G-2 RUN: WPI's Multitube Membrane Module Test

Membrane Preparation and Multitube Membrane Design

The Pd membranes developed at Worcester Polytechnic Institute (WPI), previously tested at NCCC and reported in the literature [1,2,**Error! Bookmark not defined.**,**Error! Bookmark not defined.**], were scaled up and replicated in order to synthesize eight new membranes. Each porous stainless steel (PSS) tube had a surface area of 150 cm^2 and dimensions of 38.1 cm in length, 1.27 cm OD and a Media Grade of 0.5 μm. All supports were synthesized as previously described [1,2,**Error! Bookmark not defined.**]. The supports were oxidized and graded with pre-activated alumina particles. The first grading consisted of coarse particles with sizes in the range of 1-3 μm; while fine grading introduced particles of 0.6 μm. The membranes were then activated and electroless-plated to create a dense Pd layer. Afterwards, a gold layer was deposited on top of palladium in order to improve the stability and recoverability of the membranes. Finally, a topmost layer was formed on top of Pd before the module was assembled with seven membranes and subsequently shipped to the NCCC facilities. Figure 1 shows the different thickness stages of the composite membranes; on average the membranes had a composition of 5.4 Pd, 0.4 Au and 1.6 Pd, with an intermediate grading layer of 2.5 μm. Notice that the replicability of synthesizing these membranes is effectively demonstrated by exhibiting a standard deviation in the Pd layer thickness of 0.9 μm. Furthermore, Figure 2 shows the average He leak at each step of the synthesis. As purchased, each support had a He flux of 200 L/min at one bar ΔP and it was reduced to a cumulative (all seven membranes) He flux of <0.01cm^3/min. The total permeable surface area of the seven membranes is 1050 cm^2.

The multitube membrane module was designed to hold the seven Pd/Au/Pd membranes. The module has one membrane located at the center of the module and six equally spaced membranes surrounding it. The surrounding membranes were kept at 1.31" from the central membrane and were distributed in a hexagonal profile. Notice that the additional synthesized membrane was tested at WPI under controlled conditions with pure H_2 purity for comparison purposes.

The module containing the seven Pd/Au/Pd membranes was installed in the WPI-MTR skid at the National Carbon Capture Center in Wilsonville, Al. [3, 4] as shown in Figure 3 for the G-2 RUN. During the RUN, at first, a mixture of 35:65 H_2/N_2 was fed to the system for 100 hours, followed by the actual coal derived syngas with a flow rate of 10 lb/h. The syngas feed had an average composition of H_2: 34%, N_2: 55%, CO < 1%, CO_2: 10%, H_2O: balance as described previously [3, 4].

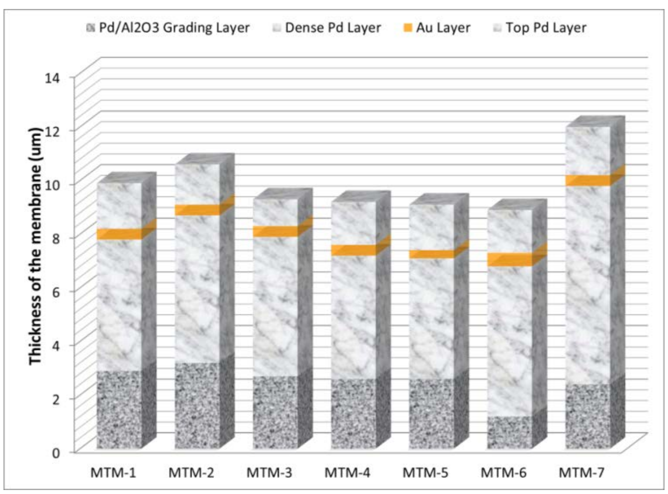

Figure 1. Composition of the multilayered composite membranes used in the present study

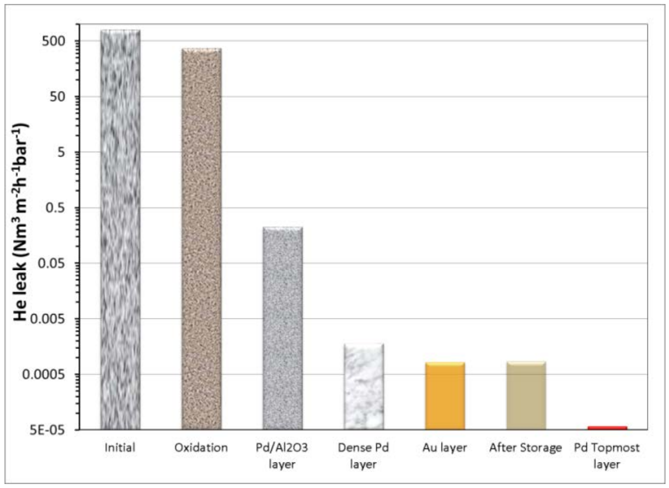

Figure 2. Average He leak through the Pd/Au/Pd membranes throughout each synthesis step

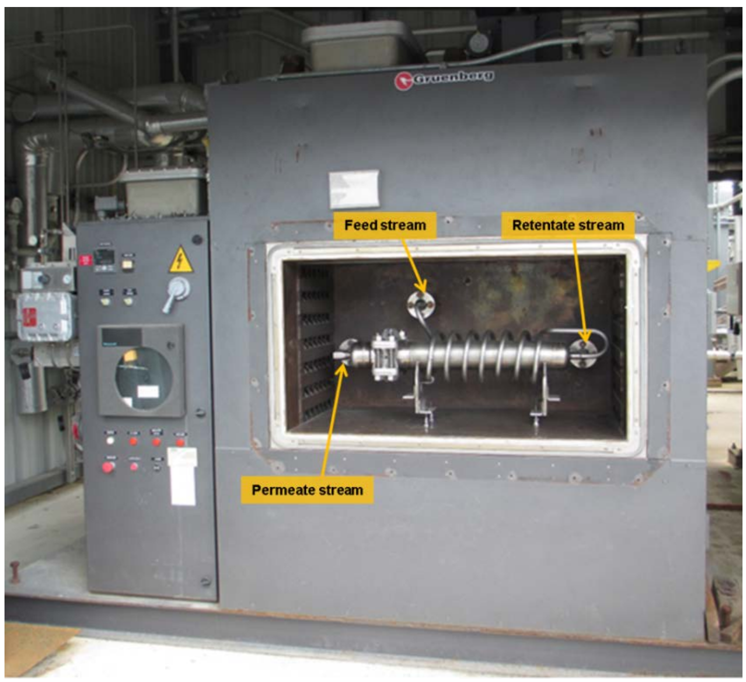

Figure 3. Photograph of the setup for testing the multitube membrane module at NCCC (Notice that the door of the oven was removed to facilitate display)

2. Results

The evaluation of the performance of the membrane module was based on its H_2 permeance ($\bar{P}_{H2}$), produced H_2 purity and H_2 recovery (R) as defined in Equations 1-3:

$$\bar{P}_{H2} = \frac{F_{H2,perm}}{A\left(\sqrt{p_{H2}^{ave}} - \sqrt{p_{H2}^{perm}}\right)} \tag{1}$$

$$Purity = \frac{F_{H2,perm}}{\sum F_{i,retentate}} \cdot 100 \quad (2)$$

$$R = \frac{F_{H2,feed} - F_{H2,perm}}{F_{H2,feed}} \cdot 100 \quad (3)$$

where $F_{H2,feed}$, $F_{H2,retentate}$ and $F_{H2,perm}$ are the H_2 flow rates at the feed, retentate and the permeate respectively. *A* is the permeable surface area of the membranes, $F_{i,retnetate}$ the flow rate of component *i* in the retentate; p_{H2}^{ave} and p_{H2}^{perm} are the H_2 partial pressures inside the module and the permeate side respectively. It is important to mention that p_{H2}^{ave} was approximated as the average of the H_2 partial pressure of the feed and the retentate.

The H_2 permeance and purity of the module are displayed as a function of time and shown in Figure 4. At first, the membrane module shows a permeance in the range of 7-10 $Nm^3m^{-2}h^{-1}bar^{-0.5}$ (6-8.6 scfh ft^{-2}-$psi^{-0.5}$) when tested under H_2/N_2 mixture as depicted in Figure 4 by using black solid data points. When syngas was fed into the module, a slight increase in permeance is observed, followed by a steady performance. The maximum flux achieved by these seven membranes was 6 lb/day of H_2. It is important to mention that the additional synthesized membrane MTM-8 with same dimensions and characteristics was tested in the facilities of Worcester Polytechnic Institute under clean and pure H_2. The membrane displayed a H_2 permeance under clean conditions of 80 $Nm^3m^{-2}h^{-1}bar^{-0.5}$ (69 scfh ft^{-2}-$psi^{-0.5}$) or an equivalent of 1.03 lb/day at pressure difference of 0.35 bar.

The H_2 purity produced by these membranes began at 99.5% under H_2/N_2 and underwent a sudden increase to 99.63% when syngas was fed and up to 99.87% after being tested for 67 hours in syngas conditions. Afterwards, the purity of the module decreased steadily reaching a minimum purity of 98.84% after 670 hours under syngas conditions. Notice that at the end of the test, the H_2 purity was of 98.13% under a H_2/N_2 mixture.

Figure 5 shows the H_2 recovery achieved under these conditions as a function of time. Notice that when the membrane module was under H_2/N_2 at the beginning of the test, the recovery reached 52%. Under syngas conditions, the H_2 recovery decreased to 35% and remained constant throughout the test. The maximum theoretical H_2 recovery achievable by the module is <90% which can be further improved by the presence of sweep gas in the permeate side and/or by increasing the retentate pressure.

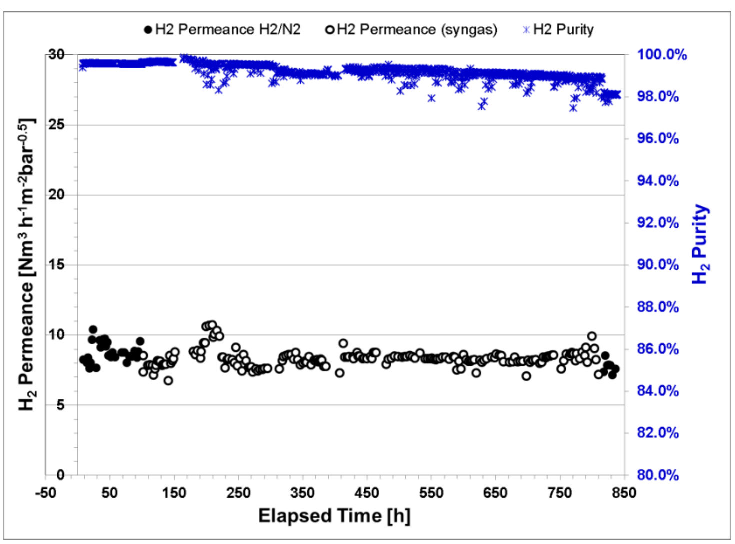

Figure 4. Hydrogen permeance and purity profiles of the multitube membrane module at NCCC

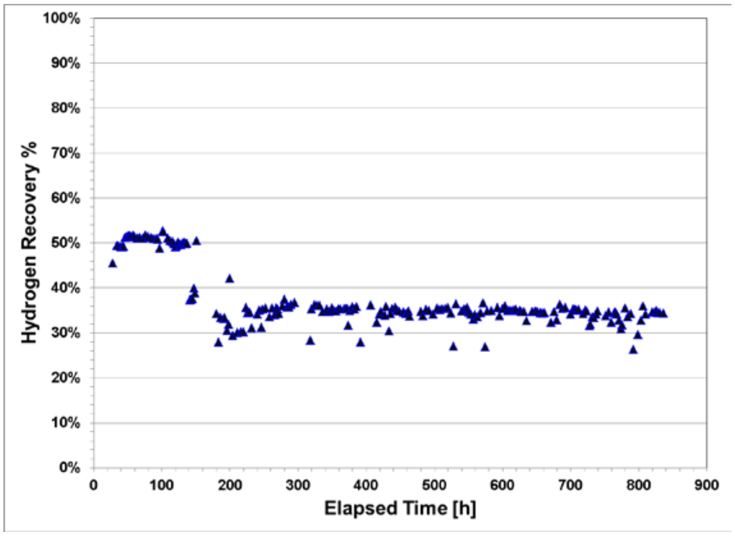

Figure 5. Hydrogen recovery profile of the multitube membrane module at NCCC

In summary, during the G-2 Run, WPI tested a multitube membrane module with a total permeable area of 1050 cm^2. The membrane module showed a stable hydrogen permeance of 8 $Nm^3m^{-2}h^{-1}bar^{-0.5}$ (6.9 scfh ft^{-2}-$psi^{-0.5}$) throughout 840 hours of testing. The purity of the produced H_2 was in the range of 99.87-98%. A H_2 production of 6 lb/day and a H_2 recovery of 37% were achieved representing a significant development in the field. The scalability and industrial applicability of this technology were successfully demonstrated.

References

[1] Ma YH, Mardilovich PP, She Y. (2000) Hydrogen gas-extraction module and method fabrication. US Patent No. 6,152,987.
[2] Ma YH, Mardilovich IP, Engwall EE. (2007) Composite gas separation modules having intermediate metal layer. US Patent No. 7,175,694.
[3] F. Guazzone , J. Catalano, I.P. Mardilovich, J Kniep, S. Pande, T. Wu, R.C. Lambrecht, S. Datta, N.K. Kazantzis, Y.H. Ma, Gas permeation field tests of composite Pd and Pd-Au membranes in actual coal derived syngas atmosphere, Int. J Hydr Energy 37 (2012) 4557-4568.
[4] I.P. Mardilovich, B. Castro-Dominguez, N.K. Kazantzis, T. Wu, Y.H. Ma, A comprehensive performance assessment study of pilot-scale Pd and Pd/alloy membranes under extended coal-derived syngas atmosphere testing, Int. J Hydr Energy 40 (2015) 6107-6117.