Final Report

April 10, 2012

Project Title:	*Hydrogen Selective Inorganic Membranes for Gas Separations in High Pressure Intermediate Temperature Hydrocarbon Containing Environments*
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1. EXECUTIVE SUMMARY

In this project, we have successfully developed a full scale commercially ready carbon molecular sieve (CMS) based membrane for applications in H_2 recovery from refinery waste and other aggressive gas streams. Field tests at a refinery pilot plant and a coal gasification facility have successfully demonstrated its ability to recovery hydrogen from hydrotreating and raw syngas respectively. High purity H_2 and excellent stability of the membrane permeance and selectivity were obtained in testing conducted over >500 hours at each site. The results from these field tests as well as laboratory testing conclude that the membranes can be operated at high pressures (up to 1,000 psig) and temperatures (up to 300˚C) in presence of aggressive contaminants, such as sulfur and nitrogen containing species (H_2S, CO_2, NH_3, etc), condensable hydrocarbons, tar-like species, heavy metals, etc. with no observable effect on membrane performance. By comparison, similar operating conditions and/or environments would rapidly destroy competing membranes, such as polymeric, palladium, zeolitic, etc.

Significant cost savings can be achieved through recovering H_2 from refinery waste gas using this newly developed CMS membrane. Annual savings of $2 to 4MM/year (per 20,000 scfd of waste gas) can be realized by recovering the H_2 for reuse (versus fuel). Projecting these values over the entire US market, potential H_2 savings from refinery waste gases on the order of 750 to 1,000MM scfd and $750 to $1,000MM per year are possible. In addition to the cost savings, potential energy savings are projected to be ca. 150 to 220 tBTU/yr and CO_2 gas emission reductions are projected to be ca. 5,000 to 6,500MMtons/year.

The full scale membrane bundle developed as part of this project, i.e., 85 x 30” ceramic membrane tubes packaged into a full ceramic potting, is an important accomplishment. No comparable commercial scale product exists in the inorganic membrane field. Further, this newly developed full scale bundle concept can be extended to other thin film inorganic membrane technology (Pd, zeolite, etc), providing a potential commercialization pathway for these membrane materials that demonstrate high potential in a variety of separation applications yet remain a laboratory “novelty” for lack of a full scale support.

Overall, the project has been highly successful and all of the project objectives have been met. We have developed the first of its kind commercial scale carbon molecular sieve membrane and demonstrated its performance in field testing under aggressive operating conditions and in the presence of chemical contaminants that would rapidly destroy alternative organic and inorganic membranes. This innovative membrane permits H_2 recovery from gas streams that up until now have not been successfully treated with membrane or conventional technology. Our end user participant is currently pursuing the field demonstration of this membrane for hydrogen recovery at its refinery site.

2. INTRODUCTION

The recovery of H_2 from various refinery waste gas streams is a difficult task due to the large array of contaminants including sulfur and nitrogen containing species as well as a wide array of higher condensable hydrocarbons. At present very little effort is made to recover H_2 from these gases due to the ineffectiveness, instability, and/or simple cost prohibitive commercial technologies such as polymeric membranes, PSA, and cryogenic distillation. Further, similar H_2 containing gas streams are available in such applications as steam crackers (ethylene, propylene production), coal and biomass gasifiers, and other petrochemical processes. However, current H_2 recovery technology again suffers from these disadvantages. In this project, Media and Process Technology Inc (M&P) developed to full commercial scale a carbon molecular sieve (CMS) membrane on ceramic substrate that was highly stable in these gas streams and could efficiently and cost effectively recover H_2 at high purity (>98%).

The objective of this project was to enhance the performance limits of inorganic membranes for gas separations at extremely high pressures (up to ~1,000 psi), intermediate temperatures (150-350°C), and in hydrocarbon-containing (HPITHC) environments, typical for most refinery conditions, and unattainable for existing commercial membranes. As a result, membrane-based gas separations, known for their energy efficiency, will become practical and realistic for refinery applications.

Use of the membrane for *in-situ* hydrogen recovery and recycle processes in refinery operations offers an effective approach to enhance the hydrogen partial pressure in the reactor via the removal of light hydrocarbons accumulated in the recycle loop, thus substantially diminishing the purge-rate and make-up amounts of hydrogen needed. As a result, the hydrogen partial pressure in the reactor can be enhanced effectively without unwanted dilution by the accumulated light hydrocarbons. Under this project, the team experimentally verified hydrogen selective inorganic membranes for hydrogen separations at extremely high pressures (up to ~1000 psi), intermediate temperatures (150-350°C), and in hydrocarbon-containing (HPITHC) environments under a simulate environment in the first phase. Its potential energy savings and carbon footprint reduction were estimated based upon the performance obtained.

Overall, the project has been highly successful and all of the project objectives have been met. We have developed the first of its kind commercial scale carbon molecular sieve membrane and demonstrated its performance in field testing under aggressive operating conditions and in the presence of chemical contaminants that would rapidly destroy alternative organic and inorganic membranes. The development of this membrane permits H_2 recovery from gas streams that up until now have not been successfully treated with membrane or conventional technology.

3. SUMMARY OF TECHNICAL RESULTS AND ACCOMPLISHMENTS

In this section the project technical results and accomplishments are summarized. Detailed discussion of the technical results is given in Section 4. Overall, the project was highly successful. From a starting point of the laboratory scale single tube, i.e., 10" long CMS deposited ceramic tubular substrates developed during feasibility testing prior to this project, we were able to complete the development and field test of the full commercial scale product, i.e., bundles comprised of 85 tubes by 30" long CMS membrane tubes capable of delivering excellent H_2 recovery from H_2 containing process waste streams. Our technical accomplishments are highlighted as follows:

- Successfully Prepared the Single Tubular CMS Membranes in the Outside Coated Candle Filter Configuration (Task 1; Section 4.1)

  During this program, the CMS membranes on the outside of our commercial ceramic tubular substrate in a candle filter configuration was successfully developed. This configuration offered several benefits which included:

  - *Higher surface area:* In comparison with the conventional inside coated tube, an outside coated part provides increased surface area for the same packing density (i.e., same number of tubes). This leads directly to lower cost and smaller footprint. For the current part (3.5mm ID x 5.7mm OD), the surface area increase is on the order of 60%.
  - *Reduced stress on the membrane tubes at the seal:* With the candle filter design, there is only one seal between the module (steel) and membrane (ceramic) tubes. Hence the difference in thermal expansion between the ceramic part and metal housing was eliminated.

  The full length membranes prepared in this project displayed >95% on-spec ratio (He permeance >1.5m^3/m^2/hr/bar; He/N_2 selectivity >70 at 220-250°C). The balance of the off-spec parts typically showed selectivities slightly lower than the target. However, the modestly lower selectivities generally correlated with much higher He permeances. Overall, we were able to successfully scale up the CMS membrane deposition to the 30" outside coated tube in a candle filter configuration.

- Successfully Developed Mathematical Model for Predicting Gas Separation Behaviors (Task 2; Section 4.2)

  The mathematical model developed accurately predicts membrane performance in mixed gas testing using pure component permeances. Further, the model has been used to diagnose problems with the membrane bundles due to feed maldistribution and lead to the development of the membrane baffles discussed in Section 4.4. This simplified model uses Excel spreadsheet and is appropriate for pressures below 400 to 500 psig and co-current flow. A more advanced model was also developed, which can be used for prediction of counter current flow at pressures above 500 psig.

- Successfully Developed a Ceramic-Glass Potting Technology for Bundling Multiple Membrane Tubes into Field Implementable Products for Commercial Use (Task 4; Section 4.3).
  The full scale commercially viable product was developed by potting 85 tubes with 30"L into a bundle. The bundle potting with pure ceramic-glass is suited for operating temperatures >400˚C. *This is a major breakthrough of the project.* No similar product is available in inorganic membrane technology.

- Successfully Developed the CMS Thin Film on the Full Scale 85-tube CMS Membrane Bundle (Task 4, Task 5; See Section 4.3.2 & 4.3.3)
  A major innovation of the project was the successful deposition of the CMS thin film on the full scale 85-tube CMS membrane bundle, not deposition by single tubes which were then bundled together. On-spec bundle production was >95% (He > 1.5 $m^3/m^2/hr/bar$; He/N_2 >70). Further, off-spec bundles generally consisted of lower selectivity (He/N_2 ~ 50 to 70) but higher permeance (He > 2.5 $m^3/m^2/hr/bar$) parts and would still perform well and be acceptable in the refinery waste gas application. Over 50 bundles have been prepared as part of this project. The performance of the 85-tube bundle was verified in a number of long term laboratory challenge tests including thermal stability, pressure cycling stability, and long term storage stability. No change in membrane performance was observed throughout this testing.

- Successfully Installed Membrane Baffles to Overcome Feed Flow Distribution Problem in Bundles (Task 5; Section 4.4).
  Mixed gas testing of the bundles revealed considerable reduction in mixed gas versus pure component permeances based upon our model predictions. This result was inconsistent with our single tube data which showed excellent agreement between mixed gas and pure component permeances. During this project, it was found that this discrepancy resulted from poor distribution of feed gas to the membrane tubes in the bundle. A bundle baffle strategy was developed and adopted that yielded excellent agreement between the model prediction and the mixed gas permeances.

- Successfully Conducted Third Party Testing of CMS Membrane with Synthetic Gas Stream (Task 6, Section 4.6.1)
  To independently verify the membrane performance upon the request by our end user participant, an outside laboratory was contracted to conduct mixed gas performance testing on our membranes with synthetic mixtures simulating the waste gas stream available in a refinery. Excellent results were obtained. High purity H_2 was delivered under the desired operating conditions (Feed conditions: 40-60% H_2, 180 to 250˚C, 150 to 350psig). Further, H_2 permeances were high and consistent with the pure component results. Finally, the model developed during this program accurately predicted membrane mixed gas performance.

- Verified CMS Membrane Performance in Actual Refinery Off-gas at Refinery's Pilot Test Facility (Task 6, Section 4.6.2)
  Actual refinery off-gas testing was conducted with our CMS membrane tubes using hydrotreater waste gas generated at our end user's pilot test facility. Over 25 days of

testing was conducted with no performance decay in the presence of H_2S (>50,000ppm), ammonia, and various higher hydrocarbons at ca. 220˚C and pressures of 150 to 300 psi. High purity H_2 (>99.5%) was obtained throughout the testing. Excellent agreement between the model predictions and actual membrane performance was obtained.

- Confirmed Bundle Performance and Stability in Industrial Gas Streams: H_2 Recovery from Coal/Biomass Gasifier Off-gas at the PSDF (Power System Development Facility; now NCCC, National Carbon Capture Center) (Task 6, Section 4.6.3)
  In addition to the extensive laboratory/pilot scale testing conducted at M&P and various outside facilities, M&P also had the opportunity to conduct field trials with its full scale 85-tube CMS bundle for the recovery of H_2 from coal/biomass gasifier off-gas without pretreatment. Over 500 hours of testing was conducted with two separate full scale bundles with no change in the permeance and/or selectivity. Overall, our full scale bundle testing at the PSDF was highly successful. We successfully verified the performance and stability of our full scale CMS membrane with the gasifier off-gas (syngas) feed rates as high as 600 scfh at ~250°C for operation of a total of >500 hours.

- Assessed the Economics, Energy Savings, and Greenhouse Gas Emission Reduction Associated with H_2 Recovery in Petroleum Refining (Section 4.7)
  An assessment of the economics of H_2 recovery from refinery waste gas was conducted. The base case analysis assumed a waste gas stream at 350psig, total feed rate of 20 MMscfd, and 60% H_2 content. For a H_2 value of $2/kscf (e.g., fuel value), annual savings of $1MM to $2MM/year can be realized by recovering approximately 8 to 12 MMscfd of H_2 can be recovered. Projecting these values over the entire US market, potential H_2 savings from refinery waste gases on the order of 750 to 1,000MM scfd and $750 to $1,000MM per year are possible. In addition to the cost savings, potential energy savings are projected to be ca. 150 to 220 tBTU/yr and CO_2 gas emission reductions are projected to be ca. 5,000 to 6,500MMtons/year.

- Completed the Preparation of Membrane Products and Logistics Required to Perform Field Test at a Refinery Site
  Based upon the excellent results from lab, pilot and field tests obtained from this project, our end user participant, a major US refinery, has begun the preparation required for performing the test at its own facility. M&P has prepared sufficient number of the full-scale CMS bundles and housing required for this test. It is anticipated that the test will be conducted within the one year after the completion of this project.

4. TECHNICAL RESULTS AND DISCUSSION

In this section, detailed results of the technical program are highlighted and discussed.

4.1 CMS Membrane Development

The primary emphasis of the project was the development of the full scale CMS membrane and bundle. Prior to this program, MPT had demonstrated preliminary feasibility for H_2 recovery from various gas streams in terms of both performance and performance stability. This work had been conducted using CMS membranes deposited on the ID of 10" ceramic tubes. During this project, a commercial scale version of this membrane was developed featuring (i) outside tube deposition for increased surface area, (ii) candle filter design to eliminate ceramic bundle to steel module seal problems, and (iii) the full scale 85-tube bundle. Details of this work are summarized and discussed in this section.

4.1.1. Single Tube Deposition: Outside Coating on Tubular Candle Filters

During this program, we developed the deposition technology to deliver 30"L full-scale CMS membranes in a candle filter configuration as part of the full scale development activities. Based upon our 10" membrane development work conducted as part of our feasibility testing as well as required separation efficiency of our commercialization partner, an on-spec membrane was determined to show a permeance of at least 1.5 $m^3/m^2/hr/bar$ at a He/N_2 selectivity of at least 50 (later increased to 70 in our bundle development). The on-spec ratio of our previous 10" tubes was >95% and this ratio became the target of our development efforts here.

Table 1. Sample of CMS membrane tubes prepared during this program as part of the initial scale-up to the 30" candle filter. On-spec

Part ID	He	N_2	H_2	He/N_2	H_2/N_2	On-spec
F-26	1.18	0.027	1.26	44	47	Y
F-28	2.40	0.034	3.04	71	90	Y
F-29*	2.80	0.060	3.63	47	60	Y
F-30	2.98	0.060	3.69	50	62	Y
F-31	2.76	0.034	4.05	81	118	Y
F-32	1.87	0.138		14		N
F-33	2.91	0.030	3.49	96	115	Y
F-34	3.17	0.044	3.45	71	78	Y
F-35	2.29	0.019	2.62	121	139	Y
F-36	1.62	0.029	2.14	56	74	Y
F-37	2.19	0.019	2.63	112	134	Y
F-39	3.19	0.11		30		Y
F-40	2.79	0.056	3.66	50	65	Y
F-41	3.33	0.096		34		Y
F-43	2.75	0.0197	3.36	139	170	Y
F-44	2.12	0.023	2.27	92	98	Y
F-47	1.13	0.0036	1.04	312	288	~Y
F-48	2.35	0.033	2.92	70	87	Y
F-51	3.04	0.060	4.06	50	67	Y
F-53	2.57	0.034	3.71	75	109	Y

Table 1 shows the performance of 30" membranes produced during the full length membrane development, following our efforts to improve the on-spec ratio. Of these tubes 19 of the 20 tubes prepared were found to be on-spec. Further, several of these tubes showed striking performance. As an example, the F-43 membrane displayed a He permeance of 2.75 $m^3/m^2/hr/bar$ and a He/N_2 selectivity of 139, suggesting that very high permeance coupled with excellent selectivity can be achieved with the CMS membrane. It is our experience that the hydrogen permeance is about 20 to 30% higher than the He permeance. However, it does appear

that we have reached the upper performance limit of CMS membranes prepared from this particular carbon precursor. For instance, the selectivity falls rapidly as the permeance is increased from 2.75 to 3 $m^3/m^2/hr/bar$ (He/N_2 ~54; part ID: F-41) and 3.3 $m^3/m^2/hr/bar$ (He/N_2 ~32; part ID: F-51). Hence, for the moment it appears that we have identified the upper bound of the membrane performance based upon this precursor, which is consistent with our previous data generated from 10" long substrates.

In summary, our test quantity production of the CMS membrane delivered an excellent result. The on-spec ratio for these 30" OD coated CMS membranes is >95%, matching the level achieved with our 10" ID coated tubes. In addition the H_2 permeance of ~3 $m^3/m^2/hr/bar$ with the selectivity of >75 can be achieved comfortably. Finally, based upon the relationship between the permeance vs. selectivity, we believe that we have maximized the membrane separation properties based upon our current preparation protocol.

4.2 Mathematical Model Development

A mathematical model was developed during the project to predict mixed gas membrane performance from pure component results. Two general assumptions were made during model development, specifically, (i) the gas permeances are independent of pressure and (ii) there is no interaction with the membrane so that gas permeances are independent of composition. Further, for simplicity only a co-current model was developed. Given these assumptions, an Excel based spreadsheet was developed to predict mixed gas performance. Table 2 shows a comparison of the single component pure gas and predicted mixed gas permeances of the F-85 membrane (30" OD coated, CMS) for a He/Ar mixture at various feed pressures up to 300psig. As can be seen, excellent agreement between the actual gas and model predictions is obtained. This result is typical for our model prediction for our 30" OD coated CMS membranes.

Table 2. Estimates of the mixed gas He and Ar permeances for the F-85 30" CMS membrane for a He/Ar gas mixture blend (60/40) at various feed pressure. Temperature is 220°C. Permeate pressure is 0 psig.

Feed Pressure [psig]	He Permeance [$m^3/m^2/hr/bar$]	Ar Permeance [$m^3/m^2/hr/bar$]
Pure gas, 20psig	1.85	0.013
Mixed Gas, Model Predictions		
20	1.75	0.012
50	1.71	0.013
80	1.81	0.015
100	1.83	0.012
200	1.78	0.013
300	1.84	0.013

4.3 Full Scale Membrane Bundle Development

In this section, results of the full scale bundle development and testing are detailed and discussed.

4.3.1. Ceramic-Glass Potting

The development of a commercial scale membrane element was an important focus and significant achievement of the research program. The single CMS tubes are an academic novelty if they cannot be packaged into a low cost multiple tube bundle that can be conveniently

sealed in a steel or similar housing. Further, the multiple tube bundle must be capable of handling the operating conditions, specifically, temperatures up to ca. 300˚C and transmembrane pressures up to at least 300 psig in the presence of potentially aggressive/corrosive gas contaminants such as sulfur-species (H_2S, etc.), ammonia, tars, organic vapors, etc. MPT's approach was the development of a glass-ceramic potting that could survive the operating conditions and be immune to chemical species in the gas stream. The development proceeded in several stages. Initially, the production of solid rod bundles ranging in diameter from 1.5 to 3" was conducted to prove that a leak free potting could be obtained. As examples, Figure 1 shows a series of increasingly higher quality 3" rod bundles prepared during this development work. Bundles 3.04 to 3.06 demonstrated leak rates 3 or more orders of magnitude less than the typical N_2 permeance of a CMS tube. Figure 2 shows the rod bundle flux at pressures up to 1,000 psig after 37 pressure cycles. Excellent pressure stability is noted over a wide range. Further, the leak rates recorded in cc/min/psi correlate with N_2 permeances for the bundle of $<<0.001 m^3/m^2/hr/bar$ and are at least an order of magnitude less than the typical membrane permeance of ca. $0.02 m^3/m^2/hr/bar$.

A key invention in the development of the CMS bundle was the ability to foam the ceramic-glass potting material during firing thereby guaranteeing good fill of all of the space between the individual tubes and the ceramic collar. Figure 3 shows a cross section of one of the 3" bundles showing clearly the foam development during glass firing. Foam development is also clearly evident in most of the 3" rod bundles shown in Figure 1. The ability to foam the glass is critical to making a leak tight potting in one firing attempt and represents a breakthrough in ceramic bundle development. Prior to this development, multiple firing and refilling of the potting was necessary to achieve a leak tight potting, a long and costly process.

Overall, the potting strategy developed during this program permitted the production of full scale 85-tube CMS membrane bundles. The performance of these bundles in various challenge and mixed gases is described in the sections that follow.

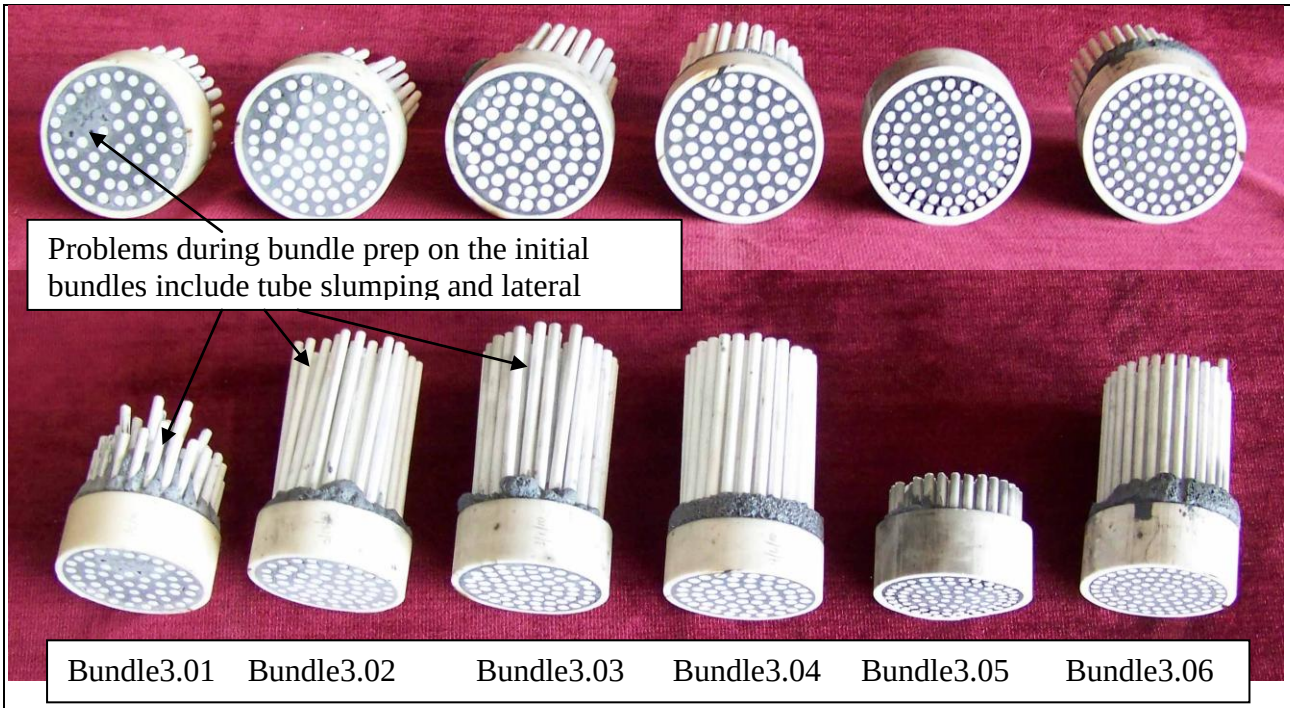


Figure 1. Standard 3" solid rod membrane bundles prepared as part of the 3" membrane production development.

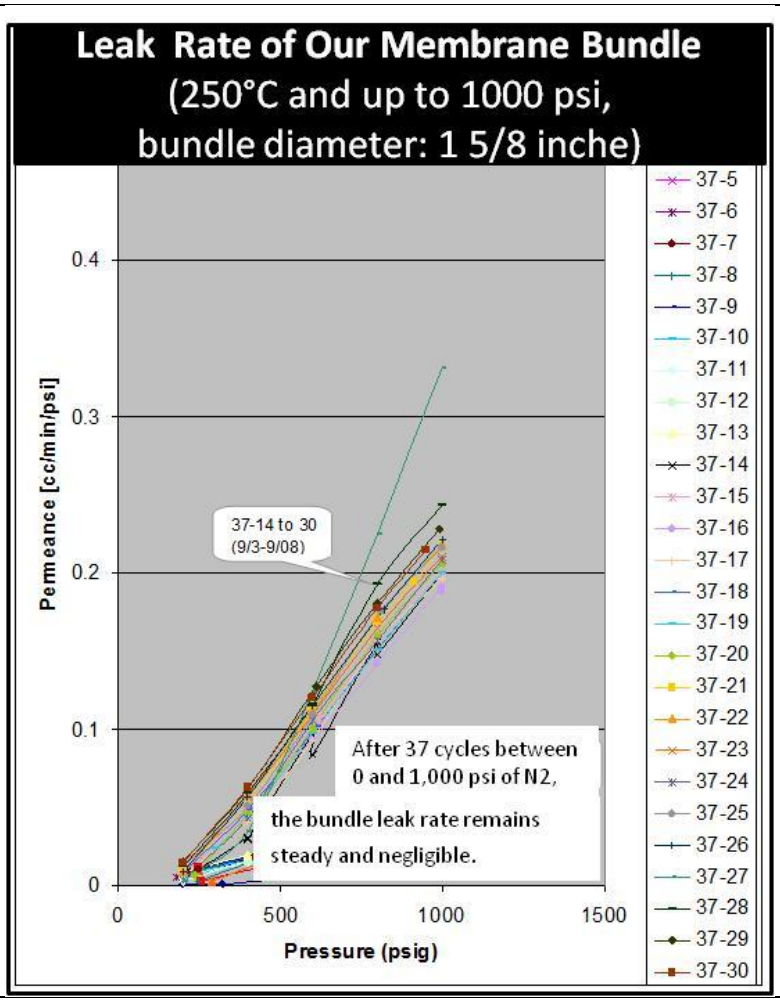


Figure 2. Pressure cycling of a solid rod bundle at transmembrane pressures up to 1,000 psig after 37 pressure cycles. No change in the bundle leak rate is observed.

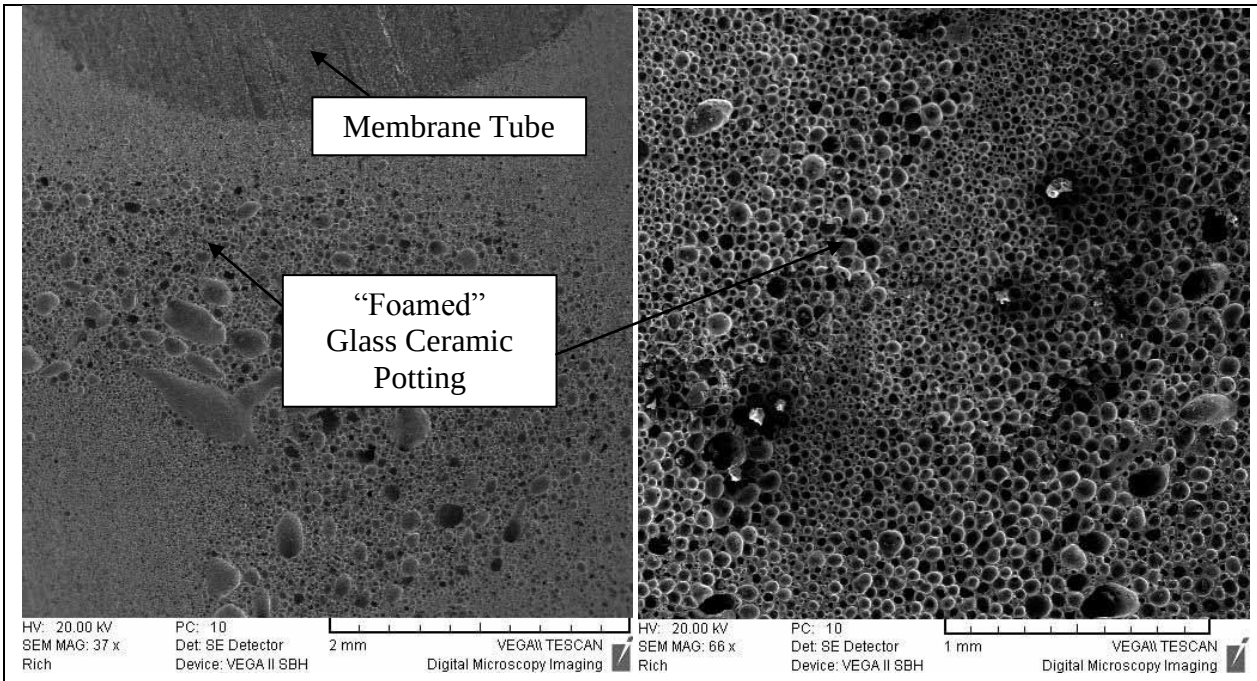


Figure 3. Cross section of the ceramic-glass potting showing the novel foaming structure. Left image shows membrane tube embedded in the potting. Right image is higher magnification of the potting showing foam structure.

4.3.2. Full Scale Membrane Bundle Development: CMS Membrane Deposition

The CMS membrane was prepared on full scale 85-tube membrane bundles in our laboratory for various testing purposes/needs and manufacturing reproducibility. Table 3 shows the performance of several bundles prepared in the final quarter of the project. As can be seen, He permeances are consistently above our 1.5 $m^3/m^2/hr/bar$ target (~550 GPU). Further, He/N_2 selectivity is consistently above the more stringent 75 target set later in the program. Only the 3-35 part fell below the permeance cutoff. The 3-37 was purposefully prepared to achieve enhanced selectivity (He/N_2 ~186) and as a result permeance was sacrificed. Overall, we continue to prepare full scale bundles that are on-spec and suitable for field testing.

Table 3. Permeance and selectivity of several 85-tube bundle prepared during this project. Test temperature is 240 to 250˚C; pressure is 20 to 30 psig.

Bundle ID	He [$m^3/m^2/hr/bar$]	N_2 [$m^3/m^2/hr/bar$]	He/N_2
3-7	2.73	0.021	130
3-9	1.46	0.012	126
3-11	1.57	0.018	89
3-13	1.61	0.008	209
3-14	2.80	0.025	116
3-15	3.15	0.041	90
3-17	2.68	0.035	87
3-18	2.30	0.022	105
3-19	1.38	0.019	75
3-31	1.94	0.028	69
3-32	1.74	0.018	99
3-33	1.69	0.020	84
3-34	1.87	0.025	75
3-35	1.26	0.013	94
3-36	2.04	0.019	108
3-37	1.12	0.006	196

4.3.3. CMS Membrane Performance: Temperature and Pressure Dependence

The typical temperature dependence of a CMS membrane is shown in Figure 4. In general, the fast gas permeance (He, H_2) increases with temperature due to activated diffusion through the nanopores. By comparison, the slow gas permeance (N_2, CH_4, etc.) tend to decrease with temperature. For these gases, diffusion is via the Knudsen and/or viscous flow mechanisms both of which display inverse temperature dependence.

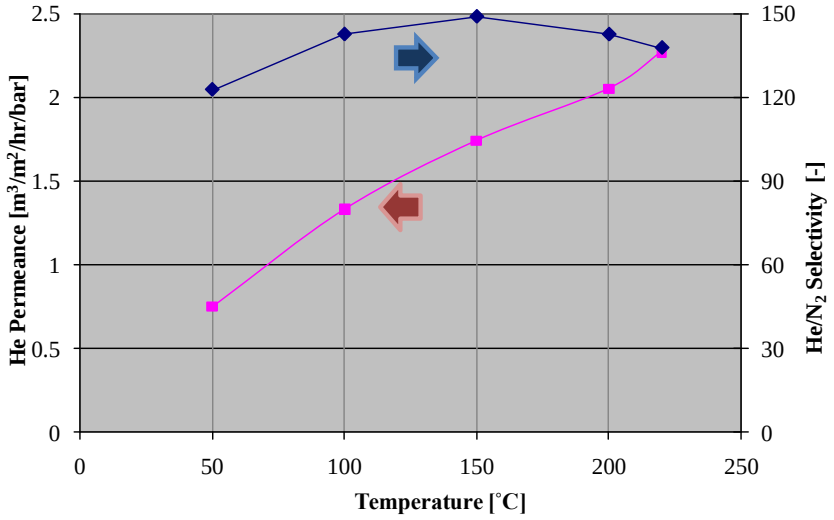


Figure 4. Effect of temperature on the permeance and selectivity of the 30" CMS membrane.

Similarly, typical pressure dependence of the slow gas (N_2) permeance of high quality CMS part is shown in Figure 7 and Figure 8. In general, at pressure below 300 to 500 psig, very little permeance increase with pressure (due to leaking) is noted in the high quality parts.

4.4 Flow Distribution Problem in Full Scale Bundles: Development of the Flow Baffles

As discussed in the previous section, excellent agreement has been obtained between the pure gas permeance and the calculated value obtained using our model to predict mixed gas permeances. Mixed gas permeances are generally no more than 5% different from the pure component value over a large range on concentrations and pressures up to 400 to 500 psig. However, initial testing with our bundles revealed considerable difference. In fact, in mixed gas He/Ar testing, mixed gas He permeances were less than 50% of the pure component values. During the project it was found that this was due to poor feed distribution in the module. A baffle technology was developed to overcome this problem as discussed in the following sections.

4.4.1. Feed Side Flow Baffle

In comprehensive testing of one of the 85-tube bundles, we demonstrated that (i) poor feed flow distribution was causing a significant loss in gas separation efficiency in comparison with our single component results and (ii) that this effect could be eliminated via baffling of the membrane bundle to prevent gas short circuiting around the outside of the bundle. Figure 5 is an illustration of the feed flow bypass phenomenon. In general, the path of least resistance from the feed to reject is around the outside of the membrane bundle, bypassing many of the interior tubes. To overcome this problem, Teflon baffles and wrap were added to the membrane bundles as shown in Figure 6. The baffles physically contact the wall of the module and prevent feed gas short circuiting shown in Figure 5. The gas separation results with several bundles modified in this way demonstrate that

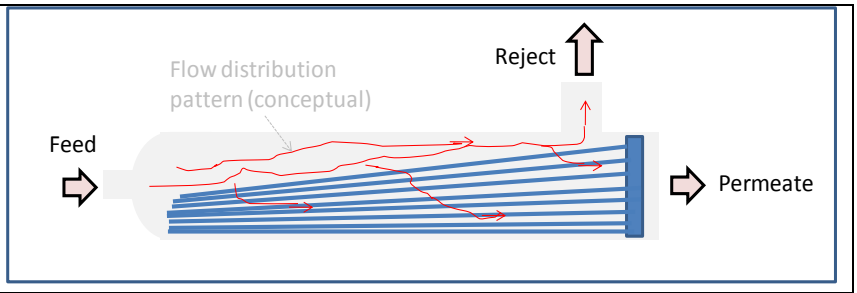


Figure 5. Schematic of the potential for feed flow distribution and short circuiting in the CMS bundle and module.

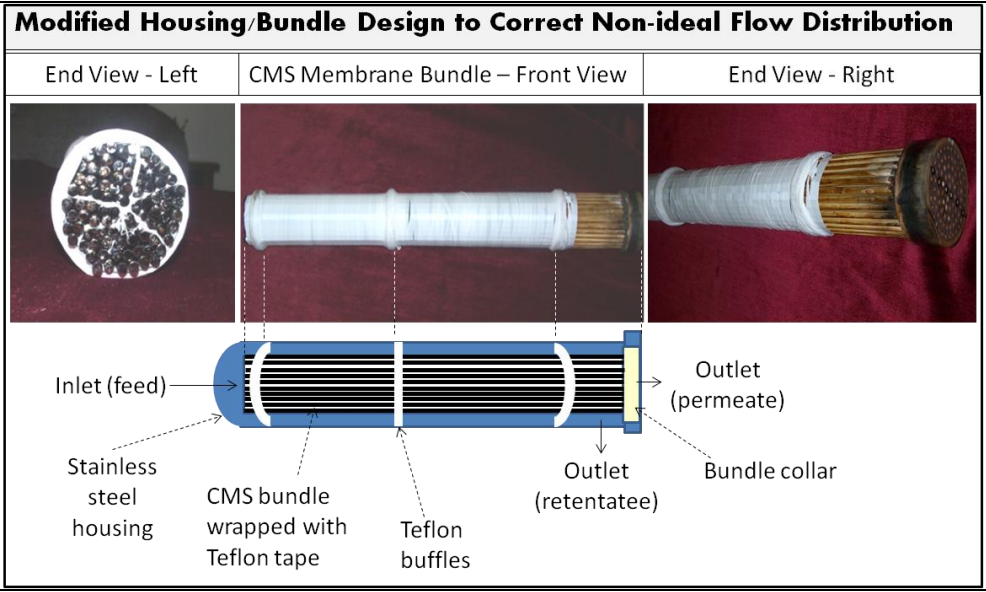


Figure 6. Teflon wrap/bundle design to prevent feed gas bypass of the membrane tubes in the full scale test module.

mixed gas permeances, particularly for the fast gases (He, H_2, etc) is within 90 to 100% of the pure component results. Typical pure component versus mixed gas data is shown in Table 4.

4.4.2. Baffle Long Term Stability

Testing was conducted to confirm longer term stability of the baffle strategy. The mixed gas permeance results after several days of testing at 220˚C of the Bundle #3-7 are shown in Table 4 and clearly demonstrate that the mixed gas permeance is relatively stable and consistent with the pure component results over 11 days of testing.

Table 4. Comparison of the pure component and mixed gas permeance of the CMS bundle #3-15. Gas testing was conducted at 220˚C at a feed pressure of 10 to 20 psig. Gas mixture composition is 60/40 vol% He/Ar.

Time	Pure Component He [$m^3/m^2/hr/bar$]	Mix Gas He [$m^3/m^2/hr/bar$]
Day 1	3.02	2.91
Day 4	3.07	3.0
Day 5	2.7	2.94
Day 6	3.1	3.2
Day 8	2.8	3.0
Day 11	3.1	3.1

These results confirm the importance of restricting the feed flow to within the space between the tubes of the bundle. Our modified module concept can achieve this objective. It should be noted that this gas bypass is a side effect of requiring some space between the bundle and the module ID, which is necessary to avoid damage to the CMS layer on the exterior of the outer tubes in the bundle during packing inside the housing. Hence, the Teflon baffles and wrap not only act to control the feed flow but also prevent damage to the membrane during installation.

4.5 Slow Gas Permeance Source in Full Scale CMS Bundles

Slow gas permeances in the full scale bundles, although on-spec, in general are higher than can be achieved with single tubes. However, the source of the N_2 permeance difference was not well understood and several sources other than the tubes could represent sources for leaking of the slow gases. In this project, considerable effort was invested in understanding the sources of the higher slow gas permeances in the bundles.

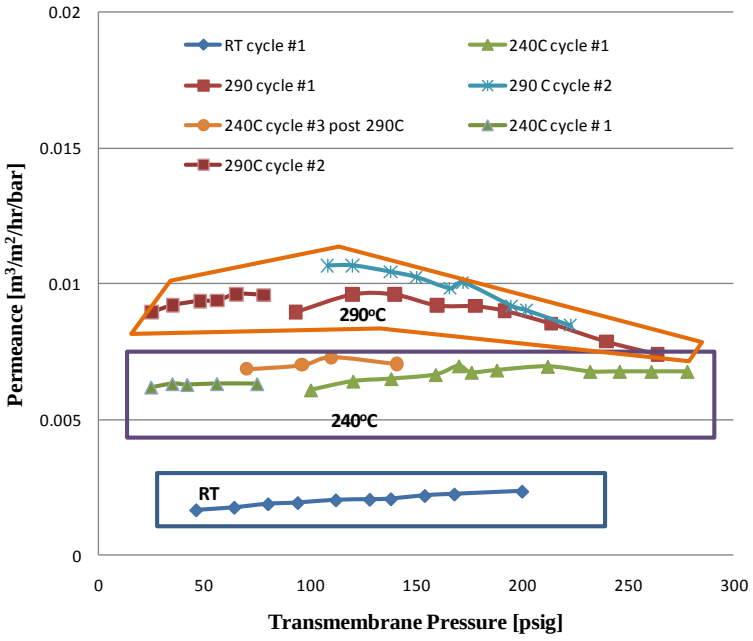


Figure 7. N_2 permeance versus pressure for the CMS Bundle 3-18.

4.5.1. Pressure Testing of the Field Testing Module Sealing Fixture.

An obvious source of potential slow gas "leaking" is the module to membrane seal. Our current technology uses a graphite packing compressed into place between the ceramic collar and steel housing. The sealing fixture is a crucial component of the field testing module. The fixture is necessary to seal the membrane bundle in the housing and prevent feed gas bypass to the permeate stream. However, once the fixture is installed in the module, it will be impossible to remove or modify it and hence considerable effort has been taken by us to verify the quality of the seal. After a few minor modifications to prototype versions, a final version was tested by us. Figure 7 shows the results of a pressure cycle to 250psig at RT, 240˚C, and 290˚C of the CMS bundle #3-18 using this sealing fixture and high temperature graphite as the seal material. As can be seen, the permeance at RT and 240˚C (both before and after thermal cycling to 290˚C) is essentially stable as a function of pressure. Although the results at 290˚C show a slight decay in the N_2 permeance, this is likely the result of inadequate preheating of the feed gas at these temperatures and higher total permeation rates and system modifications are currently underway to remedy this problem.

4.5.2. Source of N_2 Permeance in Full Scale CMS Bundles

Figure 8 shows typical nitrogen permeances of several bundles prepared near the end of this project and show values ranging from ~0.02 to 0.04 $m^3/m^2/hr/bar$ at transmembrane pressures up to 300 psi. Further, for these parts the permeance increase with transmembrane pressure increase is relatively modest and on the order of 0.005 $m^3/m^2/hr/bar$ over the 300 psi pressure range. Although these parts are on-spec, delivering He/N_2 selectivities above 75, we were interested in verifying the source of the N_2 permeance was dominated by the tubes and not some other leak. Work was undertaken to isolate the source of the N_2 permeance as discussed below.

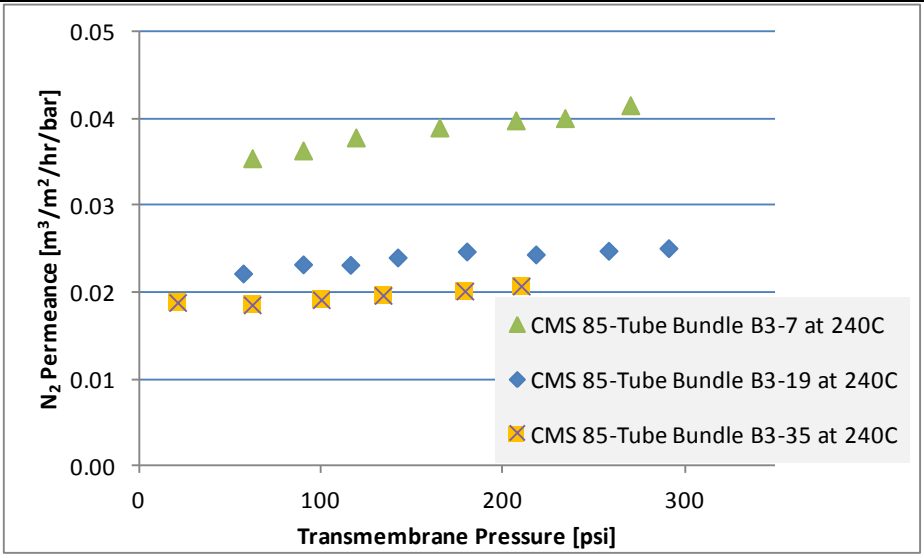


Figure 8. Transmembrane pressure dependence of the N_2 permeance of several CMS 85-tube bundles at 240˚C.

In general, low N_2 permeances are preferred so that excellent membrane selectivity and hence good gas separation can be achieved. There was some concern that the N2 permeances shown in Figure 8 may reflect leaking of the bundle potting or seal between the bundle and the steel housing. In this regard, to isolate the source of the observed N_2 permeance, we have prepared bundles that contain:

(i) Solid rods. Since it is not possible for the "tubes" to leak, this testing should reveal potential leaks in the ceramic-glass potting.
(ii) Ceramic tubes with full glass along the length. As with rods, the tubes do not leak. However, in this configuration the tube (glass end seal) to potting seal and verify the leak rate here.
(iii) Solid ceramic disc. With a solid ceramic disc (no rods/tubes) it is possible to independently check the level of the seal leak.

Solid Rod Bundle: Testing of 85-tube bundles prepared from solid rods has been conducted to pressures up to 300 psig at 240 to 250˚C. In general, these bundles display very low permeance and are typically two or more orders of magnitude lower than a comparable CMS bundles. For instance, Figure 9 shows the high pressure testing results from BT-25, a solid rod bundle. As can be seen, the permeance is extremely low at $\leq$0.0004 $m^3/m^2/hr/bar$ of N_2 at 250˚C and 300 psi and

the permeance increases by 0.0002 $m^3/m^2/hr/bar$ over the 300 psig test range. Hence, overall leaking from the potting is generally insignificant.

Bubble testing in water of the "solid rod" potting revealed about 15 to 20 small pinholes in the potting, mostly along the interface between the ceramic-glass potting and the ceramic collar. These pinholes are the source of the "leaking" in this bundle. Hence, as a screening tool, water bubble testing offers a qualitative method to identify potential problems in the potting. Clearly, several (>20) pinholes in the potting can be tolerated without compromising the performance of the bundle.

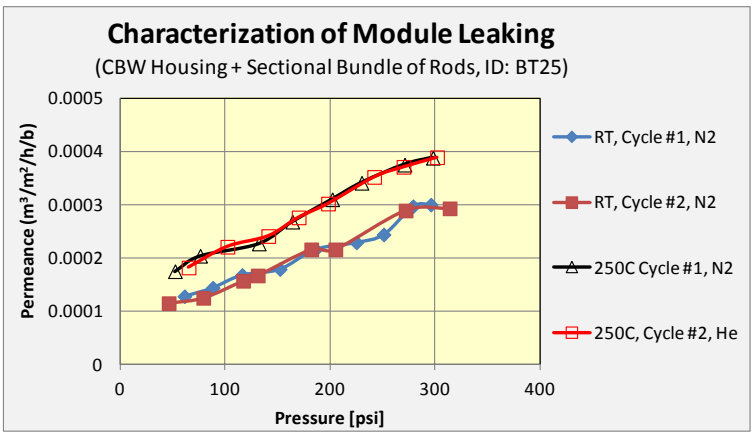


Figure 9. Transmembrane pressure dependence of a typical 85-tube "solid rod" bundle at the conditions shown.

Bubble Testing of CMS Tube Bundles: For our typical CMS bundles, bubble testing generally reveals a number of bubbles in the face of the potting consistent with that observed with the "solid rod" bundle (perhaps 20 to 50 pinholes). Hence, it is clear from this testing that the increase in N_2 permeance (and pressure dependence) of the CMS bundles is not likely due to flaws in the potting. If so, much more aggressive bubbling would be observed during bubble testing.

(Note: the solid rod bundle also shows that our graphite packing to seal the bundle in the housing is highly effective).

Glass End Sealed Tube Bundle: The solid rod bundles give us insight into possible leaking from the bulk potting ceramic-glass as well as the seam between the ceramic collar and the potting ceramic-glass. However, leaking at the seam between the tubes and potting is not accurately reflected by the solid ceramic tubes. In the standard bundle, the porous substrate tubes are end sealed with a thin coating of glass. It is this glass that is in contact with the potting and hence it is appropriate to test these materials. Testing with a bundle prepared from tubes that had been rendered impermeable with our sealing glass was conducted at pressures up to 350psig and 290˚C. As with the rod bundles, permeate flow was essentially undetectable and hence several orders of magnitude below the permeance observed in the CMS bundle testing.

Solid Aluminum Disc: Simple testing of a solid aluminum disk with the same diameter of ceramic collar was used to verify that the oring/graphite seals play no role in the pressure dependence of the leak rate. Tests conducted up to 500 psig transmembrane pressure revealed essentially unmeasurable leak rates in this configuration, consistent with a full bundle permeance of <0.0000001 $m^3/m^2/hr/bar$ and five orders of magnitude less than a typical bundle permeance (see Table 3 for typical CMS bundle permeances). Hence, the o-ring or graphite membrane to

module seal was proven to not be the source of the parabolic permeance increase during CMS bundle testing.

CMS Tubes Account for N_2 Permeance in Full Scale Bundles: Overall, our testing of the individual potential leak sources revealed that the N_2 permeances observed during the bundle testing was essentially exclusively due to permeation through the membrane tubes. There is no evidence based upon our aggressive testing that the module/ceramic seal, potting, or glass tips are leaking. These potential leak sources all reveal N_2 "permeances" at least two orders of magnitude below the results obtained for a CMS bundle.

4.6 Mixed Gas Testing in Synthetic and Actual Gas Streams. Single Tubes and Bundles

Throughout this project a number of mixed gas tests were conducted by third parties or outside of our laboratories to verify membrane performance. Single tube and bundle testing was conducted as described below.

4.6.1. Refinery Pilot Testing: H_2 Recovery from a Hydrotreater Off-gas. Synthetic Mixture

Synthetic Gas Mixture Testing… Single component and mixture gas testing was conducted at a third party site using MPT's E-59 CMS membrane. Mixed gas data was obtained with a synthetic mixture containing 60% H_2/20% CH_4/20% CO_2. Overall, good results were obtained in these tests as the permeance of both CH_4 and CO_2 remained constant and the selectivity for H_2/CH_4 remained at over 160 throughout. A small 10% loss in the mixed gas H_2 permeance (versus the pure component value) was observed during this testing and was considered negligible. Overall, excellent results with one of our high performance CMS membranes were obtained.

Synthetic Blend to Match Refinery Waste Gas*....* To follow-up on this work, mixed gas challenge testing was conducted using two synthetic blends consisting of H_2, CH_4, ethane, propane, butane, isobutane and H_2S (compositions shown in Figure 10) to better approximate the gas composition of the target refinery waste gas stream. What follows is a general discussion of the results of the mixed gas testing conducted with the #E-59 CMS membrane at the 3rd party site.

Mixture A

60% H_2
21% CH_4
6% C_2H_6
4% C_3H_8
1% i-C_4
2% n-C_4
6% H_2S

Mixture B

40% H_2
33% CH_4
10% C_2H_6
8% C_3H_8
1% i-C_4
2% n-C_4
6% H_2S

Figure 10. Synthetic gas mixtures studied during the challenge testing conducted at a 3rd party site at the request of our end user.

Mixed Gas Test #1:
Testing was conducted at a feed pressure of 350 psig and permeate pressure of 20 psig and operating temperature of 200˚C. The target feed stage cut was 19%. The results of the pure and mixed gas testing are shown in Table 5. As can be seen, very high purity H_2 can be obtained under these test conditions. However, there is a considerable reduction in the mixed gas H_2 permeance (415 GPU) versus the pure component result (571 GPU). Note that 370 GPU is

equivalent to ca. 1 $m^3/m^2/hr/bar$. Although the exact source of the 27% decline is not known, it is suspected that the larger molecular weight gases may be blocking some of the larger H_2 pores during testing. Further, the large difference in H_2/CH_4 selectivity in the mixture versus pure gas is likely due to a small leak in the permeate plumbing, since H_2/CH_4 selectivities above about 150 are very rare in pure component testing in our laboratory.

Mixed Gas Test #2:
The second test was conducted under the same conditions as Test#1 except for the slight increase in permeate side pressure. In general, the results are in good agreement with the Test#1 data.

Mixed Gas Test #3:
In this test, the gas blend was changed to Mixture B and the test temperature was increased to 250˚C. The primary goal in this test was to determine the H_2 permeance loss in the mixture at this higher temperature and compare it to the results at 200˚C from Test #1 and #2 and further in Test #4 below. As shown in Table 5, the pure component H_2 permeance increased from ca. 560 GPU at 200˚C to 691 GPU at 250˚C. This substantial increase in H_2 permeance is matched by a similar change in the mixed gas values which increased from 414 (at 200˚C) to 563 GPU (at 250˚C). Still, there is a considerable loss in mixed versus pure gas H_2 permeance of about 18% although this loss is much less that the 27% observed at 200˚C in Test #1 described above. Overall, this result is consistent with trends we have observed in the past with CMS membranes that show that membrane "poisoning" by "slow" gas contaminants will diminish considerably with increasing temperature.

Table 5. Mixed gas performance of the E-59 CMS obtained during tests conducted by a 3rd party for our end user.

Test ID	Mixture	Feed Pressure [psig]	Permeate Pressure [psig]	Test Temp [˚C]	H_2 Recovery [%]	H_2 Purity [%]	H_2 [GPU]	H_2 /CH4 [-]
	Pure			200			571	394
#1	A	350	20	200	31.8	99.4	415	148
	Pure			200			385	
	Regenate at 250˚C			200			555	
#2	A	350	50	200	31.8	99.3	414	159
	Pure			250			691	130
#3	B	350	50	250	47.3	97.8	563	194
#4	B	350	50	200			460	184
#5	B	350	50	175		96.8	373	170
	Pure			200			509	150
#6	B	350	50	200		98.1	391	156
	Pure			200			510	

Mixed Gas Test #4:
The fourth test was conducted with Mixture B but at a lower temperature of 200˚C to investigate the extent of H_2 permeance loss at reduced temperature. It is clear from the results in Table 5 that the H_2 permeance reduction in the mixed gas is again more substantial than observed at the elevated temperature.

Mixed Gas Test #5:
The operating temperature was further reduced to 175˚C and again the membrane performance was tested in the presence of Mixture B. A further substantial reduction in the permeance from the 563 GPU at 250˚C to 460 GPU at 200˚C and now 373 GPU at 175˚C was observed. However, the membrane H_2/CH_4 selectivity is still excellent at 170.

Mixed Gas Test #6:
The final mixed gas test was conducted at 200˚C with Mixture B to check the permeance recovery achieved with an increase in temperature but no regeneration of the membrane at 250˚C. However, although the mixed gas H_2 permeance increased to about 391 GPU from 373 GPU, it was still considerably less than the previous results at 200˚C of 460 GPU (Test #5) and 415 GPU (Test#1). This result suggests that some of the poisoning that occurs at 175˚C still is present and is not removed at 200˚C.

Discussion on Test Results and Implications… Mixed gas testing using $H_2/CO_2/CH_4$ blends was conducted by the 3rd party laboratory to investigate mixed gas effects on membrane permeance. Several results from these tests are summarized for comparison to testing conducted with the synthetic hydrocarbon blends. First, there was an initial decay in pure component permeance following an initial exposure to the mixed gas from about 640 to 570 GPU. This initial decay is apparently related to the "plugging/fouling" of larger pores in the membrane with gas mixture contaminants. Based upon our experience with high purity gases, it is unlikely that CO_2 and CH_4 could be the source of the permeance loss, and we suspect that higher boiling trace contaminants are likely the source. Second, the pure component H_2 permeance stabilized at this level on subsequent exposure to the mixed gas. This result is consistent with a one-time masking of the larger pores in the membrane. Third, it was observed that at 200˚C, mixed gas H_2 permeances would decay by about 20% from the pure gas values but would recover under pure gas purge to the pure gas values. At the conclusion of this preliminary testing, the pure component H_2 permeance was ca. 567 GPU at 200˚C and essentially unchanged from the first exposure to the mixed gas.

The goal was to assess the impact of higher boiling hydrocarbons in the gas blend on the H_2 permeance. A similar trend is noted. First, there is an initial decay of the pure component H_2 from 571 to 385 GPU following initial exposure of the membrane to Mixture A. This loss is actually quite substantial and oddly is less than the mixed gas value of 415G GPU (in all other testing, the mixed gas H_2 is always less than the pure component value both before and after testing). It is highly likely that there was an error in this pure gas measurement, given that the pure component permeance following an additional five mixed gas tests had stabilized at 510 GPU. Second, the initial pure component H_2 permeance loss stabilizes and does not decay with subsequent exposure to mixed gas as noted particularly in Test #6. Third, the mixed gas H_2

permeance is consistently less than the pure component value, although this loss is considerably reduced as the temperature is increased from 175 to 250˚C.

Overall, the membrane permeance characteristics are similar throughout the testing program. First, initial exposure to the mixed gas leads to an initial loss in H_2 pure component permeance is suspected to be due to irreversible plugging of larger pores. Only subsequent heating of the part to 250˚C or higher will recover the pure component H_2 permeance to its original value. Second, the loss stabilizes and the pure component H_2 permeance remains constant following additional exposure to mixed gas at constant temperature. Performance stability is an important feature of CMS membranes and is necessary for long term low cost operation. Third, in all cases (but one), there is a reduction in the mixed gas permeance below the pure component values. This loss is transitory, based upon the subsequent pure component values, and is likely due to partial blocking of intermediate size pores by one or more of the mixed gas components. Further, this permeance loss is typically on the order of 20 to 30% from the pure component value and is manageable with regard to membrane cost. Finally, the membrane selectivity remains extremely high during mixed gas testing and hence excellent H_2 purity and recovery can be achieved to meet the end user target. In summary, the 3rd party testing confirmed the membrane separation efficiency and performance stability in the presence of synthetic refinery gas.

In summary, the initial loss observed when the membrane was exposed to the mixtures could be resulted of pore plugging by larger molecular compounds (such as contaminants present in the C1 to C4 mixtures). Even though this similar plugging phenomenon could be present in the actual stream in the field, its impact in permeance reduction is within the acceptable range, and is not permanent and regenerable at a higher temperature.

4.6.2. Refinery Pilot Testing: H_2 Recovery from a Hydrotreater Off-gas. Actual Gas

During this program membrane testing was conducted at our end user pilot testing facility to verify CMS membrane performance in actual refinery off-gas generated from a pilot scale hydrotreater. These activities represented Phase I of two phases of our field demonstration activities to be conducted with our end user. Phase II activities will be conducted at an actual refinery site using our full scale multiple tube (85-tube) CMS bundle. The Phase I activities were conducted to verify the membrane stability in the presence of real off-gas. Two objectives in this phase were (i) to confirm test results obtained during third party performance evaluation of our membranes conducted with *simulated* refinery off gas and (ii) to confirm successful intermediate time frame membrane stability in the presence of actual refinery waste gas as part of the go/no go decision for the larger scale Phase II testing. In this testing, a single tube CMS membrane was used. This part was cut from a full scale 85-tube bundle and can be expected to be representative of the typical bundle performance in this application.

Table 6. Typical gas composition during the Phase I pilot testing at our end user site.

Component	Vol%
H_2	95
C1	1.6
C2	0.4
C3+	1.6
H_2S	1.4

Refinery waste gas generated from a pilot scale hydrotreater was used during this testing. Figure 11 shows the membrane test rig installed at our end user site. Table 6 shows a representative analysis of the feed composition, although in general the H_2 content varied between about 90 to

95% in the feed. Of particular note is the presence of significant quantities of higher boiling hydrocarbons as well as H_2S (10,000 to 15,000 ppm). These components are of particular interest because of their ubiquitous presence in refinery off gases and their ability to cause significant damage to competing polymeric membranes. Total gas feed pressures between ca. 150 and 300 psia and permeate pressures up to 150 psia were studied at an operating temperature of ca. 220˚C. No gas pretreatment was conducted prior to feeding to the membrane.

Figure 12 shows specific run conditions (H_2 partial pressure) and membrane performance results (H_2 recovery, H_2 permeance, H_2 permeate composition, and H_2S in the permeate) for the 24 day test run. Several important results should be highlighted. First, overall, the membrane performance is very stable. The H_2 permeate composition is consistently above 99.5% at H_2 recoveries typically above 75 to 80%. In fact, at the current pressure operating conditions, it would not be possible to achieve significantly higher H_2 recovery due to simple pressure driving force limitations. In addition, the mixed gas H_2 permeance remains stable throughout the run at ca. 0.95 to 1.1 $m^3/m^2/hr/bar$. Second, the selectivity of the membrane is high and stable throughout the run. As an example, the H_2S content in the permeate is maintained below 15ppm versus greater than 10,000 ppm in the feed. Further, it should be noted that the membrane was continuously exposed to H_2S at levels >50,000 ppm in the reject stream.

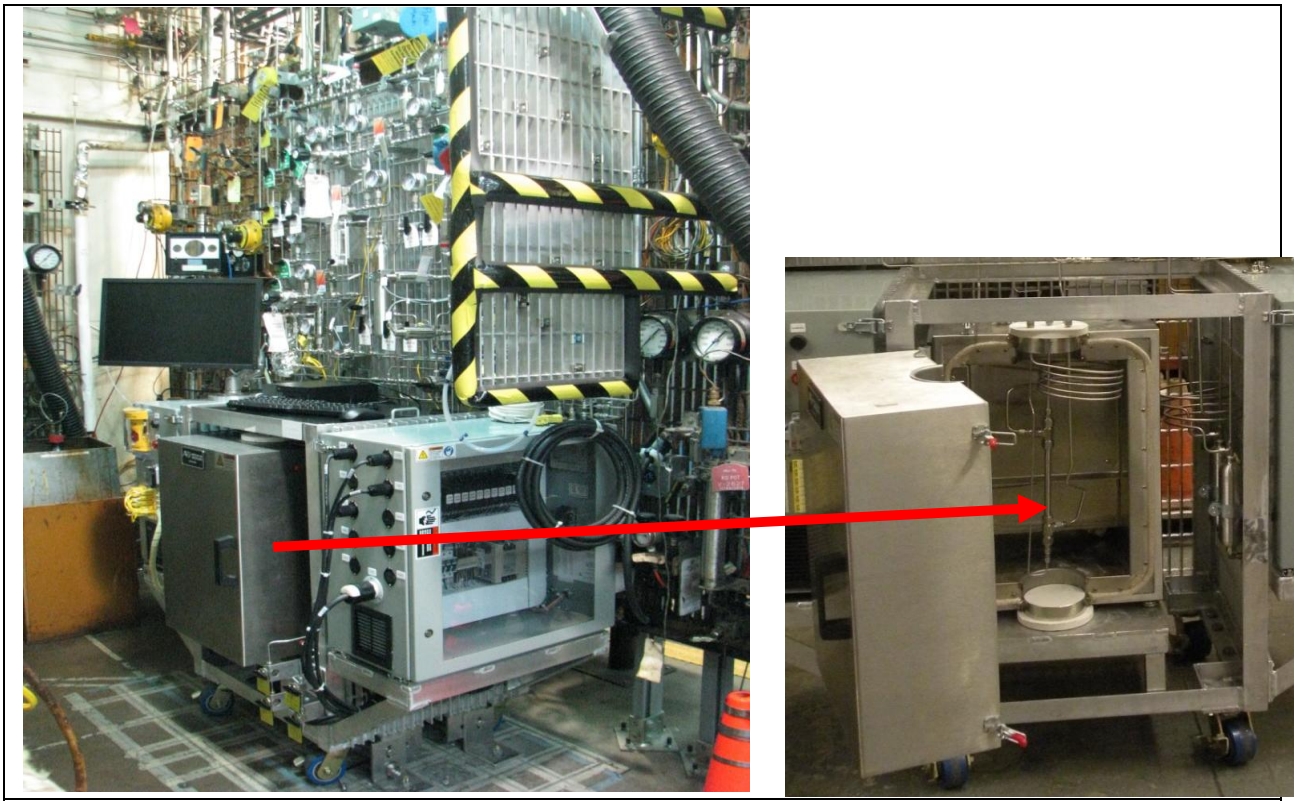


Figure 11. Pilot testing facility at our end user site and membrane test rig.

The results of this Phase I test at our end user's pilot testing facility confirmed the stability of our membranes in refinery waste gas. These results are consistent with our previous shorter term

results obtained in (i) our laboratory as well as (ii) in third party testing conducted using simulated refinery off gases as described in Section 4.6.1.

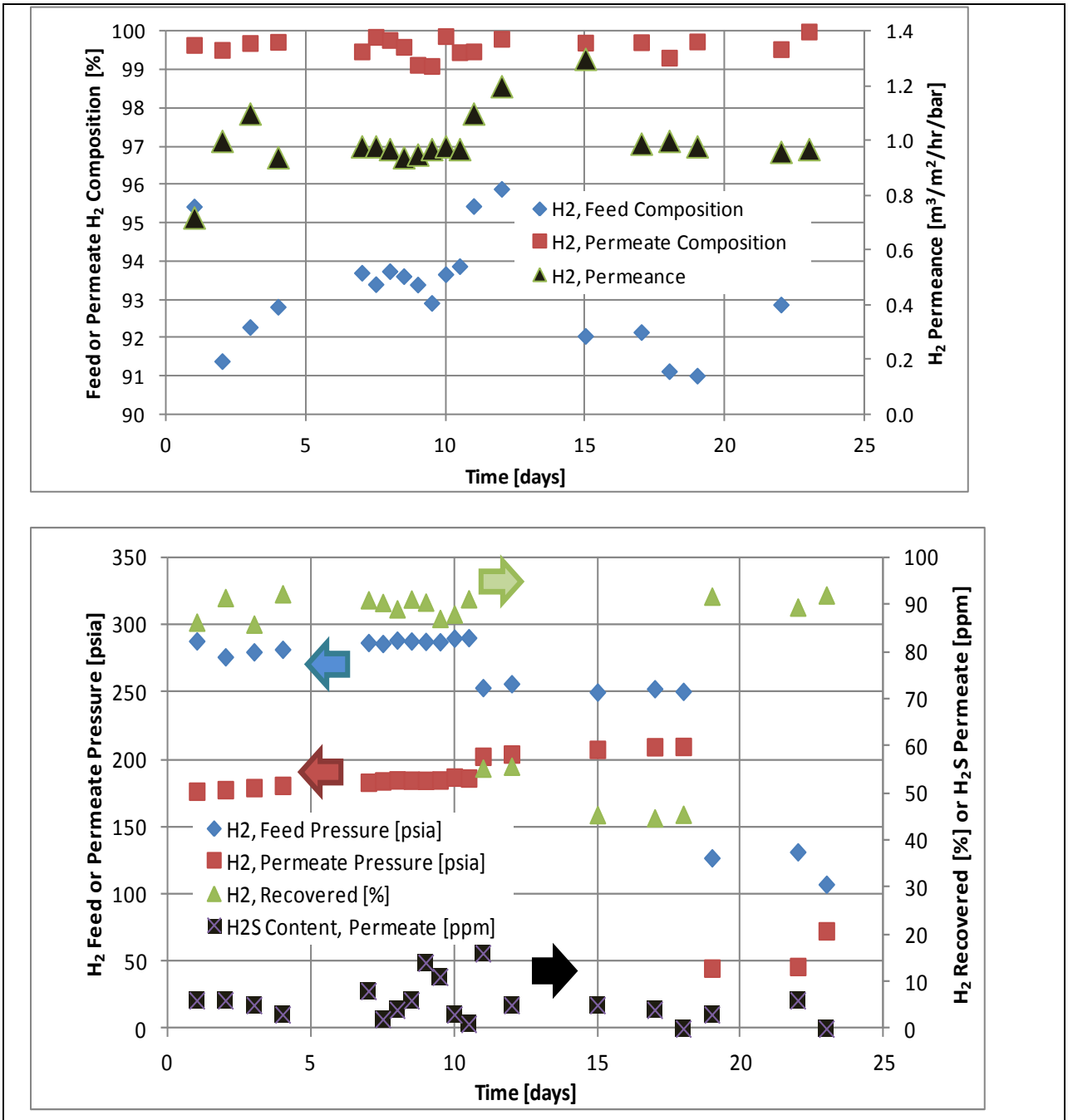


Figure 12. Performance of an MPT CMS membrane in actual refinery off gas generated from a pilot scale hydrotreater at our end user pilot testing facility. The testing was conducted over 24 days. Membrane operating temperature was ca. 220˚C.

4.6.3. Full Scale Bundle Testing at the PSDF. Coal/Biomass Gasifier Off-gas

While our end user participant was planning the field test program at its own refinery site during this project, M&P had the opportunity to conduct field tests using the off-gas (i.e., syngas) generated at a coal gasification facility. A number of tests were conducted at the Power Systems Demonstration Facility (PSDF), now the National Carbon Capture Center (NCCC), to demonstrate the separation efficiency and performance stability of our CMS membranes, both in single tube and multiple tube bundle formats. Since the coal gasifier off-gas is notoriously dirty, evaluation of our membranes under these conditions provided significant challenge testing of our membranes under the worst case scenario in benchmark against the refinery waste gas. Testing conducted to date is shown in Figure 13. Membranes used during the various stages of this testing are shown in Figure 14.

Scale	Dimension	Membrane Surface Area (m^2)	Estimated H_2 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	June 2012

Figure 13. Testing activities conducted at the PSDF.

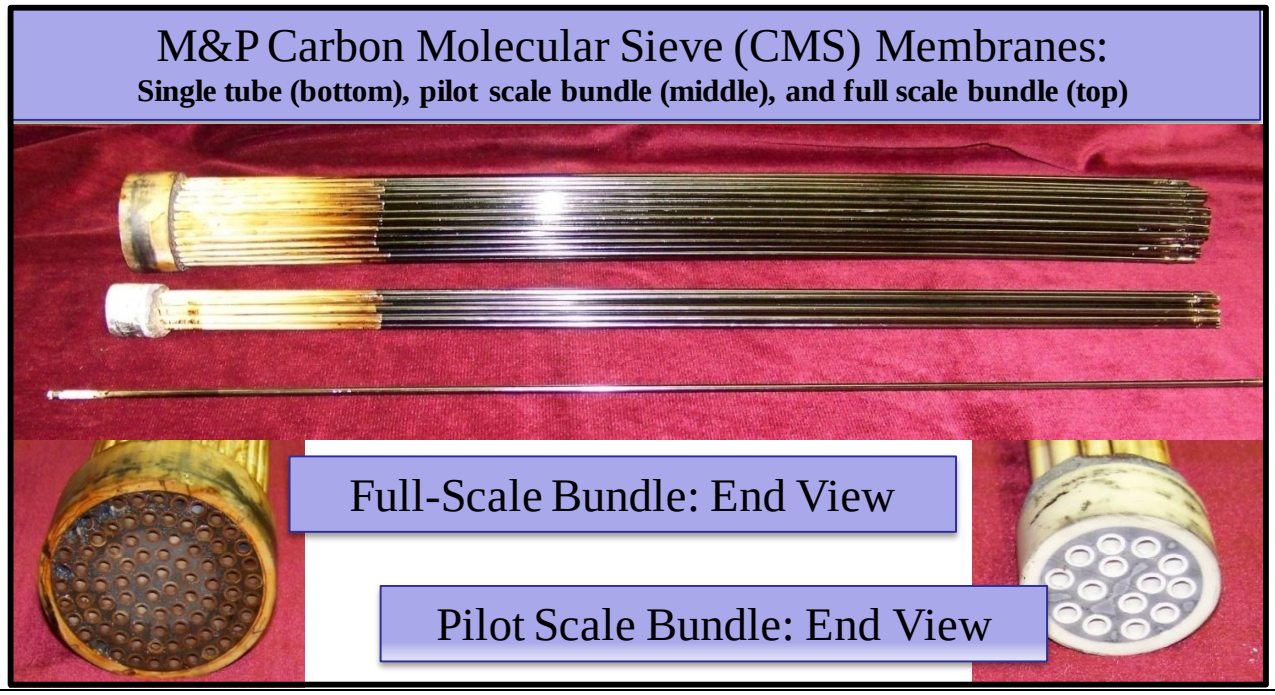


Figure 14. Testing activities conducted at the PSDF.

In the most recent of testing, 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. The full scale module is shown in Figure 15. Note that the PSDF module is SS316 construction making it suitable for operation in corrosive atmospheres, for instance H_2S.

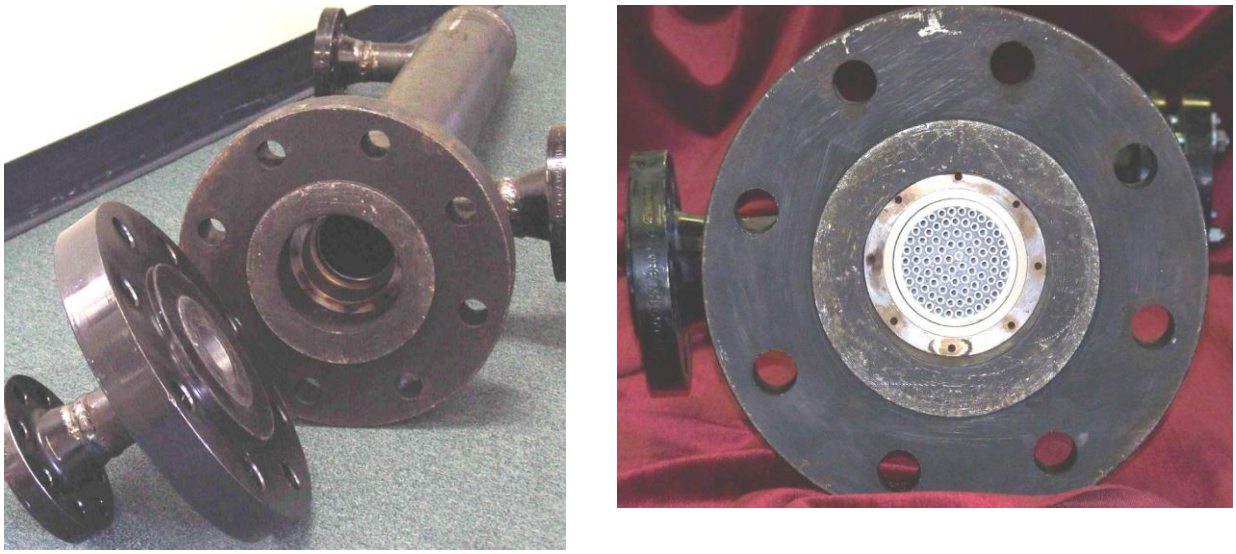


Figure 15. Full scale ca. 85-tube CMS membrane bundle (full ceramic-glass potting) suitable for high temperature and high pressure operation. Also shown is the full scale module. The module used in the PSDF is stainless steel construction (unlike the carbon steel prototype shown here).

The full scale bundle testing unit installed at the PSDF is shown in Figure 16. The B3-7 bundle was installed in the field test unit in late mid-October 2012 and testing was conducted with this membrane for approximately 215 hours in the presence of PSDF gasifier off-gas with no gas pretreatement. Figure 17 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. Figure 18 shows the H_2 and CO_2 composition of the feed and permeate gas streams. The balance was primarily N_2 (air blown gasifier) with small amounts of CO and light hydrocarbons. In addition, H_2S and other sulfur species content of the feed was typically in the 200 to 1,500 ppm range. Water content in the feed was ca. 6 to 8%. In general, the raw syngas feed H_2 content was in the range of 7 to 8%. Permeate H_2 content of about 30% was typical from this CMS bundle.

In general, the goal of this phase of the testing was to demonstrate the performance stability of the CMS membrane in the presence of highly contaminated gasifier off-gas with no pretreatment. In previous work at the PSDF, we have shown that our single tube membranes were highly

stable, particularly if operated at temperatures above 220˚C and preferably 250˚C to avoid condensation of tar-like species on the membrane surface. Figure 19 shows the helium and nitrogen permeance of the B3-7 bundle during this phase of the testing at the PSDF. As is clearly evident, the membrane performance was highly stable under these operating conditions in the presence of gasifier off-gas that has not been pretreated for the removal of gas phase contaminants.

Figure 16. Full scale CMS bundle testing unit as installed at the PSDF facility. The unit is configured to accept one full scale 85-tube bundle.

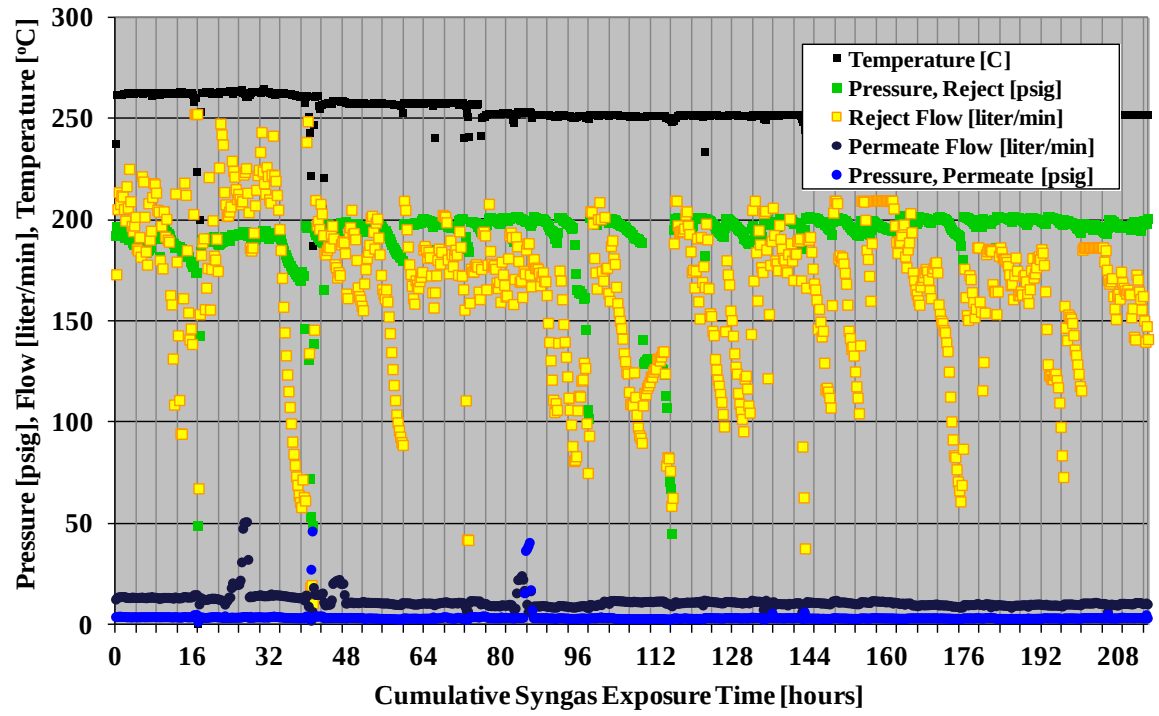


Figure 17. Summary of test conditions for the B3-7 bundle for the ca. 215 hours of testing conducted in the presence of PSDF gasifier off-gas. No gas pretreatment prior to the membranes was conducted.

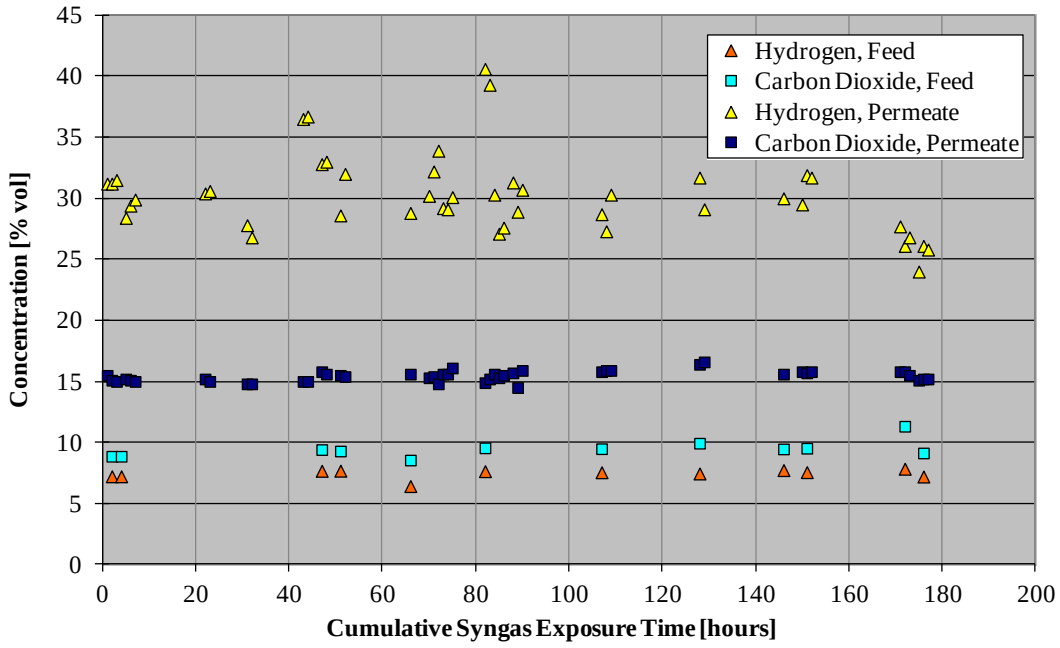


Figure 18. Feed and permeate H_2 and CO_2 composition during testing of the B3-7 bundle at the PSDF. Balance of the feed (and permeate) was primarily N_2 (air blown gasifier) with CO, light hydrocarbons, and various sulfur species.

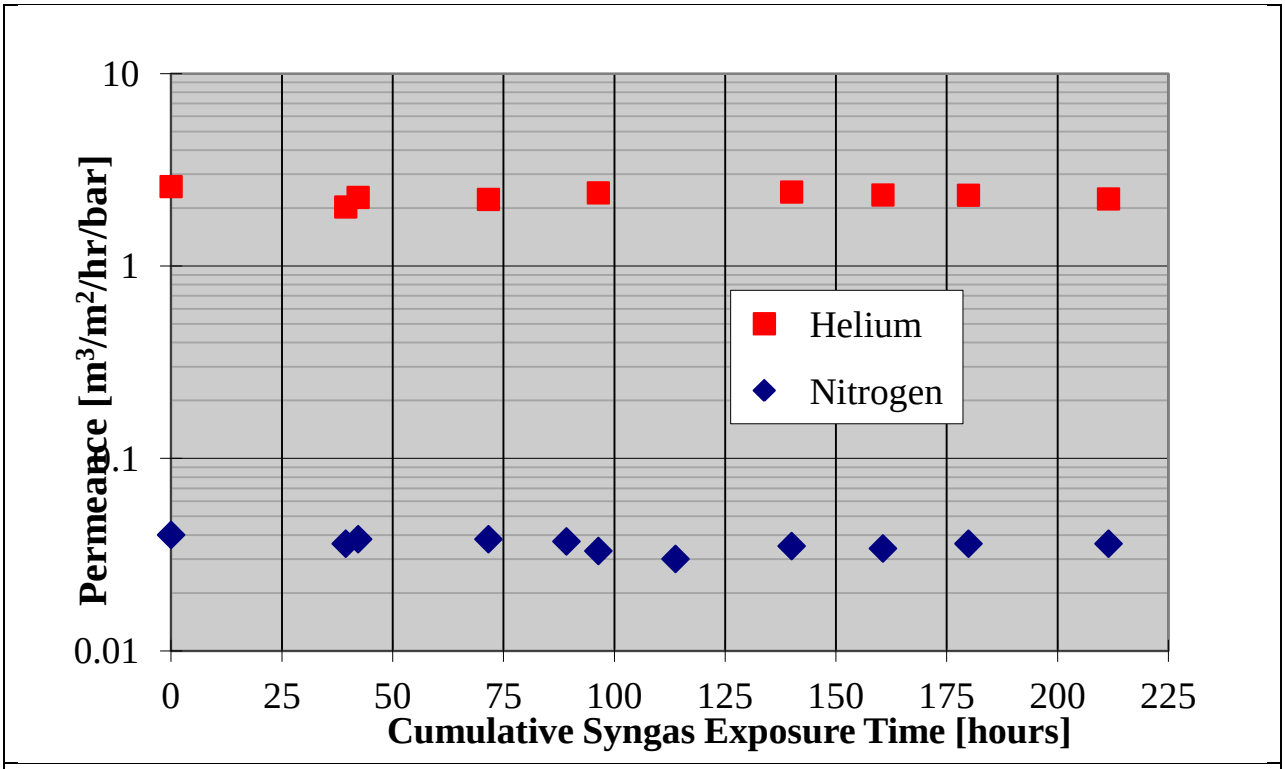


Figure 19. Permeance of helium and nitrogen during gasifier off-gas testing conducted with the B3-7 CMS bundle at 250˚C.

Overall, our full scale bundle testing at the PSDF was highly successful. Major accomplishments include:

- Successfully verified the performance and stability of our full scale field test CMS membrane bundle (86-tube, ~0.8m^2). Gasifier off-gas (syngas) feed rates as high as 600 scfh were successfully tested.

- Membrane operation at ~250°C effectively prevents "tar'-like residue deposition on the membrane and module. Hence, very stable membrane performance was demonstrated for operation >200 hours.

- The 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 >200 hours. No obvious visual or performance degradation was noted in either the CMS bundle or module.

- As previously demonstrated in smaller scale NCCC testing, no membrane degradation in the presence of H_2S or other gasifier off-gas contaminants was observed. These results are consistent with our laboratory performance test results.

4.7 Economics of H_2 Recovery from Refinery Waste Gas

An economic analysis for the recovery of hydrogen from waste refinery gas was developed by M&P during this program. The economic analysis results prepared by us are presented below.

- ***Process Conditions…*** Our economic analysis is based upon a typical refinery hydrotreater off-gas stream of 20 million scfd at 150 to 360 psig with a hydrogen content of 40 to 60% as recommended by our end user participant. Our analysis below is based upon the simulation results described in Sec. 3.6. The membrane surface area and the hydrogen purity along with the % hydrogen recovered generated from the simulation were used as input performance parameters for our economic model. This model can be used to calculate the operating cost, capital recovery cost and the lost fuel cost. Our recovered hydrogen cost is based upon the sum of these three items. Then, this hydrogen cost is compared with the existing competing technology, pressure swing adsorption, PSA.

- ***Key Cost Assumptions…*** Key assumptions used in this economic model include:

  1. **Our CMS Membrane**… Our CMS membrane cost is \$800/m^2 based upon our existing commercial membrane price + additional CMS deposition cost. The housing/plumbing cost is based upon \$250/m^2 recommended in Ref. 1.
  2. **Compressor and Utility Costs**... The installed compressor capital cost is based upon the equation used in Ref. 1 and the projection based upon the indices listed in Ref. 3. However, this price is about 50% of that listed in Ref. 2 on a comparable basis. We have performed the sensitivity analysis on the variation of the compressor cost, the 50% variation does not change the trend of the economic analysis result, i.e., \$/kscf H_2, since the capital cost is amortized for a long period 5 to 10 years. The utility cost is based upon \$0.08/kwh.
  3. **PSA Capital and Operating Costs**… The PSA operating cost is based upon the correlation suggested in Ref. 6, which is comparable with the cost listed in Ref. 2. The capital cost for PSA used in Ref. 1 is about 50% lower than that used in Ref. 2. In our comparison of PSA against our membrane process, we have chosen the lower operating and the capital costs, i.e., ½, for comparison.
  4. **Annual Savings Analysis**… The base case used in our analysis is hydrogen produced from steam methane reforming (SMR). The current hydrogen cost, \$4/kscf H_2, is based upon \$4/Million Btu CH_4 and the comparable plant sized listed in Ref. 5. Hydrogen cost from SMR listed in Ref. 2 is comparable to the estimated listed in Ref. 5. However, \$2/kscf H_2 based upon the input from refineries, is also used in our analysis.

- ***Results: Hydrogen Recovered and Annual Savings Achieved by Our Membranes***… Figure 20 and Figure 21 summarize the results of the economic analysis for the 60% H_2 feed case, permeate recovery pressures of 3, 50 and 100 psig, and H_2 valued at \$2/kscf. As can be seen in Figure 20, increasing permeate pressure in general leads to lower H_2 recovery. However, annual savings are less affected by permeate pressure in this analysis due to increased compression cost required at lower permeate pressures (higher H_2 recovery). As shown in the pie charts in Figure 21, the % contribution of the capital charge and power consumption

increase with decreasing permeate pressure due to increased compression cost. Still in this analysis, at a feed pressure of 350 psig approximately 8 to 12 MMscfd of H_2 can be recovered at annual savings of $1MM to $2MM/year. If a H_2 value of $4/kscf is assumed, then annual savings range from $4MM to $5MM per year as shown in Figure 22.

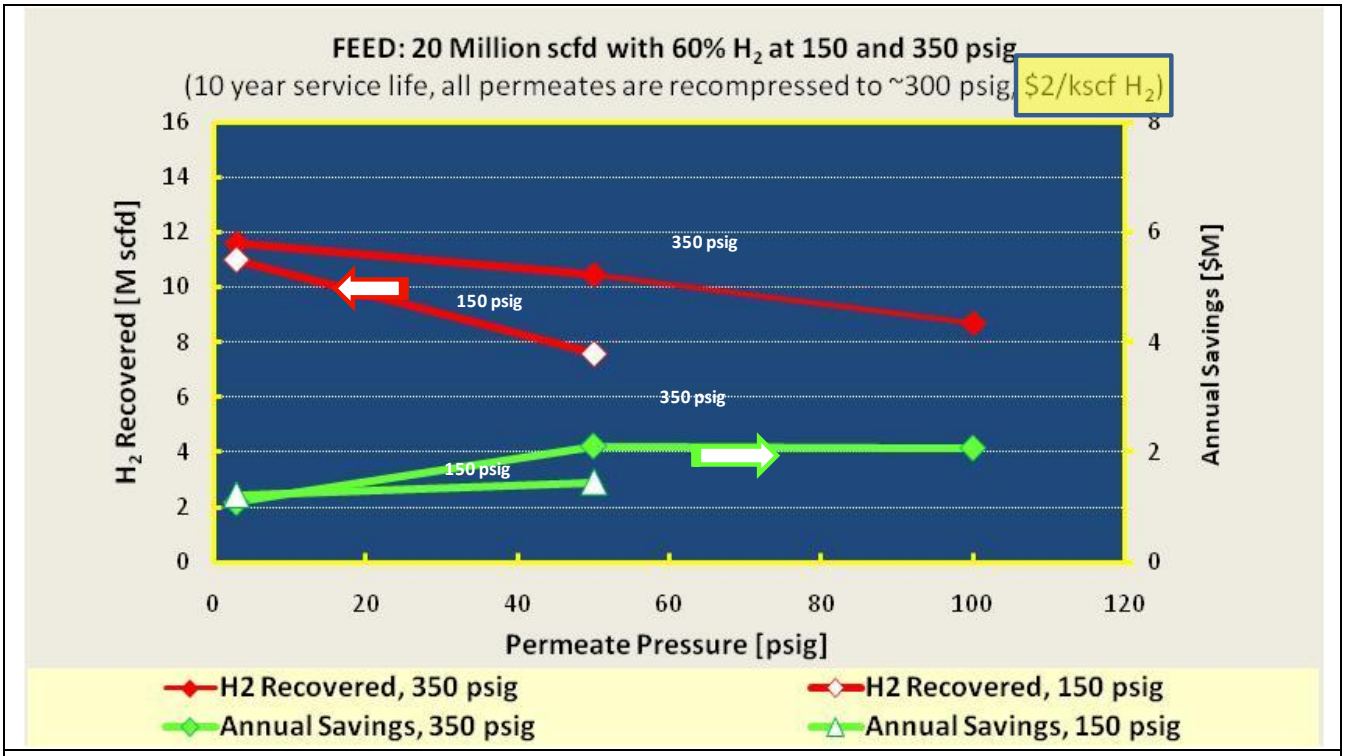


Figure 20. Economics of hydrogen recovery from a refinery waste gas stream as a function of permeate side pressure for two total feed pressures cases of 350 and 150 psig. Annual savings are calculated based upon a H_2 value of $2/kscf H_2.

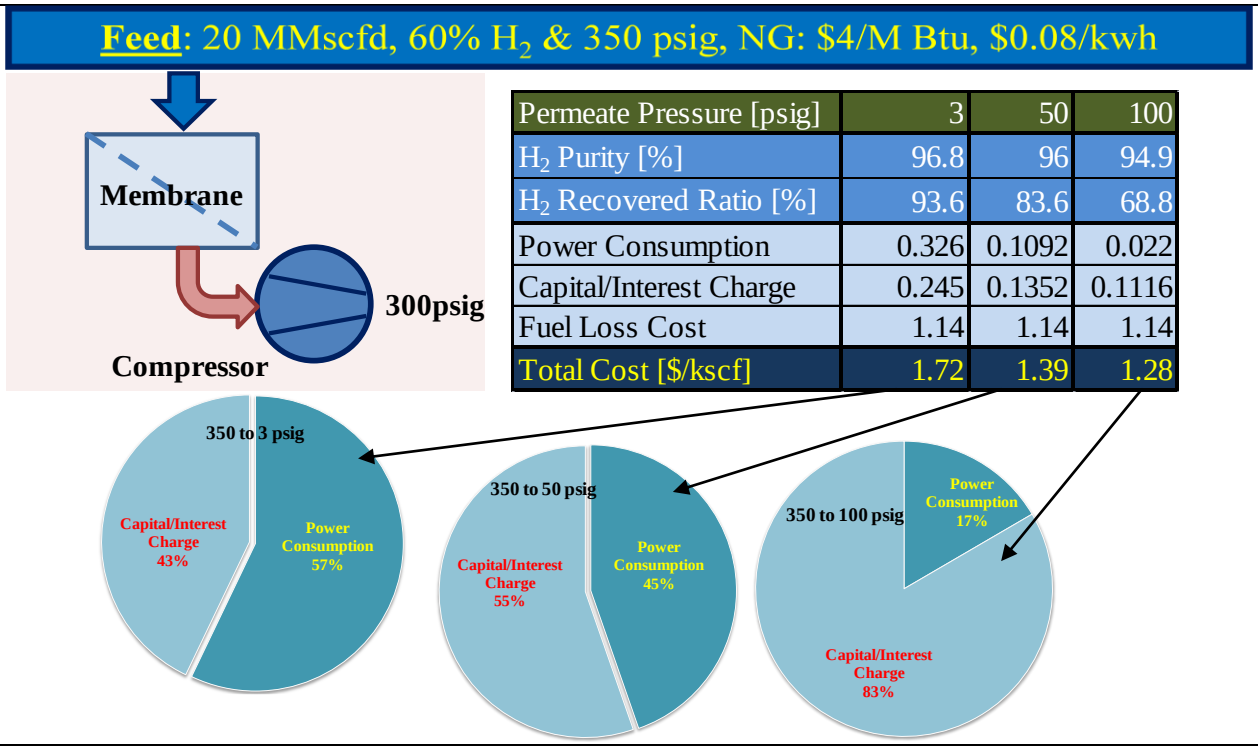


Figure 21. Simplified process flow diagram and breakdown of cost contribution of the major components. Note that as the permeate pressure decreases, membrane cost contribution decreases but power (compressor) cost increases.

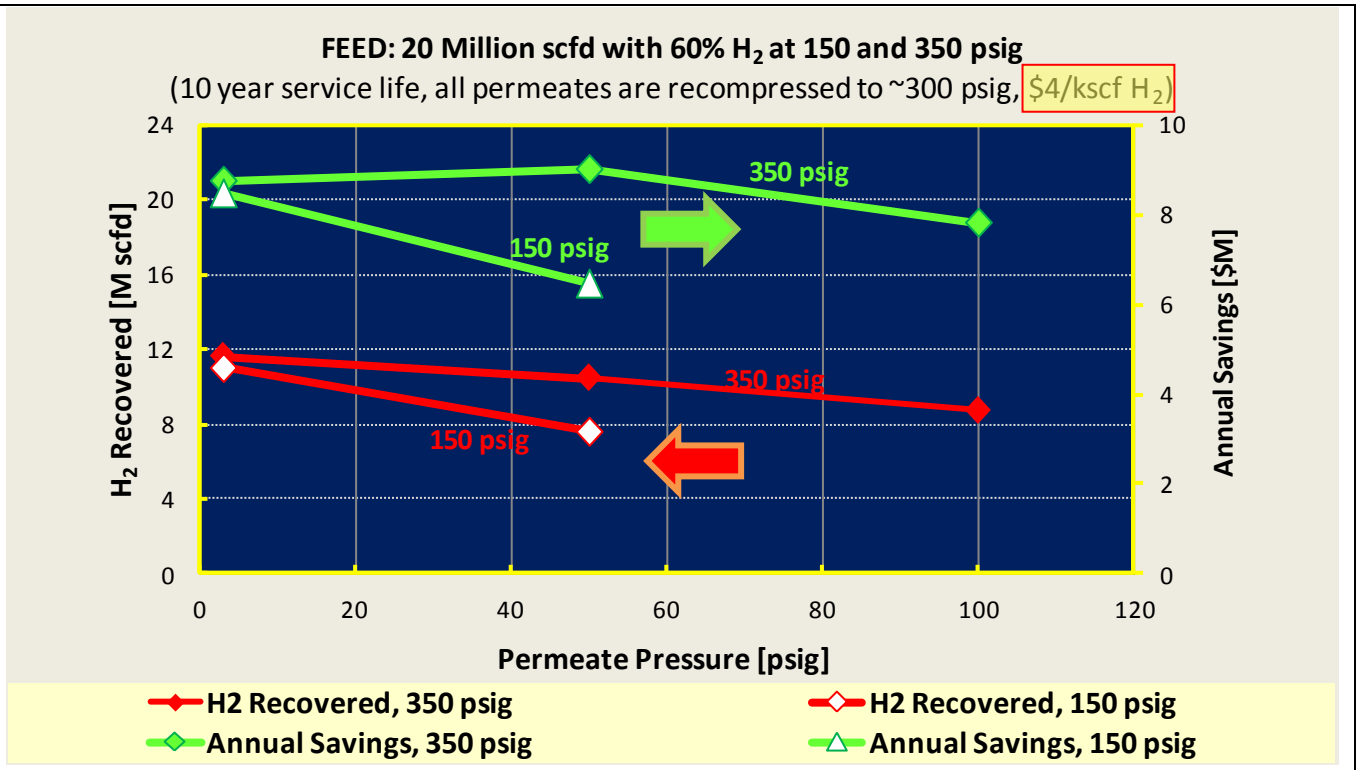
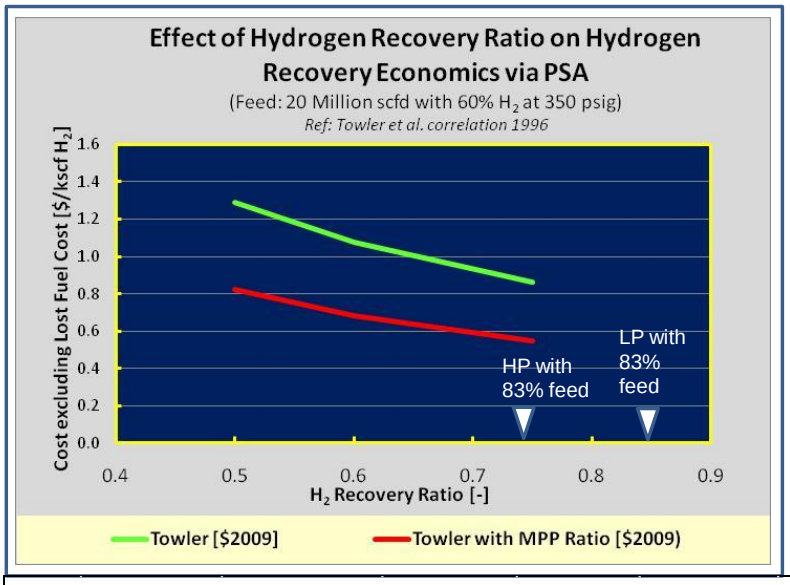


Figure 22. Economics of hydrogen recovery from a refinery waste gas stream as a function of permeate side pressure for two total feed pressures cases of 350 and 150 psig. Annual savings are calculated based upon a H_2 value of \$4/kscf H_2.

- ***Competing Technology and Economics…*** Although polymeric membranes have been considered for the proposed application, the operation at the low temperature puts the polymeric membrane in a vulnerable position as a result of the hydrocarbon condensation on the membrane surface. Unless a very extensive pre-treatment is implemented, which tends to increase the operating cost significantly, the polymeric membrane is considered to be not viable in our proposed application. The other competing technology often considered is the pressure swing adsorption (PSA). Due to (i) its wide use in refinery for hydrogen recovery from steam methane reformers, and (ii) the ability to deliver hydrogen product at the pressure similar to the feed (thus, no recompression of the product hydrogen stream is required) the PSA is evaluated here as a competing technology.

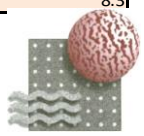


PSA Capital and Operating Economics and Comparison of PSA and M&P CMS Membranes

Comparison between PSA and M&P CMS Membranes: 350 psig and 60% H_2							
Feed [M scfd]	H_2 in feed [mol fraction, -]	H_2 Recovery Ratio [-]	Operating Cost [$/kscf]	Lost Fuel cost [$/kscf]	Total Operating Cost [$/kscf]	Capital Cost [$MM]	Hydrogen Recovered [M scfd]
PSA - High Pressure purge gas for purged fuel delivery (best case scenario, 1/2 cpital cost and 1/2 operating cost)							
20	0.6	0.5	0.822	1.144	1.965	7.09	6.0
Membrane - 100 psig for permeate pressure and then recompressed to 300 psig (Worst case scenario, 2 x compressor and 5 yrs service life)							
20	0.6	0.69	0.209	1.144	1.345	1.83	8.3

- Using Peramanu et al's with 50% discount for capital and operating cost
- Cases for <350 psig and <60% H2 are not practical for PSA

Media and Process Tech Inc.



Limitations of PSA Technology: PSA technology suffers two major deficiencies for this proposed application: (i) the hydrogen concentration in the hydrotreater off-gas ranging from 40 to 60% or lower, which is below the optimum concentration range for PSA applications, and (ii) the purge gas from PSA is usually at nearly atmospheric pressure, which is difficult to deliver to the fuel header. Although it is possible to keep the purge gas at a high pressure (PSA-HP), one pays the price in total hydrogen recovery. In light of these deficiencies, we have performed an economic analysis to evaluate PSA hydrogen recovery economics for a stream with 60% H_2. As illustrated in the figure above, the hydrogen recovery ratio influences the hydrogen recovery

economics significantly. In our analysis, we have assumed that the hydrogen recovery ratio is 60% of the feed with 50% hydrogen purity for the PSA-HP case based upon the 75% recovery ratio for the feed with 84% hydrogen purity presented in the literature. Analyzing three references available in the literature, we have taken the most favorable operating and capital cost cases for the PSA operation due to the inconsistencies among the three resources as illustrated in the figure above. The hydrogen recovery cost ($/kscf) for the PSA is about 1/3 higher than the membrane case while its operating cost is several times higher. In addition the amount of hydrogen recovered is much reduced due to its low recovery ratio. In conclusion, the PSA technology is not economically competitive for the proposed application.

In summary our economic analysis indicates that our proposed membrane based hydrogen recovery process can achieve significant cost savings in addition to the energy savings and CO_2 avoidance as estimated in our proposal. According to our analysis, about $1-9 million cost savings can be achieved for a typical 20 million scfd waste stream generated from the hydrotreating process at 350 to 150 psig with 40 to 60% hydrogen. This level of economics represents the worst case scenario; significantly higher cost savings could be achieved for the waste stream available at pressure >350 psig and at concentrations >40-60%. This analysis is currently under review by our end user participant.

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1. *Membrane Permeation Processes*, Chapter 15, p. 1259
2. Peramanu, S., B. G. Cox, and B. B. Pruden, "Economics of hydrogen recovery processes for the purification of hydroprocessor purge and off-gases", *International Journal of Hydrogen Energy*, *24*, 405(1999).
3. Producer Price Index Finished Goods: Capital Equipment, http://alfred.stlouisfed.org
4. Gottschlich, D. E., D. L. Roberts, J. G. Wihmans, C. M. Bell, and R. W. baker, "Economic comparison of several membrane configurations for H_2/N_2 separation", *Gas Separations & Purification*, *3*, 170(1989)
5. Doty, F. D, "A realistic look at hydrogen price projection", Doty Scientific, Inc., Columbia, SC., Sep. 1, 2004.
6. Towler, G. P., R. Mann, A. J-L. Serriere, and C. M. D., Gabaude, "refinery Hydrogen Management: Cost analysis of Chemically-Integrated Facilities", *Ind. Eng. Chem. Res.*, *35*, 2378(1996)

4.8 Potential H_2 Recovery and Annual Savings

The use of H_2 in refineries has increase dramatically over the past decade and is expected to continue to expand as the quality of crude oil feedstocks decline and environmental regulatory pressures mount. Vital statistics of H_2 consumption in the US are given in Figure 23. Total H_2 production in 2011 was estimated to be ca. 8.3 billion scfy with growth projected to be 10 to 15% per year (see the references at the end of this section). Of this total, approximately 45% is refinery H_2 yielding a total H_2 refinery usage on the order of 10,000 MMscfd. Given an estimated 80 to 85% utilization rate, approximately 1,500 to 2,000 MMscfd is sent to waste gas and recovered for fuel value. Assuming 50% potential recovery using MPT membrane technology, recoverable H_2 is ca. 750 to 1,000MM scfd. Annual savings are on the order of $750 to $1,000MM per year.

H_2 Vital Statistics [US]	
Total H_2 Production	8,350 Bscfy
Trend	10 to 15%/yr
Market	$22 Billion
Average Cost	$2.6/kscf
Refinery H_2 (Ammonia H_2)	45% (28%)
Total Refinery H_2	10,000 MMscfd
Estimated H_2 to Fuel (80 to 85% H_2 Utilized)	1,500 to 2,000 MM scfd
Recoverable H_2 (at 50% with membrane)	750 to 1,000 MM scfd
Recovered H_2 Value	750 to 1,000 $MM/yr

Figure 23. Vital statistics H_2 usage in the US and potential savings achievable with MPT membrane technology.

1. http://www.bharatbook.com/detail.asp?id=192727&rt=Hydrogen-as-a-Chemical-Constituent-and-as-an-Energy-Source.html
2. CryoGas International, February, 2011
3. http://www.slideshare.net/fredyornath/applied-hydrogen-slide-presentation-31208

4.9 Energy Savings and CO_2 Emission Reductions of H_2 Recovery from Refinery Waste Gas

In addition to the cost savings and H_2 recovery aspects, there are concomitant energy and CO_2 emission savings that can be achieved. Energy savings calculated on a net chemical minus fuel value basis per scf H_2 are ca. 130 BTU/scf H_2 as shown in Figure 24. Given this and projecting a total market of 750MM to 1,000MM scfd of H_2 recoverable (see Figure 23) and an 8% per year technology penetration rate, we estimate total energy savings on the order of 150 to 220 tBTU/yr by 2030. Similarly, CO_2 emission savings can be calculated and are shown in Figure 25. CO_2 emission reductions on the order of 5,000 to 6,500 MMton/yr can be expected by the year 2030.

CH_4 Make-up	Energy Consumption [Btu/scf H_2]	Assumptions
Hydrogen Production via SMR	420	Energy consumption to produce H_2 via steam methane reforming (SMR)
H_2 Heating Value requiring CH_4 make-up	-290	Since the make-up H_2 required for hydrotreating can be used as fuel (if H_2 is not reused by hydrotreater), this Btu credit should be deducted from our savings.
Net Energy Savings per unit H_2 recovered	130	Energy savings resulted from reduction in H_2 consumption with our proposed technology

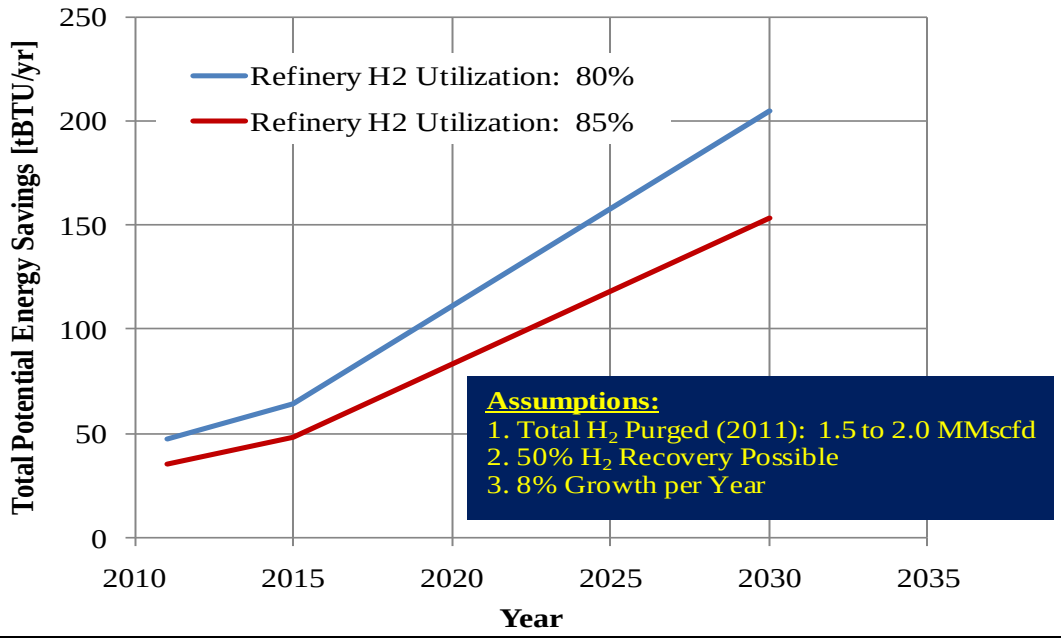

Figure 24. Net energy savings per unit of H_2 recovered and projected annual total energy savings.

CO_2 Emission for H_2 Production	CO_2 Emissions [ton/scf H_2]	Assumptions
	8.75×10^{-3}	Since refineries today are operated under hydrogen-limited conditions, the make-up hydrogen consumed by the hydrotreater will have other uses if not needed by the hydrotreater. Thus, there is no difference in CO_2 emissions with or without CH_4 make-up.

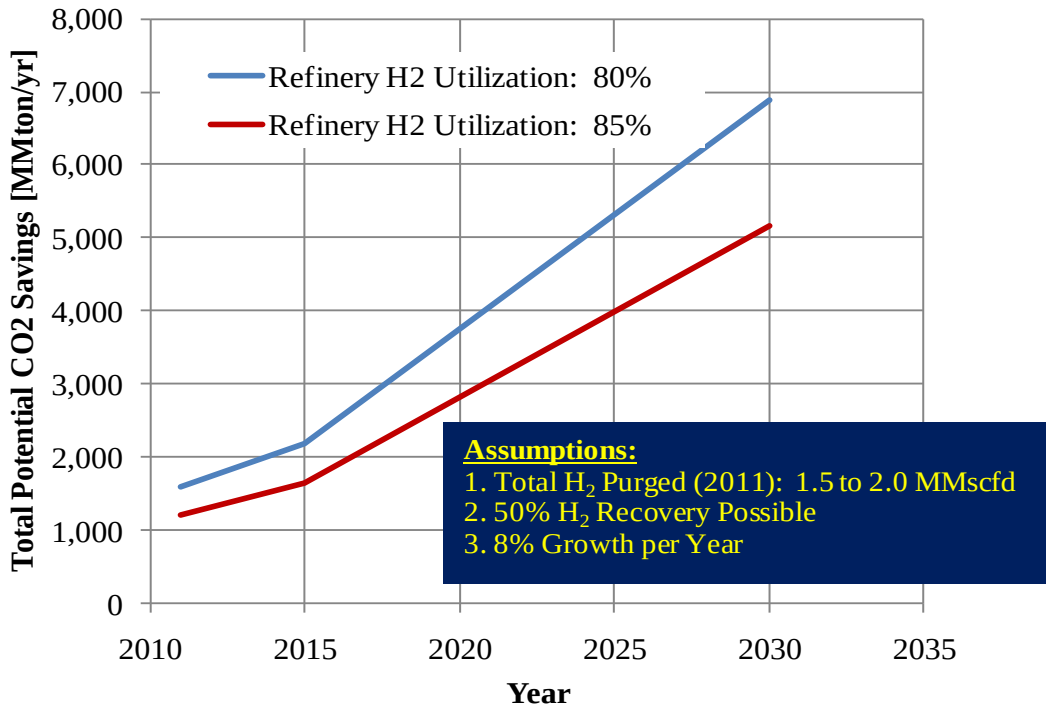

Figure 25. Net CO_2 emission savings per unit of H_2 recovered and projected annual total energy savings.