High-Temperature Water-Gas Shift Membrane Reactor Study

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ABSTRACT

NETL's Office of Research and Development is exploring the integration of membrane reactors into coal gasification plants as a way of increasing efficiency and reducing costs. Water-Gas Shift Reaction experiments were conducted in membrane reactors at conditions similar to those encountered at the outlet of a coal gasifier. The changes in reactant conversion and product selectivity due to the removal of hydrogen via the membrane reactor were quantified. Research was conducted to determine the influence of residence time and H_2S on CO conversion in both Pd and $Pd_{80wt\%}Cu$ membrane reactors. Effects of the hydrogen sulfide-to-hydrogen ratio on palladium and a palladium-copper alloy at high-temperature were also investigated. These results were compared to thermodynamic calculations for the stability of palladium sulfides.

INTRODUCTION

Hydrogen production from coal gasification has gained renewed interest in recent years as a result of the vast amount of available coal which can be gasified to produce a syngas stream with relatively high concentrations of H_2 (~35vol%) and CO (~51%). The CO can be further reacted with steam via the water-gas shift reaction (WGSR) to increase the H_2 concentration in the syngas. At the same time, this reaction produces a concentrated stream of CO_2 that, once separated from the H_2, can be geologically sequestered to mitigate the greenhouse effect.

Pd-based membranes have gained a great deal of attention for membrane reactor (MR) application because these membranes are highly permeable to H_2, are virtually impermeable to other gases and are stable at relatively high temperatures. Such Pd-based MRs have been successfully demonstrated to enhance CO conversions via the WGSR (Equation (1)) to values above the thermodynamic equilibrium at various temperatures (Uemiya et al. 1991; Basile et al. 1996; Basile et al. 2001; Iyoha et al. 2007; Iyoha et al. 2007[2]) as a result of the selective and rapid extraction of H_2 from the reaction zone.

$$CO + H_2O \leftrightarrow CO_2 + H_2, \ \Delta H^{o}_{298} = \text{-41kJ/mol} \qquad (1)$$

However, most of these experiments have been conducted using pure reagent feeds (i.e. CO and H_2O) and have been limited to temperatures below 600K. Only a few studies have explored conducting the WGSR in a MR when the CO is present in a mixture with components other than steam. And none of the previous studies were conducted in the presence of H_2S.

H_2S is a common contaminant present in coal-derived syngas and is a known poison of Pd-based membranes, resulting in reduced H_2 permeance (McKinley 1967; Morreale 2006), sulfidation (Morreale 2006), pitting (Kulprathipanja et al. 2005), and catastrophic rupture of the membrane within seconds of contact (Edlund et al. 1994). To successfully integrate a MR immediately downstream of the coal gasifier for high-purity H_2 production, robust MRs capable of tolerating poisoning by contaminants such as H_2S, would have to be developed. The $Pd_{80wt\%}Cu$ membrane used in the present work was selected because it was expected to exhibit tolerance to higher concentrations of H_2S relative to the pure Pd membrane. A recent study by Iyoha et al. (Iyoha et al. 2007[3]) suggested that the sulfidation of Pd-based membranes is dependent on the H_2S-to-H_2 ratio associated with the thermodynamic

stability of the sulfide. Further, Iyoha et al. showed that it is possible to operate Pd and $Pd_{80wt\%}Cu$ MRs at 1173K in the presence of H_2S-to-H_2 molar ratios below 0.0011.

The objective of this work is to demonstrate enhanced CO conversion via the WGSR, and high-purity H_2 recovery in Pd and $Pd_{80wt\%}Cu$ MRs using simulated, coal-derived syngas at 1173K, in the absence and presence of varying concentrations of H_2S. This temperature was selected to be representative of a MR positioned just downstream of the coal gasifier.

EXPERIMENTAL

WGS reaction in multi-tube Pd and Pd-Cu membrane reactors
The four-tube MR (Figure 1) and experimental apparatus used in this study has been described previously (Iyoha et al. 2007[2]). Briefly, the 3.175 mm OD, 125-µm thick Pd and $Pd_{80wt\%}Cu$ alloy tubes used in the present study were each 15.25 cm in length. The effective surface area of the four tubes for H_2 transport was about 51.9 cm^2 and the total reactor volume was 3.5 cm^3.

The gases used were He, Ar, 1000 ppm H_2S-10%He-balance H_2 and a simulated syngas containing 53%CO, 35%H_2 and 12%CO_2 purchased from Butler Gas Products. All gases were 99.999% certified calibration gases. He and Ar were used during heat-up of the various reactor systems to the desired reaction temperature of 1173K. At the desired operating temperature, syngas and steam were introduced into the four-tube reactor. The resultant feed composition was about 29.5% CO, 19.5% H_2, 6.7% CO_2 and 44.3% H_2O. For experiments involving H_2S, the 1000 ppm H_2S-10%He-balance H_2 gas was introduced after steady-state CO conversion was attained at the specified condition, at a flow rate to ensure the desired H_2S-to-H_2 ratio.

The desired amount of steam was introduced by injecting distilled water into the flowing gas stream using a calibrated ISCO 500D syringe pump. The water was vaporized in the heated feed line before entering the reactor. Excess steam was used to prevent carbon formation in the membrane tubes. Prior control studies suggested that the 1.5 steam-to-CO ratio was adequate to suppress carbon formation in the reactor systems. A trap was placed on the exit line to collect the unreacted steam before the effluent gases were directed to a Hewlett-Packard 5890 Series II GC equipped with a 3 m long by 3.2 mm OD zeolite-packed column and thermal conductivity detector for quantification. The Ar sweep gas was introduced in a counter current flow mode. The flow rate of each gas was controlled by Brooks mass flow controllers. The volumetric flow-rate of the effluent stream was measured with a wet gas meter. The mass balance closure was within ±3%.

Equations (2) to (5) were used to calculate the CO conversion and the H_2 recovery from the reaction zone, while Equation (6) was used to determine the H_2 permeance of the membranes. The amounts/concentrations of H_2, CO and CO_2 in the reactor effluent were determined by gas chromatography. The CO conversion, X_{CO}, calculated by Equation (2) was assumed to have taken place only within the reactor. Negligible conversion occurred in the tubing leading to and from the reactor because of the steep temperature changes before and after the reaction zone. Further, the feed lines were lined with quartz to minimize interaction of the reactant gases with the stainless-steel walls.

The residence times of the reactor systems were varied by changing the operating pressure while keeping the inlet feed flow rate and reaction temperature constant. Note that previous work conducted by Bustamante et al. (Bustamante et al. 2005) provides a rate expression for the forward WGSR based on high pressure data obtained at NETL. Increasing the reaction pressure increased the residence time, increased the H_2 partial pressure driving force for H_2 flux, and also increased the rate of reaction.

$$X_{CO} = \left(\frac{x_{CO,in} \cdot Q_{feed,in} - x_{CO,out} \cdot Q_{effluent}}{x_{CO,in} \cdot Q_{feed,in}} \right) * 100 \qquad (2)$$

$$H_{2\,total}\,(sccm) = x_{H2,in} \cdot Q_{feed,in} + 0.01 \cdot X_{CO} \cdot x_{CO,in} \cdot Q_{feed,in} \qquad (3)$$

$$H_2 \text{ extracted (sccm)} = \frac{x_{H2,sweep}}{1 - x_{H2,sweep}} * Q_{Ar,sweep} \tag{4}$$

$$H_2 \text{ recovery (\%)} = \frac{H_{2\ extracted}}{H_{2\ total}} * 100 \tag{5}$$

$$J_{H2} \text{ (mol/m}^2\text{/s)} = k' \left(P_{ret}^{0.5} - P_{perm}^{0.5} \right) \tag{6}$$

Where:
X_{CO} is the molar CO conversion.
x_{CO} and x_{H2} are the mole fractions of CO and H_2, respectively.
J_{H2} is the H_2 flux through the membrane.
k' is the H_2 permeance (mol/m^2/s/Pa$^{0.5}$).
P_{ret} and P_{per} are the H_2 partial pressures (Pa) in the retentate and permeate streams, respectively.
Q_{feed} is the inlet syngas flow rate (sccm).
$Q_{effluent}$ is the effluent retentate flow rate measured by the wet gas meter (sccm).
Q_{Ar} is the argon sweep gas flow rate (sccm).

Note that all results presented in this paper were collected during periods of complete H_2 selectivity of the MR.

RESULTS AND DISCUSSION

H_2 permeance testing
Figure 2a and b show control experiments in which the H_2 permeance of the Pd and $Pd_{80wt\%}Cu$ MRs was measured using 3.175 cm tubes (Equation (6)) at 1173K in 90%H_2-He and 90%H_2-1000 ppm H_2S-He environments. The figures show steady state H_2 permeance values in both MR systems within about 2 hours of the introduction of the 90%H_2-He mixture. The results indicate that the permeance of the $Pd_{80wt\%}Cu$ membrane, $1.42*10^{-4}$ mols/m^2/s/Pa$^{0.5}$, was about 46% that of the pure Pd membrane ($3.10*10^{-4}$ mols/m^2/s/Pa$^{0.5}$) at 1173K. These values are in very good agreement with published permeance values for $Pd_{80wt\%}Cu$ (Howard et al. 2004) and Pd (Morreale et al. 2003) membranes. Figure 2a and b also show that introducing H_2S to the system by switching the feed mixture to 90%H_2-1000 ppm H_2S-He results in no discernable change in H_2 permeance for both membrane systems. Furthermore, Figure 2b shows that when the 90%H_2-1000 ppm H_2S-He mixture was reverted to the 90%H_2-He mixture (~24hrs), and subsequently reintroduced (28hrs), there was no change in H_2 permeance of the $Pd_{80wt\%}Cu$ membrane. Therefore, it was concluded that the presence of H_2S (H_2S-to-H_2 ratio ~ 0.0011) does not affect the H_2 permeance of the Pd and $Pd_{80wt\%}Cu$ membranes at 1173K.

WGSR in Pd MR using simulated, H_2S-free, syngas feed
Following H_2 permeance testing of the Pd and $Pd_{80wt\%}Cu$ membranes, the efficacy of the MR for enhancing the conversion of CO contained in the simulated coal-derived syngas was determined at 1173K. The WGSR was conducted using a H_2S-free, simulated syngas feed in both Pd and $Pd_{80wt\%}Cu$ four-tube MRs operated in countercurrent mode, i.e. with the reactant gases and the sweep gas flowing in opposite directions. The effect of feed-side residence time on CO conversion was investigated by varying the feed-side pressure while keeping the inlet feed flow rate and permeate side pressure of 159 kPa constant.

Figure 3 depicts the real-time CO, CO_2 and H_2 effluent concentration trend in the Pd MR for feed-side pressures of 143, 239 and 412 kPa, which correspond to MR residence times of 0.7, 1.2 and 2s (based on inlet flow rates), respectively. The specified operating condition was maintained until steady state effluent concentrations were attained, after which the pressure was increased in order to increase the residence time. Figure 3 illustrates increasing CO_2 concentration with increasing residence time, while CO and H_2 concentrations were observed to decrease. The decrease in CO concentration with increasing residence time was the result of increasing CO conversion via the WGSR. The decreasing H_2 concentration from approximately 9% H_2 to 5% H_2 to <0.5% H_2 was attributed to the combination of the longer residence time of reactants in the MR and the higher trans-membrane H_2 partial pressure differential (as a result of the higher operating pressure) resulting in higher H_2 flux through the Pd membrane. This is further substantiated by the increasing H_2 recovery observed in Figure 4.

Figure 4 shows the CO conversion and H_2 recovery for the four-tube Pd MR as a function of time-on-stream for residence times of 0.7, 1.2 and 2s, which correspond to feed-side pressures of 143, 239 and 412 kPa, respectively. These results demonstrate the efficacy of the MR to significantly enhance CO conversion of the equilibrium limited WGSR to nearly complete conversion, while simultaneously producing a high-purity H_2 stream. Compared to the equilibrium CO conversion of 32% for the syngas feed mixture at these conditions, the results show an increase in CO conversion to 56.4, 75.2 & 99.7% for increasing residence times of 0.7 to 1.2 to 2s, respectively. The shift in the CO conversion above the equilibrium value was attributed primarily to the high rate of H_2 extraction from the reaction zone through the Pd membranes. It is worth noting that all of the CO_2 was removed from the MR in the high pressure retentate stream, which also contained steam. Figure 3 and Figure 4 also show that the Pd MR operated in counter-current configuration is capable of nearly complete H_2 recovery if a sweep gas is used to remove the permeate.

WGSR in $Pd_{80wt\%}Cu$ MRs using simulated, H_2S-free, syngas feed
Figure 5 depicts the real-time component effluent concentration trend in the $Pd_{80wt\%}Cu$ MR at 1173K for residence times of 0.96, 2 and 2.8s, corresponding to feed-side pressures of 198, 412 and 483 kPa. The figure shows a similar trend of effluent concentrations (decreasing CO and H_2 and increasing CO_2 concentrations) and CO conversion (Figure 4) observed in the Pd MR system. Figure 6 shows the corresponding component conversions for $Pd_{80wt\%}Cu$. The results also show that the $Pd_{80wt\%}Cu$ MR effectively enhanced CO conversions above the equilibrium value of 32% over the conditions of the study.

It is evident that when the Pd MR was replaced with a $Pd_{80wt\%}Cu$ MR, however, the CO_2 concentration in the retentate stream (Figure 5), and the level of CO conversions attained (Figure 6) were always lower than that of the Pd MR. Specifically, the maximum CO conversions attained in the $Pd_{80wt\%}Cu$ MR were 62% and 78% at 2 and 2.8s residence times, respectively, compared to the 99.7% CO conversion attained in the Pd MR at 2s residence time. This phenomenon had been previously observed for WGSMR involving pure CO and steam reagent gases at a similar temperature (Iyoha et al. 2007[2]), and was primarily attributed to the lower H_2 permeance of the $Pd_{80wt\%}Cu$ membrane relative to Pd at this temperature. Further, Figure 6 also shows that the H_2 recovery of the $Pd_{80wt\%}Cu$ MR, 75%, was lower than the H_2 recovery in the Pd MR, nearly 100%, at feed-side pressure of 412 kPa corresponding to a residence time of 2s.

With regards to the longevity of the membrane, the $Pd_{80wt\%}Cu$ MR was successfully operated for about 6 days in the WGSR environment without experiencing failure. The Pd MR lasted 3 days under comparable conditions before pinhole defects formed. This suggests that alloying Pd with Cu may result in a more robust MRs that can withstand the harsh, high-temperature operating conditions of the post-gasifier environment (H_2S-free).

WGSR in Pd and $Pd_{80wt\%}Cu$ MR using simulated syngas feed containing H_2S
The WGSR was also conducted in Pd and $Pd_{80wt\%}Cu$ MRs in the presence of varying concentrations of H_2S. The amounts of H_2S introduced to the Pd and $Pd_{80wt\%}Cu$ MRs were specified to either be below or above the threshold H_2S-to-H_2 ratios expected to result in membrane sulfidation, based on the H_2 concentration in the effluent retentate stream of the respective MR systems.

WGSR in Pd MR using simulated syngas feed containing H_2S
For experiments involving H_2S, the desired amount of H_2S was introduced by co-feeding the 1,000 ppm H_2S-He-H_2 with the syngas. The slight increase in total feed flow rate (less-than 6%) was compensated for by increasing the retentate pressure to achieve the same residence time. When the H_2S flow rate was controlled such that the H_2S-to-H_2 ratio remained below the equilibrium ratio expected for stable Pd_4S formation, i.e. 0.0014 at 1173K for Pd (Taylor 1985; Iyoha et al. 2007), a precipitous drop in CO conversion was observed. Figure 7 illustrates the real-time CO conversion and H_2 recovery trend for the Pd MR in the absence and presence of 30 ppm H_2S at a residence time of 0.4s. With a H_2 effluent concentration of 10 mol% before the H_2S introduction (Figure 8(18hrs)), the introduced H_2S concentrations of 30 ppm to the Pd MR resulted in H_2S-to-H_2 ratios of about 0.0003 (equivalent to about 300 ppm H_2S-in-pure H_2) at the reactor exit. It is evident in Figure 7 that after a steady state conversion of about 49% CO conversion was attained, introducing 30 ppm H_2S quickly resulted in the decrease in CO conversion, reaching a new steady-state value of about 12% after approximately 3 hours. This reduction in CO conversion is also observed in the data depicted in Figure 8 which shows the real-time component concentration trend for the Pd MR exposed to the syngas mixture.

When the H_2S was introduced along with the syngas (~19hrs), a rapid reduction in CO_2 concentration, accompanied by the increase in CO concentration was observed, likely due to the deactivation of the catalytic activity of the Pd membrane towards the WGSR. H_2 concentration in the retentate stream was also observed to decrease from about 10% to 3.5%. As expected (control experiments shown in Figure 2a and b resulted in no discernable influence of H_2S on H_2 permeance), this catalyst deactivation phenomenon did not appear to impact H_2 transport through the MR, and no decrease in H_2 recovery was observed. Furthermore, when the H_2S was switched off (39hr, Figure 7), the CO conversion was observed to recover to about 83% of its original conversion. This corroborates the assertion that the decrease in CO conversion observed was not the result of sulfidation of the MR, but deactivation of the catalytic Pd walls towards the WGSR. In addition, the MR was observed to maintain its mechanical integrity and H_2 selectivity for the duration of the 30 ppm H_2S-syngas testing period.

When the H_2S concentration was increased to 50 ppm (68hrs), the MR failed within minutes, as evidenced by a rupture in one of the four membrane tubes. The failure of the MR was probably the result of the sulfidation of the MR due to the presence of a H_2S-to-H_2 ratio of greater than 0.0014. At the time of the 50 ppm H_2S introduction to the MR, the effluent H_2 concentration of about 3.5% (Figure 8(68hrs)) resulted in a H_2S-to-H_2 ratio of approximately 0.00145 at the exit of the MR. This value is slightly above the minimum H_2S-to-H_2 ratio that is expected to result in sulfidation of Pd at 1173K (Iyoha et al. 2007[3]). It was therefore not surprising that the MR failed.

WGSR in $Pd_{80wt\%}Cu$ MR using simulated syngas feed containing H_2S
Figure 9 depicts CO conversion and H_2 recovery for the $Pd_{80wt\%}Cu$ at 2s residence time in the presence and absence of H_2S. In the absence of H_2S (27 to ~48hrs), the CO conversion and H_2 recovery were both observed to reach steady state values of about 67%. Similar to the Pd MR, when 40 ppm H_2S was introduced to the MR, a rapid reduction in CO conversion was observed, decreasing within 3 hours of introduction to a steady state value of ~16%. However, in contrast to the Pd MR which experienced no change in H_2 recovery when H_2S was introduced, the H_2 recovery in the $Pd_{80wt\%}Cu$ MR was observed to decrease slightly from about 68% to a new steady-state value of approximately 56% (Figure 9). Figure 9 also shows that when the H_2S is switched off, CO conversion did not recover to its original level within the 10-hour period. In fact, only a modest increase of about 15% points was observed. Increasing the H_2S concentration to 60 ppm (77hrs) decreased the CO conversion from 30% back to about 16%.

Figure 10 shows the real-time effluent concentration data for the $Pd_{80wt\%}Cu$ MRs exposed to the syngas mixture containing 40 and 60 ppm H_2S. Similar to the Pd MR system, when the H_2S was introduced (~49hrs), a rapid reduction of CO_2 concentration, accompanied by the increase in CO concentration was observed. Assuming no change in H_2 concentration measured in the effluent retentate stream (~12% H_2 between 40 & 50 hr (Figure)), the introduced 40 ppm H_2S resulted in a H_2S-to-H_2 ratio of approximately 0.0004 (equivalent to ~400 ppm H_2S-in-H_2). When the 60 ppm H_2 was introduced after about 77 hours, the H_2 concentration was observed to decrease to about 10% (Figure 10(85 hr)), resulting in a H_2S-to-H_2 ratio of approximately 0.0006 (equivalent to ~600 ppm H_2S-in-H_2). These ratios were below the H_2S-to-H_2 ratios expected to sulfide the $Pd_{80wt\%}Cu$ membrane (Iyoha et al. 2007[3]), therefore it is no surprise that the membrane maintained its H_2 selectivity and mechanical integrity.

Control experiments shown in Figure 2a and b suggest no influence of the H_2S on H_2 permeance of both MRs. This observation, coupled with the fact that the H_2 recovery was observed to only be slightly reduced in the presence of H_2S, support the theory that the observed reduction of CO conversion experienced by the MR when H_2S was introduced with the syngas mixture likely resulted from the blocking of catalytic surface sites for the WGSR by sulfur. The presence of adsorbed sulfur on the membrane surface may impede the transfer of WGS reactants from the bulk to the membrane catalytic surface, appreciably reducing the catalytic activity of the MR for the WGSR. It is uncertain, however, why the CO conversion did not increase more appreciably in the $Pd_{80wt\%}Cu$ system after the H_2S was turned off.

When the inlet H_2S concentration was increased to 90 ppm H_2S for the $Pd_{80wt\%}Cu$ MR system, the MR module was observed to fail within minutes, resulting in the complete loss of membrane selectivity, and the depressurization of the reactor. With a steady-state H_2 effluent concentration of about 8% before the H_2S introduction (100 hrs, figure not shown), introducing 90 ppm H_2S to the syngas feed resulted in a H_2S-to-H_2 ratio of about 0.0012 (~1,200 ppm H_2S-in-H_2), a value just below the H_2S-to-H_2 ratio expected to sulfide the membrane. However, note that further

reduction of CO conversion would have resulted in a lower H_2 concentration as less H_2 is produced, thereby increasing the H_2S-to-H_2 ratio, which would explain the observed failure of the MR.

CONCLUSIONS

A CO conversion of 99.7% in a simulated syngas feed containing 53%CO, 35%H_2 and 12%CO_2 (dry basis) was attained in a 125-μm Pd four-tube membrane reactor at 1173K with a steam-to-CO ratio of 1.5 and 2s residence time. Furthermore, nearly complete H_2 recovery was also attained through the Pd membrane reactor module.

The $Pd_{80wt\%}Cu$ membrane reactor also effectively enhanced CO conversions above the equilibrium value of 32% (associated with non-membrane reactors) over the conditions of the study. However, the maximum conversions attained were appreciably lower than those obtained in the Pd membrane reactor, reaching maximum CO conversions of 62% and 78% at 2 and 2.8s residence times, respectively. This was primarily attributed to the lower H_2 permeance compared to that of Pd. The H_2 recovery was also observed to always be lower for the $Pd_{80wt\%}Cu$ MR.

Exposure of both membrane reactors to syngas mixtures containing H_2S levels such that the H_2S-to-H_2 ratio was less than ~0.001 (a value less than the 0.0014 value expected to form stable sulfides at 1173K) did not appear to affect the H_2 permeance, mechanical integrity, and H_2 selectivity of the membrane reactors at 1173K. However, a steep drop in CO conversion was observed. This reduction in CO conversion was attributed to sulfur deactivating the catalytic activity of the Pd membrane surface towards the WGSR. When the H_2S-to-H_2 feed ratio was increased to 50 and 90 ppm H_2S for the Pd and $Pd_{80wt\%}Cu$ membrane reactor systems equivalent to 0.0014 and 0.0012 H_2S-to-H_2 ratios, respectively (values equal to or just below ratios expected for stable sulfides to form), the membrane reactors were observed to fail within minutes. These membranes must, therefore, be operated at conditions that prohibit the formation of thermodynamically stable sulfides.

Our results show that at high temperatures, with no added catalyst particles, it is possible to enhance CO conversions significantly above the equilibrium value and attain high H_2 recovery from simulated syngas in the absence of H_2S. The results also show that it is possible to stably operate (with respect to H_2 selectivity and mechanical integrity) the Pd and $Pd_{80wt\%}Cu$ MRs in the presence of H_2S-to-H_2 ratios well below 0.0014. However, the deactivation of the catalytic activity of the Pd and $Pd_{80wt\%}Cu$ membranes towards the WGSR by the H_2S will reduce CO conversions when H_2S is present in the feed.

DISCLAIMER

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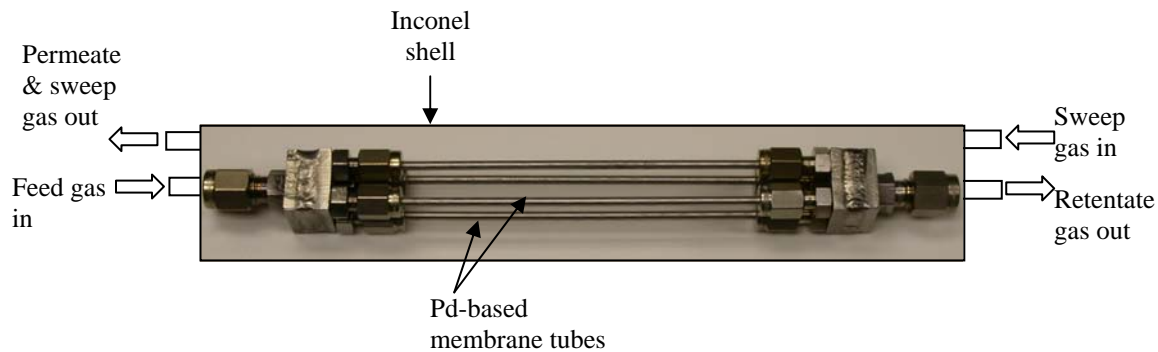
Figure 1. Detail of NETL four-tube Pd-based membrane reactor.
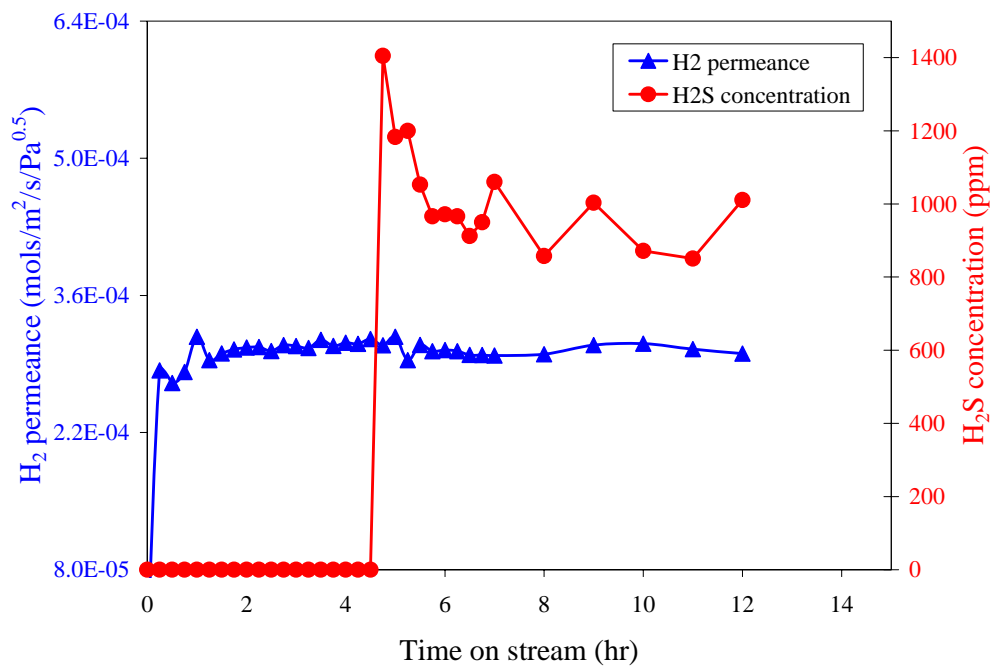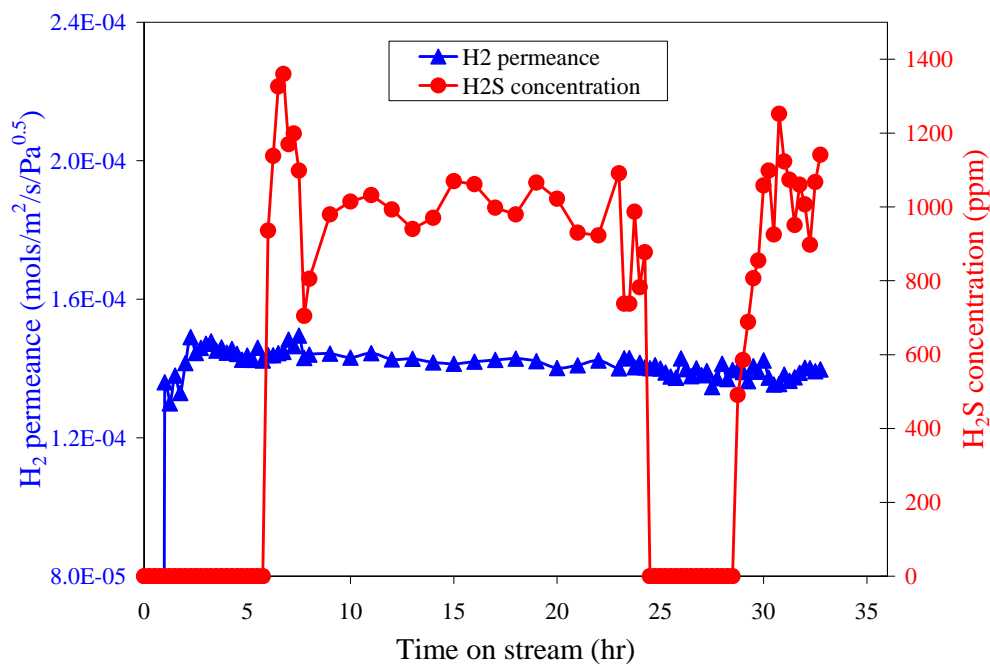
Figure 2. H_2 permeance of Pd (a) and $Pd_{80wt\%}Cu$ (b) MRs in $90\%H_2$-He and $90\%H_2$-1000 ppm H_2S-He atmospheres at 1173K.
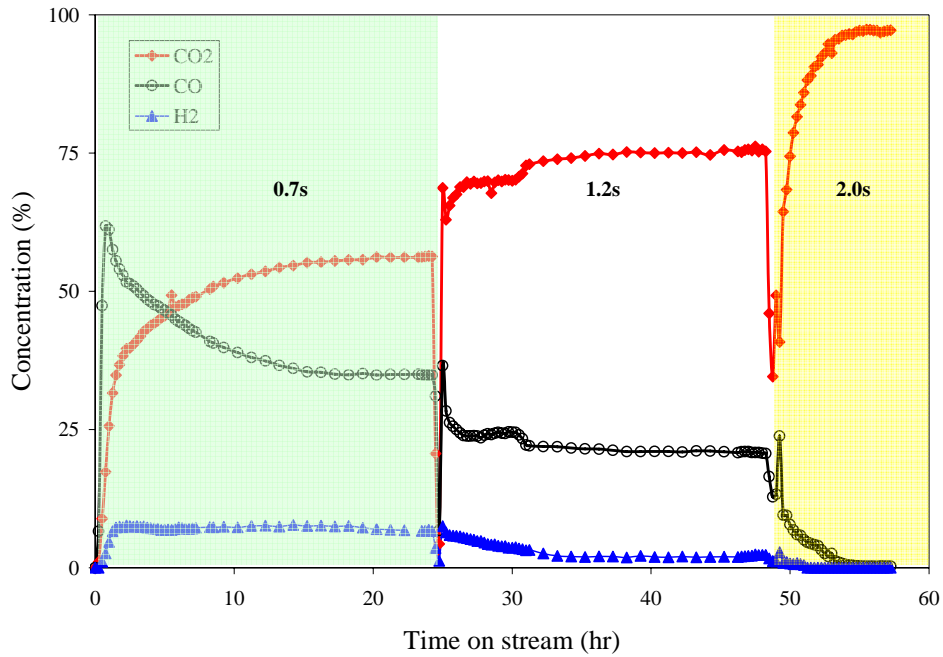
Figure 3. Real-time concentration (CO, CO_2 and H_2) trend in the four-tube Pd MR at 1173K for 0.7s, 1.2s and 2s residence times using simulated syngas feed with steam added to produce an initial steam-to-CO ratio of 1.5 (29.5% CO, 19.5% H_2, 6.7% CO_2, and 44.3% H_2O). MR was exposed to the syngas environment for ~60 hours and developed pinholes after about 3 days at 1173K.
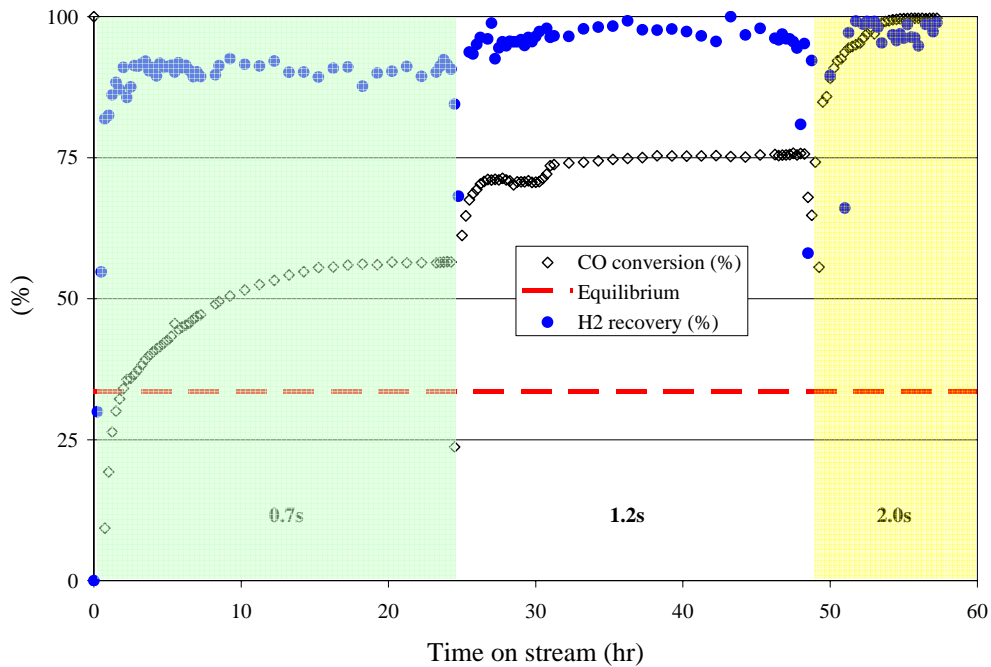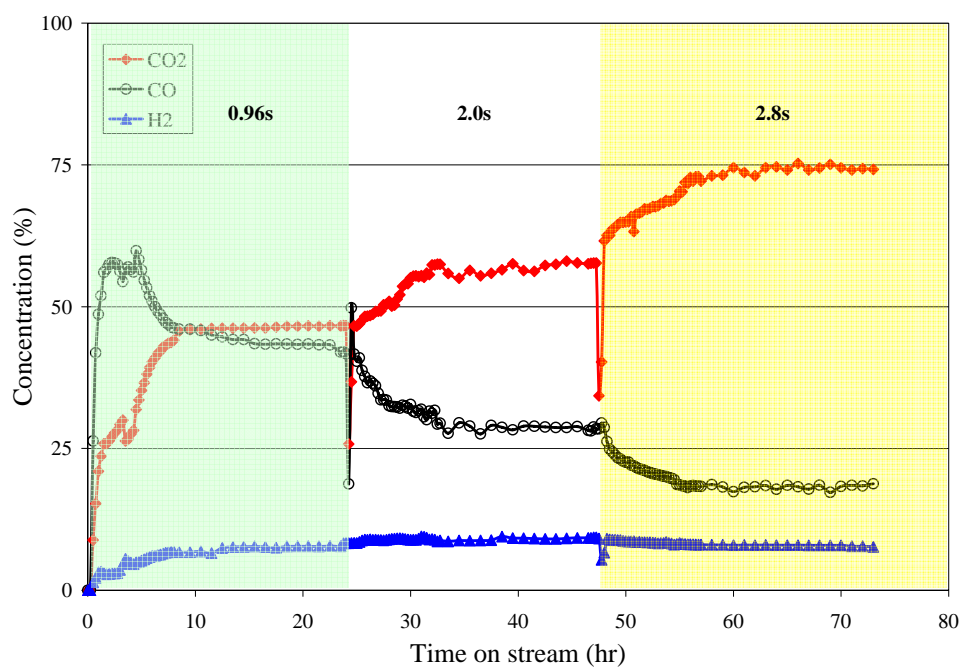

Figure 4. Real-time CO conversion and H_2 recovery trend in the four-tube Pd MR at 1173K for residence times of 0.7s, 1.2s and 2s using simulated syngas feed with steam added to produce an initial steam-to-CO ratio of 1.5 (29.5% CO, 19.5% H_2, 6.7% CO_2, and 44.3% H_2O). MR was exposed to the syngas environment for ~60 hours and developed pinholes after about 3 days at 1173K. The equilibrium CO conversion at this condition is ~32%.

Figure 5. Real-time concentration (CO, CO_2 and H_2) trend in the four-tube $Pd_{80wt\%}Cu$ MR at 1173K for 0.96, 2 and 2.8s residence times using simulated syngas feed with steam added to produce an initial steam-to-CO ratio of 1.5 (29.5% CO, 19.5% H_2, 6.7% CO_2, and 44.3% H_2O). MR operated for about 6 days without failure.
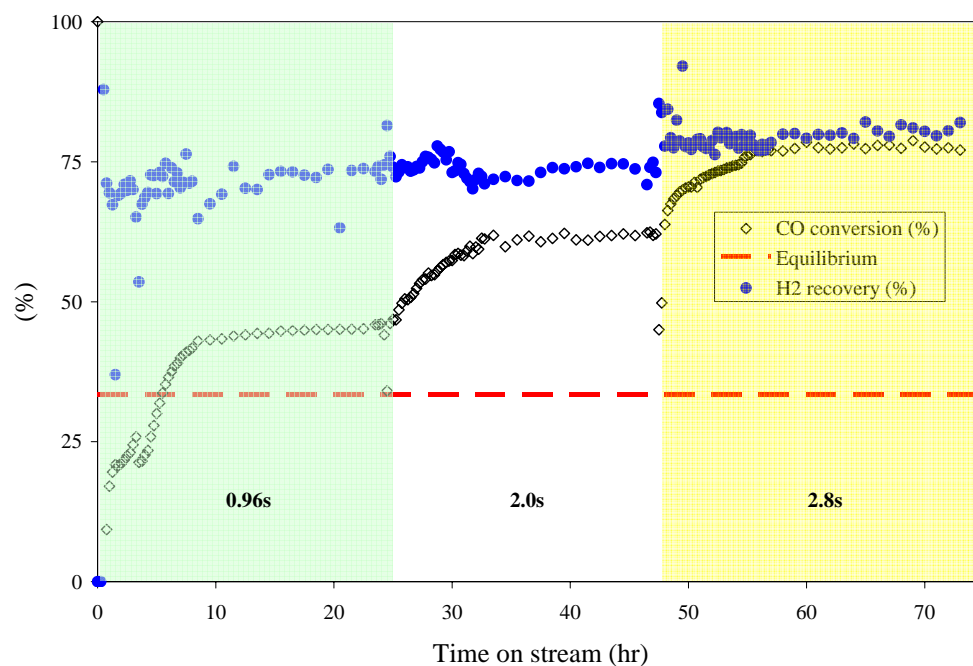

Figure 6. Real-time CO conversion and H_2 recovery trend in the four-tube $Pd_{80wt\%}Cu$ MR at 1173K for residence times of 0.96, 2 and 2.8s using simulated syngas feed with steam added to produce an initial steam-to-CO ratio of 1.5 (29.5% CO, 19.5% H_2, 6.7% CO_2, and 44.3% H_2O). The equilibrium CO conversion at this condition is ~32%. The $Pd_{80wt\%}Cu$ MR was successfully operated for about 6 days without failure.
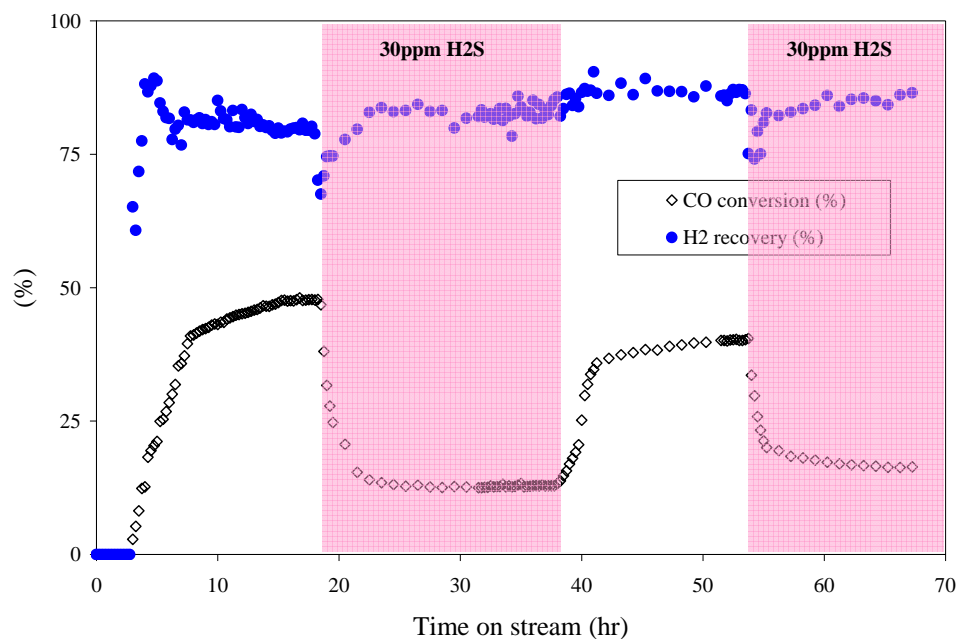
Figure 7. Real-time CO conversion and H_2 recovery trend in the four-tube Pd MR at 1173K for residence times of 0.4s before and after reaction testing with 30 ppm H_2S-syngas. Membrane failed within minutes of exposure to 50 ppm H_2S that began at 68hrs.
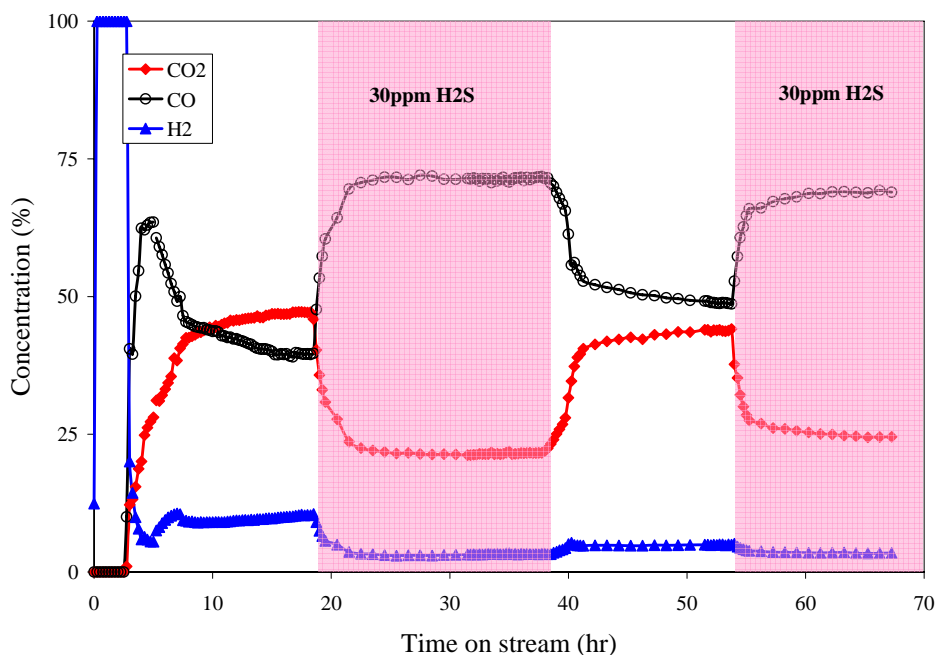

Figure 8. Real-time concentration (CO, CO_2 and H_2) trend for the four-tube Pd MR at 1173K and 0.4s residence time before and after reaction testing with 30 ppm H_2S-syngas. Membrane failed within minutes of exposure to 50 ppm H_2S that began at 68hrs.
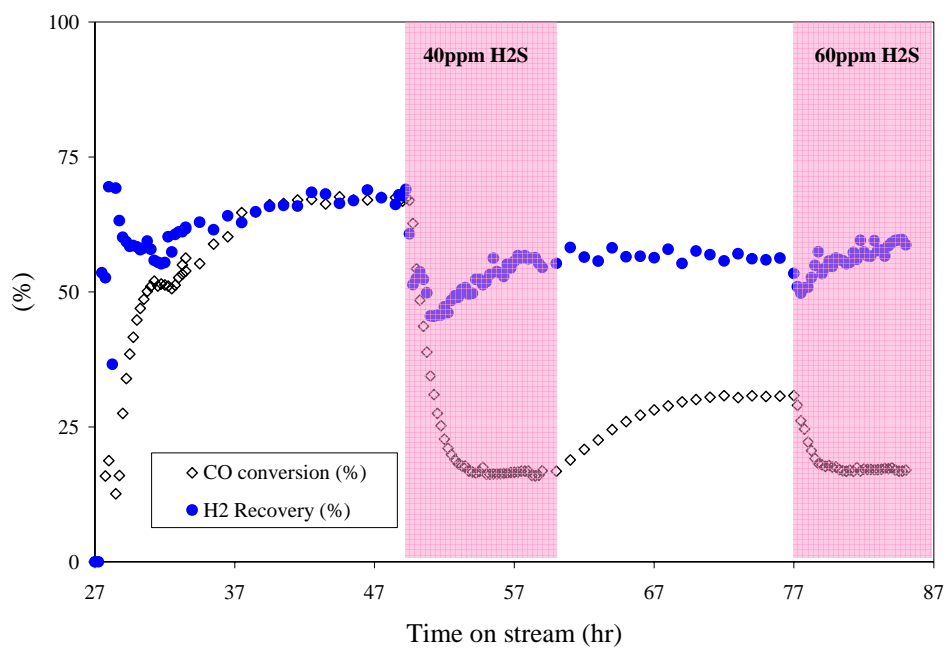
Figure 9. Real-time CO conversion trend and H_2 recovery in the four-tube $Pd_{80wt\%}Cu$ MR at 1173K and residence time of 2s before and after 40 and 60 ppm H_2S-syngas reaction testing. Membrane failed after exposure to 90 ppm H_2S.
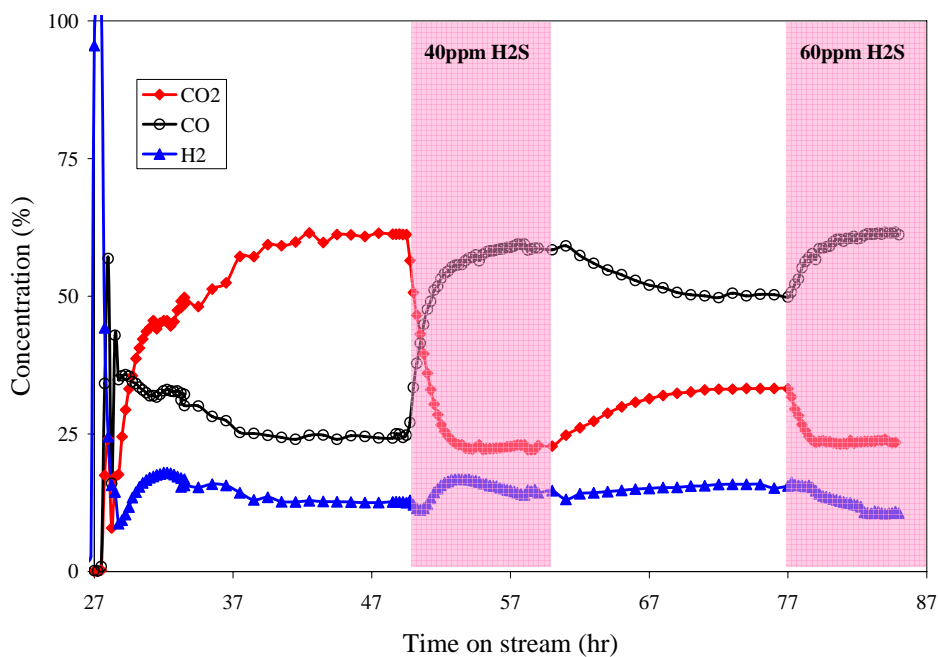

Figure 10. Real-time concentration (CO, CO_2 and H_2) trend for the four-tube $Pd_{80wt\%}Cu$ MR at 1173K and 2s residence time before and after 40 and 60 ppm H_2S-syngas reaction testing. Membrane failed after exposure to 90 ppm H_2S.