between the pure and mixed gas H₂ permeance in the testing at the NCCC in 4Q 2011.

- Improvement with Reinforced Internal Baffles

To remedy this problem, additional baffles were added to the bundle which was equipped with our standard baffle originally. The individual tube testing as described above was again conducted. As shown in Table 3.4, the variance between the He permeances obtained from pure component and mixed gas was considerably lower.

Table 3.3. He permeance for the B3-32 bundle with modified internal baffles during pure component and mixed gas testing at MPT's facility and the NCCC. Synthetic gas mixtures of He/Ar (60/40) and He/N₂ (70/30) were used respectively.

Feed Rate [liter/min]	Temp [°C]	Reject Pressure [psig]	Permeate Pressure [psig]	He, mixed gas Permeance [m ³ /m ² /hr/bar]
MPT Laboratory Testing				
Pure component He at 220°C				1.57
Mixed gas results:				
76	220	50	0	1.55
50	220	48	0	1.39
PSDF Testing				
Pure component He at 195°C				1.52
Mixed gas results:				
180	195	94	9	1.51
226	195	110	5	1.42
227	195	110	5	1.36
266	195	140	9	1.35

Based upon this testing, it was clear that controlling the feed gas flow distribution in the interior of the bundle was necessary and could be accomplished with the baffling scheme developed under this project. Given the successful demonstration of the interior baffles with this bundle, full scale testing was conducted at our facility using a He/Ar (60/40) gas blend. The membrane permeance was determined for both the pure gas as well as the mixed gas at ca. 50 psig and feed rates of 50 and 76 liters/min. As can be seen in **Table 4**, reasonably good agreement between the mixed gas and pure component results is obtained from the tests at our pilot plant. The mixed gas He permeance is no more than 10% less than the pure component value.

Following the successful bundle testing at our facility, additional bundle testing was conducted at the NCCC (formerly PSDF) facility with this bundle using a synthetic gas blend of He/N₂ (70/30) to verify the performance under typical run conditions for our field testing. Similar

results are obtained at feed flow rates up to 266 liter/min and feed pressures up to 140 psig. Again, the maximum deviation between the pure and mixed gas data is ca. 10%. By comparison, 30 to 40% reduction in the mixed gas permeance was observed during the 4Q 2011 test at NCCC with gasifier off-gas. Hence, it is apparent that well-designed internal baffling is required to deliver good gas dispersion to the tubes in the interior of the bundle (e.g., Ring 3 to 5).

3.3. Conclusions

Based upon the results presented in this quarter, several conclusions can be drawn as follows:

1. *Temperature and pressure cycling test up to 30 cycles was performed to demonstrate the mechanical stability of our membrane module under 1,000 psi and 220°C environment.* Our comprehensive pressure/temperature cycling test demonstrates that (i) the bundle nitrogen leak rate is negligible and (ii) the bundle can sustain the application environment selected under this project without degradation.
2. *Flow distribution within the shell side of our full-scale module is considered acceptable after the module was reinforced with internal baffles.* Our lab evaluation determined about 10% discount in separation efficiency of the full-scale module in comparison with the single tube's. Further, this improved flow distribution was demonstrated in a full-scale testing facility using the temperature, pressure and flow rates comparable to the full-scale operation.

The successful development of the above two fronts forms the foundation of our full-scale CMS bundle/module designed for the proposed application.

n Production Using a Catalytic Membrane Reactor Based Process

4.1. *Literature Review on Catalytic Membrane Reactors involving Water Gas Shift Reaction*

Integrated gas combined cycle (IGCC) power plants show promise for environmentally-benign power generation. The syngas produced from the gasifier must be cooled down in order to remove its contaminants, especially H_2S , and then reheated to be further reacted with steam in a WGS reactor to maximize its hydrogen content. The WGS reaction is exothermic and its equilibrium conversion decreases with temperature. Therefore, typically two reactors, one operating at high temperature (HTS) and another at lower temperature (LTS) are used in order to overcome equilibrium limitations, and to increase CO conversion of the feed at space velocities in the range of $(400\text{--}2500 \text{ hr}^{-1})$ [2]. The gas stream exiting the WGS reactors must be treated further in separation units to produce nearly pure hydrogen. The total process, as it now stands, is complex and energy intensive. In order to avoid using the dual WGS reactor system, membrane reactors (MR) have been considered for this application. Through the use of the MR, and by removing H_2 *in situ* from the WGS reaction mixture, the equilibrium is shifted towards the products, ultimately resulting in higher conversions in a single-stage reactor.

Dense Pd [3-8], microporous silica [9-12], and carbon molecular sieve (CMS) membranes [13-15] have been studied for use in the MR applications for the WGS reaction. For example, Bi *et al.* [7] used a $\text{Pt/Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ catalyst with a hydrogen-selective Pd membrane and attained an improved performance using feeds with compositions that match those at the exit of industrial reformers. For a reactor temperature of 350°C , a feed-side pressure of 1200 KPa, and a steam to CO ratio equal to 3, the conversion remained above the thermodynamic equilibrium value for feed hourly space velocities up to $9100 \text{ l kg}^{-1}\text{h}^{-1}$. However, H_2 recovery decreased rapidly with increasing feed space velocity. The highest hydrogen purity attained was 99.7%. Brunetti *et al.* [8] used a syngas mixture as the feed for the WGS reactor and upgraded it in one-stage MR using a Pd–Ag membrane. For a reactor temperature of 325°C , feed-side pressure of 600 KPa, and an hourly space velocity of 2600 h^{-1} , they obtained a CO conversion of 90% and a H_2 recovery of 80%. Iyoha *et al.* [5] used an MR containing multiple tubular Pd and 80 wt% Pd–20 wt% Cu membranes to perform the WGS reaction in the absence of heterogeneous catalyst particles at 1173K, which is the temperature an MR positioned just downstream of a coal gasifier would typically encounter. At an hourly space velocity of 720 h^{-1} , they attained a CO conversion of 93% and a H_2 recovery of 90% using the Pd membrane, and a CO conversion of 66% and a H_2 recovery of 85% using the Pd-Cu membrane.

Despite being able to attain high CO conversions and to deliver high hydrogen purity, Pd membranes have drawbacks which have limited their widespread industrial applications. Palladium is an expensive material, which makes membranes made out of the metal typically more expensive than other inorganic membranes. H_2O and CO blocking dissociation sites on the membrane surface was reported, resulting in a reduction in the hydrogen recovery [16], especially at temperatures below 623 K. H_2S is known to adversely affect Pd membrane

characteristics, even at single-digit ppm concentration levels. Exposure of the Pd to H₂S has been shown, for example, to not only reduce the permeability, but to also result in the formation of an irreversible grey surface scale of palladium sulfide [17]. Pd membrane exposure to H₂S has also been shown to result in dramatic pitting of the membrane surface [18].

The drawbacks associated with Pd membranes have motivated the use of other types of high-temperature resistant membranes. Giessler *et al.* [9], for example, compared the performance of molecular sieve silica membranes in the WGS reaction to that of Pd-composite membranes [3]. Their results suggest that the molecular sieve silica membranes perform better than the Pd-composite ones. Since silica membranes are known to be sensitive to steam, Giessler *et al.* [9] proposed the functionalization of the membranes using surfactants (e.g., triethylhexylammonium bromide) in order to form a hydrophobic silica surface. They reported that the steam presence resulted in a decrease in the H₂ and CO₂ permeances. However, the H₂/CO₂ selectivity remained constant between prior to and after steam exposure. Brunetti *et al.* [10] studied the performance of a traditional packed-bed reactor (PB) and a membrane reactor making use of a silica membrane on a porous stainless steel (SS) support for the WGS reaction. They observed that increasing the temperature, especially at lower pressures, increased the conversion difference between the MR and the PB. At a space velocity of 2070 h⁻¹, a temperature of 280 °C, and a pressure of 400 kPa, the MR yielded a CO conversion of 95%, which represents an increase of 8 % over the conversion in the PB. The CO concentration in the permeate side ranged from 1 to 10% depending on the operating conditions. The membrane exhibited higher permeances, but no change in selectivity (H₂/CO, H₂/CO₂) before and after the reaction. The membrane flux (H₂, CO and CO₂) was shown to be a linear function of the driving force, and no inhibition effect of other gases on the hydrogen flux was observed.

CMS membranes, which have attracted recent attention for gas separation applications [19], have also found use in MR for the WGS reaction. Harale *et al.* [13, 14] studied a hybrid adsorbent-membrane reactor (HAMR) system to carry out the WGS reaction. They used a hydrotalcite sorbent for CO₂ adsorption and nanoporous hydrogen-selective CMS membranes. The HAMR system attained CO conversions that are significantly higher than the corresponding equilibrium conversions and proved to be more efficient than PB as well as the conventional MR. Sa *et al.* [15], in a modeling study, compared the performance of an MR containing Pd membranes with an MR containing CMS membranes for H₂ production by methanol steam reforming. They concluded that the major difference in the performance of these MR occurs when the amount of hydrogen produced is low. At low contact time, the Pd-MR presents a higher driving force for H₂ than the CMS-MR, and delivers higher H₂ recovery. For the Pd-MR, low hydrogen production rate means lower driving force since hydrogen is the only permeating species. Changing the contact time has very little effect on the Pd-MR recovery of H₂, and only becomes noticeable at very high contact times. On the other hand, all species permeate in the CMS-MR, therefore, H₂ partial pressure increases with the permeation of the other species (mainly water) towards the permeate side which results in a higher driving force for H₂ and in increasing the CMS-MR hydrogen recovery. The Pd-MR performance was further enhanced by higher retentate and lower permeate pressures, while the CMS-MR performed better for intermediate trans-membrane pressure gradients.

To our knowledge, all the WGS-MR studies, so far, have been performed with pure feeds in the absence of impurities that one may typically encounter in coal-derived syngas, particularly H_2S , which has proven detrimental to both conventional WGS (HTS and LTS) catalysts [20] and Pd membranes [17,18]. In this paper, we study, instead, a WGS-MR treating a feed which contains substantial quantities of H_2S (several thousand ppm) typical of what may be encountered in the off-gas of a coal gasifier. The idea is to make this MR the “heart” of a “one-box” process in which the gasifier syngas is fed directly into the WGS reactor, which then effectively converts the CO into hydrogen in the presence of H_2S and other impurities, and delivers a substantially contaminant-free hydrogen product. For the MR we have chosen to use CMS membranes which are prepared by the deposition of polymeric precursors on tubular alumina substrates commercially available by Media and Process Technology, Inc. (for further details about the preparation technique, see [21-23]). In ongoing field studies by our team these membranes have already proven stable in the treatment of commercial refinery streams containing high levels of contaminants, such as H_2S and NH_3 . CMS membranes have also been shown previously [13, 14] to be highly stable in the presence of steam in the WGS reaction environment. Since H_2S in the syngas poisons the common WGS catalysts [20], in our study we are making use of a so-called sour-shift catalyst [24], in order to overcome the problem of catalyst poisoning. These sulfur-resistant WGS catalysts, containing sulfided Co-Mo or Ni-Mo supported on alumina [20], and on various other supports, such as zeolites [25], titania and zirconia [26], were first proposed almost twenty years ago; they have since been shown to exhibit good performance (at relatively low temperatures, 250-350 °C) with syngas feeds containing high H_2S concentrations (if adequately pre-sulfided prior to use, they perform satisfactorily even in feed streams that contain low level of H_2S).

In what follows, we first discuss the experimental studies to determine the reaction kinetics and rate parameters of the commercial sulfur-tolerant Co/Mo/ Al_2O_3 catalyst that we utilize. Then, we discuss the experimental membrane reactor performance for a range of pressures and sweep ratios, and compare it with results from a simple isothermal MR model. Finally, the same model is used to further investigate the design features of the proposed process.

4.2. Experimental

A schematic of the MR system used in this study is shown in Figure 4.1. The tubular CMS membrane is sealed inside the tubular SS reactor using graphite o-rings and compression fittings. The catalyst particles are first thoroughly mixed with ground quartz particles, and are then loaded into the annular space in between the membrane and the reactor body. We dilute the catalyst with inert quartz particles in order to completely fill the annular reactor volume, and to be able to operate the reactor bed under isothermal conditions. The experimental system consists of three sections: (i) The feed section, which consists of gas cylinders, mass flow controllers, syringe pumps, and the steam generating units; (ii) the reactor section, which consists of the MR, a furnace for heating the reactor, pressure gauges for measuring the pressure, two condensers and two moisture traps to remove the water from the reject- and permeate-side streams of the reactor, and two traps to remove the H_2S from the same streams; (iii) the analysis section, that consists of a gas chromatograph to analyze the concentration of the exit gas streams, two bubble flow-meters for measuring the total flow-rates, and Dräger tubes to measure the H_2S concentration.

Figure. 4.1 Experimental set-up used in the membrane reactor experiments

For the experiments, the reactor is maintained isothermal by placing it in a six-zone furnace, the temperature in each zone controlled with the aid of six temperature controllers and thermocouples installed in six different locations in the bed. An additional thermo-well is installed in the bed in order to monitor the temperature along the length of the bed using a sliding thermocouple. The feed and sweep gas streams flow at specified rates controlled by mass-flow controllers (MFC). Pressures are controlled by adjusting the needle valves at the exit of the reactor and sweep sides. Pressure gauges are installed at the inlet and outlet of both the feed and permeate sides in order to monitor the pressure.

Two syringe pumps are used in order to supply a controlled flow of water into two steam-generating units (one connected to the feed line, the other to the sweep stream line). The steam generators are well-insulated SS vessels which are packed with quartz beads, in order to accelerate the water evaporation and to dampen out any fluctuations in the flow of the steam that is generated. They are heated by heating tapes wrapped around them, and their temperature is controlled with the aid of temperature controllers. All the stream lines, including feed, sweep, permeate, and reject lines are insulated and heat-traced using heating tapes. Their temperature is also controlled with temperature controllers. In particular, the feed and sweep gas flows are preheated to the reaction temperature before entering the reactor.

The above experimental system is also utilized to carry-out permeation studies for characterizing the membrane properties. For such experiments, the sweep gas (permeate-side) inlet is closed, gas flows into the feed-side and the flow rates and the compositions of the permeate and reject streams are measured. For calculating the water permeance, the permeated stream by-passes the

condenser and goes directly into the adsorbent bed where the water is captured. The amount of water that permeates is calculated by measuring the weight of the adsorbent before and after water permeation. During the MR experiments, the gas streams exiting the reject and permeate sides flow first through condensers and then through moisture-traps in order to capture the water. The flow rates of the water-free stream are then measured by a bubble flow-meter. A small slip-stream from both the reject and permeate sides is intermittently removed to measure the H₂S content through the use of Drager tubes [27]. These are graduated tubes that contain a Cu compound that reacts with the H₂S and produces CuS, which results into a color change from blue to black. The degree of color change, read on a linear scale on the colorimetric detection tube, is translated into an accurate measurement of the level of H₂S (as low as 0.2 ppm) present in the gas stream. Another small slip-stream from both the reject and permeate sides is allowed to pass through an adsorption bed (in order to remove its H₂S content), and is then used to measure the composition with an online gas chromatograph.

To carry-out the packed bed reactor experiments (to compare its performance with that of the MR) and for measuring the catalytic reaction kinetics, the same procedure is followed, except that the inlet and exit valves for the sweep gas are closed.

4.3. Modeling and Data Analysis

To analyze the data, we use an isothermal co-current flow (feed to permeate) MR model previously utilized by our group for describing such reactors [28]. Several assumptions are made in order to simplify the mathematical analysis. Briefly, it is assumed that the reactor operates isothermally (this has been validated experimentally) under ideal gas law conditions, and that the external mass-transfer resistances are negligible for the catalyst and the membrane. Catalyst internal diffusion limitations are included in the overall rate coefficients. Mass transfer through the membrane is described by the following empirical equation.

$$F_j = U_j (P_j^F - P_j^P) \quad (1)$$

where F_j is the molar flux for component j (mol/m². h), P_j^F (bar) the partial pressure for component j in the feed side, P_j^P (bar) the partial pressure for component j in the permeate side, and U_j (mol/m². h. bar) the permeance for component j .

Mass balances for each component in the feed and permeate sides are described by Equations 2 and 3, respectively.

$$\frac{\partial n_j^F}{\partial V} = -\alpha_m U_j (P_j^F - P_j^P) + v_j (1 - \varepsilon_v) \beta_c \rho_c r^F \quad (2)$$

$$\frac{\partial n_j^P}{\partial V} = \alpha_m U_j (P_j^F - P_j^P) \quad (3)$$

where n_j^F is the molar flow rate (mol/h) for component j in the feed side, n_j^P the corresponding molar flow rate (mol/h) in the permeate side, V the reactor volume variable (m³), α_m the surface area of the membrane per unit reactor volume (m²/m³), v_j the stoichiometric coefficient for

component j (negative for reactants and positive for products), ε_v the bed porosity in the feed side, β_c the fraction of the solid volume occupied by the catalysts, ρ_c the catalyst density (g/m^3), and r^F the WGS reaction rate ($\text{mol/g} \cdot \text{h}$)

The pressure drop in the packed-bed is calculated using the Ergun equation (Equations 4-6, below).

$$-\frac{dP^F}{dV} = 10^{-6} \frac{f (G^F)^2}{A^F g_c d_p \rho^F} \quad (4)$$

$$f = \left(\frac{1 - \varepsilon_v}{(\varepsilon_v)^3} \right) \left(1.75 + \frac{150(1 - \varepsilon_v)}{N_{\text{Re}}^F} \right) \quad (5)$$

$$N_{\text{Re}}^F \equiv d_p G^F / \mu^F \quad (6)$$

where P^F is the feed-side pressure (bar), A^F the cross-sectional area available to flow for the reactor feed side (m^2), μ^F the viscosity ($\text{g/m} \cdot \text{h}$), d_p the particle diameter in the feed side (m), $G^F = \rho^F u^F$ the superficial mass flow velocity in the feed side ($\text{g/m}^2 \cdot \text{h}$), u^F the average velocity of the fluid (m/h), ρ^F the average fluid density (g/m^3), and g_c the gravity conversion factor. The above set of equations are solved numerically together with the following boundary conditions:

$$n_j = n_{j0} \text{ and } P^F = P_0^F \text{ at } V = 0$$

where P_0^F is the inlet feed-side pressure (bar) and n_{j0} is the inlet molar flow rate for component j (mol/h).

CO conversion is defined by Equation 7.

$$X_{\text{CO}} = \frac{n_{\text{CO}o}^F - (n_{\text{CO},\text{exit}}^F + n_{\text{CO},\text{exit}}^P)}{n_{\text{CO}o}^F} \quad (7)$$

where $n_{\text{CO}o}^F$ is the CO molar flow rate at the inlet (mol/h), $n_{\text{CO},\text{exit}}^F$ is the CO molar flow rate at the exit of the reactor's feed side (mol/h), and $n_{\text{CO},\text{exit}}^P$ is the CO molar flow rates at the exit of the reactor's permeate side (mol/h). Hydrogen recovery (Re_{H_2}) is given by Equations 8 [7].

$$\text{Re}_{\text{H}_2} = \frac{n_{\text{H}_2,\text{exit}}^P}{(n_{\text{H}_2,\text{exit}}^F + n_{\text{H}_2,\text{exit}}^P)} \quad (8)$$

where $n_{\text{H}_2,\text{exit}}^F$ is the hydrogen molar flow rate at the exit of the reactor's feed side (mol/h) and $n_{\text{H}_2,\text{exit}}^P$ is the hydrogen molar flow rate at the exit of the reactor's permeate side (mol/h).

4.4. Results and Discussion

In what follows, we present the results, and describe and discuss their implications.

4.4.1. Kinetic studies

The kinetics of the WGS reaction has received substantial attention in recent years [e.g., 29-31].

Several researchers, in particular, have also studied the WGS kinetics over sour WGS catalysts [e.g., 32-36]. Various rate expressions have been reported and different mechanisms [29] have been proposed to explain the observed reaction rate equations. Most researchers, however, make use of an empirical, power-law rate expression, without reference to any specific reaction mechanism. In this study, a commercial Co-Mo/Al₂O₃ sour shift catalyst is utilized to perform the WGS reaction (the physical properties of the catalyst are shown in Table 4.1). The catalyst and quartz particles are crushed separately into smaller particles and their sizes are sorted with the aid of mesh-screens in the range of 600-800 μm . Prior to loading into the reactor, the catalyst is mixed and diluted with the quartz particles in order to completely fill the reactor space and to be able to conveniently operate the reactor bed under isothermal conditions. The catalyst particles are irregular in shape, but are roughly considered spherical for the estimation of the bed properties. Since the Co and Mo metal components of the fresh catalyst, as received, are in the oxidized form, they must be sulfided prior to the reaction. The activation procedure involves the *in-situ* reduction of the metals using a gas mixture containing H₂ and H₂S using the temperature and pressure protocol as specified by the catalyst manufacturer.

Catalyst form	Extrudates
Catalyst size	0.003 m
Chemical Composition	CoO: 3-4 wt% MoO ₃ : 13-15 wt% Al ₂ O ₃ : 80-85 wt%
Bulk Density	592.68*10 ³ g/m ³
Surface Area	160-220 m ² /g
Pore Volume	0.55-0.65*10 ⁻⁶ m ³ /g

Since the catalyst manufacturer did not provide any reaction rate information on the catalyst, a series of kinetic experiments have been carried out in a PB using 12 g of the catalyst intermixed with 90 g of the quartz at temperatures in the range of (220-300 °C), pressures in the range of (1-5 atm) and $\frac{W_c}{F_{CO}}$ (weight of undiluted catalyst (g) over the molar flow rate of CO (mol/h)) in the

range of (77-311). Results are shown in Figures. 4.2 and 4.3 in terms of CO conversion vs. $\frac{W_c}{F_{CO}}$

for a feed composition of H₂: CO: CO₂: CH₄: H₂S = 2.6:1:2.13:0.8:0.05 (corresponding to a fractional composition of 39.5 % H₂, 15.2 % CO, 32.4 % CO₂, 12.2 % CH₄ and 0.7 % H₂S) and a near stoichiometric H₂O/CO ratio in the feed of 1.2. To validate the reaction rate, the CO conversion data were fitted using nonlinear regression analysis and the following empirical rate expression was found to provide the best fit for all the experimental data generated (including the PB experiments carried out in tandem with the MR experiments):

Figure 4.2 CO conversion as a function of W_c/F_{CO} for various packed-bed reactor pressures at $T=250\text{ }^{\circ}\text{C}$

Figure 4.3 CO conversion as a function of W_c/F_{CO} for various packed-bed reactor temperatures at $P=3\text{ atm}$

$-r_{co} = 16.63 e^{\frac{-33280}{RT}} p_{co}^{0.692} p_{H_2O}^{0.266} p_{co_2}^{-0.334} p_{H_2}^{-0.570} (1 - \beta)$ where $\beta = \frac{1}{K_{eq}} \frac{(P_{CO_2} \cdot P_{H_2})}{(P_{CO} \cdot P_{H_2O})} \cdot P_j$ (bar) is the partial pressure for component j , and K_{eq} is the overall reaction equilibrium constant [37].

4.4.2. Membrane reactor experiments

The purpose of these experiments was to show that both the membrane and catalyst perform stably under the WGS reaction environment. In all the MR experiments reported here, we used a feed with composition (on a dry basis) of $H_2: CO: CO_2: CH_4: H_2S = 2.6:1:2.13:0.8:0.05$ (intended to simulate a coal gasifier's exit composition [38]) and a near stoichiometric H_2O/CO ratio in the feed of 1.2. Commercial WGS reactors generally operate in the presence of substantial excess steam. One potential advantage of WGS-MR is that they give the same conversion, at or near stoichiometric H_2O/CO ratios, thus the choice of the low H_2O/CO ratio in our experiments. Two different CMS membranes of the exact same dimensions ($L=254\text{ mm}$, $ID=3.5\text{ mm}$, $OD=5.7\text{ mm}$)

were utilized in the isothermal experiments reported here. The first membrane (CMS#1) with relatively high flux but moderate selectivity was used for a preliminary series of membrane reactor experiments, and also for an extended series of membrane characterization studies, with the entire series of experiments lasting for over one month. Table 4.2 presents three sets of mixed-gas permeation data. The first composition is that of the dry feed for the MR experiments. The second composition is the exit (on a dry basis) reactor composition corresponding to 70% CO conversion, while the third composition is the same as the second one, but with water being present (the lower H₂S content in the second and third compositions is because H₂S is purchased premixed in the CO gas cylinder). As can be seen in Table 4.2, varying the mixed-gas composition (including the H₂S concentration) has little effect on the permeance of most of the gases (other than hydrogen for which the permeance varies by <15%).

Table 4.2 Mixed-gas permeation data for CMS#1

Table 4.2 Mixed-gas permeation data for CMS#1		
	Gas Mixture Composition	
(1)	H₂:CO:CO₂:CH₄:H₂S = 39.5%:15.2%:32.4%:12.2%:0.7%	
Gas	Permeance m³/(m².h.bar)	Separation Factor (S.F)
H₂	1.37	1.0
CO	0.02	68.5
CO₂	0.05	27.4
CH₄	0.01	137.0
H₂S	0.01	137.0
(2)	H₂:CO: CO₂:CH₄:H₂S= 45.36%:4.52%:38.91%:11%:0.21%	
Gas	Permeance m³/(m².h.bar)	Separation Factor (S.F)
H₂	1.40	1.0
CO	0.02	70.0
CO₂	0.04	35.0
CH₄	0.01	140.0
H₂S	0.01	140.0
(3)	H₂:CO:CO₂:CH₄:H₂O:H₂S = 42.45%:4.233%:36.4%:10.29%:6.43%:0.197%	
Gas	Permeance m³/(m².h.bar)	Separation Factor (S.F)
H₂	1.56	1.0
CO	0.02	78.0
CO₂	0.05	31.2
CH₄	0.01	156.0
H₂O	1.1	1.4
H₂S	0.01	156.0

Figure 4.4 shows the CO conversion and H₂ recovery at three different $\frac{W_c}{F_{CO}}$ for the MR experiments at P=5 and permeate steam sweep gas ratios $SR = \left(\sum n_{j0}^P / \sum n_{j0}^F \right) = 0.1$ (the error bars reflect the carbon and hydrogen loss or gain due to the experimental errors in measuring the flow rates and compositions). In the experiments we used 15 g of the catalyst diluted with 80 g of ground quartz glass, packed inside the MR in the annular space between the reactor wall and the membrane (membrane shell-side). Shown on the same figure are the simulated conversion

Figure. 4.4 Comparison of the experimental (a) conversion (top) and (b) recovery (bottom) with the model predictions at T=250 °C, P=5 atm and sweep ratio=0.1 using CMS #1

and recovery lines using the model, utilizing the experimental rate expression, and the last set of mixed-gas permeances in Table 4.2. Figure 4.5 shows the conversion and hydrogen recovery at 250 °C for a different set of experimental conditions as shown in the figure caption.

Figure. 4.5. Comparison of the experimental (a) conversion and (b) recovery with the model predictions at T=250 °C, P=3 atm and sweep ratio=0.3 using CMS #1

In order to further explore the range of appropriate operating conditions for the CMS-MR, and to further validate the ability of membranes and catalysts to function stably, a second series of MR experiments for the WGS reaction were carried out at 300 °C, a temperature which pushes the limits of application for both the sour-shift catalyst and the CMS membranes. In these experiments, we again used the same feed gas composition and H₂O/CO ratio, with the experiments being carried out at two different feed pressures (3 and 5 atm, with the permeate side pressure under atmospheric conditions), and two different permeate steam sweep gas ratios of 0.1 and 0.3. In this series of experiments, in tandem with the MR experiments, we also carried out under identical conditions PB experiments (every MR experiment was followed by a PB experiment during which the permeate side is kept closed, as previously described). A different membrane (CMS#2), this time with high selectivity but relatively low permeability was utilized, and 10 g of the catalyst diluted with 80 g of ground quartz glass was packed in the membrane shell-side (the reactor shell-side volume was slightly smaller in these series of experiments, thus the use of a smaller amount of catalyst).

Figure 4.6 Compositions of (a, top) reject and (b, bottom) permeate side at $P=3$ atm and sweep ratio=0.3

Since the emphasis in these experiments was on the MR performance, we carried out only a limited number of permeation studies using single gases before and after the MR experiments. Prior studies by our group with several of these membranes indicate that the mixed-gas permeances of the various gases generally remain relatively close to the values measured during the single-gas experiments [14]. Table 4.3 indicates the single gas permeances for this membrane measured prior to the initiation of the reactor experiments. For H₂S, the MR experiments indicated that it does not permeate through the membrane (within the detection limit of the Drager tube utilized) and, hence, its permeance was taken to be zero, since it has no impact on the modeling results. (In extensive studies in which both the surface of the membrane module and the plumping were specifically coated to avoid potential wall adsorption, the H₂S permeance was always found to lie in between the permeance of CO/N₂ and CH₄). The permeance of water was deduced by fitting all the compositional data available for both the reject and permeate sides of the MR (e.g., see Figure 4.6 for the fit for one set of such data). The MR experiments lasted more than one month during which period membrane gas permeances changed less than 7% before and after the experiments, indicative of the good stability of the membranes under the WGS-MR environment. The model discussed earlier was again used to simulate the experimental results, together with the experimental empirical power-law rate expression and the experimental single-gas permeances (Table 4.3) as discussed above.

Figure 4.7 shows the CO conversion and H₂ recovery at three different $\frac{W_c}{F_{CO}}$ for the MR and PB experiments at 3 atm and a steam sweep ratio of 0.1. Figure 4.8 presents the CO conversion and H₂ recovery at the same conditions mentioned above, but at a steam sweep ratio equal to 0.3.

Figure 4.7 Comparison of the experimental (a, top) conversion and (b, bottom) recovery with the model predictions at T=300 °C, P=3 atm and sweep ratio=0.1 using CMS #2

Figures 4.9 and 10 show the CO conversion and H₂ recovery for the MR and the PB experiments at 5 atm and steam sweep ratios equal to 0.1 and 0.3, respectively (the solid lines in the figures represent the modeling results).

Table 4.3 Single-gas permeation data for CMS#2 (*Fitted value)

Pure Gas		
	Permeance m ³ /(m ² .h.bar)	Separation Factor (S.F)
H₂	0.5354	1
CO	0.0037	145.88
CO₂	0.0107	50.03
CH₄	0.0014	31385.18
H₂O*	0.0922	5.8

These figures make it clear that the model does, generally, a good job in predicting the experimental MR as well as the PB behavior. The MR attains conversions which are higher than those for the packed-bed. The relatively low conversions are due to limitations with the size of our laboratory system, which accommodates only one small CMS membrane, and the limited amount of catalyst that can be filled inside the small reactor. The pressure drop measured in the laboratory (and also the one calculated using the Ergun equation) was also negligible due to the same reasons. Higher conversions can be attained for higher $\frac{W_c}{F_{CO}}$, as the simulation results also

indicate (see below). We are limited, however, in our laboratory system by the amount of catalyst that can be utilized. Once the amount of catalyst is fixed, the maximum value of $\frac{W_c}{F_{CO}}$

attained is determined by the minimum flow rate one is able to provide, reflecting the lower limits of the MFC in our experimental system (it should be noted, however, that high $\frac{W_c}{F_{CO}}$ values

are also not interesting for practical applications).

A key conclusion from this series of experiments is that the membrane and the catalyst exhibited robust behavior and remained stable throughout the series of experiments which lasted almost one month in the presence of hydrogen sulfide under the harsh WGS environment.

Figure 4.8 Comparison of the experimental (a, top) conversion and (b, bottom) recovery with the model predictions at $T=300$ °C, $P=3$ atm and sweep ratio=0.3 using CMS #2

Figure 4.9 Comparison of the experimental (a, top) conversion and (b, bottom) recovery with the model predictions at $T=300\text{ }^{\circ}\text{C}$, $P=5\text{ atm}$ and sweep ratio=0.1 using CMS #2

Figure 4.10 Comparison of the experimental (a, top) conversion and (b, bottom) recovery with the model predictions at $T=300\text{ }^{\circ}\text{C}$, $P=5\text{ atm}$ and sweep ratio=0.3 using CMS #2

4.5.

Reactor

Design and Scale-up

Since the model performs reasonably well in describing the experimental results, it can be used to further study the effect of various parameters on WGS-MR performance, in terms of reactor conversion, hydrogen recovery, and purity. The target here is to choose appropriate conditions which maximize both the CO conversion and H_2 recovery, and minimize the CO content of the hydrogen product. In the simulations that follow the experimental power-law reaction rate expression together with the experimental single-gas permeances for the CMS#2 membrane were used. The membrane length is increased to 1 m and it is assumed that the catalyst and quartz are packed along the entire length of the membrane. The conditions utilized,

unless otherwise noted in the figures' captions, are listed in Table 4. 4.

Table 4.4 The base-case and the range of the experimental conditions used in the simulations

Parameter	Base case	Applied range
Feed side pressure (P^F)	5 atm	5-30 atm
Permeate side pressure (P^P)	1 atm	-
Reactor temperature (T_R)	300 °C	-
Steam sweep to feed ratio (SR)	0.3	0.3-2
Number of membranes	1	1-4
Length of the membrane (L)	1 m	-
Inner diameter of the membrane (ID)	0.0035 m	-
Outer diameter of the membrane (OD)	0.0057 m	
Inner diameter of the reactor	0.0318 m	
Weight of the catalyst (W_c)	10 g	-
Hydrogen permeance	0.54 m ³ /(m ² .h.bar)	0.5-3
H ₂ /CO separation factor (S.F)	146	100-300

Figure 4.11 shows the effect of pressure. Since the coal gasifier typically operates in the

Figure 4.11 Effect of pressure on (a, top) conversion and (b, bottom) recovery, $L=1$ m, $T=300$ °C and sweep ratio =0.3

pressure range of 20-30 atm [39], the advantages of operating the CMS-MR at high pressures is obvious. Increasing the pressure helps increase both the conversion and the hydrogen recovery by increasing the partial pressure difference of hydrogen across the membrane. The pressure effect is more prominent at lower $\frac{W_c}{F_{CO}}$, and for a constant weight of catalyst that means higher

feed flow rates. As expected, even at the highest pressures the reactor does not attain complete conversion due to the omnipresent loss of CO, which indicates that a more appropriate type of reactor may be a hybrid system consisting of a packed-bed, followed by an MR [40].

Figure 4.12 shows the effect of the sweep ratio. As the figure indicates, increasing the SR increases both the conversion and recovery, as expected, since sweeping helps maintain the permeate-side partial pressures low. Increasing the sweep ratio does not affect the CO transport through the membrane as much as increasing the reactor side pressure, and as a result the impact of CO loss is not as severe and CO conversion continues to increase as the sweep ratio increases. Figure 4.13 shows the effect of the membrane area on the MR performance. In these simulations, we have kept the amount of catalyst constant and have increased the number of membranes that are packed into the reactor. The amount of quartz utilized has been adjusted to fill the annular space between the membrane and the reactor wall (we estimate that we can comfortably fit up to four membranes inside the reactor). As Fig. 4.13 indicates, increasing the number of membranes (n), which translates into increasing the membrane area per unit catalyst weight, increases both

CO conversion and H₂ recovery, due to the more rapid transfer of products to the permeate side. This favorably shifts the reaction equilibrium towards the product side. Similarly to the pressure

Figure 4.12 Effect of sweep ratio on (a, top) conversion and (b, bottom) recovery, $L=1$ m, $T=300$ °C and $P=5$ atm

effect, the effect of increasing the membrane area is stronger at lower $\frac{W_c}{F_{CO}}$, which at constant weight of the catalyst corresponds to higher feed flow rates.

Figure 4.14 shows the effect of varying the H₂ permeance on the MR performance (while keeping the separation factors towards the other species constant, as indicated in Table 4.3). As expected, increasing the H₂ permeance helps increasing both CO conversion and H₂ recovery, the effect being more pronounced for the hydrogen recovery. Figure 4.15 shows the effect of varying hydrogen permeance (while maintaining the separation factors constant) on CO concentration (on a dry basis) in the product stream. Note that while higher permeances have a positive impact on CO conversion and hydrogen recovery, they have, on the other hand, a negative impact on hydrogen purity. Finally, Figure 4.16 shows the effect of varying the H₂/CO separation factor by varying the CO permeance, while maintaining the permeances of all other species constant (see Table 4.3), on the CO concentration (on a dry basis) in the product stream. Decreasing the CO permeance impacts the conversion (not shown here) by decreasing the inadvertent CO loss to the permeate side, but as expected, its most significant impact is lowering the CO concentration in the product stream.

As noted previously, the proposed “one box” approach is being studied in the context of IGCC power plants, where the goal is to carry out the WGS step without the need to cool the gasifier off-gas stream to remove its various contaminants (e.g., H_2S) and then having to reheat it back to the WGS reaction temperature. Turbines, internal combustion (IC) engines and proton exchange membrane (PEM) fuel cells have been studied for power generation using the hydrogen-enriched syngas. Turbines and IC engines are significantly more tolerant to low levels of sulfur, CO and other contaminant than PEM fuel cells. If PEM fuel cells are the option of choice for power generation, however, then as the simulations above indicate an additional polishing step (absorption/adsorption for the H_2S and other contaminants and preferential oxidation for CO) may be required. However, the energy needed for such a step, when treating the permeate stream of the proposed “one-step” process, is likely to be a fraction of what would be needed to treat the off-gas of a conventional sour-shift reactor.

Figure 4.13 Effect of the membrane area on (a, top) conversion and (b, bottom) recovery, $L=1$ m, $T=300$ °C, $P=5$ atm and sweep ratio=0.3

Figure 4.14 Effect of the H₂ permeance on (a, top) conversion and (b, bottom) recovery, L=1 m, T=300 °C, P=5 atm and sweep ratio=0.3

Figure 4.15 Effect of the H₂ permeance on CO concentration in the product stream, L=1 m, T=300 °C, P=5 atm, sweep ratio=0.3 and H₂/CO separation factor (S.F) = 146

Figure 4.16 Effect of the CO permeance on CO concentration in the product stream, L=1 m, T=300 °C, P=5 atm, sweep ratio=0.3 and H₂ permeance = 0.54 m³/(m².h.bar)

4.6. Conclusions

In this study, the “one-box” process which combines reaction and membrane separation in the same unit was experimentally evaluated for the WGS reaction. The kinetics of the same reaction over sulfided Co-Mo/Al₂O₃ catalyst was investigated and a data-validated rate expression and kinetic parameters were obtained. Nanoporous carbon molecular sieve

membranes were used for the *in-situ* hydrogen separation. The membranes' performance was investigated under the operating conditions and their transport properties were used for the model predictions. The modeling studies indicated good agreement with the experimental data. The MR performance was investigated for a range of pressures and sweep ratios, and showed higher CO conversions and H₂ purity compared with those of the traditional packed-bed reactor. The effect of the membrane properties and experimental conditions on the performance of the system was also investigated. The "one-box" process proved to possess several advantages over the traditional systems including increasing CO conversion, decreasing the amount of steam required for the reaction, and being able to deliver a product with significantly lower CO content. Using impurity-resistant catalyst adds another advantage to this system by allowing one to perform the reaction in the presence of hydrogen sulfide; for the IGCC power plants this would result in considerable energy savings. The catalyst and the CMS membranes have demonstrated good stability in the presence of hydrogen sulfide in continuous reactor experiments lasting over a month.

5. Field Tests

5.1. Overview of Our Field Test Program and Accomplishments in 2008-10

The ultimate objective of this project is to demonstrate the technical feasibility of our proposed hydrogen separation process for coal derived syngas without the gas pretreatment for contaminants removal. Unfortunately simulating the actual coal-derived syngas contaminants profile in the lab is next to impossible. Thus, parts of the tasks of this project were involved in conducting the field test using the full-scale membrane product developed from this project fed with actual coal gasification off-gas. Our field test activities under this project were progressive in phases, i.e., from the initial testing with single tubes to the final testing using the full-scale module as shown in Table 5.1 below:

Table 5.1 Field Tests Conducted at NCCC under This Project				
Scale	Dimension	Membrane Surface Area (m²)	Estimated H₂ Throughput [SCFH]	Test Status at PSDF
Single tube	0.3cm id x 0.57cm od x 30"L	0.009	1.5	Completed
Pilot scale bundle	1.5" dia x 30"L packed with 13 single tubes	0.115	19	Completed
Full scale bundle	3" dia x 30"L packed with 86 single tubes	0.762	128	Completed
Multiple-bundle module	Stainless steel housing packed with 3 to >9 full scale bundles	2 to >10	400 to >1,500	Future test phase

During this project, we have completed the tests using single tube, pilot scale bundles and full scale bundles at National Carbon Capture Center (NCCC) (Wilsonville, Alabama) as described in Table 5.1. The test remained to be completed is the demonstration using the multiple-bundle module, which is outside the scope of this project. The pictures of the membranes representing the three different scales used in the field tests are shown below:

The details of the early tests involving single tubes and pilot scale bundles are summarized in major accomplishments below as background information for the full scale module tests which are discussed separately in Sec. 5.2:

- Membrane operation at ~275°C effectively prevented the “tar”-like deposition on the membrane surface/in the membrane pores and steady permeance was demonstrated for operation >100 hours.

In the beginning (2009), our membrane fed with the coal-derived syngas pretreated with a “scrubber” showed steady state permeation at a lower temperature, i.e., 175°C. During 2010, one of our objectives was the elimination of pretreatment required for our CMS membrane filtration. During the test in April 2010, we observed nearly 80% reduction in permeate flux for the membrane operated at this low temperature, but fed with coal gas without pre-treatment. Obviously the “tar” like deposition fouled the membrane surface. Further, we noticed the elevation of the operation temperature to 230°C eliminated most fouling, i.e., about 10% instead of 80% loss in permeance. During the August trial, we modified our test unit to accommodate the membrane permeation at a much higher temperature, i.e., 275°C, no permeance reduction was observed, indicating the higher temperature operation was necessary to prevent the deposition of tar. Subsequently, our membrane was operated for >100 hours continuously at this higher temperature without any degradation in membrane performance and materials. In summary, our tests in 2010 have demonstrated that the membrane maintained its performance and material stability at this elevated temperature, i.e., 275°C, with the coal gasifier off-gas without gas pretreatment for contaminants removal.

Significance... The success of this higher temperature operation confirms the process feasibility of warm gas separation via membrane and the advantage of “no pretreatment for contaminants removal” from coal gas. Moreover, this warm gas temperature is compatible with the operating temperature for water gas shift reaction via sour gas shift catalysts. Therefore, process intensification via integration of gas clean-up, water gas shift reaction, and H₂ separation into a single step is technically feasible.

- Pilot scale CMS membrane bundles were employed, which delivered ~20 scfh H₂. The bundle configuration and housing design employed for these tests have proven adequate for the selected operating condition, i.e., 270 to 300°C and 250 psi for a period of >300 hours. During the two tests conducted in 2010, we have methodically scaled up our test membrane unit to “multiple single tubes” first and then “pilot scale multiple tube bundle” from the single tube membrane used in the previous tests. The pilot scale CMS membrane bundle used in the August 2010 test delivered 20 scfh H₂, which is about 17X higher than that used in the previous test. The bundle configuration and housing design have proven adequate for the selected operating condition, i.e., 270 to 300°C and 250 psi for a period of >300 hours. The bundle design, i.e., potting of 17 single tubes into a bundle, was satisfactory, i.e., no leakage and no crack, with respect to the operation temperature and pressure. Further, our design for seal between metal housing and membrane element proves satisfactory, i.e., no significant leakage was detected. In summary, our scaled-up version of membrane, i.e., potting single tubes into a multiple

tube bundle, was successfully demonstrated throughout the two tests performed during 2010.

Significance... One of the major commercialization barriers associated with the inorganic membranes for high temperature gas separations is the field implementable module/housing/element design, in particularly for applications under the coal gasification environment. Our tests in 2010 have methodically proven the adequacy of our housing/module design for field operation under the selected operating condition. Further, the successful demonstration of the pilot scale bundle during 2010 established an important milestone to justify the test of the full scale membrane bundle (i.e., 5X of the pilot scale), which was held in yr 2011.

- Our hydrogen selective membrane bundle was able to enrich the gasifier off-gas to >90% H₂ along with H₂S and CO₂ rejection. No membrane degradation in the presence of H₂S was observed throughout the two tests in 2010.

During our two tests in 2010, our CMS membranes consistently enriched hydrogen to >90% purity from 30-40% in the feed with the multiple single tubes and pilot scale bundles. Through permeation of H₂ to the permeate side, our membrane retains CO₂ in the reject side. In general, the CO₂ concentration in the feed during our test was ca. 6 to 8% for hydrogen sweetened syngas, the CO₂ concentration in the permeate ranged 2 to 3% in the sweetened gas. H₂S in the concentration of 280 to 350 ppm was reduced to 20-90 ppm in the permeate, evidently the removal efficiency of CO₂ and H₂S is lower than those levels demonstrated previously using single tubes, i.e., >98% H₂ purity and <15 ppm H₂S consistently. Our post mortem analysis indicated that the membrane peak selectivity was located at the lower temperature as originally designed. Our 2010 tests performed at the higher temperature, i.e., 275°C, recommended fine tuning of the membrane porous structure to elevate its peak performance temperature at the selected operating temperature determined in the 2010 tests.

Significance... Although our hydrogen selective membrane has demonstrated its hydrogen separation ability from raw syngas along with the rejection of CO₂ and H₂S in 2010, the degree of selectivity was lower than what demonstrated previously in 2009. Fine tuning of the peak performance temperature of the membrane in response to the elevated operating temperature identified in 2010 was necessary. The modified membrane porous structure in response to this requirement was incorporated for the test in 2011 using a full-scale bundle.

In short through the field tests conducted in 2009-2010, we confirmed the process viability of hydrogen separation and the removal of CO₂ and other contaminants from coal-derived syngas without gas pre-treatment for contaminants removal. Based upon the success of the test using the pilot scale bundle in 2010, we moved forward for the full-scale bundle test in 2011.

5.2. Overview on Tests Conducted in Yr 2011-12 using Full-Scale Membranes and Modules

Our tests at NCCC in Yr 2011-12 focused on the testing of the full scale CMS membrane bundle fed with gasifier off-gas with no gas pretreatment for contaminants removal. Also included in this testing was our Pd-Cu alloy membrane for H₂ enrichment to >99% from the product

Figure 5.2 Full scale ca. 85-tube CMS membrane bundle (full ceramic-glass potting) suitable for high temperature and high pressure operation. Also shown is the full scale module. The module used in the NCCC is stainless steel construction (unlike the carbon steel prototype shown here).

generated from our CMS membrane. The primary goal of this phase of the testing was to demonstrate the performance stability of the full-scale CMS membrane and bundle in the presence of coal-derived syngas with no pretreatment, specifically:

- Demonstrated the mechanical stability of the full scale 3" bundle and module product in actual gasifier off-gas. The full scale bundle consists of ca. 85-single tubes potted into a ceramic collar as shown in Figure 5.1 for high temperature high pressure applications.
- Reproduced the separation performance established previously with the single tubes and pilot scale elements.

- Evaluated the post treatment concept to enrich hydrogen to >99+% purity with a palladium membrane.

During our previous tests, we have used single tube CMS membranes (0.35 cm ID, 0.57cm OD, and 30”L) and pilot-scale bundles composed of 14 full length singlet tubes to evaluate the membrane separation efficiency and performance stability in the presence of coal gasification off-gas. During 2011-12, testing was scaled up to our full scale bundle consisting of ca. 85 tubes potted into a ceramic collar using our ceramic glass formulation. The bundle is suitable for temperature up to ca. 300°C and pressures (transmembrane) of 300+ psi. One of the bundles and the full scale module are shown in Figure 5.2. Note that the module used for test during this period was SS316 construction making it suitable for operation in corrosive atmospheres, for instance H₂S.

5.3. Full Scale Membranes, Modules and Field Testing Unit used in Yr 2011-12

Construction of the full scale field testing unit was completed at our pilot plant and shipped to the NCCC for field test operations conducted during October thru December of 2011. Final installation at the NCCC was completed in early October 2011 with the help of NCCC personnel. In addition to the CMS membrane, the unit was also configured to accept single tube Pd membranes for polishing of the permeate from the CMS subsystem and to enrich the H₂ content beyond 99%. The unit installed at the NCCC is shown in **Figure 5.3**.

Figure 5.3 Full scale CMS bundle testing unit as installed at the PSDF facility. The unit is configured to accept one full scale 85-tube bundle.

5.4. Test Results obtained from Full-Scale Membrane Unit in Yr 2011

The full-scale membrane bundle (B3-7) was installed in the field test unit in late mid-October 2011 and testing was conducted with this membrane for approximately 220 hours in the presence

of NCCC gasifier off-gas with no gas pre-treatment. Figure 5.4 shows the operating test conditions for this bundle during the test period. In general, the operating temperature was maintained at ca. 250°C throughout at a target pressure of ca. 200psig. The permeate pressure was maintained at ca. 3 to 5 psig. The feed rate (permeate + reject flow) of gasifier off-gas was varied at times to check the influence on membrane performance but in general was maintained at ca. 150 to 250 liters/min. Test results are highlighted below:

- Gas Permeations with the full scale bundle B3-7 were stable throughout the ~220 hrs of continuous testing.

Figure 5.5 below shows the H₂ and CO₂ composition of the feed and permeate gas streams. The balance was primarily N₂ (air blown gasifier) with small amounts of CO and light hydrocarbons. In addition, H₂S and other sulfur species content of the feed was typically in the ~300 ppm range. Water content in the feed was ca. 6 to 8%. In general, the raw syngas feed H₂ content was in the range of 7 to 8%, typical of syngas generated from the air blown gasifier. Permeate H₂ content of about 30% was typical from this CMS bundle. According to our simulation, H₂ purity in the permeate was expected to be at ~40%. The below-than-expected hydrogen purity was attributed to the non-ideal feed flow distribution within the module as a result of the extremely high feed flow rate used in this test. Additional discussion is presented as a separate bullet item later under this section.

Figure 5.6 shows the helium and nitrogen permeance of the B3-7 bundle during this phase of the testing. Single gas components of helium and nitrogen were used to determine the permeation properties of the membrane throughout the test. As is clearly evident, the membrane performance was highly stable under these operating conditions in the presence of gasifier off-gas that had not been pretreated for the removal of gas phase contaminants.

- About 40% reduction in hydrogen separation efficiency was observed consistently throughout the test, attributed to the non-deal flow distribution within the module under the feed flow rate much higher than the rates tested previously.

Although membrane permeance stability was excellent throughout the 220 hours of testing of the full scale B3-7 bundle, the selectivity in the mixed gas testing was consistently lower than expected as discussed above. Specifically, the permeate quality was lower than predicted by (i) mathematical modeling and (ii) the preliminary mixed gas performance testing of the bundle in the laboratory. Based upon the pure component He permeance and He/N₂ selectivity (ca. 2.1 to 2.3 m³/m²/hr/bar and 55-70, respectively) our modeling data predicted a permeate H₂ content of 38 to 40% versus the generally <32% shown in Figure 5.5. Additionally, based upon the permeate quality and flow rate, the H₂ permeance was estimated to be ca. 1.3 to 1.5 m³/m²/hr/bar during this test as shown in Figure 5.7, which was considerably lower than the pure component He permeance of 2.1 to 2.3 m³/m²/hr/bar. Note that H₂ permeances are typically 10 to 25% greater than the He permeance in our CMS parts. The low H₂ purity and permeance obtained from

syngas versus the pure component results obtained from the gas cylinders throughout the test was unexpected. In mixed gas He and N₂ testing of this bundle prior to shipment to the NCCC facility, we found excellent agreement between the pure and mixed gas permeances based upon our mathematical model. The specific source of the problem was attributed to mal-distribution of feed gas throughout the bundle as the problem discussed in Chapter 3, which is further discussed in the next section.

Figure 5.7 Permeance of helium and nitrogen during gasifier off-gas testing conducted with the B3-22 CMS bundle at 250°C.

- Mal-distribution of the feed gas in the bundle was identified as the source of the reduction in separation efficiency based upon our previous experience and the extremely higher flow rate used in this field test.

It is interesting that we have noted this type of problem in the past during the early development and testing of the 85-tube bundles in our laboratory. Specifically, the fast gas permeances, such as He and H₂, were reduced in the mixed gas testing of our bundles. This was found to be attributed to feed gas short circuiting around the bundle to the reject outlet. To remedy this problem, the bundles are now equipped with reinforced baffles to

prevent feed gas bypass as detailed in Chapter 3. Without these baffles, mixed gas permeances of the fast gases will generally be 30 to 50% less than the pure component values. This is most likely due to the situation that the tubes in the center of the bundle rapidly deplete the H_2 or He and are “starved” for feed gas.

Visual inspection of the B3-7 bundle after the test was conducted and is shown in Figure (right hand picture). As is apparent in the picture, there is no evident problem with the installed baffle and specific failure of this baffle was rejected as a source of the difference between the mixed and pure component gas results at the NCCC.

Figure 5.8 (Top left) Contaminant buildup during previous testing at the PSDF with the multiple single tube module. No contaminant buildup was noted in the full scale module (bottom left) or the membrane (right) during the current phase of testing with the operating temperature maintained at 250°C.

Given that (i) this baffle appears to be undamaged in the B3-7 bundle and (ii) we experienced the same mixed gas H_2 permeance loss in the B3-22 bundle, we suspected

that the problem may have been related to poor feed gas distribution to the interior tubes, particularly at very high feed flow rates tested at the NCCC. In our laboratory testing, gas feed rates of ca. 30 to 50 liters per minute were used and pure and mixed gas permeances, particularly of H_2 , were within 5%. However, a much higher feed rate, i.e., from 150 to 250 liters per minute, was used during NCCC testing. At these high feed rates, we suspect that there was a gas distribution problem to the interior tubes in the bundle. The source of this problem was the close packing of the bundle and hence the potentially high pressure loss that occurred in the center of the bundle as the gas exited through the external tubes to the reject. This problem was corrected in a subsequent test conducted in 2012, which is discussed in Sec. 5.5.

- Enrichment of the H_2 content to >99% via post treatment with a Pd membrane was demonstrated for about 10 hours during this test.

The primary advantage of the CMS membrane is its excellent stability in the presence of aggressive gas phase contaminants such as sulfur and nitrogen species (H_2S , NH_3 , etc.) and tars (naphthalenes, etc). However, the CMS membrane selectivity is not high enough to deliver high purity H_2 (>99%) from gasifier off-gas for applications, such as PEM fuel cell, and will need to be polished with other technology if this purity is required. As part of our NCCC testing program, a Pd-alloy membrane developed by us was incorporated in-series with the CMS membrane as a post-treatment to consistently deliver high purity H_2 (>99%) from gasifier off-gas with no gas pretreatment. The primary disadvantage of the Pd-alloy membranes is the high sensitivity to sulfur and other species in the coal-derived syngas. As a post-treatment, the Pd-membrane is exposed to the treated syngas gas which is free from sulfur contaminants and contains a much higher percentage of hydrogen. Thus, hydrogen purity can be further enhanced by the Pd membrane which is not susceptible to chemical degradation. 5.9 shows the results for an MPT Pd-Cu alloy membrane (PdCu-500-6) operating on the NCCC gasifier permeate generated from the CMS membrane bundle, B3-22. The feed H_2 content to the Pd membrane is ca. 78 to 84%. The permeate composition was consistently above 99% throughout the approximately 10 hours of testing. Further, no degradation in the performance of the Pd membrane was noted over this time frame. The technical feasibility of using Pd membrane as post-treatment for upgrading the hydrogen permeance from the CMS membrane was demonstrated during this field test.

- The full-scale membrane bundle/module demonstrated its fouling resistance to tar-like species, which were identified as the fouling source during our previous tests. Operation at the temperature $\geq 250^{\circ}\text{C}$ recommended from our lab and previous field tests was thus confirmed during this field test using a full-scale CMS bundle/module.

In the previous testing conducted with single CMS tubes configured into a multi-tube housing at the NCCC in 2010, we experienced flux decay as a result of buildup of tar-like species on the membrane surface. In laboratory testing, we have demonstrated that this was a result of operating at temperatures below a critical temperature that leads to condensation of the tar-like species in the module as summarized in Chapter 2. Visual evidence of “tar” buildup in previous testing at the NCCC is shown in Figure 5.8 (top left). This problem was solved by operating at temperatures above 220°C , preferably $>250^{\circ}\text{C}$. Given this previous experience at the NCCC, the current B3-7 bundle was removed from service and visually inspected for any buildup of contaminants in the module or on the membrane. **Figure** (bottom left) shows the results. Previous testing resulted in considerable buildup of a “greenish” contamination inside the module (see top left picture). During this current round of testing, no evidence of similar build up is noted on either the module or the CMS

membrane element after >220 hour run as shown in Figure 5.8 (bottom left). This result is consistent with our laboratory testing as well as the performance stability of the CMS bundle noted in **Figure 5.5**. This field test confirms the fouling resistance of our CMS membrane in the presence of tar-like materials in coal-derived syngas.

The results obtained from this field test demonstrated the technical feasibility of the proposed "one box"-like process for hydrogen separation from coal-derived syngas without gas pre-treatment. However, the separation efficiency of the full-scale bundle/module tested during 2011 was found much lower than the performance obtained from the single components and the binary gas mixtures performed at our pilot plant prior to this test. Mal-flow-distribution within the module was aggravated under the extremely high feed flow rate used in this test. Additional tests in 2012 were performed to correct this deficiency of the full-scale bundle.

5.5. *Field Tests using Full-scale Module with Reinforced Internal Baffles in 2012*

The field testing conducted in Yr 2011 demonstrated the performance and material stability of the full-scale membrane/module for ~220 hrs of continuous operation. However, the separation efficiency, i.e., the enrichment of hydrogen from the coal-derived off-gas without gas pre-treatment, was much lower than the expected level obtained from the previous tests using single tubes and pilot scale module. Mal-flow-distribution within the module was the main source of the below-the-expected efficiency, in particular when the module was fed with syngas at a high flow rate. The off-line analysis and internal diagnosis at our pilot plant confirmed the source, which was then corrected with the reinforced internal baffles as discussed in Sec. 3.2. During Yr 2012, we performed the off-line test at NCCC using He/N₂ binary mixtures to verify the separation efficiency of the module. $\geq 90\%$ of the efficiency obtained by the single tubes was achieved as discussed in Sec. 3.2. Under this section, we present the hydrogen enrichment results obtained from this improved module fed with the actual gasifier off-gas at NCCC.

Hydrogen concentration in the gasifier feed is ~10% as shown in Figure 5.10, typical for the air blown gasifier off-gas generated at NCCC. The balance of the feed is primarily N₂, at about 75%; CO₂ content is about 10%. The remaining is CO, about 5%, according to our estimate. Due to the significant feed composition fluctuation, no water content was analyzed. H₂S contaminant level is at 387 to 415 ppm according to our analysis with Drager tube. It should be noted that the membrane was exposed to the syngas with significant water; thus, the actual concentrations of these gas components the membrane was exposed are much lower than what reported in Figure 5.10. Feed with this composition at 150-200 liter/min was fed to the module without pre-treatment during our test for about 10 hours. Hydrogen purity was enriched from 2-7% in the reject to 30 to 50% in the permeate on the dried basis as shown in Figure 5.11. Nitrogen content was reduced to 25 to 50% level as shown in Figure 5.12 along with the concentration of other components. Hydrogen was enriched to the level similar to the early field tests we conducted using the single tube, indicating that the module efficiency approached that of the single tube. In contrast, hydrogen was enriched to a much lower level, about $30 \pm 5\%$ with the reject at ~7% in the last field test shown in Figure 5.5 using the original module (i.e., without the reinforced baffles). H₂S was reduced to the level of 62 to 90 ppm with the Drager tube. The significant improvement in the hydrogen enhancement during this test indicates that the module with the

reinforced baffles improved the separation efficiency significantly. Due to the lack of the actual composition on the wet basis, no simulation was performed to verify the level of the separation efficiency improvement with the syngas. However, the off-line test using He/N₂ mixtures indicated ~90% separation efficiency was achieved as documented in Sec. 3.2.

Due to the lower hydrogen concentration generated from the air blown gasifier, we did artificially dose the syngas with the bottled hydrogen to the level generated by the oxygen blown gasifier, i.e., ~40%, during our previous tests. We did not perform a similar test for the 2012 test. However, a mathematical simulation was performed using the gas permeances obtained from this improved module for the feed generated from oxygen blown gasifier with the composition as shown here, which simulates the coal-derived

syngas after some degree of water gas shift reaction. Hydrogen can be enriched to 92 to 96% on the dried basis, and 62 to 64% on the wet basis at the recovery ratio of 90 to 40% respectively as shown in Figure 5.13. For the purpose of hydrogen production, the enrichment to the purity of 92% at the 90% recovery is substantial. Although a post treatment may be necessary, such as the use of the Pd membrane as

Components	[-]	Permeance [$\text{m}^3/\text{m}^2/\text{hr}/\text{bar}$]
H ₂	0.41	0.9
CO	0.14	0.01
CO ₂	0.28	0.01
H ₂ O	0.16	0.85
N ₂	0.01	0.009
Total	1	

discussed in Sec. 5.4, to enhance its purity to 99+% as demonstrated in Figure 5.9 for sale as chemicals and for PEM fuel cell applications. On the other hand, a high degree of hydrogen enrichment to the 60+% concentration on the wet basis is ideal for power generation application with carbon capture and storage (CCS) (see Case 3a in Sec. 6.2). Significant steam present at this temperature and pressure can reduce or eliminate the diluent requirement for power generation by turbines. The generation of the diluents requires significant parasitic energy consumption as discussed in Sec. 6.2 of Chapter 6.

In summary, the field test conducted in Yr 2012 supported the improvement with the reinforced baffles for our full-scale CMS module through off-line He/N₂ mixtures and the actual air blown gasifier off-gas. Further, our simulation based upon the gas permeance obtained from this improved module indicates that hydrogen at 95+% and 60+% purity on the dried and wet basis can be produced from the coal-derived syngas generated from an oxygen-blown gasifier.

5.6. Conclusions

Our multiple field tests conducted at NCCC have been focused on the testing of the hydrogen separation and contaminants removal by the CMS membrane bundle/module in the presence of gasifier off-gas with no gas pretreatment. Also included in this testing was our Pd-Cu alloy membrane as post treatment for H₂ enrichment to >99%. This field testing has been highly successful, and has demonstrated the technical feasibility of our proposed "one-box" like process using the full-scale CMS membranes/modules with actual coal-derived syngas. Specific conclusions are summarized below:

- *We successfully verified the separation performance and material stability of our full scale CMS membrane bundle (86-tube, ~0.8m²). This full-scale bundle/module has been successfully challenged with gasifier off-gas (syngas) feed rates as high as 600 scfh at >200 psig and >250°C. Over 300 cumulative hours of performance testing was conducted with two full scale membrane bundles with no observed degradation in their permeances.*
- *Membrane operation at ~250°C effectively prevents "tar"-like residue deposition on the membrane and module, evidenced by the post-mortem module analysis and the permeances without degradation throughout the test. This is consistent with our laboratory experience conducted with synthetic organic and tar species (see Sec. 2).*

- *The CMS bundle configuration and housing design employed for these tests have proven adequate for the selected operating condition, i.e., 250 to 300°C and >200 psi for a period of ~220 hours of continuous operation. No obvious visual or performance degradation was noted in either the CMS bundle or module. The full-scale CMS membranes/bundles/modules developed under this project are ready for future field tests.*
- *No membrane degradation in the presence of H₂S and other syngas contaminants was observed during the multiple tests conducted between 2009-2012, which confirms the chemical stability of the CMS membrane established in our lab evaluation using H₂S as a model contaminant (see Chapter 2).*
- *H₂ purity in excess of 99% was achieved using our Pd-Cu alloy membrane as a post treatment to our CMS membranes at NCCC. No performance degradation was noted with this Pd membrane in the 10 hours of feasibility testing conducted.*
- *Our simulation indicates that >94% hydrogen (dried basis) with 90% recovery with the CMS membrane alone can be achieved for the oxygen blown gasifier under a similar operating condition employed by NCCC. On the other hand, hydrogen concentration at 60+% purity on the wet basis can be achieved, which is ideal for power generation with turbines with carbon capture and storage requirement.*
- *The full-scale membrane/module experienced non-uniform flow distribution under a high feed rate, i.e., 150 to 250 liters/minute, to the module during the Yr 2011 tests, which was corrected with reinforced internal bafflers during the test in 2012. The gas separation efficiency was within 10% of that based upon the single component testing.*

Overall, the testing at the NCCC facility was highly successful. Several hundred hours of testing of our CMS membrane bundles revealed exceptionally stable membrane performance in the presence of gasifier off-gas that had gone through no pretreatment prior to being exposed to our membranes. Hydrogen purity was enriched to >50% from the feed containing ~10% hydrogen generated from the air-blown gasifier. This hydrogen separation efficiency is expected to deliver >94%xxx purity with as high as 90% hydrogen recovery for syngas generated from oxygen blown gasifier with ~40% hydrogen as feed.

6. Economic Analysis for Selected Process Schemes

6.1. Development of Promising Process Schemes

Process design concepts for our CMS membranes were developed and analyzed under this chapter for the production of electric power and/or hydrogen from the gasification of coal. The conceptual cases producing electric power are compared with benchmark cases developed by the DOE National Energy Technology Laboratory (NETL) for Integrated-Gasification Combine-Cycle (IGCC) power plants with (Case 2a) and without (Case 1a) Carbon Capture and Storage (CCS)². Hydrogen producing benchmark cases, with (Case 2b) and without (Case 1b) CCS, were also developed from the NETL IGCC cases. One advanced concepts for the integration of the CMS membranes was considered for power (Case 3a) or hydrogen (Case 3b) production. In addition, the power production scheme was modified and analyzed for the co-production of both power and hydrogen (Case 3b). Process Concepts based upon the palladium (Pd) membrane were also included in Case 3b and 3c for power generation and hydrogen production respectively for comparison with the cases with the CMS membranes. Table 6.1 summarizes these cases and their economics, which is discussed in detail in Sec. 6.2.

Table 6.1 Process Schemes Selected for Performance and Economic Analysis for Power Generation

Case Descriptions	Production		HHV Efficiency %	Required Selling Price				CO ₂ Capture %	CO ₂ Avoided \$/tonne
	Electricity	Hydrogen		Electricity	Hydrogen	Electricity	Hydrogen		
	MWh/Ton	M SCF/Ton		mills/kWh	\$/MM Btu	% Increase			
1a: IGCC w/o CCS - 1-Stage Selexol™ (base case)	2.66	-	39.0	76.3	-	-	-	0	-
2a: IGCC w/CCS - 2-Stage Selexol™	2.23	-	32.6	105.5	-	38	-	90	42.46
3a: IGCC w/CCS - CMS & Pd Membranes & 1-Stage Selexol™	2.37	-	34.6	95.1	-	25	-	98	24.64

Table 6.2 Process Schemes Selected for Performance and Economic Analysis for Hydrogen Production

Case Descriptions	Production		HHV Efficiency %	Required Selling Price				CO ₂ Capture %	CO ₂ Avoided \$/tonne
	Electricity	Hydrogen		Electricity	Hydrogen	Electricity	Hydrogen		
	MWh/Ton	M SCF/Ton		mills/kWh	\$/MM Btu	% Increase			
1b: Gasification w/o CCS - 1-Stage Selexol™ & PSA (base case)	-	45.38	63.0	-	10.9	-	-	0	-
2b: Gasification w/CCS - 2-Stage Selexol™ & PSA	-	38.36	53.3	-	13.8	-	26	90	27.00
3c: Gasification w/CCS - Pd Membranes & HGCU	-	45.93	63.8	-	12.1	-	11	100	10.11

Table 6.3 Process Schemes Selected for Performance and Economic Analysis for Co-Production

Case Descriptions	Production		HHV Efficiency %	Required Selling Price				CO ₂ Capture %	CO ₂ Avoided \$/tonne
	Electricity	Hydrogen		Electricity	Hydrogen	Electricity	Hydrogen		
	MWh/Ton	M SCF/Ton		mills/kWh	\$/MM Btu	% Increase			
3b: w/CCS - CMS & Pd Membranes & 1-Stage Selexol™	1.52	12.78	40.0	95.1	15.2	25	39	98	24.94

*Avoided Cost = $(COE/MWh_{w/capture} - COE/MWh_{w/o capture}) / (tonne CO_2 emitted/MWh_{w/o capture} - tonne CO_2 emitted/MWh_{w/capture})$;
for H₂ production, COE is replaced with the RSP of H₂ and the basis of MWh is replaced by M SCF.

6.2. Description of Process Schemes

The benchmark and conceptual cases are described in more detail below.

Case 1a: Power Generation via IGCC without CCS - 1-Stage Selexol™ (Base Case)

² Cost and Performance Baseline for Fossil Energy Plants, Volume 1: Bituminous Coal and Natural Gas to Electricity, DOE/NETL-2010/1397, Revision 2, November 2010.

The block flow diagram (BFD) for this benchmark is shown in Figure 6.1 below³. In the baseline, un-shifted syngas from the gasifier is cooled and purified using cold-gas clean-up (CGCU) processes that are commercially available. The sulfur removal technology used is a single-stage Selexol™ absorption process.

The clean syngas is reheated, expanded in an expansion turbine (XT) to recover incremental power from the hot pressurized gas, diluted with by-product nitrogen (N₂) gas from the air separation unit (ASU) and then fed to a commercial combustion turbine (CT) to produce power. Heat from the hot exhaust of the CT is recovered in a heat-recovery steam generator (HRSG; not shown) and used to produce additional electric power in a conventional steam turbine (ST) system. The exhaust from the HRSG is vented to the plant stack and no carbon capture is accomplished in this case. The analysis of Case 1a replicates the performance and costs reported in the NETL study (NETL Report Case 1).

Case 1b: H₂ Production w/o CCS - 1-Stage Selexol™ & PSA (Base Case)

The process shown in Figure 6.1 was modified to produce high-purity hydrogen (H₂) for transfer to a hydrogen pipeline at moderate pressures. The BFD for this benchmark case is shown in Figure 6.2 below. Case 1b only produces sufficient electric power to satisfy all internal requirements for operation of the plant. The following changes are made to the coal gasification-based processes of Figure 6.1 to produce hydrogen. Water-gas-shift (WGS) reactors are added upstream of the HRSG to convert carbon monoxide (CO) in the syngas to additional H₂. Steam is co-fed to the reactors, to increase the conversion for the WGS reactions. Operations of the CGCU and XT remain the same though the flowrate and composition of the syngas has changed. The expanded H₂-rich syngas is sent to a pressure swing adsorption (PSA) unit to recover H₂ from the gas for sale. The reject gas from the PSA is used for plant fuel. However, the CT is

³ Note that in this and subsequent BFDs, only affected portions of the process flowsheet are shown.

eliminated and replaced with a conventional boiler to raise steam for operation of the ST. No carbon dioxide (CO₂) is captured in this case.

Figure 6.2 Block Flow Diagram – Case 1b: Hydrogen Production w/o CCS

Case 2a: Power Generation via IGCC w/CCS - 2-Stage Selexol™

The IGCC case depicted in Figure 6.1 is modified to enable CO₂ capture and compression. This new case serves as the benchmark for IGCC with CCS. The modified design is shown in Figure 6.3. Since most of the carbon produced by the above process will be captured as CO₂, WGS reactors are required to convert essentially all of the CO in the syngas to additional H₂ and CO₂. The single-stage Selexol™ unit is replaced with a dual-stage unit capable of recovering 90% of the CO₂ generated. This relatively low-pressure CO₂ is compressed and transported to a suitable underground CO₂ storage site for injection. The analysis of Case 2a replicates the performance and costs reported in the NETL study (NETL Report Case 2).

Figure 6.3 Block Flow Diagram – Case 2a: Power Generation via IGCC w/CCS – Dual Stage Selexol™

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Case 2b: H₂ Production w/CCS - 2-Stage Selexol™ & PSA

Similar to what was done for Case 2a, the Case 1b BFD was modified to recover CO₂ by adding a second stage to the Selexol™ unit and CO₂ compression. Case 2b is shown in Figure 6.4. Note that WGS reactors do not need to be added for this case, since they were already present in Case 1b.

Figure 6.4 Block Flow Diagram – Case 2b: Hydrogen Production w/CCS – Dual Stage Selexsol™ & PSA

Case 3a: Power Generation via IGCC w/CCS - CMS & Pd Membranes & 1-Stage Selexol™

An IGCC system with CCS, employing MPT CMS membranes is shown in Figure 6.5. In order to achieve a high CO₂ recovery for CCS a Pd membrane is supplemented as a second stage as shown in Figure 6.5. In this concept, the WGS reactors shown in Figure 6.3 are replaced with CMS WGS membrane reactors (MR), with the single-stage CGCU system processing the retentate from the MR. The clean CO₂-rich gas from the CGCU is sent to compression. At intermediate stages during compression, one or two banks of Pd membrane separators (MBS) are used to recover residual H₂ left in the CO₂ stream before it is transported to a storage site. The high-purity CO₂ retentate is sent to compression and transport. The permeate from the CMS MR, containing the bulk of the H₂ and residual CO₂, is combined with the H₂ permeate from the Pd MBS and is used as fuel to fire the CT. Note that this concept eliminates the XT as well as several CO₂ compression stages. Nitrogen gas from the ASU is used both as a sweep gas to the membranes and as a fuel gas diluent. Injection steam, in addition to being used to improve WGS conversion, also is used as sweep gas and fuel diluent.

Figure 6.5 Block Flow Diagram – Case 3a: Power Generation via IGCC w/CCS – Hybrid CMS/Pd Membrane System

Case 3b: Co-Production w/CCS - CMS & Pd Membranes & 1-Stage Selexol™

Co-production of electric power and hydrogen was mentioned as one of the possible advantages of the Case 3a concept. This BFD is similar to Figure 6.5 shown for Case 3a. Only minor flowsheet modifications are required to export about 25% of the H_2 produced by the plant as a high-purity, medium pressure co-product.

Case 3c: H_2 Production w/CCS - Pd Membranes & HGCU

Concept Case 3c employs Pd membranes alone to produce a single high-purity H_2 product from the gasification of coal. This BFD for this concept is shown in Figure 6.6. In order to integrate the Pd WGS MR into the Case 2a flowsheet, a number of other novel technologies are required. Due to sulfur poisoning, CGCU is replaced with HGCU (humid gas clean-up) upstream of the MBR. NETL is currently funding the development of HGCU technologies, which operate at temperatures consistent with those required by the WGS reaction. The retentate from the MR, at elevated pressure and temperature is suitable for firing in a CT. However, to avoid dilution of the concentrated CO_2 stream with N_2 from firing air, high-purity O_2 from the ASU must be used. This additional O_2 demand increases the required size of the ASU supplying O_2 to the gasifier. CTs that can be fired using pure O_2 are under development in Europe. An approach being taken is to recycle CO_2 back to the CT as a substitute for the missing N_2 , which serves to moderate firing temperatures. Alternatively, the CT may be replaced with an XT and an oxy-fired boiler used to generate steam. The latter, is less efficient than the use of a combined-cycle CT/ST systems. In addition, Case 3c eliminates the steam sweep used in Cases 3a and 3b, and the permeate is recovered at low pressure, requiring re-compression. Overall, the Case 3c concept is considered to have higher R&D risk versus that required for Cases 3a and 3b, due to the need to develop several other supporting technologies in addition to H_2 separation membranes.

Methodology and Assumptions:

Analysis of the conceptual designs presented above was conducted using a simplified approach, coupled with idealistic assumptions to estimate performance and cost impacts of the process modifications. The estimates developed are preliminary and are valuable for identifying promising R&D and for determining the feasibility of the novel concepts represented by the MPT membrane Cases 3a, 3b and 3c. As such, they should not be used for scaling up these gas separation membrane concepts without further refinement.

Cases 1a and 2a are derived from the NETL baselines mentioned previously¹. Results for these cases match exactly with NETL results for IGCC plant capacity, efficiency and cost, reported as the required cost of electricity (COE). In order to establish baselines for the corresponding Cases 1b and 2b, which produce H₂ instead of electricity, the 1a and 1b BFDs were modified and new material balances were calculated reflecting the changes made. Then, plant energy requirements (parasitic electricity and steam), capital, and operating costs for Cases 1b and 2b were scaled from the corresponding information in Cases 1a and 1b. Adjustments were also made to reflect changes in operating pressure or temperature where significant. Similarly, Cases 3a, 3b and 3c were also scaled from the Cases 1a and 2a, with MPT membrane technologies substituted for the corresponding conventional systems. Overall, cases involving the production of electricity should be more accurate than those involving H₂ production, since the latter involved more process modifications to the NETL baseline designs. It may be assumed that the analysis results reported as deltas between cases with and without CCS, are more accurate than the calculated results for individual cases.

Other assumptions made for this analysis include:

1. CO conversion for WGS MR of greater than 99%
2. CMS H₂ permeance of 1.5 m³/m²/hr/bar at operating temperatures ranging from 200 to 280°C⁴
3. CMS separation factors relative to H₂ of 70, 140, 70, 35, 1.3, 140, and 70 for the gases argon, methane, CO, CO₂, water, H₂S, and N₂, respectively⁵
4. H₂ permeance of 10 m³/m²/hr/bar at operating temperatures greater than 300°C³ for Pd membranes
5. Infinite selectivity of H₂ relative to all other gases for Pd membrane
6. For Cases 3a and 3b, 75% recovery of H₂ from CMS, and N₂ sweep gas split equally between the CMS and Pd membrane units
7. Delivered cost for both MPT CMS and Pd membrane modules of \$100/ft², with an additional installation cost of 50%⁴
8. For Case 3c, costs for HGCU are assumed equivalent to those for existing CGCU technologies; similarly, for the costs of CT technology differences.

No detailed simulations of the CMS and Pd MBS or MR were performed in this analysis. Heat integration concepts depicted in Figures 6.5-6.7 are conceptual and were assumed to mitigate any process heating differences relative to the NETL baseline designs.

⁴ In-house data.

⁵ "Concept Verification, Product Development and Field Evaluation," presentation for DOE contract No. DE-FC26-07NT43057, 2012 by Meida and Process Technology Inc.

6.3. *Performance and Economics Analysis*

Cases for Power Generation

The results of the analyses conducted in this project are summarized in Table 6.1. For power generation via IGCC cases, significant comparisons can be made between Cases 1a, 2a, and 3a. The addition of state of the art (SOTA) CCS technologies to an IGCC plant lowers the efficiency by about 6 percentage points from 39.0 to 32.6%. This reduction results primarily from the addition of the CO₂ compression step, along with increased pumping requirements for circulation of the Selexol™ solvent. The addition of the WGS reaction step also negatively affects overall plant efficiency. In combination, this results in a reduction of net MWh per ton of coal processed from 2.66 to 2.23. Inversely, for coal-fired IGCC plants with the same electricity output, a plant with CCS must be 19% larger than a plant without CCS. CO₂ avoided cost for the SOTA plant with CCS is \$42.46 per ton of CO₂ captured, and the required COE increases by about 38% from that of Case 1a.

Case 3a has the potential to improve the cost and performance of an IGCC plant with CCS significantly relative to the SOTA case. Plant efficiency only drops by about 4 percentage points to 34.6%, and the size of the plant increases only by about 12%, relative to the baseline plant. These improvements result from a major reduction in CO₂ compression requirements; as well as the elimination of all parasitic energy requirements for CO₂ capture. Unlike absorption processes, gas separation membranes when effectively integrated into a process, require no additional heating or cooling, solvent pumping, or gas compression. In addition, the loss of power production due to the elimination of the XT is compensated for by increased ST power output due to the reduction in excess steam required by the WGS reaction. The avoided cost of CO₂ capture is reduced by about half to \$24.94 per tonne, and COE increases only by 25% relative to the IGCC baseline. In addition, the Case 3a concept achieves these improvements while potentially capturing greater than 90% of the CO₂ produced.

Cases for Hydrogen Production

For the H₂ production-only cases, comparisons can be made between Cases 1b, 2b and 3c. The addition of SOTA CCS technologies to the H₂ plant lowers the efficiency by about 10 percentage points from 63.0 to 53.3%, and decreases the H₂ yield from about 45 to 38 M SCF/ton of coal (M SCF – 1,000 standard cubic feet). It should be noted in general, plant efficiencies are higher for H₂ versus electricity production, since the H₂ produced is not combusted within the plant. CO₂ avoided cost for the SOTA plant with CCS is \$27.00 per tonne of CO₂ captured, and the required selling price (RSP) for H₂ increases by about 26% from that of Case 1b. The cost of avoided CO₂ emissions is significantly lower than that for the SOTA power plant analyzed in Case 2a (\$42.5 versus \$27 per tonne, respectively). The underlying reasons for this are three-fold: first, the baseline H₂ plant already employs WGS reactors to maximize H₂ production; thus, they are not an added cost of CCS for this system; second, the CT required for IGCC power generation in the electricity production cases is more expensive in Case 2a versus 1a; and third, gross power production decreases in Case 2a.

Case for Co-Production

Case 3c employing Pd membrane reactors, is potentially very attractive relative to the SOTA design of Case 2b. However, 3c also requires successful R&D to develop HGCU and CT technologies with performance and cost comparable with SOTA technologies. Therefore, cost of this system may be higher and performance lower than indicated by this analysis. Case 3c is capable of capturing essentially all of the CO₂ produced at an avoided cost of \$10/tonne and a RSP for H₂ only 11% higher than the baseline, Case 1b. Plant efficiency and yield are comparable with the baseline. These are the result of the inclusion of a higher efficiency combined-cycle system in Case 3c versus Case 2b, which employs a single-cycle ST system.

Case 3b with a configuration similar to that of Case 3a is able to co-producing H₂ and power, and exports about 25% of the H₂ produced for sale. This results in a reduction in net power output of about 35%. Avoided costs are comparable to Case 3a and to Case 2b, indicating no clear advantage for co-production in regards to the cost of carbon capture. The higher RSP for H₂ in Case 3b versus 2b, would suggest the latter as the more economic alternative. Similarly, Case 3c has potentially a much lower RSP. However, all these results depend significantly on the assumed COE used in the Case 3b analysis. A higher electricity selling price and less optimistic performance and costs for Case 3c could change the ordering of these results.

Unique Advantages of Process Scheme with CMS Membranes

Advantages of the power generation using our CMS membranes supplemented with our Pd membranes (i.e., Case 3a) versus the state-of-the-art (SOTA) scheme using 2-stage Selexsob™ Case 2a are:

- The need to add a second stage to the Selexol™ unit to remove CO₂ is eliminated. It may also be possible to use a cheaper alternative to Selexol™, such as the amine solvent MDEA, in the single-stage H₂S absorption system, or possibly eliminate the H₂S system entirely, if H₂S and CO₂ can be co-injected for storage. The single-stage unit if used will also be smaller due to the reduced volume of gas flow.
- CO conversion and bulk separation of raw syngas occurs at elevated temperatures in the CMS-MR, delivering humid H₂ to the CT at specification pressure and temperature, and CO₂ enriched gas to the CGCU system at relatively high pressure; reducing the amount of total compression required.
- The continuous removal H₂ from the WGS-MR and higher operating temperatures, have the potential additional advantages that the steam requirement for the WGS reaction and the reactor volume may be reduced.
- The H₂ gas remaining in the CMS-MR retentate is recovered during compression using highly-H₂ selective Pd membranes. Again, the H₂ permeate is delivered to the CT at specification pressure and temperature without the need for additional re-compression. The co-use of steam and/or N₂ CT diluents as sweep gas maximizes the performance of both membrane separations.
- 99+% purity H₂ can be co-produced from off the Pd membranes and sold, if steam is used as the sweep gas (see Case 3b).

Technology development challenges for the Case 3a concept are achieving high overall H₂ recoveries from the gas separation membrane systems; potential plugging and temperature management in the WGS-MR; improved H₂/CO₂ selectivity for the CMS membrane;

minimization of H₂S slip through the CMS membrane; and reduction of re-heating requirements for Pd MBS feed stream. Technical feasibility of these requirements has been demonstrated under this project, which is summarized in Sec. 2 to 4. However, our field tests in this project are limited to the use of the CMS membrane and the CMS/Pd hybrid membrane system to demonstrate the direct feed of the raw syngas without gas cleanup as pre-treatment. The process concept involving the membrane reactor, which has been demonstrated using a bench top membrane reactor (see Chapter 4) remains to be demonstrated in the field.

6.4. *ns*

Conclusio

The preliminary analysis presented here has identified an attractive process flowsheet and designs for the integration of our CMS membranes into coal conversion plants for the production of electricity and/or hydrogen. The first IGCC concept integrates CMS WGS-MRs with upstream of the syngas clean-up and CO₂ compression steps, supplemented with multiple Pd MBSs within the CO₂ compression train. Advantages of this approach are process intensification combining WGS and CO₂ removal in single unit operation; improved pressure and H₂ management in the IGCC system, resulting in less CO₂ compression and no need for separate re-compression of the H₂ fuel gas; and the ability to co-produce high-purity H₂ along with electric power. Further, locating the highly-selective Pd membranes after the CGCU step ensures that Pd poisoning by sulfur cannot occur under normal operation. These advantages have the potential to significantly reduce the COE and the avoided cost of CO₂ capture.

Technical challenges involving in this scheme include achieving high overall H₂ recoveries; fouling and temperature management in the WGS MR; improved H₂/CO₂ selectivity for the CMS membrane; minimization of H₂S slip through the CMS membrane; and reduction of re-heating requirements for the Pd MBS. This project has demonstrated the technical feasibility of these challenge areas in the lab and/or field tests with our state-of-the-art CMS and Pd membranes. Nevertheless, further development in these areas is needed to maximize the benefits identified by this process scheme. It is also recommended that more detailed process analyses be conducted to quantify the challenges facing the membrane technologies (both CMS and Pd) developed by Media and Process Technology Inc under this project. Such analyses should include both rigorous material and energy balances and bottom-up estimation of all capital and operating costs. Rigorous modeling of the MRs and MBSs is also needed to predict their performance, and to optimize individual membrane module recoveries and the distribution of sweep gas to the system. In addition, a pinch analysis would be extremely valuable for identifying efficient energy integration schemes and minimizing water usage within these complex processing plants.

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Nomenclature

A^F	cross-sectional area for the feed side (m^2)
ID	inner diameter of the membrane (m)
OD	outer diameter of the membrane (m)
G^F	superficial mass flow velocity in the feed side ($\text{g}/\text{m}^2\cdot\text{h}$)
K_{eq}	equilibrium constant
L	length of membrane (m)
N_{Re}^F	Reynolds number for the feed side
F_j	molar flux for component j ($\text{mol}/\text{m}^2\cdot\text{h}$)
P_j	partial pressure for component j (bar)
P^F	feed side pressure (bar)
P_j^F	partial pressure for component j in the feed side (bar)
P^P	permeate side pressure (bar)
P_j^P	partial pressure for component j in the permeate side (bar)
V	reactor volume (m^3)
Re_{H_2}	hydrogen recovery
X_{CO}	carbon monoxide conversion
X_e	equilibrium conversion
d_p	particle diameter in the feed side (m)
f	friction factor
g_c	gravity conversion factor
n_j^F	molar flow rate for component j in the feed side (mol/h)
n_j^P	molar flow rate for component j in the permeate side (mol/h)
r	overall reaction rate expression ($\text{mol}/\text{g}\cdot\text{h}$)
U_j	membrane permeance for component j ($\text{mol}/\text{m}^2\cdot\text{h}\cdot\text{bar}$)
u^F	flow velocity on the feed side (m/h)
W_C	weight of the catalyst (g)
SR	steam sweep gas ratio $(\sum n_{j0}^P / \sum n_{j0}^F)$
T	temperature
<i>Subscripts</i>	
0	entrance condition
exit	exit condition
j	chemical species
eq	equilibrium

Superscripts

F	feed side
P	permeate side

Greek Letters

α_m	membrane area per feed side reactor volume (m^2/m^3)
β	equilibrium coefficient
β_c	fraction of solid volume occupied by catalyst
ε_v	bed porosity in the feed side
μ^F	viscosity of the fluid ($\text{g}/\text{m}\cdot\text{h}$)
ρ^F	average density of the fluid (g/m^3)
ρ^c	catalyst density (g/m^3)
ν_j	stoichiometric coefficient for component j

List of Acronyms

CCS	carbon capture and storage
CGCU	cold gas clean up
CMS	carbon molecular sieve
CT	combustion turbine
HAMR	hybrid adsorbent-membrane reactor
HGCU	hot gas clean up
HRSG	heat recovery steam generator
HTS	high temperature shift
IGCC	integrated gas combined cycle
LTS	low temperature shift
MBS	membrane separator
MFC	mass flow controller
MPT	Media and Process Technology Inc
MR	membrane reactor
NCCC	National Carbon Capture Center
NETL	National Energy Technology Laboratory
PB	packed bed
Pd	palladium
PSA	pressure swing adsorption
SOTA	state of the art
SS	stainless steel
WGS	water gas shift reaction
XT	expansion turbine