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Testing of a 7-Tube Palladium Membrane Reactor for Potential Use in TEP

June 2009

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TESTING OF A 7-TUBE PALLADIUM MEMBRANE REACTOR FOR POTENTIAL USE IN TEP

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1 Introduction

A Palladium Membrane Reactor (PMR) consists of a palladium/silver membrane permeator filled with catalyst (catalyst may be inside or outside the membrane tubes). The PMR is designed to recover tritium from the methane, water, and other impurities present in fusion reactor effluent. A key feature of a PMR is that the total hydrogen isotope content of a stream is significantly reduced as 1) methane-steam reforming[1] and/or water-gas shift[2] reactions proceed on the catalyst bed and 2) hydrogen isotopes are removed via permeation through the membrane. With a PMR design matched to processing requirements, nearly complete hydrogen isotope removals can be achieved.

A 3-tube PMR study was recently completed[3]. From the results presented in this study, it was possible to conclude that a PMR is appropriate for TEP, perforated metal tube protectors function well, platinum on aluminum (PtA) catalyst performs the best, conditioning with air is probably required to properly condition the Pd/Ag tubes, and that CO/CO_2 ratios maybe an indicator of coking.

The 3-tube PMR had a permeator membrane area of 0.0247 m^2 and a catalyst volume to membrane area ratio of 4.63 cc/cm^2 (with the catalyst on the outside of the membrane tubes and the catalyst only covering the membrane tube length). A PMR for TEP will require a larger membrane area (perhaps 0.35 m^2). With this in mind, an intermediate sized PMR was constructed. This PMR has 7 permeator tubes and a total membrane area of 0.0851 m^2. The catalyst volume to membrane area ratio for the 7-tube PMR was 5.18 cc/cm^2. The total membrane area of the 7-tube PMR (0.0851 m^2) is 3.45 times larger than total membrane area of the 3-tube PMR (0.0247 m^2).

The following objectives were identified for the 7-tube PMR tests:

- Refine test measurements, especially humidity and flow.
- Refine maintenance procedures for Pd/Ag tube conditioning
- Evaluate baseline PMR operating conditions
- Determine PMR scaling method
- Evaluate PMR with realistic feed compositions
- Evaluate PMR performance with varying permeate pressures
- Study coking-related issues
- Identify any unexpected behavior that may require further investigation (used to study transient behavior)

This report presents the tests results defined by these objectives.

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[1] $CH_4 + H_2O = 3H_2 + CO$

[2] $CO + H_2O = H_2 + CO_2$

[3] Bryan Carlson et.al., *Testing of a 3-Tube Palladium Membrane Reactor for Potential Use in TEP*, Report prepared by Los Alamos National Laboratory for US ITER, US-ITER-TD0022.

2 Test Apparatus

The schematic drawing of the system used for these tests is depicted in Figure 1. After initial startup activities, the retentate flow controller (FC-RET) was moved downstream of the water trap to avoid failure of the mass flow controller due to the presence of condensed water. This means that the FC-RET measurement will not directly include total water in the retentate stream. FC-RET will include the total water exiting the water trap. All data reported here are after the FC-RET transducer was moved.

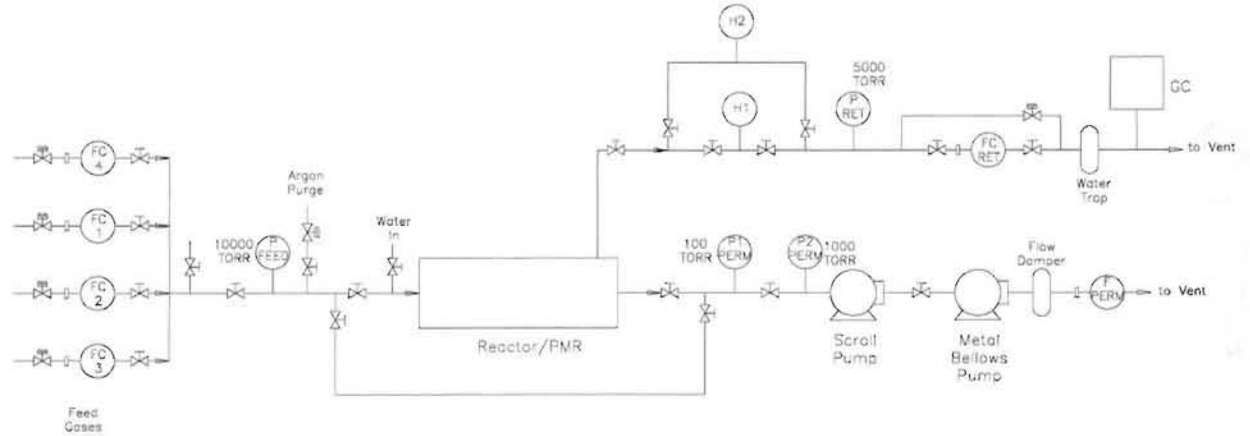

Figure 1 Laboratory-Scale PMR Processing System (FC-RET subsequently moved after the Water trap)

Transducers: Brooks 5850E or 5850EM mass flow controllers were used to flow feed gases to the processing system and to measure/control the retentate flowrate. A Brooks 5860 mass flow meter was used to measure permeate flow. MKS Baratron model 122 and 222 pressure transducers were used throughout the system. A water trap (chilled water condenser operating at 4 °C) was placed up stream of the GC to prevent excessive water from entering the GC. Two GE Sensing humidity probes were used in the retentate line upstream of the water trap to measure water at that point. One measured dew points in the range of $-80^{\circ}C$ to $20^{\circ}C$ and the other measured $-15^{\circ}C$ to $70^{\circ}C$.

Pumps: An ISCO Model 2350 HPLC pump was used to inject water upstream of the PMR. The PMR permeate was fitted with a scroll pump (Normetex 15) backed by a metal bellows pump (Senior Aerospace MB-601).

Gas Analysis: Gas stream composition was determined by gas chromatography (GC) with an Agilent 3000A MicroGC equipped with two analytical columns using ultra high purity (99.995%) argon as the carrier gas. The two channel GC was equipped with a 10 meter x 0.32 mm ID column packed with 5A molecular sieve/PLOT and a 10 meter x 0.32 mm ID column packed with PoraPLOT Q. Detectors (one on each column) for both columns were thermal conductivity detectors operated in the standard or high sensitivity mode. The molecular sieve column was used to quantify CO, N_2, O_2, H_2, and CH_4. The PoraPLOT Q column was used to quantify CO_2. The GC was setup to constantly sample and analyze retentate gases during testing. The time between samples varied between 1.5 to 2 minutes.

PMR: A drawing of the 7-tube PMR is shown in Figure 2. The PMR was fabricated by Johnson Matthey. The PMR included seven Pd/Ag tubes. The tubes were 75% Pd and 25% Ag. The Pd/Ag tubes had an OD of 6.35 mm (0.25 inches), an ID of 5.99 (0.236 inches), and a wall thickness of 170 μ (0.007 inches). The active length (e.g. excludes brazing length) of Pd/Ag tubes after fabrication varied from 61.44 cm (24 3/16 inches) to 62.71 cm (24 11/16 inches).

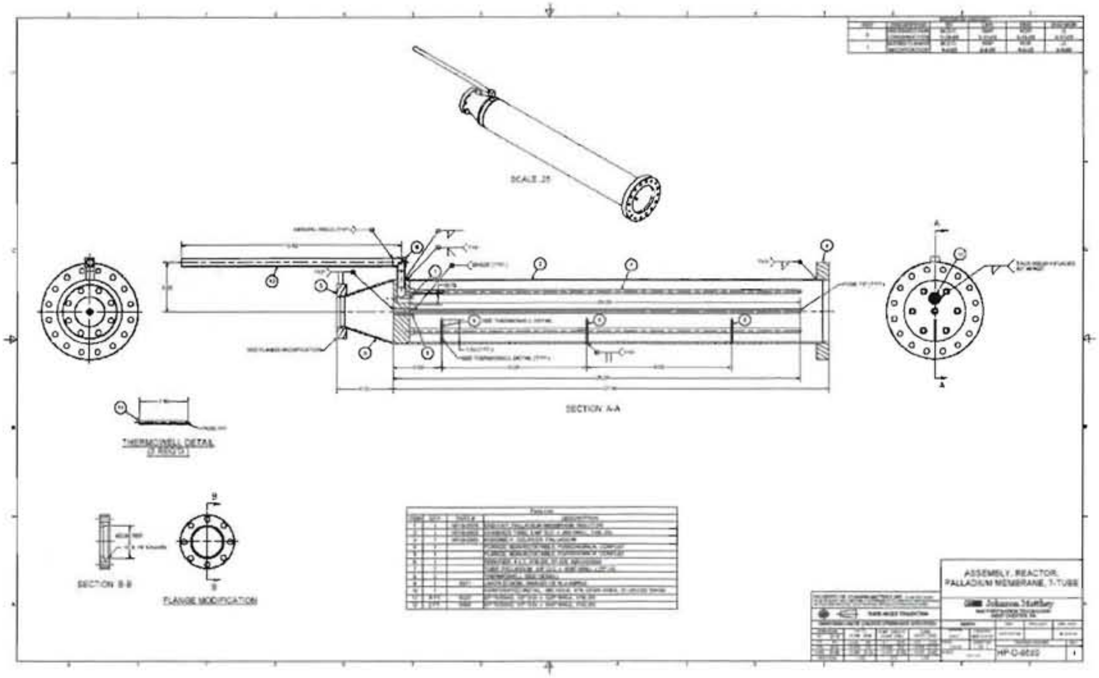

Figure 2 PMR Drawing

The body of the PMR was constructed of 10.16 cm (4.0 inch) OD 304 stainless tubing with an ID of 97.38 cm (3.834 inches). The feed end was fitted with a 15.24 cm (6.0 inch) Conflat-style flange. This was used to mate to a Conflat-style flange which ultimately leads to a 1.27 cm (½ inch) OD tube used to supply feed gases to the PMR. The permeate end was reduced to 5.04 cm (2 inch) OD and fitted with a 8.573 cm (3 3/8 inch) Conflat-style flange. The tube collection plate for the Pd/Ag tubes was drilled radially so that retentate gas could be exhausted radially in a 1.27 cm (1/2 inch) OD tube. A screen was placed over the retentate exhaust port to prevent catalyst and other materials from entering the retentate exhaust. The retentate gas was collected near the center of the PMR.

The PMR was installed in a furnace in the vertical position with the feed inlet at the top and the retentate and permeate outlets at the bottom. Previous experience showed that repeated heating and cooling of a PMR could lead to crushing of the Pd/Ag tubes presumably due to thermal expansion and contraction. Thus, the PMR tubes were protected by placing a perforated metal tube around the outside of the Pd/Ag tubes. A shop drawing used to construct the perforated metal tubes is shown in Figure 3. The perforated metal tubes were 9.525 mm (0.375 inches) OD x 0.4572 mm (0.018 inches) wall thickness with a total length of 64.77 cm (25.5 inches). This was perforated with 2.972 mm (0.117 inch) diameter holes on a 3.962 mm (0.156 inch) stagger, leaving 51% open area. To form the tube, the flat stock was rolled around a mandrel and tack welded. These were installed in the PMR by slipping one end over the stainless steel sleeve which held the Pd/Ag tubes. Installation was completed by packing a small amount of quartz wool in the annular space between the Pd/Ag tube and the perforated metal.

Final assembly of the PMR was accomplished with the following steps: 1) assemble all parts of the PMR except for the feed flange, 2) orient the PMR with the permeate end down, 3) use a fixture to hold the Pd/Ag tubes in place, 4) pour in the catalyst, 5) remove fixture, and 6) continue filling catalyst until the catalyst reaches the end of the Pd/Ag tubes. The volume of catalyst present when the PMR is filled to the end of the Pd/Ag tubes is calculated at 4314 cc. Pictures showing the 7-tube PMR in various stages of assembly are given in Appendix B.

Catalysts: The catalyst tested in the 7-tube PMR was Engelhard A-16825, which consists of 0.5% Pt on alumina (referred to here as PtA). Details of this catalyst were described previously.[4]

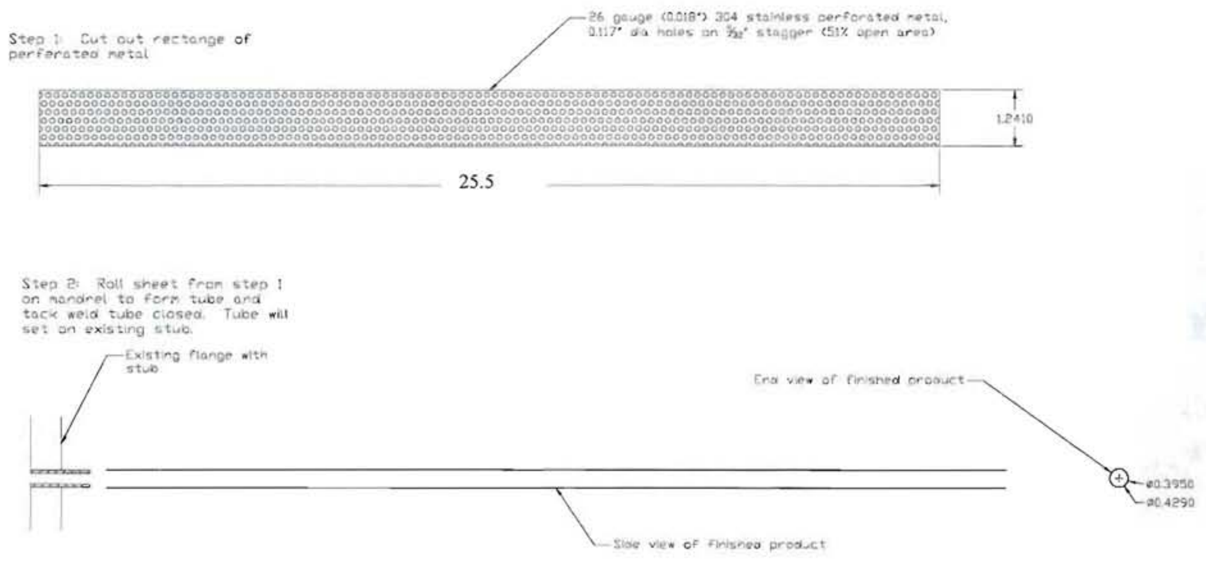

Figure 3 Perforated Metal Protector Shop Drawing

3 Calibration and Measurement Accuracy

All pressure transmitters, flow controllers and meters, and humidity probes were calibrated prior to the start of testing. The Agilent micro GC was calibrated with a certified gas mixture standard provided by Scott Specialty Gases. The gas standard was a mixture of 79.9% CO_2, 10.1% CO, 1.0% CH_4, 0.99% N_2, 0.99% O_2 with the balance Ar. The accuracy of the calibration mixture was ± 2% for CO_2 and ±5% for the other gas species. All calibration curves were found to be

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[4] Dogruel, David, et al., *Testing of Four Catalysts for Potential Use in TEP*, US ITER report US ITER 13201-TD0016-R01 (2008).

linear. Seven times over the course of the 7-tube experiments, the calibration gas was fed to the GC. A single flow controller was used for this feed and nothing was mixed with the calibration gas designed to minimize systematic effects. These experiments were used to determine the values presented in Table 1:

Table 1 Accuracy of GC Measurements

Gas	Calibration Gas (Concentration %)	One standard deviation from GC measurements (Concentration %)	Two standard deviations from GC measurements (% of measurement)
CO_2	79.9	0.57	1.4
CH_4	1.00	0.0275	5.5
CO	10.1	0.192	3.8
H_2	1.00	0.0249	5.0

The last column of numbers indicates the 95% confidence that all GC measurements are going to fall in a band above or below the measured value. For example, an experimenter would be 95% sure that the actual H_2 value would fall in a band 5.0% above and 5.0% below the measured H_2 value (i.e. for a measured value of 1% H_2 the 95% confidence level is 1.00-(1.00)*5.0% to 1.00+(1.00)*5.0%), i.e. 0.95 to 1.05.

The accuracy of the mass flow controllers and flow meters is given by the manufacturer as 1% of full scale when they are calibrated to a specific gas or 5% of full scale when correction factors are used. All flow meters used were calibrated to nitrogen and then the actual flow was determined by applying a correction factor supplied by the manufacturer. A 2000 sccm mass flow controller was used to feed CO and CH_4. In addition, during testing of air-like feed gases, a 200 sccm mass flow controller was used to feed CO. A 5,000 sccm mass flow meter was used to measure permeate flow. Retentate flows were measured with either with a 5000 sccm or a 10000 sccm mass flow controller.

The accuracy of the pressure transducers was given by the manufacturer as 1% of reading. Thermocouples were placed into the top, middle, and bottom of the PMR catalyst bed to record temperatures. Furnace temperatures were adjusted to maintain these thermocouples with 5 °C of the operating temperature (i.e. 500 °C).

The accuracy of the -15 °C to 70 °C humidity probe (H-2) is given by the manufacturer as ±1 °C dew point for temperatures greater than 30 °C and a relative humidity (RH) greater than 40%. For temperatures less than 30 °C and a RH greater than 30%, the error is also given as ± 1 °C dew point. The accuracy of the -80 °C to 20 °C humidity probe (H-1) is given by the manufacturer as ± 2 °C dew point. Dew point (DPC) readings for the two humidity probes (when both probes were on scale in the overlap region) were compared. It was observed that H-1 was approximately 18 DPC lower than H-2 over the range of about 0 °C to 20 °C when the process gas temperatures were about 40 °C. The H-1 probe does not have functional temperature compensation. Discussions with the manufacturer and examination of probe data indicate that, whenever available, the H-2 reading should be used. The H-1 probe becomes very insensitive to process temperatures when dew points are less than -15 °C. When H-2 readings are off-scale low, the H-1 reading should be used. To verify this information, the humidity probes were crosschecked with an EdgeTech DewPrime III chilled dew point hygrometer (Serial Number 25128). This instrument was calibrated to a NIST traceable standard on 2/13/09. The calibration is good for 1 year. Comparisons of readings taken with this instrument are presented in Table 2. It should be noted that small variations in the process gas temperatures greatly affect the dew points observed with the H-1 probe. The H-2 probe is relatively insensitive to process gas temperatures. The H-2 probe was used to collect all data presented in this report.

Table 2 Humidity Probe Dew Point Comparisons

DewPrime Dew Point °C	H-1 Dew Point °C	H-1 Gas Temperature °C	H-2 Dew Point °C	H-2 Gas Temperature °C
7.6	5.85	17.3	7.3	17.8
-2.9	-2.07	17.4	-1.7	17.8
8.9	0.2	22.1	8.9	33.6
9	5.75	19	8.7	21.2
8.8	6.76	18.8	8.6	19.9
8.8	7.9	18.4	8.7	19

The accuracy of the thermocouples is assumed to be within 1 °C.

The accuracy of the ISCO HPLC pump used for the feed of water is given by the manufacturer as ± 1% at 2 ml/min. To determine the accuracy at other flow rates, measurements were taken. This was done by setting the ISCO pump at a set point, flowing water into a calibrated volume over a measured period of time, and measuring the mass of water collected. Results collected prior to 3-tube PMR testing are reported in Table 3. Feed flow rates during the testing of the 7-tube PMR ranged between 0.04 and 0.32 ml/min. Note that the actual flows delivered were always greater than the flows requested. At or above set points of 0.03 ml/min, the delivered flow is 3-6% above the set point. At or below a set point of 0.020 ml/min, the delivered flow was much greater than the set point. The data suggest that below set points of about 0.030 ml/min, the delivery rate is about 0.027 ml/min regardless of the set point setting. Thus, experimental data collected over this region must take this consideration into account.

Table 3 Accuracy of the ISCO HPLC pump at different flow rates

Set Point (ml/min)	Mean Flow Rate (ml/min)	Standard Deviation (ml/min)	% Error
1.000	1.038	0.001	3.8
0.316	0.334	0.001	5.7
0.100	0.105	0.001	5.0
0.030	0.031	0.001	3.3
0.020	0.028	0.001	40
0.014	0.026	0.005	86

At the end of the 3-tube PMR testing a repeat of these calibration checks was performed. The ISCO pump was set to 0.32 ml/min and water was delivered to a covered collection vessel for 30 min. At that time the collected water was weighed and found to be 9.7724 gm. Thus, the delivery rate was 0.3257 ml/min which is 1.8% above the set point. This was the factor that was used to analyze the 7-tube PMR data. In other words, all ISCO pump settings were multiplied by 1.022 to determine the actual water delivery rate (value which minimizes the coking calculation (see elsewhere)).

4 PMR Conditioning

Pd/Ag Tube Permeation Measurements: Previous work had shown that treatment with air was necessary to condition Pd/Ag tubes so that they permeated hydrogen at expected rates. To verify the need for air treatment, the 7-tube PMR was conditioned overnight with 0.24 Pam^3/sec (200 sccm) hydrogen feed at 450 °C and 80.0 kPa (600 torr) (with the permeate side of the 7-tube PMR closed in). Thereafter, two permeation flowrate measurements were taken by feeding 8.43 Pam^3/sec (4992 sccm) of hydrogen to the 7-tube PMR at a feed/retentate pressure of approximately 82.7 kPa (620 torr) with the scroll and metal bellows pumps running and connected to the permeate. The results are given in Table 4. Following these measurements, the PMR was conditioned by maintaining a feed of 0.76 Pam^3/sec (450 sccm) of argon and 0.084 Pam^3/sec (50 sccm) of air (10% air mixture) for one hour. During this period a portion of the feed was used to periodically fill the permeate side of the PMR. The filling was followed by evacuation (three or four cycles). Following this procedure, the hydrogen permeation rates were measured under the same conditions used earlier. The results of these tests are listed in Table 4 along with the estimated theoretical performance. Variations in permeator tube thickness estimated at ±25.4 μ (0.001 inches) makes it impossible to calculate a single value of estimated performance. Instead, a estimate performance range was calculated based on this uncertainty in tube thickness. Following the completion of all testing, a final permeation test was performed. No degradation in permeation rates was observed.

Theoretical performance was calculated based on the following permeation equation.

$$F_H = \frac{2\pi K_H n z}{\ln(r_2 / r_1)}(\sqrt{p_{H,R}} - \sqrt{p_{H,P}})$$

Where:

F_H = Permeation Flow of Hydrogen
K_H = Permeation Constant for hydrogen = 3.85E-8*exp(-5730/RT) mole/(m*s*sqrt(Pa))[Ref 5]
r_1 = inside diameter of the permeator tube
r_2 = outside diameter of the permeator tube
n= number of permeator tubes
$p_{H,R}$ = Pressure of hydrogen on the retentate side of the permeator tube
$p_{H,P}$ = Pressure of hydrogen on the permeate side of the permeator tube
R = Universal Gas Constant = 8.31 J/(^{o}K*mole)
T = Temperature of Permeator K
z = length of permeator tube

Table 4 PMR Permeation Test Results

Temp (°C)	Feed Pressure (kPa)	Feed Flow (Pam^3/sec)	Permeate Pressure (kPa)	Permeate Flow (Pam^3/sec)	Theoretical Performance (Pam^3/sec)	Comments
450	82.7 620 (torr)	8.43 4992 (sccm)	0.87 6.5 (torr)	3.33 1970 (sccm)	3.73-5.08 2210-3010 (sccm)	H_2 Conditioning
450	82.4 618 (torr)	8.43 4992 (sccm)	0.97 7.4 (torr)	3.63 2147 (sccm)	3.70-5.04 2189-2982 (sccm)	H_2 Conditioning
450	81.5 611 (torr)	8.43 4995 (sccm)	1.77 13.26 (torr)	5.25 3109 (sccm)	3.52-4.79 2084-2839 (sccm)	Ar/Air conditioning before 7-tube test
450	80.1 601 (torr)	8.43 4993 (sccm)	1.49 11.2 (torr)	5.10 3021 (sccm)	3.53-4.81 2093-2851 (sccm)	Ar/Air conditioning after completion of 7-tube test

*Note: Theoretical Performance is based on observed permeate pressures. An estimate of the variations in tubing thickness (170 μ ± 25.4 μ) results in an uncertainty in this calculation.

Treatment with a 10% air mixture appears to be an effective conditioning method. No degradation in permeator performance was noted after this treatment during further testing. Other researchers noticed similar behavior. F. Galluci, et.al. [6] observed that if they didn't use air

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[5] K. Munakata et. al., "Numerical Simulation of Membrane Reactor for Detritiation of Plasma Exhaust", *Fusion Science and Technology, Vol. 48, July/Aug 2005.*

[6] F. Gallucci et.al., "The effect of mixture gas on hydrogen permeation through a palladium membrane: Experimental study and theoretical approach", International Journal of Hydrogen Energy, Vol. 32, 2007, pgs 1837-1845

during the conditioning process, a decrease in permeation was noticed over time. A.L Mejdell, et.al[7] showed that treatment in air increased the size of the grain boundaries.

5 Results

Note: Various values have been used as "standard conditions" when expressing measurements in units of, say, sccm. The Brooks flowmeters used in these tests were calibrated to the manufacturer's default standard conditions of 21.1 °C (70 °F) and 101325 Pa (1 atm). Throughout this report, these are the standard conditions that are used.

5.1 Experimental Procedure

Typical PMR experiments were performed to establish performance above, below, and at the "knee" where a significant change in the slope of mole fraction vs. feed flowrate occurs. PMR performance is quite different above and below the "knee". Below the knee the PMR has more than enough membrane area. The performance worsens slowly as the total feed flowrate is increased. This results in increased H_2 loading to the permeate pump which results in higher permeate pump feed pressure. This can be thought of as a "pump curve" limited region. Above the knee, the PMR is primarily limited by the membrane area. In other words the PMR feed has increased to the point where the retentate and permeate are no longer at (or near) H_2 partial pressure equilibrium. Additional PMR feed results in more rapidly worsening performance as the membrane becomes increasingly overwhelmed by H_2 loading. "Breakthrough" is the demarcation point for below and above the "knee." "Breakthrough" is the point at which there is significant departure between permeate and retentate H_2 partial pressure.

It is presumed that PMRs will usually be designed for operation in the "pre-broken through" region.

Typical PMR experiments were performed by characterizing PMR performance below and above breakthrough. This was accomplished by fixing the PMR temperature and pressure, by maintaining permeate vacuum by running the permeate vacuum pump, and by fixing the feed composition. Then the total feed flowrate was increased, steady state was achieved, and performance was characterized (primarily by recording retentate composition and flowrate).

Typical PMR experiments (to characterize performance above and below breakthrough) were performed as follows:

1. Establish an Ar purge through the PMR feed/retentate and start the vacuum pumping system on the permeate.
2. Heat the PMR to the target temperature
3. Shut off the Ar purge
4. Establish target feed flows (e.g. CO and water flows for WGS experiments or CH4 and water flows for MSR experiments)
5. Use the FC-RET flow controller to establish the target feed/retentate operating pressure

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[7] A.L. Mejdell et. Al., "Hydrogen permeation of thin, free-standing Pd/Ag 23% membranes before and after treatment in air", Journal of Membrane Science 307 (2008) 96-104

6. Observe transducer and GC measurements. Allow the system to operate until steady state is achieved. Typically this was between 0.5 to 3 hrs. Steady state was typically considered achieved when a series of GC measurements showed no further significant change.
7. Collect a "snapshot" of steady state transducer and GC data
8. If further data are to be collected repeat steps 4-7. If data collection is complete, shut off the feed gases and establish an Ar purge.
9. Once all non-Ar gases have been purged from both the feed/retentate and permeate side of the PMR, the system may be shutdown.

5.2 Outline of Experiments Performed

A series of tests were performed to evaluate the 7-tube PMR performance for water-gas shift reactions. Tests were performed to establish the optimum $CO:H_2O$ feed ratio and then a series of tests were performed at various flow rates and temperatures.

A series of tests were performed to evaluate the 7-tybe PMR performance for methane-steam reforming reactions. Tests were performed to establish the optimum $H_2O:CH_4$ feed ratio and then a series of tests were performed at various flow rates and temperatures.

A series of tests were performed to evaluate the performance of the PMR under realistic feed conditions. Based on the expected air-like processing stream from the ITER cryopumps consisting of 15 Pam^3/sec of Ar, 1 Pam^3/sec of CH_4, and 1 Pam^3/sec of CO, a series of tests were performed with this composition at various flow rates and permeate pressures to evaluate PMR performance.

Tables listing all tests and test results are presented in Appendix A.

5.3 Data Collected

The parameters listed in Table 5 were measured for all catalyst tests and constitute a data "snapshot" as described above.

Table 5 List of Measured Parameters

SCADA Tag Name	Units	Description
FA-3	sccm	Feed Flow of CO or CH_4 (recorded value corrected for gas in use)
none	ml/min	Feed Flow of Water (value recorded at the left in Appendix A do not include the calibration correction factor (1.022))
P-FEED	torr	Feed pressure
P-RET	torr	Retentate pressure
F-RETc	sccm	Retentate flowrate if retentate gas is N2 (Value of actual flow depends on gas composition which varies)
FS-PERM	sccm	Permeate (smoothed) flowrate if permeate is N2
T-TOP, T-MID, T-BOT	C	Temperature of the top, middle and bottom of the internal 7-tube PMR (within the Catalyst Bed). Average of these values listed as "TCAT" in °C in Appendix A.
P1-PERM	torr	Permeate pressure upstream of Scroll Pump (0-100 torr range).
P2-PERM	torr	Permeate pressure upstream of Scroll Pump (0-1000 torr range).
None	%	H_2 in retentate "Dry Basis" following water trap
None	%	CH_4 in retentate "Dry Basis" following water trap
None	%	CO in retentate "Dry Basis" following water trap
None	%	CO_2 in retentate "Dry Basis" following water trap
H-1	DPC	Retentate humidity-low range transducer
H-2	DPC	Retentate humidity-high range transducer
T-TRACEx	C	Temperature of heat traces

The retentate flow, as recorded, is the flowrate if the stream were composed of nitrogen. Factors based on actual stream composition (available from Brooks Instruments) are required to determine the actual retentate flowrate. The flow of the retentate was estimated by calculation as follows:

$$Fret(actual) = \frac{Fret(measured)}{\left(\frac{x_{H2}}{1.008} + \frac{x_{CO}}{0.995} + \frac{x_{CH4}}{0.963} + \frac{x_{CO2}}{0.773} + \frac{x_{H2O}}{0.856} + \frac{x_{Ar}}{1.395}\right)}$$

Where: 1.008, 0.995, 0.963, 0.773, 0.856, and 1.395 are the correction factors given by the manufacturer.

A summary all runs performed during the 7-tube PMR experimental campaign is presented in Table 6.

Table 6 Summary of 7-Tube PMR Tests Performed

Dates	Test	T(C)	P (kPA)	Total Feed Flowrate Points Collected	Purpose
3/10-20/09	WGS	500	160 1200 (torr)	4	Scaling, compare with 3-tube test at these conditions
3/23-24/09	WGS	500	200 1500 (torr)	5	Establish base case WGS performance
4/21-22/09	WGS	550	200 1500 (torr)	3	Establish temperature-dependence of base case WGS performance
3/23-4/23/09	WGS	500	200 1500 (torr)	3	Establish optimal water-to-CO feed ratio
4/7-13/09	MSR	500	200 1500 (torr)	6	Establish base case MSR performance
4/16-20/09	MSR	550	200 1500 (torr)	6	Establish temperature-dependence of base case MSR performance
4/7-5/7/09	MSR	500	200 1500 (torr)	3	Establish optimal water-to-methane feed ratio at 500 C
4/14-15/09	MSR	500	200 1500 (torr)	3	Establish optimal water-to-methane feed ratio at 550 C.
3/26-4/2/09	ALP	500	200 1500 (torr)	3	Establish dependence of base case ALP performance on variation in permeate pressure
5/11-14/09	ALP	500	200 1500 (torr)	5	Establish base case ALP performance (useful for direct scaling for sizing design)

Details of each "point" are given in Appendix A.

5.4 Data Processing

To be fully utilized the raw PMR data must be processed to determine values of interest. This includes determining concentrations at the exit of the PMR rather than at the exit of the water trap where they are measured. It includes calculations of F_{ret} since direct measurements proved to be unreliable (probably due to using a high capacity flow controller at the low end of its range). It includes determination of decontamination factors, % H_2 recovery and coking rates. The equations for determining these values are given in Appendix C.

The measured data and calculated quantities are included as Appendix A.

5.5 Experimental overview – mole fraction vs. total feed flowrate charts

The overall behavior of each experimental run is given in a mole fraction vs. total feed flowrate chart. Such a chart of each experimental run is given in this section. For each chart all parameters or fixed except the feed flowrate. Note that specialized runs addressing feed ratio and the effect of permeate pressure are not presented in this section.

WGS: Water-gas shift test results are given in Figures 4, 5, and 6. These tests were performed with a CO:H_2O Ratio of 1.09:1 at 1) 160 kPa (1200 torr) and 500 °C, 2) 200.0 kPa (1500 torr) and 500 °C, and 3) 200.0 kPa (1500 torr) and 550 °C, respectively. Tests at 160 kPa were performed to allow the evaluation of scale up from a 3 tube to 7 tube PMR. No historical data was available at 200 kPa from the 3 tube PMR testing. The evaluation of scaleup is discussed in section 6.3. At operating temperature and pressure of 500 °C and 200 kPa, all hydrogenated species begin to breakthrough at a total feed flowrate of about 3.2 Pam^3/sec (1900 sccm).

While the tentative expectation is that a TEP PMR will be designed to run at 500 C and 200 kPa (1500 torr), this expectation had not be established early during the 3-tube campaign. Thus, a 7-tube WGS run was performed at 160 kPa (1200 torr) for direct comparison with 3-tube results.

In all data reported here (three cases) the retentate shows the order (highest to lowest) of concentrations in the retentate to be water:hydrogen:methane. Presumable changing the ratio of the feed gases would affect this observation. Thus, water (and then hydrogen) was the large contributor to H lost in the retentate for these runs.

In all cases the CO_2 in the retentate was quite high, in the >80% region. And in all cases the CO in the retentate was around 10%.

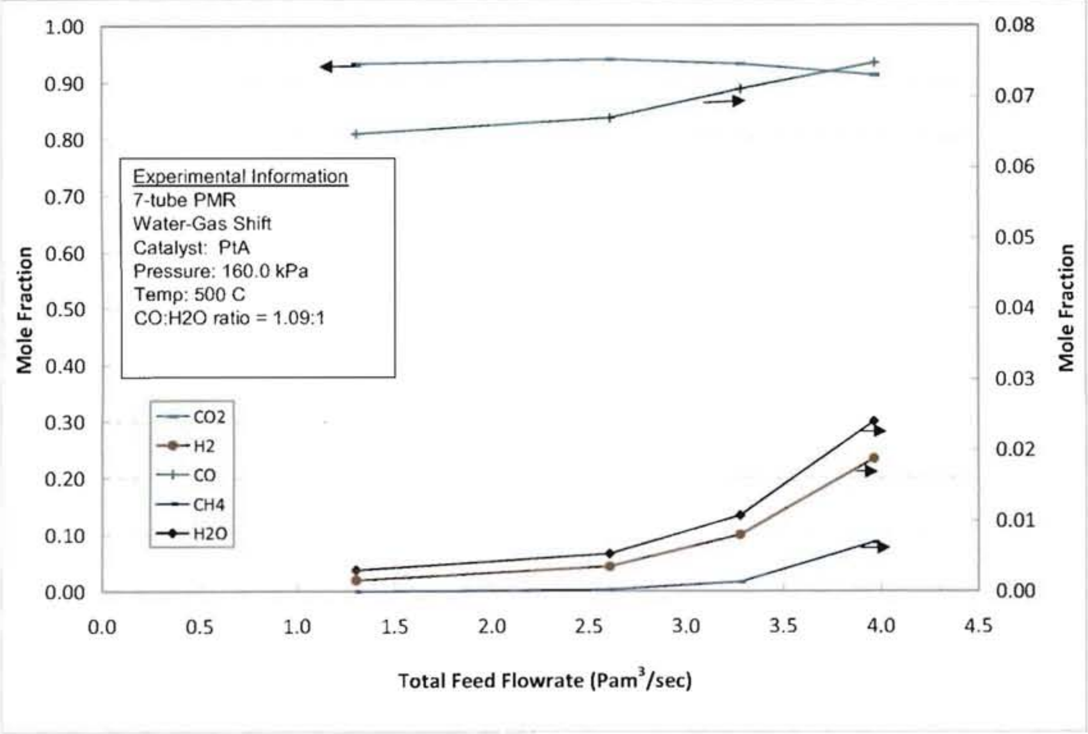


Figure 4 Species Mole Fraction versus Total Feed Flowrate for water-gas shift reaction on PtA catalyst, 500 °C, 160 kPa (1200 torr), and CO:H_2O = 1.09:1

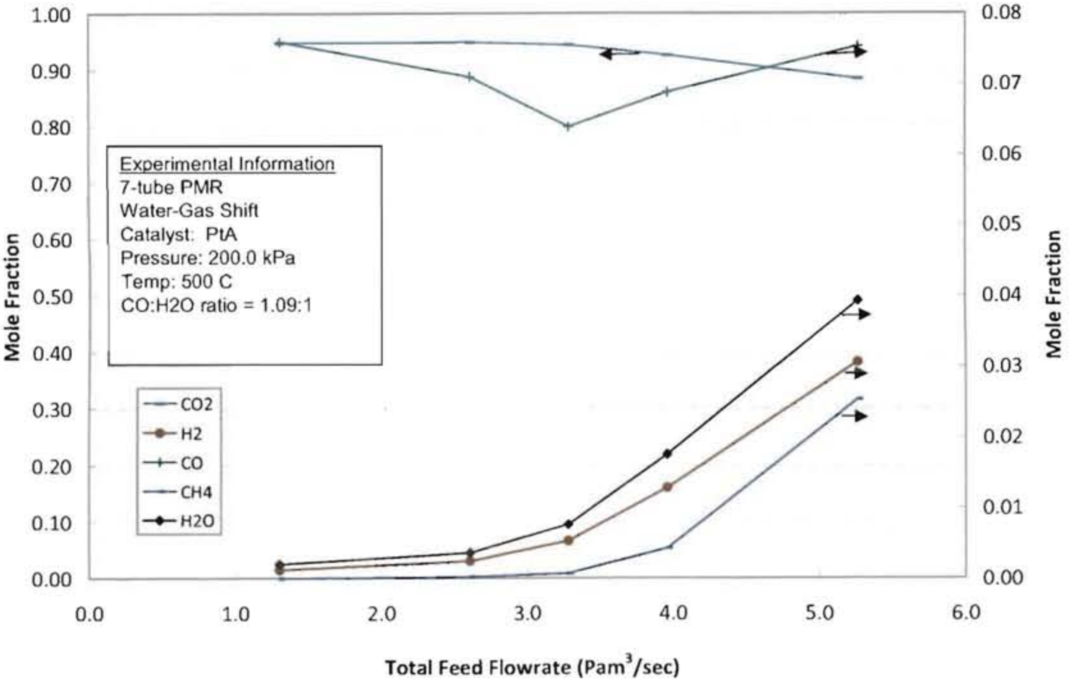


Figure 5 Species Mole Fraction versus Total Feed Flowrate for water-gas shift reaction on PtA catalyst, 500 °C, 200 kPa (1500 torr), and CO:H_2O = 1.09:1

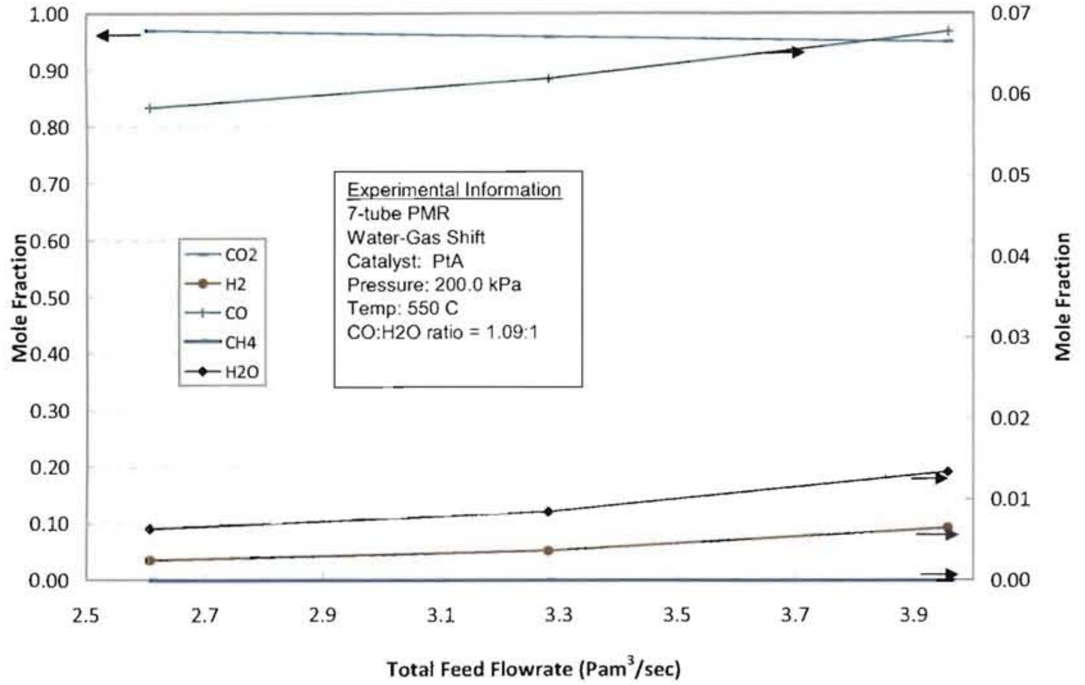


Figure 6 Species Mole Fraction versus Total Feed Flowrate for water-gas shift reaction on PtA catalyst, 550 °C, 200 kPa (1500 torr), and CO:H_2O = 1.09:1

MSR: Methane-steam reforming test results are given in Figures 7 and 8. These tests were performed with a H_2O:CH_4 Ratio of 1.84:1 at 1) 200 kPa (1500 torr) and 500 °C, and 2) 200 kPa (1500 torr) and 550 °C. At 500 °C and 200 kPa (1500 torr), breakthrough occurred at a total feed flowrate of about 1.86 Pam^3/sec (1100) sccm. Increasing the temperature to 550 °C increased the total feed flowrate at breakthrough to about 2.42 Pam^3/sec (1433 sccm).

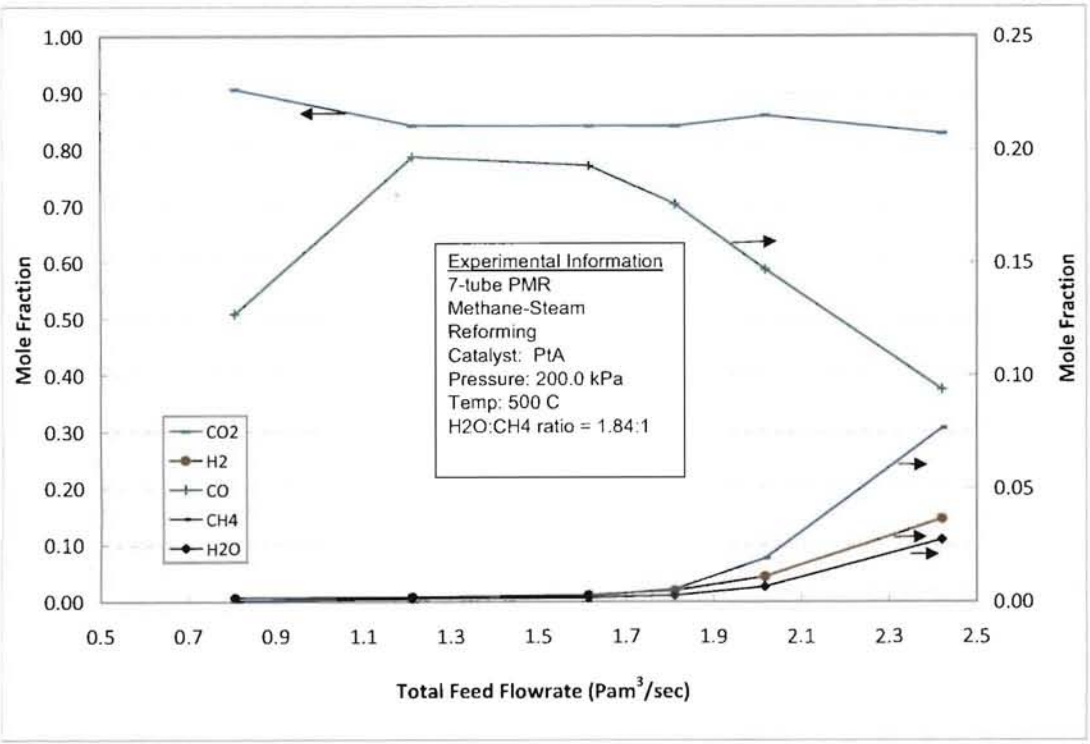


Figure 7 Species Mole Fraction versus Total Feed Flowrate for methane-steam reforming on PtA catalyst, 500 °C, 200 kPa (1500 torr), and $H_2O:CH_4 = 1.84:1$

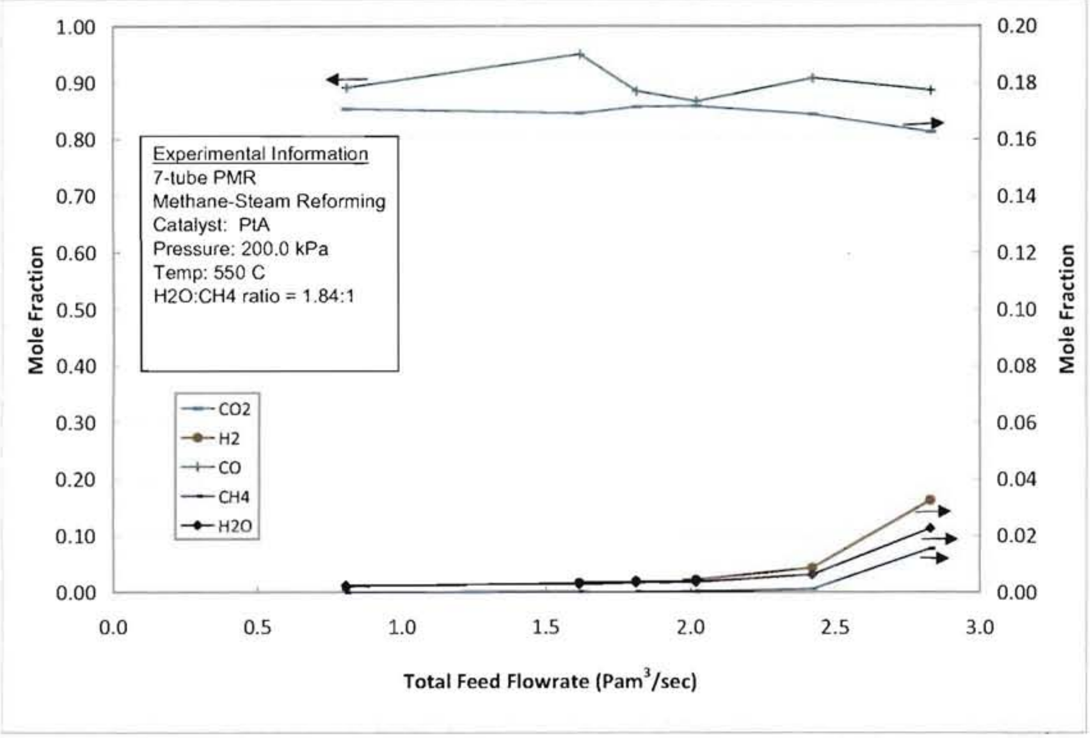


Figure 8 Species Mole Fraction versus Total Feed Flowrate for methane-steam reforming on PtA catalyst, 550 °C, 200 kPa (1500 torr), and H_2O:CH_4 = 1.84:1

ALP: ALP is "air like processing". ALP is one of the key gases that TEP needs to process, and the processing requirements are addressed in the System Requirements Document. "Air-like gas" was prepared for the 7-tube PMR tests by mixing 15 parts Ar, 1 part CH_4, and 1 part CO. Water was added to this mixture so that the H_2O:CH_4 ratio was maintained at 2.97:1. All experiments were performed at 200.0 kPa (1500 torr) and 500 °C. Results are given in Figure 9. Breakthrough was at a total feed flowrate of about 4.39 Pam³/sec (2600 sccm).

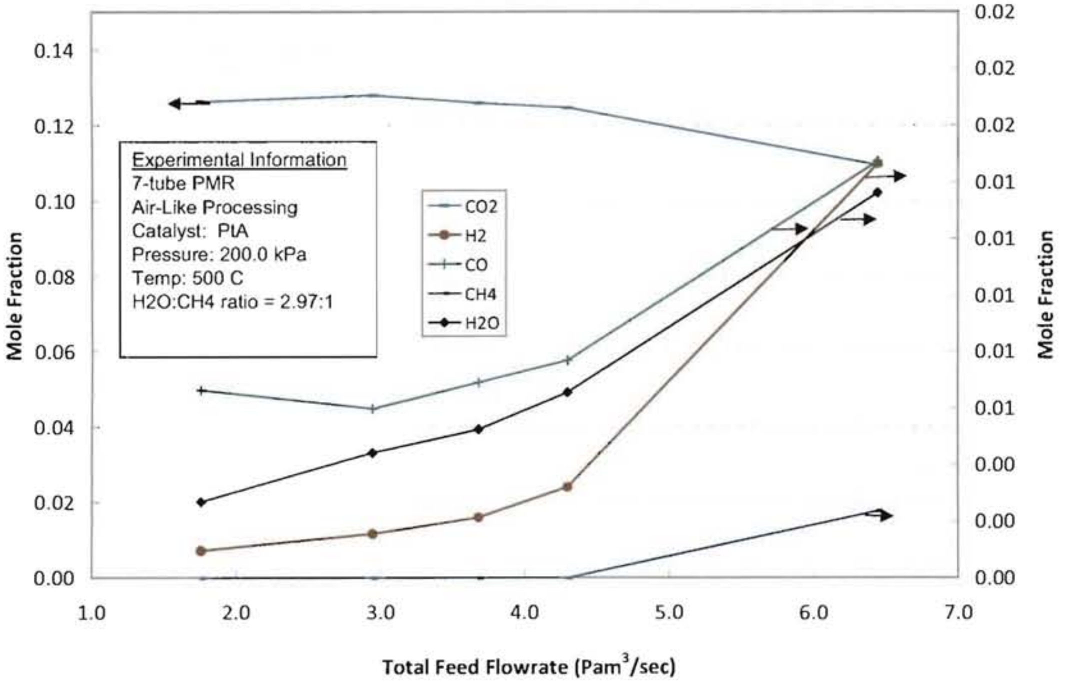


Figure 9 Species Mole Fraction versus Total Feed Flowrate for air-like processing on PtA catalyst, 500 °C, 200 kPa (1500 torr), and $H_2O:CH_4 = 2.97:1$

6 Analysis and Discussion

Figures of Merit: This section serves to identify parametric trends in the test results. Most results are expressed in terms of "% Hydrogen Recovery". This compares the total H in the permeate to the total H in the feed. Due to the magnitude of errors, the feed stream minus the retentate stream is used to more accurately determine the permeate stream. Thus, % Hydrogen Recovery is determined as follows:

$$\%\ Hydrogen\ \mathrm{Re}\,cov\,ery = \frac{F_{Feed}\left(x_{H2O}+2x_{CH4}+x_{H2}\right)-F_{ret}\left(x_{H2O}+2x_{CH4}+x_{H2}\right)}{F_{Feed}\left(x_{H2O}+2x_{CH4}+x_{H2}\right)}*100$$

This results in a relatively straightforward figure of merit for PMR overall performance. The decontamination factor (DF) which is another figure of merit for overall PMR performance. DF is defined as the total hydrogen in the feed divided by the total hydrogen in the retentate or:

$$DF = \frac{F_{Feed}\left(x_{H2O}+2x_{CH4}+x_{H2}\right)}{F_{\mathrm{Ret}}\left(x_{H2O}+2x_{CH4}+x_{H2}\right)}$$

As hydrogen removal approaches completion, DF values rise very rapidly. For DFs greater than 50 (or H_2 recovery = 98%), small experimental errors can lead to significant changes in DF.

For the purposes of this report, "% hydrogen recovery" was found to be the more useful figure of merit.

Run summary: The results of each 7-tube run were plotted as % hydrogen recovery versus the total feed flowrate on Figure 10. The "Experimental Procedure" (above) describes the "knee" or "breakthrough" and behavior at higher and lower flowrates. This behavior is clearly evident on Figure 10. At lower flowrates % hydrogen recovery drops gently and is evidence that the PMR is in the pre-breakthrough region. The increased load on the vacuum pump is a key reason for the slight degraded performance with increasing flowrate. The permeate and retentate hydrogen partial pressures are nearly equal before the end of the membrane. At higher flowrates the PMR performance rapidly degrades. The key contributor to this is that partial pressure equilibrium is not reached prior to the end of the membrane tube (i.e. all of the membrane is being used). Thus, additional hydrogen-containing species introduced to the PMR result in significant hydrogen-containing species in the retentate (i.e. rapid drop in performance). Breakthrough is the onset of transition from pre-breakthrough to the after breakthrough region.

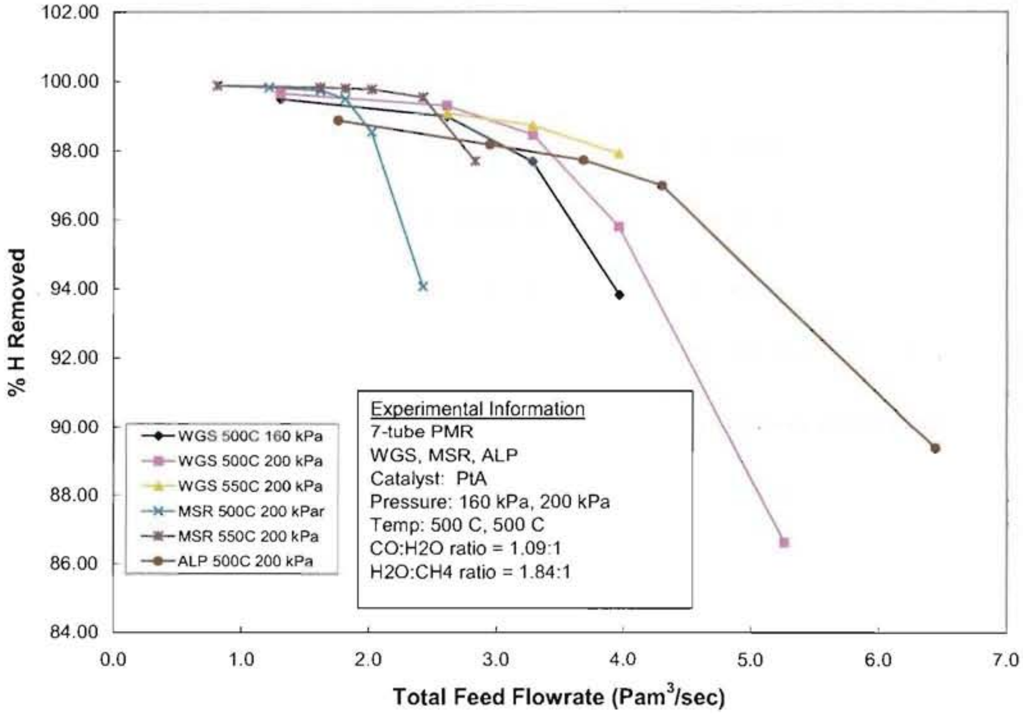


Figure 10 % H Recovered versus Total Feed Flowrate for all tests

Figure 10 was used to estimate the total feed flowrate for which breakthrough occurs for all tests and the results are summarized in Table 7.

Table 7 Summary of Breakthrough Flowrates

C	T(C)	P (kPa)	Estimated Breakthrough Total Feed Flowrate (Pam^3/sec)
WGS	500	160 (1200 torr)	2.87 (1700 sccm)
WGS	500	200 (1500 torr)	3.20 (1900 sccm)
WGS	550	200 (1500 torr)	>3.97 (2350 sccm)
MSR	500	200 (1500 torr)	1.86 (1100 sccm)
MSR	550	200 (1500 torr)	2.42 (1433 sccm)
ALP	500	200 (1500 torr)	4.39 (2600 sccm)

In an attempt to understand whether or not the H_2 partial pressure is the same on both side of the membrane at the exit in the pre-broken through region, for each snapshot, the H_2 partial pressure in the retentate was divided by the H_2 partial pressure in the permeate. The results are plotted on Figure 11 for each total flowrate. At lower flowrates the ratio is nearly unity (but enough above unity that more effects are being observed), at higher flowrates the ratio is far above unity, and there is a transition (slope change) between the two regions. This is considered further evidence that at low flowrates performance is strongly influence by pump limitations while at higher flowrates performance is limited by the available membrane.

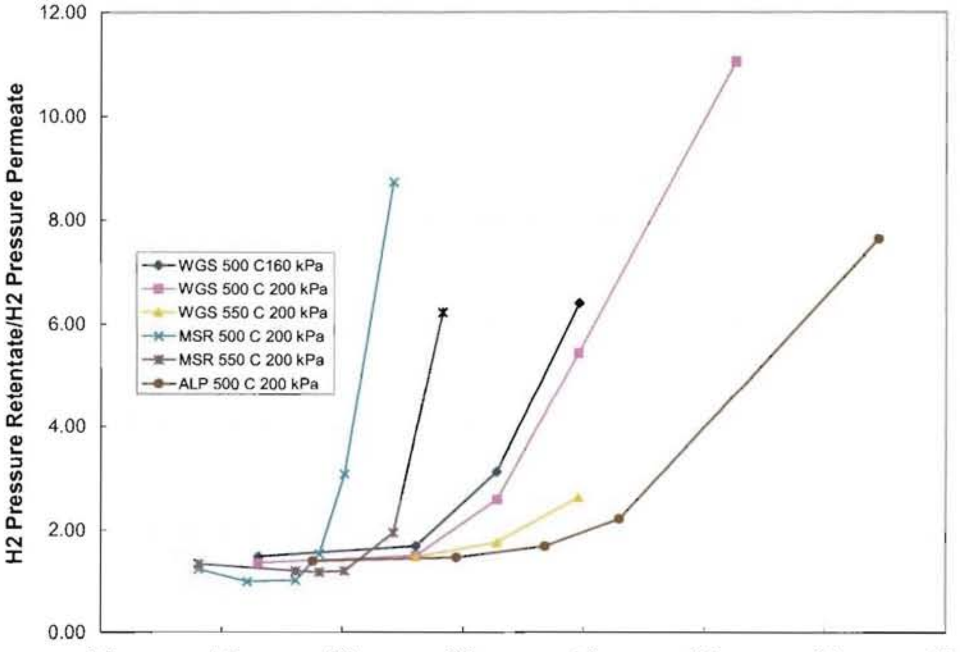


Figure 11 Ratio of H_2 Pressure in the Retentate/H_2 Pressure in the Permeate versus Total Feed Flowrate for all tests.

6.1 Effect of temperature

The effect of temperature on % H removed values is presented in Figure 12 for the water-gas shift reaction at 200 kPa (1500 torr). One curve is for 500 °C and the other is for 550 °C. Performance appears to be only weakly affected by temperature.

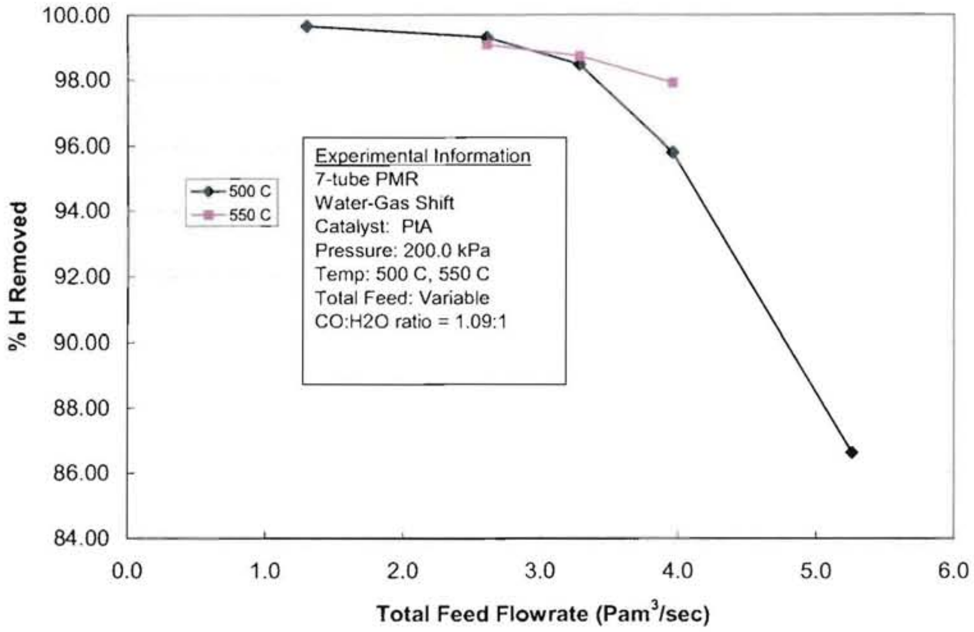


Figure 12 % H Removed versus Total Feed Flowrate water-gas shift processing on PtA catalyst, 500 °C and 550 °C, 200 kPa (1500 torr), and $CO:H_2O = 1.09:1$

% H removed values for methane-steam reforming reactions at 200 kPa (1500 torr) are presented in Figure 13. One curve is for 500 °C while the other is for 550 °C. Higher temperature significantly increases the breakthrough flowrate. At the higher temperature, the highest flowrate results are either at or below breakthrough.

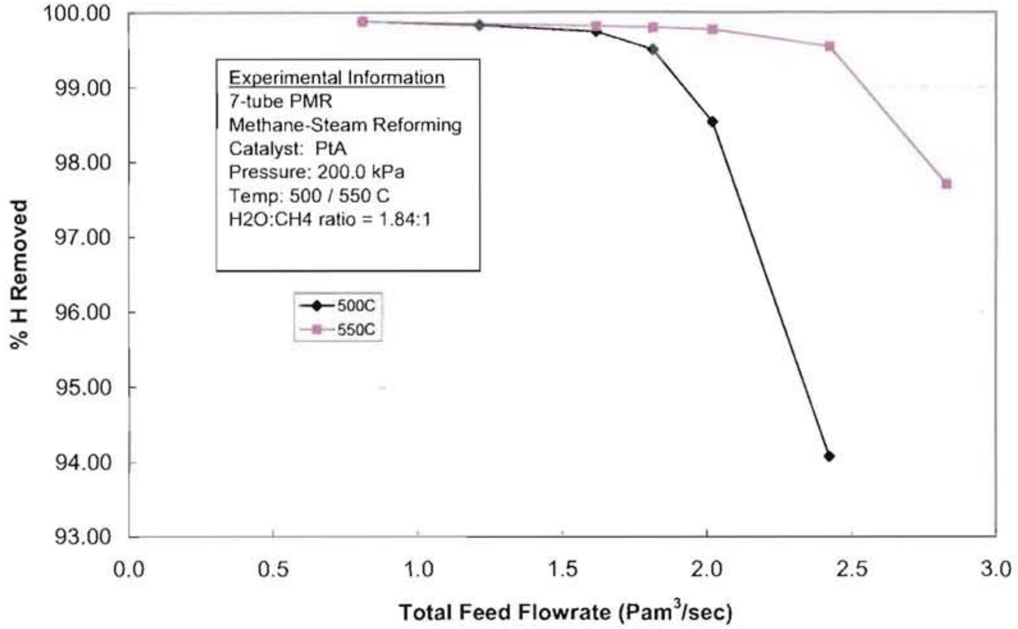


Figure 13 % H Removed versus Total Feed Flowrate methane-steam reforming processing on PtA catalyst, 500 °C and 550 °C, 200 kPa (1500 torr), and $H_2O:CH_4 = 1.84:1$

6.2 Effect of feed composition

To determine the effect of % H removed on the carbon monoxide-to-water ratio in the feed for water-gas shift, tests were performed with varying carbon monoxide-to-water ratios in the feed. The tests were performed at 500 °C and 200 kPa (1500 torr). The results are presented in Figure 14 and are plotted as % H removed versus $CO:H_2O$ ratio. It is observed that over the range of tests performed, % H removed improved with increasing ratio with the best results observed occurring at ratios of 1.09-1.20. At higher ratios previous studies have shown that coking occurs. Based on this consideration, a carbon monoxide-to-water ratio of about 1.09:1 is deemed to be a good target condition. It is noted that good performance is obtained over a wide feed ratio range and control at an exact ratio is not necessary.

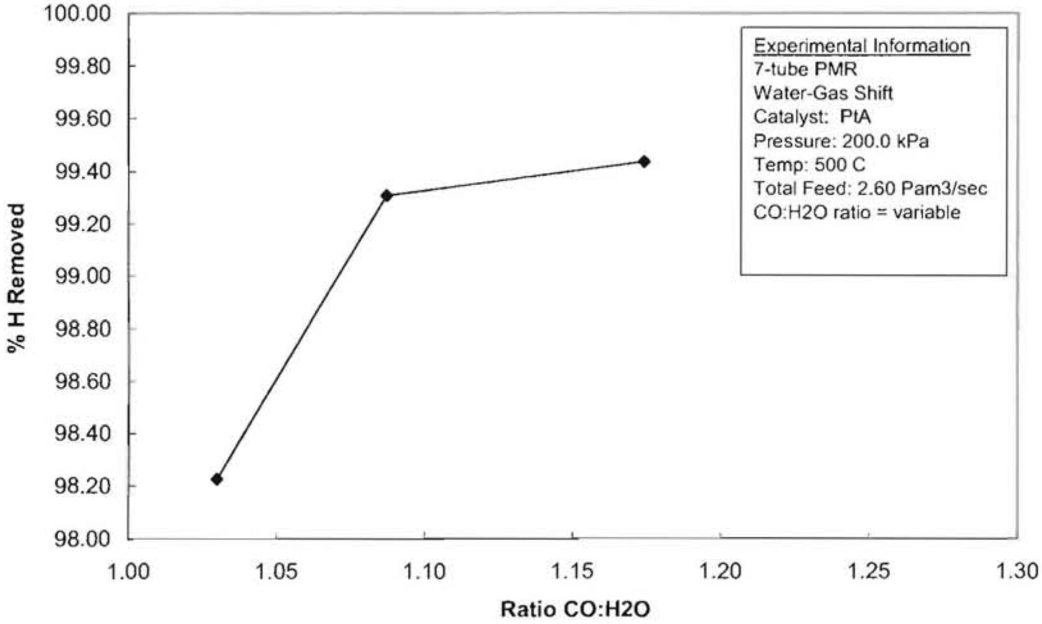


Figure 14 % H Removed versus CO:H_2O ratio for water-gas shift processing on PtA catalyst, 500 °C and 200 kPa (1500 torr).

Methane-steam reforming was also the subject of a feed ratio study, though, of course, tests were performed with varying water-to-methane ratios. The results are presented in Figure 15. Test results are plotted as % H removed versus the H_2O:CH_4 ratio for two temperatures, 500 °C and 550 °C. While good results were obtained over the entire range of ratios studies (1.75 – 1.95), the best results were obtained over 1.75-1.84. Considering that coking would become an increasing concern as water is decreased, 1.84:1 appears to be a reasonable target. However, as in the water-gas shift case, good results are obtained over a wide range, so control at an exact ratio is not essential.

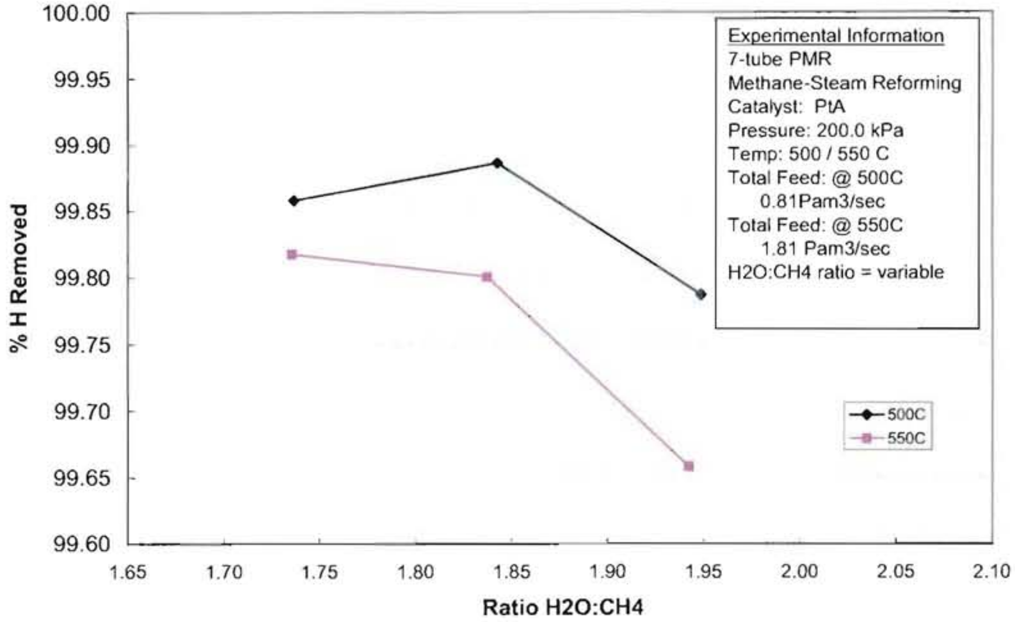


Figure 15 % H Removed versus $H_2O:CH_4$ ratio for methane-steam reforming processing on PtA catalyst, 500 °C and 550 °C, and 200 kPa (1500 torr).

6.3 PMR Scaling Method

Part of the reason for the 7-tube PMR test was to determine whether or not 3-tube PMR[3] results could be scaled based on membrane area. The ratio of the membrane areas of the two PMRs was 3.5 ($0.0851\ m^2/0.0247\ m^2 = 3.5$). Note that the ratios of catalyst to permeation area was similar for the 3-tube and 7-tube PMR (i.e. 4.63 cc/cm^2 and 5.18 cc/cm^2, respectively)

A comparison of 3-tube and 7-tube water-gas shift processing results is presented in Figure 16. Results are plotted as % H Removed versus total flowrate. The 3-tube and 7-tube tests at 160 kPa (1200 torr), 500 °C and a $CO:H_2O$ ratio of 1.09:1 are plotted. The 3-tube results are plotted against the lower x-axis range of 0-2 while the 7-tube results are plotted against the upper x-axis range of 0-7 Pam^3/sec. These ranges are the ratio of the membrane area, so if this is the dominate scaling factor, the two curves should be quite similar on such a plot. As observed, the two curves are quite similar. Both curves appear identical below the breakthrough point, and both curves appear to have similar breakthrough points (though more data would be needed to be more definite about this). After breakthrough the 7-tube curve falls below the 3-tube curve, but this is to be expected since the membrane area ratio is not the dominate factor in this region)

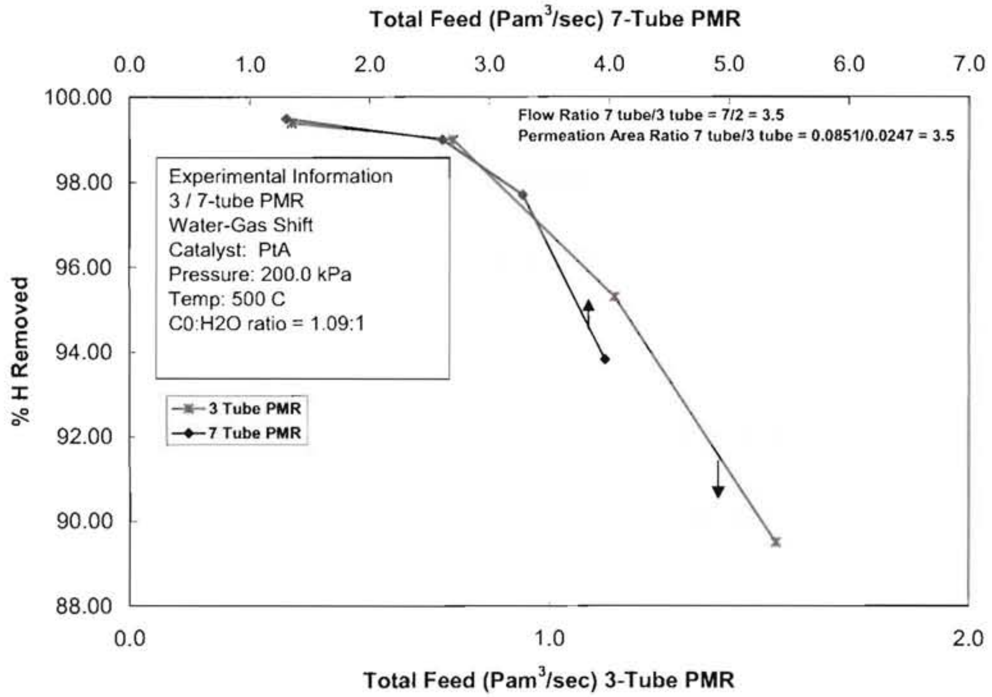


Figure 16 3-tube to 7-tube PMR comparison. % H Removed versus total feed flowrate for water-gas shift processing on PtA catalyst, 500 °C, and 160 kPa (1200 torr).

A similar study was conducted for methane-steam reforming. Figure 17 is a plot of % H removed versus total flowrate for 3-tube and 7-tube tests at 200 kPa (1500 torr) (7-tube) and 213.3 kPa (1600 torr) (3-tube), 500 °C and at a H_2O:CH_4 ratio of 1.84:1. Again the 3-tube results are plotting against the lower x-axis and the 7-tube results are plotted against the upper x-axis, and again the upper axis covers a range 3.5x the lower axis. As for WGS, the curves at flowrates less than breakthrough appear identical and both curves show breakthrough at about the same location. Thereafter, as before, the 7-tube curve is significantly below the 3-tube curve (as expected).

Both the WGS and MSR studies support the same conclusions, i.e. for otherwise identical conditions, performance up to and including breakthrough scales linearly and essentially exclusively with membrane area. This observation will be very important for sizing PMRs.

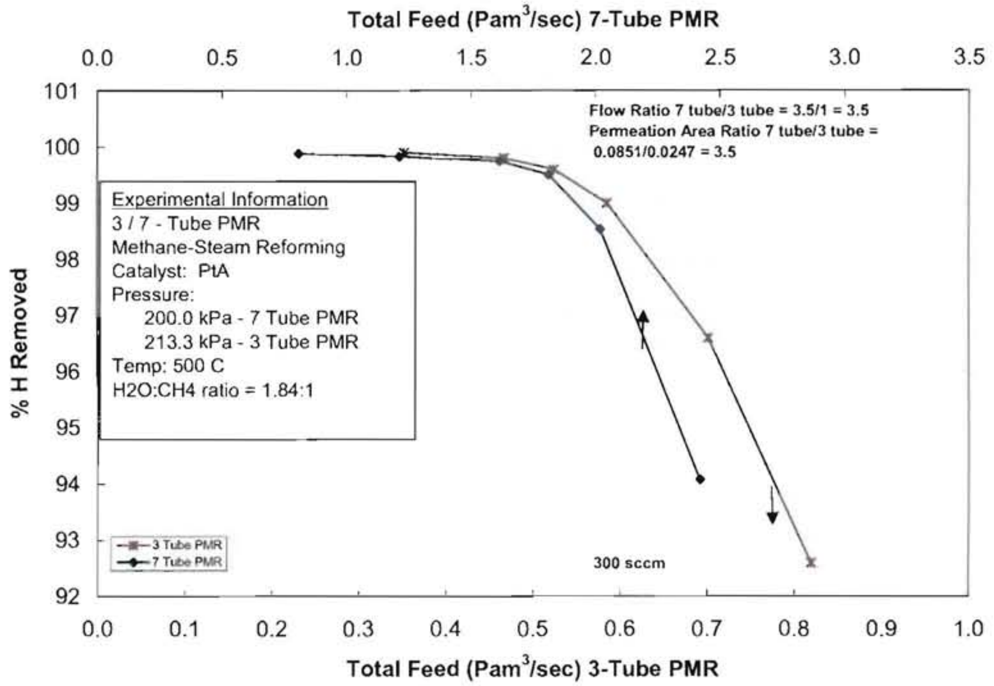


Figure 17 3-tube to 7-tube PMR comparison. % H Removed versus total feed flowrate for methane-steam reforming processing on PtA catalyst, 500 °C, 200 kPa (1500 torr) and 213.3 kPa (1600 torr).

6.4 Realistic Feed Composition

Results presented this point have been for idealized feed consisting only of water-gas shift or methane-steam reforming gases. Such results are important for understanding fundamental behavior and to benchmark models. These studies are also realistic for ITER water processing. But ITER air-like processing will be a more complicated mixture which may consist of methane, inert (e.g. Ar), N_2, water, carbon oxides and perhaps other gases. Attempting to feed the PMR a more realistic model of ITER air-like gases, the PMR was fed gases consisting of 15 parts Ar, 1 part CH_4, and 1 part CO. Water was added this mixture to maintain a H_2O:CH_4 ratio of 2.97:1. Results are presented on Figure 18. Breakthrough appears to occur at a feed flowrate of about 4.39 Pam^3/sec (2600 sccm). At comparable flowrates, performance appears somewhat degraded from previous (idealized) results. This is expected due the large fraction of inert in the realistic mixture.

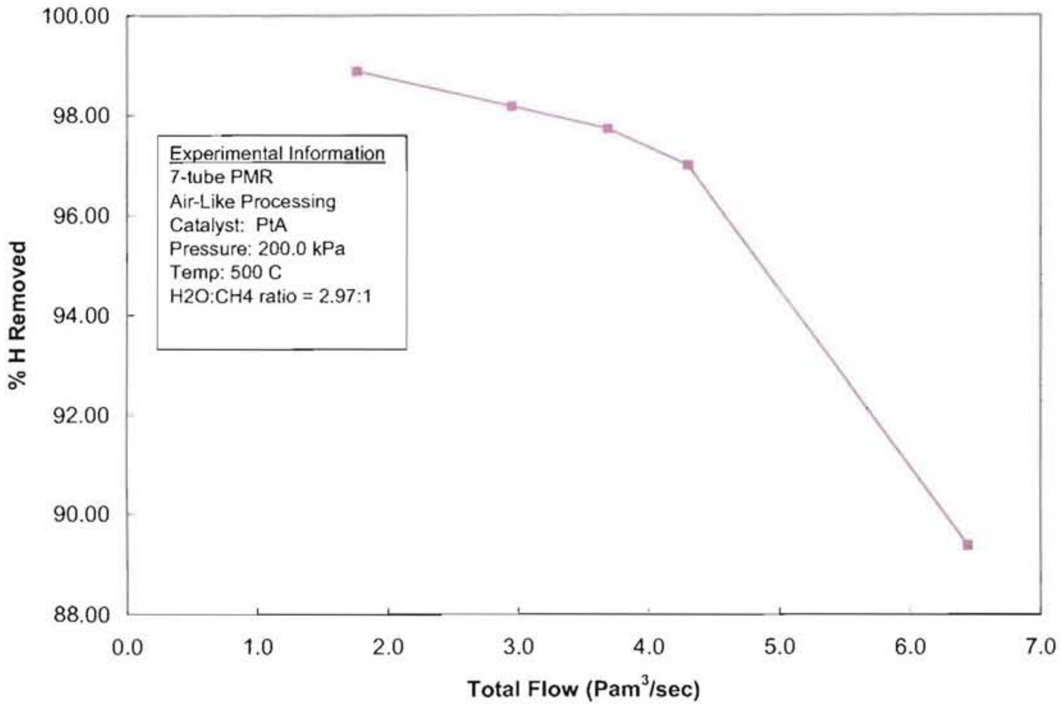


Figure 18 % H Removed versus total feed flowrate for air-like processing on PtA catalyst, 500 °C, 200 kPa (1500 torr), $H_2O:CH_4 = 2.97:1$.

6.5 Effect of Permeate Pressure

To quantify the effect of permeate pressures on % H removed, a series of runs was performed where all conditions were equal, but the only change made was the valve between the PMR and the permeate vacuum pump was progressively closed. This in turn increased the permeate pressure of the PMR. This study was performed with the air-like gas feed. The results are presented on Figure 19 as % H removed versus permeate pressure. For example, a % H removal of almost 97% was measured for a permeate pressure of 0.53 kPa (4 torr). As expected improved permeate vacuum results in better PMR performance. As observed on Figure 19 this improvement is approximately linear for the conditions studied.

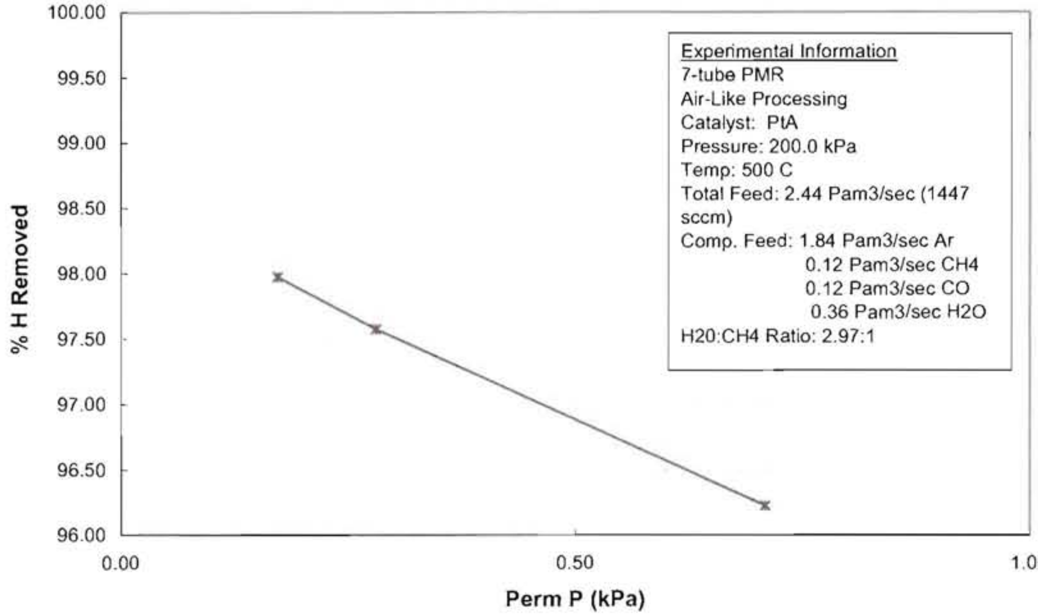


Figure 19 % H Removed versus total permeate pressure for air-like processing on PtA catalyst, 500 °C, 200 kPa (1500 torr), $H_2O:CH_4 = 2.97:1$.

6.6 Coking

Coking can ultimately lead to PMR plugging and coking can occur even while typical measures of performance (% H removed) are good. Previous studies have shown that coking can be avoided by conditions, but that coking will occur if, for instance, the feed becomes too rich in carbon. These studies were performed using measures of coking that were after-the-fact, i.e. an observation of plugging or a measure of the amount of H_2 required to decoke the PMR. To date on online indication of coking (or the lack thereof) has not been identified. In an effort to ultimately develop such a measurement, in the present study the $CO:CO_2$ ratio behavior in the retentate was noted.

When reactions proceed to near completion, $CO:CO_2$ ratios can be estimated by stoichiometry (assuming only the WGS and MSR reactions). For water-gas shift reactions with a $CO:H_2O$ feed ratio of 1.09:1, the ratio of $CO:CO_2$ in the retentate should approach 0.11. Actual $CO:CO_2$ ratios for water-gas shift reactions at 500 °C and 550 °C are presented in Figure 20. The data indicate that the $CO:CO_2$ ratio varies between 0.065 and 0.080. These results are below the theoretical ratio.

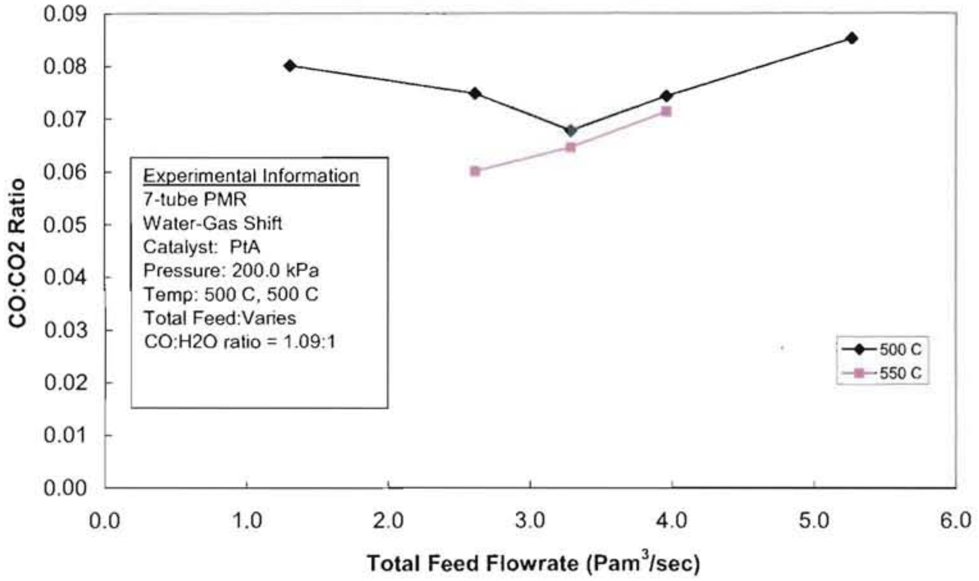


Figure 20 $CO:CO_2$ Ratios versus total feed flowrate for water-gas shift processing on PtA catalyst, 500 °C and 550 °C, 200 kPa (1500 torr), $CO:H_2O = 1.09:1$.

For methane-steam reforming reactions with a $H_2O:CH_4$ ratio of 1.84:1, the same stoichiometry arguments as above lead to the conclusion that the ratio of $CO:CO_2$ in the retentate should approach 0.25. Experimental measurement of the $CO:CO_2$ ratios for methane-steam reforming at 500 °C and 550 °C are presented in Figure 21. All $CO:CO_2$ ratios were somewhat below the theoretical value of 0.25.

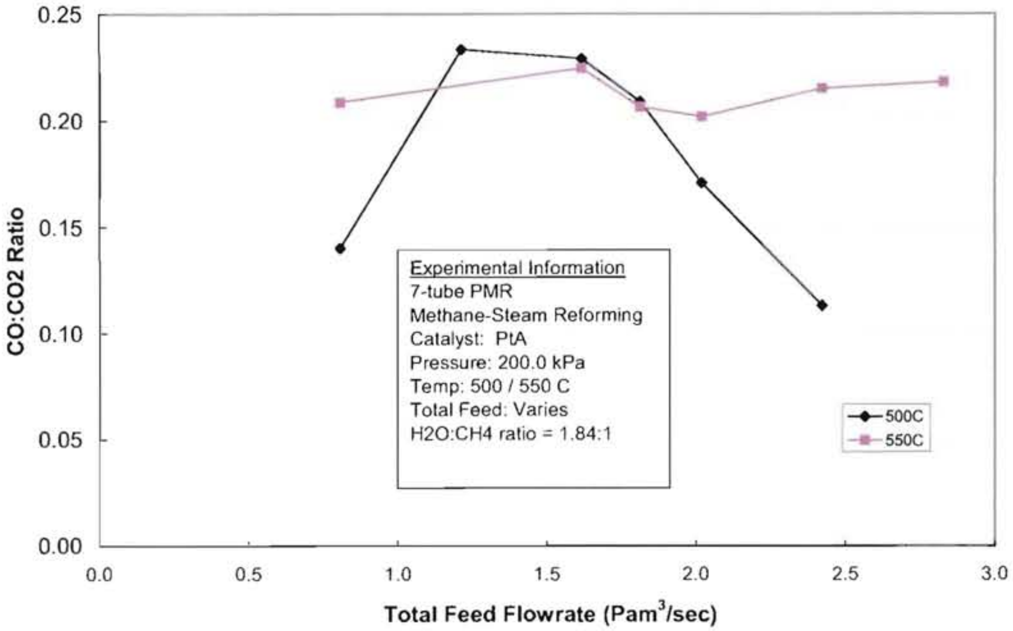


Figure 21 CO:CO_2 Ratios versus total feed flowrate for methane-steam reforming processing on PtA catalyst, 500 °C and 550 °C, 200 kPa (1500 torr), H_2O:CH_4 = 1.84:1.

For air-like processing with a H_2O:CH_4:CO ratio of 2.97:1:1, the ratio of CO:CO_2 should approach 0.053. Actual CO:CO_2 ratios for air-like processing at 500 °C are presented in Figure 22. The data show that the CO:CO_2 ratio was approximately at the theoretical value except after breakthrough.

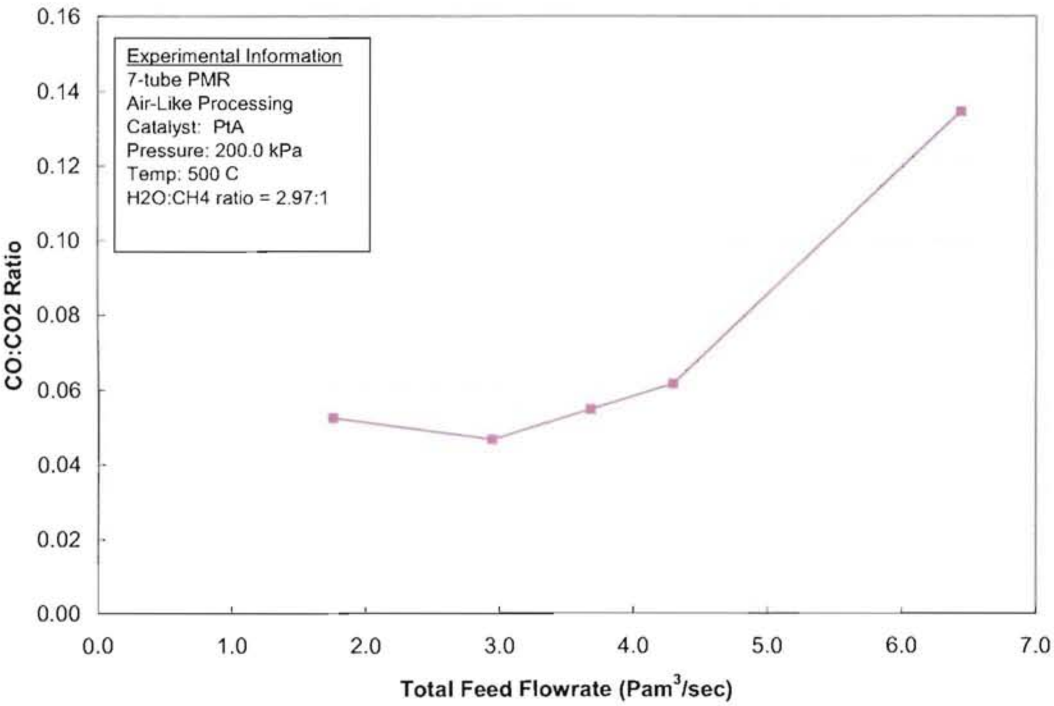


Figure 22 $CO:CO_2$ Ratios versus total feed flowrate for air-like processing on PtA catalyst, 500 °C, 200 kPa (1500 torr), $H_2O:CH_4 = 2.97:1$.

6.7 Initial Observations of Transient Behavior

Data presented to this point are steady state results, i.e. they are data collected only have the PMR has had significant time (minutes or hours) to reach steady performance. For a given set of conditions, this is the PMR performance that should be expected. However, performance might be significantly worse during transients such as step changes in conditions (e.x. feed flowrate changes) or during startup or shutdown.

Data depicting transients during startup and step changes in feed flow rates are presented in Figures 23 and 24 for water-gas shift and methane-steam reforming. Both graphs indicate spikes in H_2, CH_4, and CO levels during transient conditions. No spike in H_2O levels was noted during these transients. It was also noted that after shutdown, followed by an Ar purge, significant amounts of water were desorbed from the catalyst bed. It is hypothesized that water adsorption/desorption is important for PMR dynamic performance. Further testing is required to understand these observations, and such tests are presently being planned.

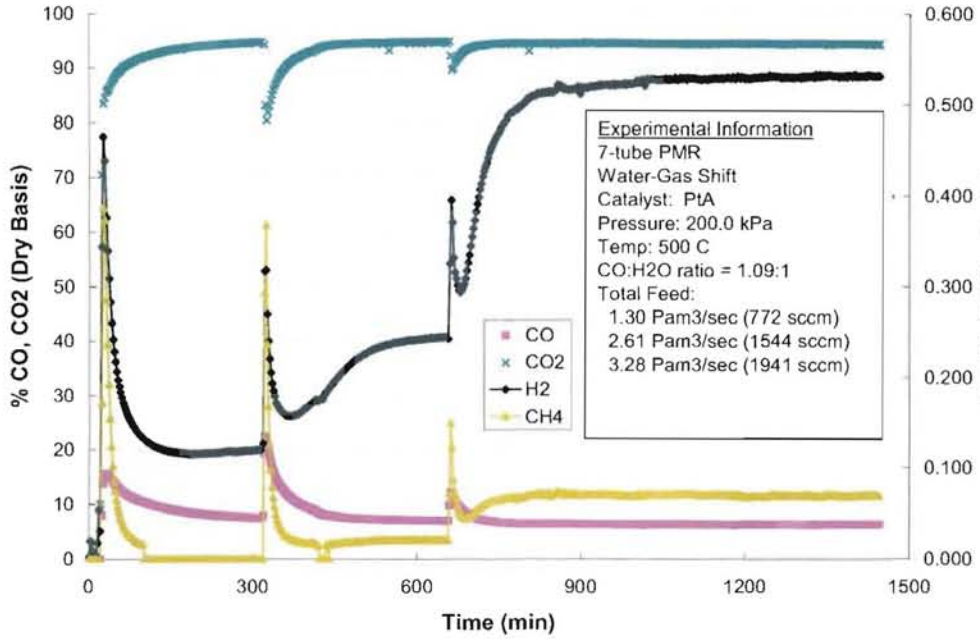


Figure 23 Water-Gas Shift Process Transients recorded on 3/23/09 during startup and changes in feed flowrates.

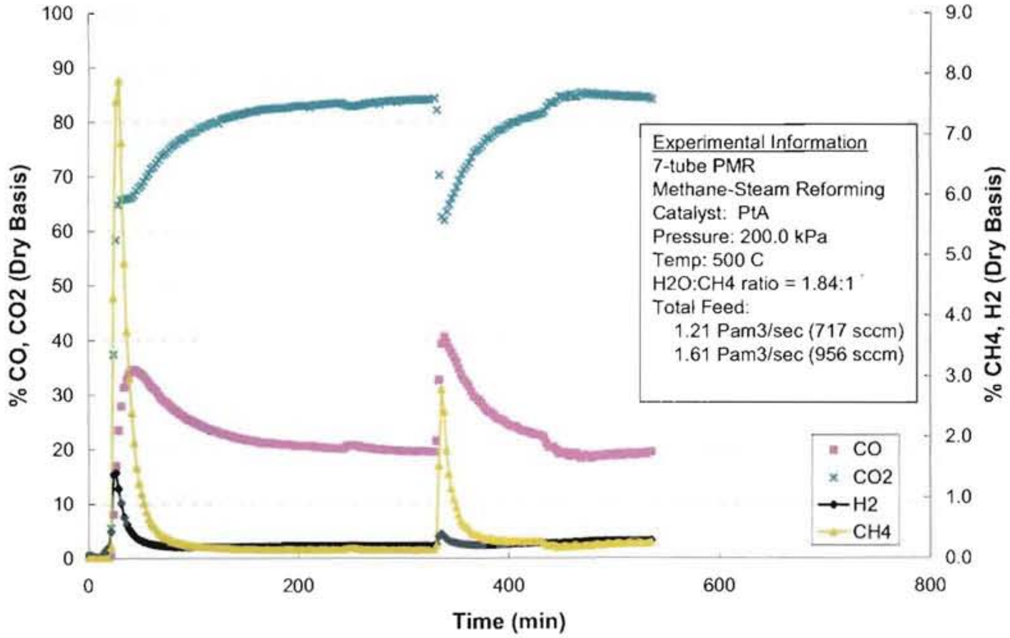


Figure 24 Methane-Steam Reforming Process Transients recorded on 4/8/09 during startup and changes in feed flowrates.

7 Summary and Conclusions

The purpose of testing the 7-tube PMR was to achieve the following objectives:

- Refine test measurements, especially humidity and flow.
- Refine maintenance procedures for Pd/Ag tube conditioning
- Evaluate baseline PMR operating conditions
- Determine PMR scaling method
- Evaluate PMR with realistic feed compositions
- Evaluate PMR performance with varying permeate pressures
- Address coking issues (if necessary)
- Indentify any unexpected behavior that may require further investigation

To accomplish these objectives a PMR which includes seven tube (Pd/Ag membrane tubes) was constructed. This PMR is about 1/5th scale for TEP. Results from these tests were collected and are presented here. The 7-tube PMR was a scale up of 3.5 from 3-tube PMR results which were collected and presented earlier. Both tests were conducted in the Hydrogen Processing Laboratory at Los Alamos National Laboratory.

Accuracy problems with the humidity reading were identified and corrected. This improved the quality of the data collected and simplified the analysis.

F_{ret} was moved to a point where plugging due to water condensation in the flow controller was avoided. This enabled successful completion of runs (which otherwise might have terminated). Use of the F_{ret} flow measurement was still found to be unreliable. Reliable measurement of this flow could be useful for future experiments.

A tube conditioning method was successfully trying and documented. This may be incrementally improved, but the important features have been identified.

If was concluded that for water-gas shift, the target $CO:H_2O$ feed ratio should be 1.09:1 and for methane-steam reforming the target $H_2O:CH_4$ feed ratio should be 1.84:1. However, it was also found that a rather broad range of feed ratios gave good results. This should decrease the need for a precise feed control system. It was noted however, that too much carbon in the feed may result in coking.

A number of tests results for water-gas shift processing and methane-steam reforming processing at different flowrates were collected. These data appear sufficient for scaling to ITER conditions, and they appear valuable for computer model benchmarking. Significant data were collected that 500 C and 200 kPa (1500 torr)(tentative TEP baseline conditions) and parametric measurement were collected off of this baseline to characterize dependencies.

Comparison of these data to previous data collected for a 3-tube PMR indicate that, all other things being equal, the PMR breakthrough flowrate scales linearly with membrane area. This will be useful for TEP PMR sizing.

Tests to evaluate the performance of a PMR under realistic air-like feed conditions were conducted on a simulated air-like feed mixture. These results were similar to idealized WGS and MSR results. These results will be useful to predicting PMR performance under realistic conditions and for computer modeling benchmarking

Performance was significantly improved with increasing temperature for MSR, but only marginally improved for WGS.

Performance degraded as the permeate pressure increased. Over the range studied, this dependency appears linear (% H removed vs. permeate pressure

Coking can be a significant problem for PMRs, and an attempt to understand on-line behavior related to coking was made. The $CO:CO_2$ ratio in the retentate for various processing conditions was plotted and analyzed. It was noted that the observed value was generally somewhat below what would be expected from assumed stoichiometry. The implications of this remain a topic for future study.

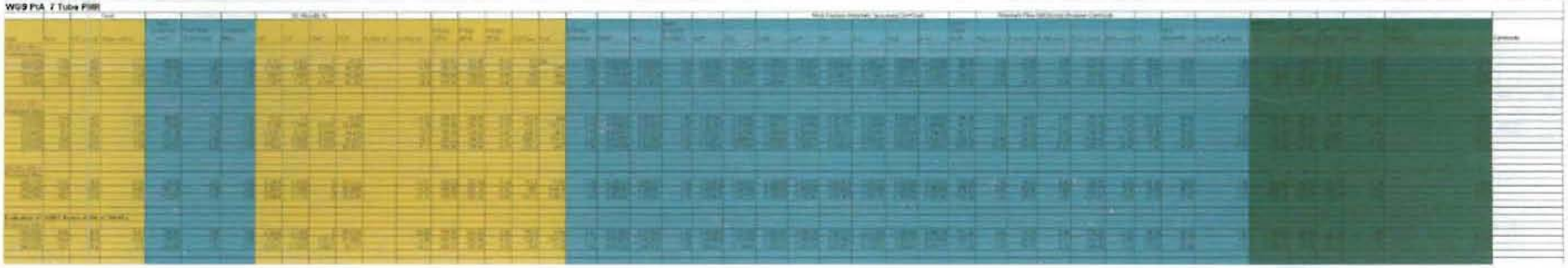
Previous PMR studies in this series have focused on steady state results, but this study includes some dynamic study. Spikes in hydrogen, methane, and carbon monoxide species were noted during startup and feed flow rate changes. These caused significant PMR performance degradation (% H_2 removed). It is believed that part of the cause of these transients is due to the adsorption of water on the catalyst bed. Future work will be required to explain and develop solutions to minimize these transients.

The results presented here are believed to be sufficient to size PMRs for steady state operation in TEP. There is sufficient understanding of baseline conditions (500 °C, 200 kPa (1500 torr) and feed ratios) and expectations associated with variations in these conditions. In addition these results will be useful for benchmarking computer models of the PMR which will be used for sizing and other purposes. It was noted during this study that there are significant degradations in PMR performance during transients. Understanding and addressing such issues will be dealt with in future studies.

8 Appendix A- PMR Test Results with PtA Catalyst

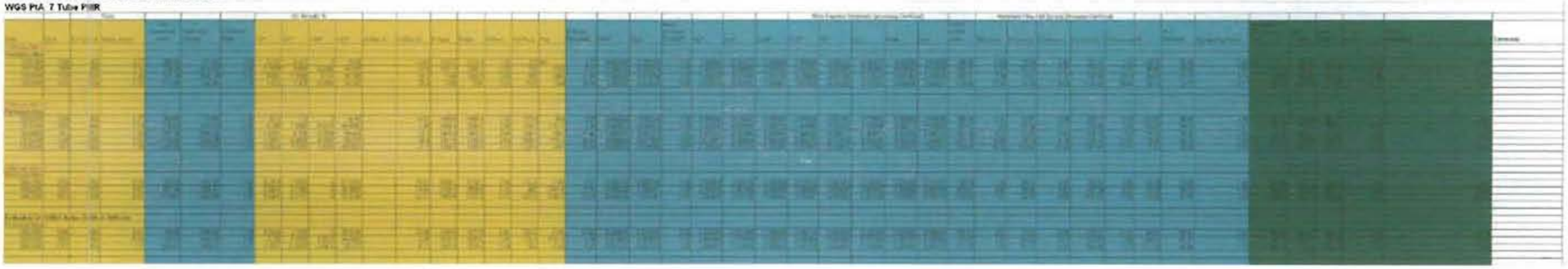
8.1 Water-Gas Shift Test Results

7-Tube PMR Data with Total Flow and Pressures converted to SI Units



WGS PtA 7 Tube PMR

7 Tube PMR Data as Collected

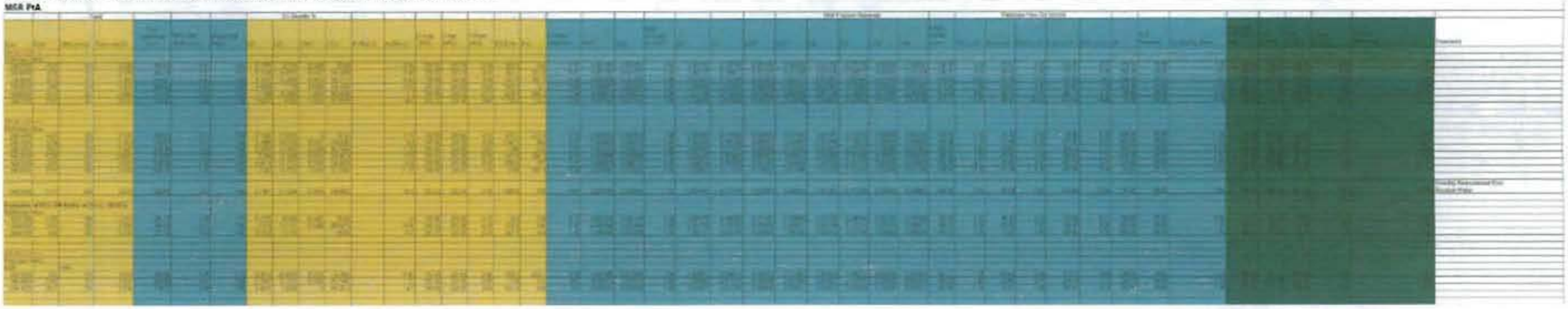


WGS PtA 7 Tube PMR

8.2 Methane-Steam Reforming Test Results

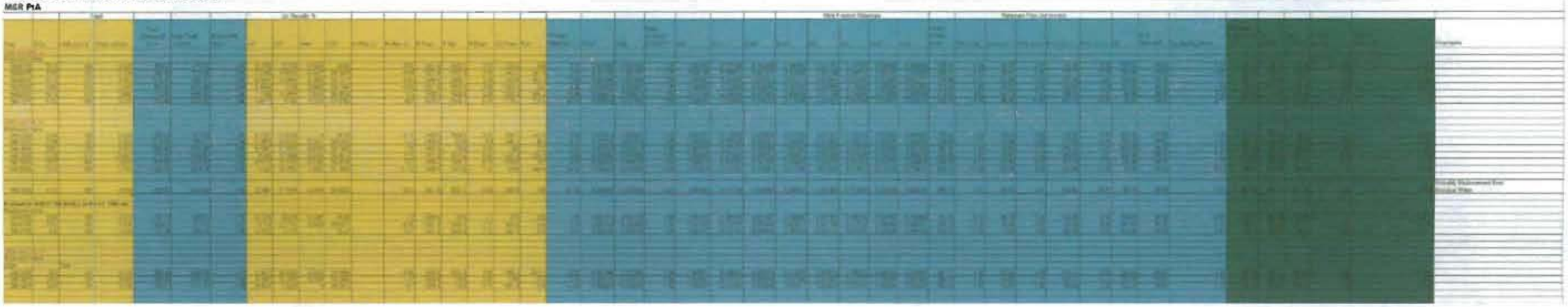
7-Tube PMR Data with Total Flow and Pressures converted to SI Units

MSR PtA



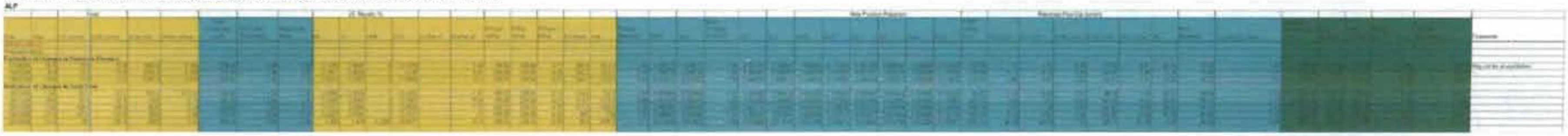
7 Tube PMR Data as Collected

MSR PtA

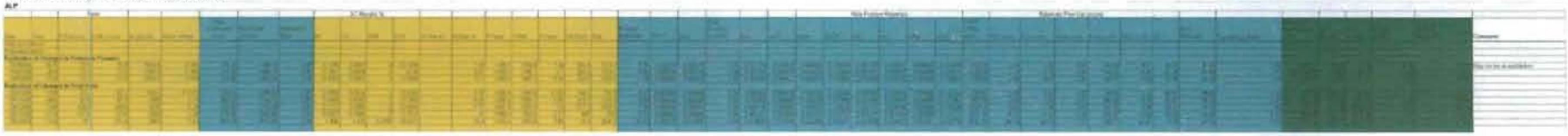


8.3 Air-Like Processing Test Results

7-Tube PMR Data with Total Flow and Pressures converted to SI Units

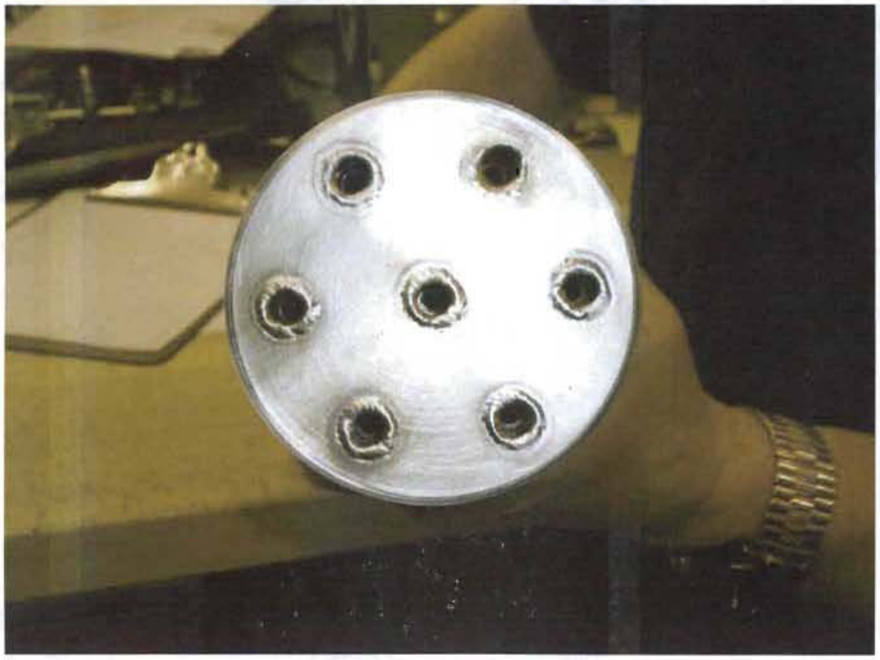


7 Tube PMR Data as Collected

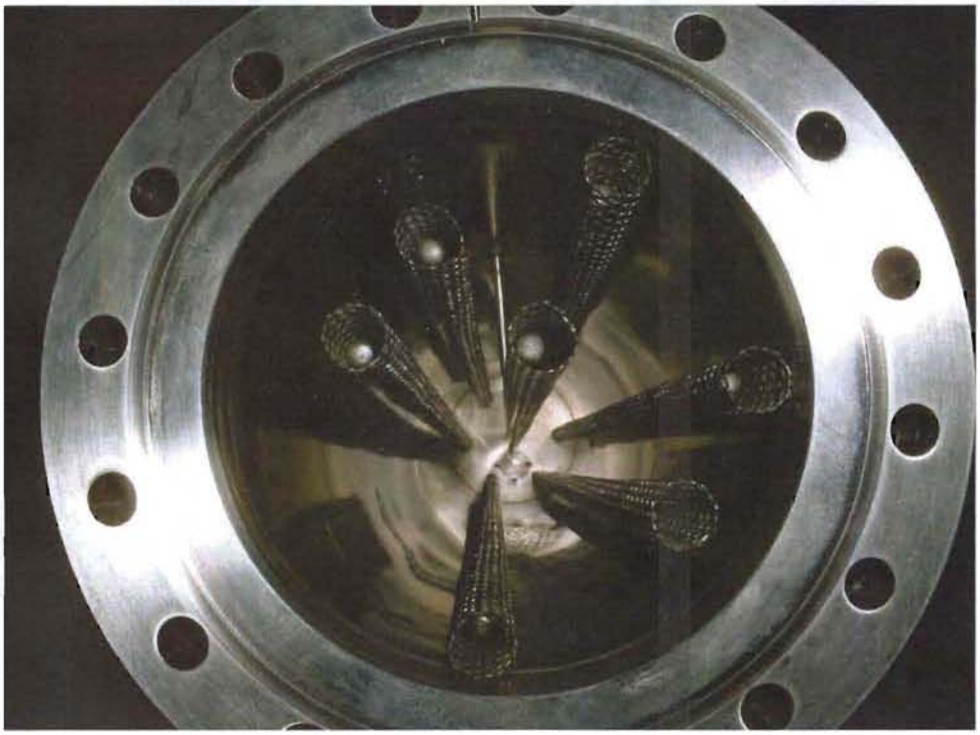


9 Appendix B – 7-tube PMR Pictures

Picture showing Pd/Ag tubes brazed to collection plate during fabrication (at the factory).

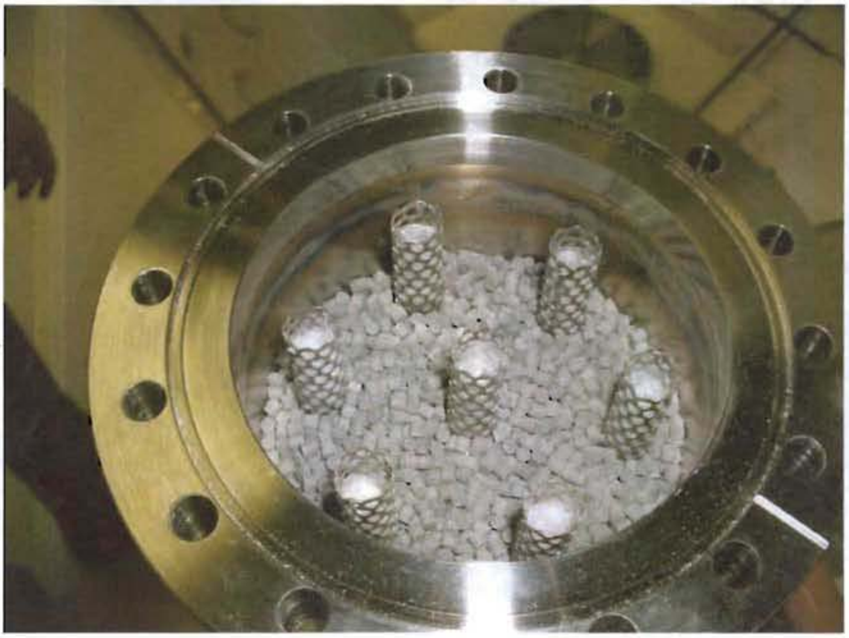


Picture showing brazing sleeves welded into the collection plate.



Picture showing the perforate metal tubes installed over the Pd/Ag tubes.

Picture showing fixture in place to center Pd/Ag tubes during catalyst loading.

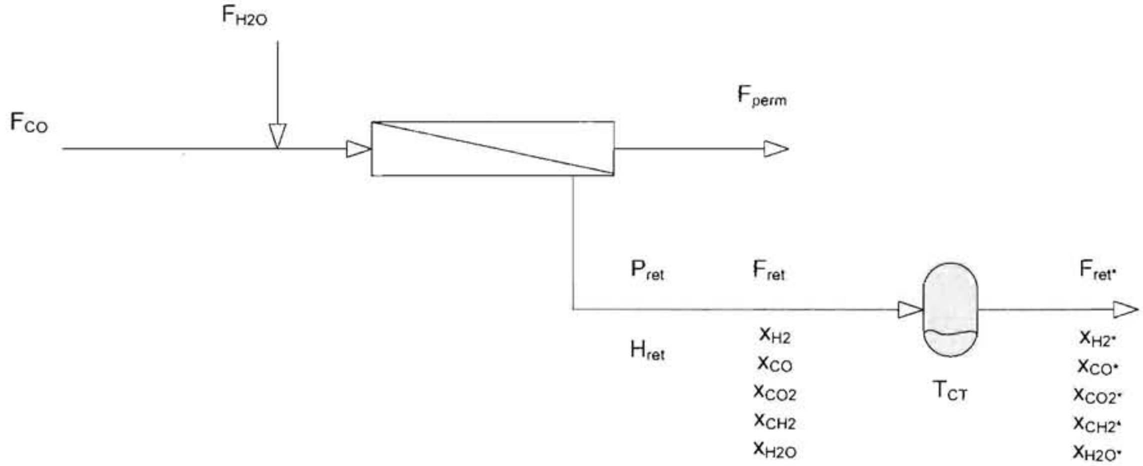


Picture showing PMR loaded with PtA catalyst and with quartz wool placed in the end of the perforated metal tube protectors to center the Pd/Ag tubes.

Picture showing the fully assembled PMR inside of the heating furnace.

10 Appendix C: Equations for analysis of water-gas shift PMR experiments

PMR data are not necessarily measured at the primary point of interest. And certain quantities can be determined more than one way which offers opportunities for cross checking results. For these purposes, key variable of interest for water-gas shift experiments are shown in the following figure:



Determine concentrations at exit of PMR

GC measurements were made after a water trap to minimize the amount of water introduced to the GC. But PMR performance must be based on concentrations exiting the PMR, i.e. prior to the water trap. To determine the necessary information first write the following mass balance equations:

$$F_{ret}x_{H2} = F^*_{ret}x^*_{H2} \tag{1}$$

$$F_{ret}x_{CO} = F^*_{ret}x^*_{CO} \tag{2}$$

$$F_{ret}x_{CO2} = F^*_{ret}x^*_{CO2} \tag{3}$$

$$F_{ret}x_{CH4} = F^*_{ret}x^*_{CH4} \tag{4}$$

$$F_{ret}x_{H2O} = F^*_{ret}x^*_{H2O} + F^L_{H2O} \tag{5}$$

$$F_{ret} = F^*_{ret} + F^L_{H2O} \tag{6}$$

Equations (5) and (6) can be combined to give:

$$F^{*}_{ret} = F_{ret}\frac{(1-x_{H2O})}{(1-x^{*}_{H2O})} \tag{7}$$

Substituting (7) into (1), (2), (3) and (4) yields:

$$x_{H2} = \frac{(1-x_{H2O})}{(1-x^{*}_{H2O})}x^{*}_{H2} \tag{8}$$

$$x_{CO} = \frac{(1-x_{H2O})}{(1-x^{*}_{H2O})}x^{*}_{CO} \tag{9}$$

$$x_{CO2} = \frac{(1-x_{H2O})}{(1-x^{*}_{H2O})}x^{*}_{CO2} \tag{10}$$

$$x_{CH4} = \frac{(1-x_{H2O})}{(1-x^{*}_{H2O})}x^{*}_{CH4} \tag{11}$$

The mole fraction of water before the water trap is known from Hret and the mole fraction of water after the water trap is known from the temperature of the water trap. Thus, equations (8) - (11) can be used to convert mole fractions from GC measurements made after the water trap into mole fractions in front of the water trap. This provides all necessary concentration information on the gas leaving the PMR.

Determine retentate flowrate by oxygen balance

While Fret was measured with a mass flow controller these measurements were found to be unreliable presumably due to water condensation. Thus, Fret was determined by considering the following oxygen balance

$$F_{CO} + F_{H2O} = F_{ret}(x_{CO} + 2x_{CO2} + x_{H2O}) \tag{12}$$

Solving for Fret gives:

$$F_{ret} = \frac{F_{CO} + F_{H2O}}{(x_{CO} + 2x_{CO2} + x_{H2O})} \tag{13}$$

This equation was used to determine Fret for all PMR experiments.

Determine coking rates

If it is assumed that no coking occurs in the PMR then the following carbon balance applies:

$$F_{CO} = F_{ret}(x_{CO} + x_{CO2} + x_{CH4}) \tag{14}$$

This equation can be used to determine Fret, and the result can be compared to Fret from the oxygen balance. This was done, and it was generally observed that Fret from the carbon balance was either equal to or smaller than the Fret from the oxygen balance. This suggested that in some cases perhaps coke was being deposited in the PMR. A carbon balance which includes coking is:

$$F_{CO} = F_{ret}(x_{CO} + x_{CO2} + x_{CH4}) + F_{coke} \tag{15}$$

Using Fret from the oxygen balance, this equation was used to estimate coking rates for each PMR experiment.

H balance-based Fret determination

As a check on other calculations and measurements, a hydrogen balance can be written as follows:

$$F_{H2O} = F_{perm} + F_{ret}(x_{H2} + 2x_{CH4} + x_{H2O}) \tag{16}$$

This was used to determine Fret. However, this method proved to be problematic. When the PMR is operating in the pre-broken through region, F_{H2O} is only slightly larger than F_{perm}. In fact, in many cases the difference is smaller than instrument accuracy. Thus, Fret determined by this method was erratic except for measurements which were well beyond breakthrough.

DF and % H2 Recovered

The overall performance of the PMR can be expressed as a decontamination factor or as % hydrogen recovery. The decontamination factor (DF) is total hydrogen entering the PMR divided by the total hydrogen in the retentate. Using feed and retentate-based measurements, this was calculated as followings (using Fret based on oxygen balance):

$$DF = \frac{F_{H2O}}{Fret(x_{H2} + 2x_{CH4} + x_{H2O})} \tag{17}$$

% H2 recovered based on feed and retentate-based measurements were calculated as follows (again using Fret based on oxygen balance):

$$\%H2\,recovered = 100\left(1 - \frac{Fret(x_{H2} + 2x_{CH4} + x_{H2O})}{F_{H2O}}\right) \tag{18}$$

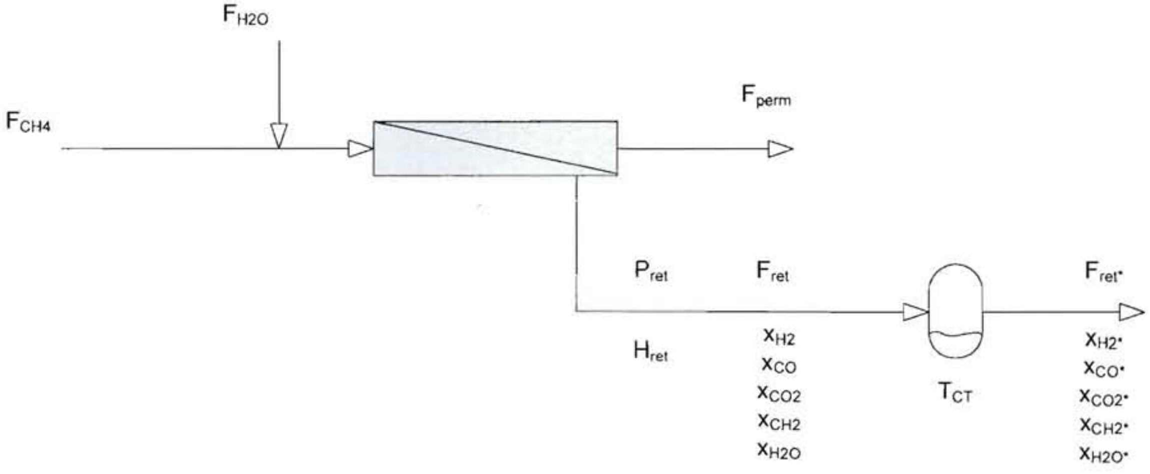
Alternatively, the same value can be calculated using feed and permeate information as follows:

$$\%H2\,recovered = 100\left(1 - \frac{F_{H2O} - F_{perm}}{F_{H2O}}\right) \tag{19}$$

These latter two equations were found useful to determine the accuracy of the underlying data. In particular there were questions regarding the accuracy of Fperm. Thus, for each series of PMR experiments a multiplier was applied to Fperm to minimize the difference between these two calculations of % H2 recovered.

Equations for analysis of methane-steam reforming PMR experiments

Similar treatment is needed for methane-steam reforming experiments, but somewhat different relationships result from the different feed gases. The key variables for these experiments are shown in the following figure:



Where methane-steam reforming relationship is different from water-gas shift relationship, they are highlight in the following abbreviated sections.

Determine retentate flowrate by oxygen balance

Fret by oxygen balance is determined as follows:

$$F_{ret} = \frac{F_{H2O}}{(x_{CO} + 2x_{CO2} + x_{H2O})} \tag{20}$$

Determine coking rates

The carbon balance without coking is:

$$F_{CH4} = F_{ret}(x_{CO} + x_{CO2} + x_{CH4}) \tag{21}$$

While the carbon balance with coking is:

$$F_{CH4} = F_{ret}(x_{CO} + x_{CO2} + x_{CH4}) + F_{coke} \tag{22}$$

H balance-based Fret determination

The hydrogen balance-based balance is:

$$2F_{CH4} + F_{H2O} = F_{perm} + F_{ret}(x_{H2} + 2x_{CH4} + x_{H2O}) \tag{23}$$

DF and % H2 Recovered

The feed and retentate-based DF calculation is:

$$DF = \frac{2F_{CH4} + F_{H2O}}{Fret(x_{H2} + 2x_{CH4} + x_{H2O})} \tag{24}$$

The % H2 recovered based on feed and retentate measurements is:

$$\%H2\ recovered = 100\left(1 - \frac{Fret(x_{H2} + 2x_{CH4} + x_{H2O})}{2F_{CH4} + F_{H2O}}\right) \tag{25}$$

The % H2 recovered based on feed and permeate measurements is:

$$\%H2\ recovered = 100\left(1 - \frac{2F_{CH4} + F_{H2O} - F_{perm}}{2F_{CH4} + F_{H2O}}\right) \tag{26}$$

Nomenclature

Symbol	Meaning
F_{CO}	CO feed rate (sccm)
F_{CH4}	CH4 feed rate (sccm)
F_{H2O}	H2O feed rate (sccm)
F_{ret}	Retentate flowrate before the water trap (sccm) (incl water from PMR)
F^{*}_{ret}	Retentate flowrate after the water trap (sccm) (incl water from water trap)
F_{perm}	Permeate flowrate (sccm)
x_{H2}	Mole fraction of H2 at PMR exit
x_{CO}	Mole fraction of CO at PMR exit
x_{CO2}	Mole fraction of CO2 at PMR exit
x_{CH4}	Mole fraction of CH4 at PMR exit
x_{H2O}	Mole fraction of H2O at PMR exit
x^{*}_{H2}	Mole fraction of H2 at water trap exit
x^{*}_{CO}	Mole fraction of CO at water trap exit
x^{*}_{CO2}	Mole fraction of CO2 at water trap exit
x^{*}_{CH4}	Mole fraction of CH4 at water trap exit
x^{*}_{H2O}	Mole fraction of H2O at water trap exit, (for spreadsheet, same as x_{H2O} when x_{H2O} is less than 10 torr
F^{L}_{H2O}	Flowrate of water vapor into the liquid form in the water trap (sccm)
F_{coke}	Flowrate of carbon in the gas phase into the solid phase in the PMR (sccm)
DF	Decontamination factor, "total H in feed" divided by "total H in retentate"
$\%H2\ recovered$	% hydrogen recovered
$Pret$	Retentate pressure (torr)
$Hret$	Retentate humidity (dew point in degrees C)
Tct	Water trap temperature (C)

Note: All spreadsheet calculations assume standard conditions are 70 F and 1 atm.