

Water-Gas Shift Membrane Reactor Studies

M.V. Ciocco¹, B.D. Morreale¹, K.S. Rothenberger², B.H. Howard²,
R.P. Killmeyer², R.M. Enick³, and F. Bustamante³

ABSTRACT

The high-temperature water-gas shift reaction, $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$, plays a key role in the production of hydrogen from coal via gasification technology. One study focuses on using a membrane reactor to remove the H_2 produced, thus improving the overall conversion of the water-gas shift reaction.

Palladium-based membranes continue to be considered as candidates for membrane reactors because of their catalytic activity with respect to hydrogen dissociation, high hydrogen permeability and possible resistance to poisoning. This study quantified the membrane performance of various Pd-Cu alloys at the extreme temperature and pressure conditions associated with various configurations of coal gasification plants.

INTRODUCTION

The production of hydrogen is expected to increase in the future as the U. S. moves toward greater use of hydrogen as an energy carrier. Industrial processes, such as coal gasification, produce hydrogen mixed with carbon dioxide and other gases. Advances in the area of membrane technology may improve the efficiency of hydrogen separation and recovery, and thus reduce the cost associated with hydrogen production.

The water-gas shift (WGS) reaction, Equation 1, is important as a method for further enhancing the yield of hydrogen from such aforementioned industrial processes. Syngas mixtures, for instance, are typically generated at elevated temperatures via the combustion of natural gas, coal, bio-mass, petroleum and organic wastes[1]. Steam is then added to the $\text{CO} - \text{H}_2$ syngas mixture prior to being introduced to WGS reactors to convert the CO and H_2O to CO_2 and H_2 . However, thermodynamic equilibrium favors high conversion of CO and steam to hydrogen and carbon dioxide at low temperatures. The WGS reaction is reversible, and several correlations for the equilibrium constant have been published[2-5].



The first steps in the design of membrane reactors are the characterization of the membrane permeance and an accurate representation of the reaction kinetics. There are numerous kinetic studies of the catalyzed forward WGS reaction at temperatures up to 873K[6]. However, kinetic

¹ NETL Site Support Contractor, Parsons, Inc., P.O. Box 618, South Park, PA 15129, Phone: (412) 386-4774, Fax: (412) 386-4542, ciocco@pp.netl.doe.gov

² United States Department of Energy, National Energy Technology Laboratory, 626 Cochran Mill Rd., Pittsburgh, PA 15236, Phone: (412) 386-6409, Fax: (412) 386-5920

³ NETL Research Associate, Chemical and Petroleum Engineering Department, University of Pittsburgh, Room 1249 Benedum Hall, Pittsburgh, PA 15261, Phone: (412) 624-9630, Fax: (412) 624-9639

studies of the forward or reverse WGS reaction at elevated temperatures ($>873\text{K}$) are uncommon. This scarcity of data is probably attributable to the low equilibrium conversions of CO that can be achieved in conventional reactors operating in this temperature range. However, high conversions at elevated temperature can be achieved in a hydrogen-permeable membrane reactor[7]. Further, high temperatures would enhance the kinetics to the extent that the reaction would proceed rapidly in the absence of heterogeneous catalysts. So, in this study, the initial effort was focused on determining such kinetics for the reverse reaction. Note that research on the forward WGS reaction has also begun.

A significant technical barrier impeding hydrogen separation membrane development is resistance to impurities. Many impurities, most importantly sulfur compounds such as H_2S , are part of the gasification product gas mixture. Very dilute concentrations (ppm level) of these sulfur-containing compounds can rapidly deactivate a catalytic metal surface, such as palladium[8-11]. Pd-Cu alloys have exhibited resistance to sulfur poisoning upon exposure to H_2 -rich retentate streams containing H_2S at levels of up to 5 ppm[12], 1000 ppm[13] and (at temperatures greater than 773 K) intermittent exposure to 100,000 ppm[14]. Permeability has also been evaluated with H_2S in the hydrogen retentate stream[12,13] and with sulfur-free retentate streams[12-20]. The highest reported values of Pd-Cu alloy permeability were comparable to pure Pd permeability and occurred for a composition of approximately 60wt%Pd – 40wt%Cu. The high permeability of this composition is attributable to the high mobility of hydrogen atoms within its body-centered-cubic (bcc) crystal structure[21-24].

In this study three Pd–Cu alloys were selected, 53%Pd-47%Cu (the composition in the middle of the β phase region), 60%Pd-40%Cu (the composition most commonly cited as yielding the greatest H_2 permeability), and 80%Pd-20%Cu (a composition far removed from the β phase region and intermediate to the 60%Pd-40%Cu alloy and pure Pd). The permeance values of pure palladium and pure copper membranes were also evaluated.

EXPERIMENTAL

Reverse WGS Reaction Apparatus - The Hydrogen Membrane Test Unit Number 1, HMT-1, at US DOE NETL was designed to attain high-pressure (up to 3.0 MPa), high-temperature (up to 1198 K) conditions in Inconel or quartz reactors, Figure 1. Operating details are described elsewhere[25].

Kinetic studies were conducted using an equimolar feed mixture introduced to the reactor over a range of flow rates or for mixtures in which the concentration of one reactant was held constant while the concentration of the other was varied. Partial pressures were established by adjusting feed gas composition and total pressure; no inert diluent gases were employed. An oxygen trap was located before the reactor to eliminate the pronounced catalytic influence of O_2 on the reaction.

The reactants, CO_2 and H_2 , were premixed and then fed to the quartz reactor through quartz tubing and a narrow annulus with a volume of 0.2 cm^3 , approximately one tenth that of the reaction zone volume. The gases were rapidly heated from 873 K to the reaction temperature as

they passed through the annulus (annular gap = 0.13 mm). Control experiments indicated that no conversion of the CO₂ in the quartz reactor was detectable for reaction temperatures below 873 K. The design for the all Inconel reactor is similar and is detailed below.

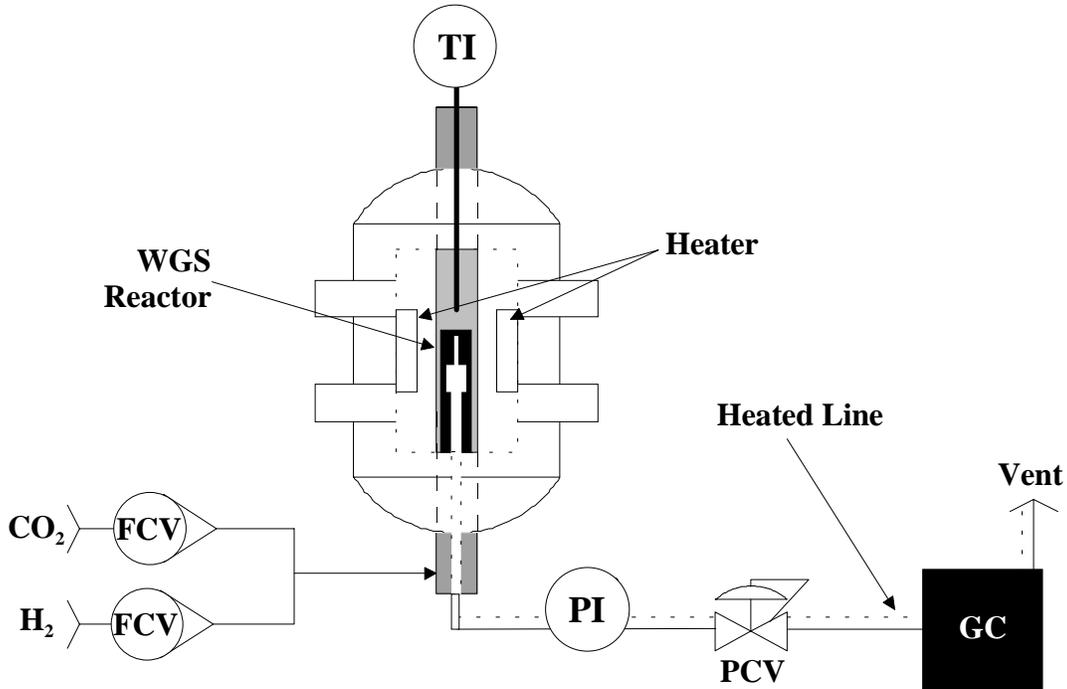


Figure 1. Schematic of HMT-1 unit. FCV – Flow Control Valve. PCV – Pressure Control Valve. PI – Pressure Indicator. GC - Gas Chromatograph. TI – Temperature Indicator.

Table 1. Dimensions of the reaction zone of the quartz and Inconel reactors

	Quartz	Inconel
a-Reactor Height (mm)	19.0	25.4
b-Reactor ID (mm)	11.0	13.5
c-Inner Tube Height (mm)	14.0	19.1
d-Inner Tube ID (mm)	1.85	2.87
e-Inner Tube OD (mm)	3.85	4.14
f-Plug OD (mm)	10.75	9.52
g-Plug Length (mm)	45.0	NA*
Volume (mm ³)	1805	3386

*The inconel plug extended well beyond the heat zone.

The geometry of these reactors is illustrated in Figure 2 and the dimensions are provided in Table 1. When the quartz reactor was operated at elevated pressure, an overburden fluid, CO₂, was maintained at the same pressure as the reacting gases within the reactor to prevent stresses across the reactor walls. The pre-heated feed gases entered the reaction zone and flowed upward toward

the top of the narrow inner tube that led to the reaction zone exit. Residence times of 0.3 - 0.5 s were chosen for the reactions conducted in the quartz reactor at low pressure. This yielded conversions of 0.1 - 2%, which were great enough to assure accurate measurements of conversion but low enough to mitigate the effect of the forward reaction on the reaction rate. Residence times of 2-10 s were realized at high-pressure conditions because of the increased gas density. Comparable residence times were selected when the Inconel reactor was used.

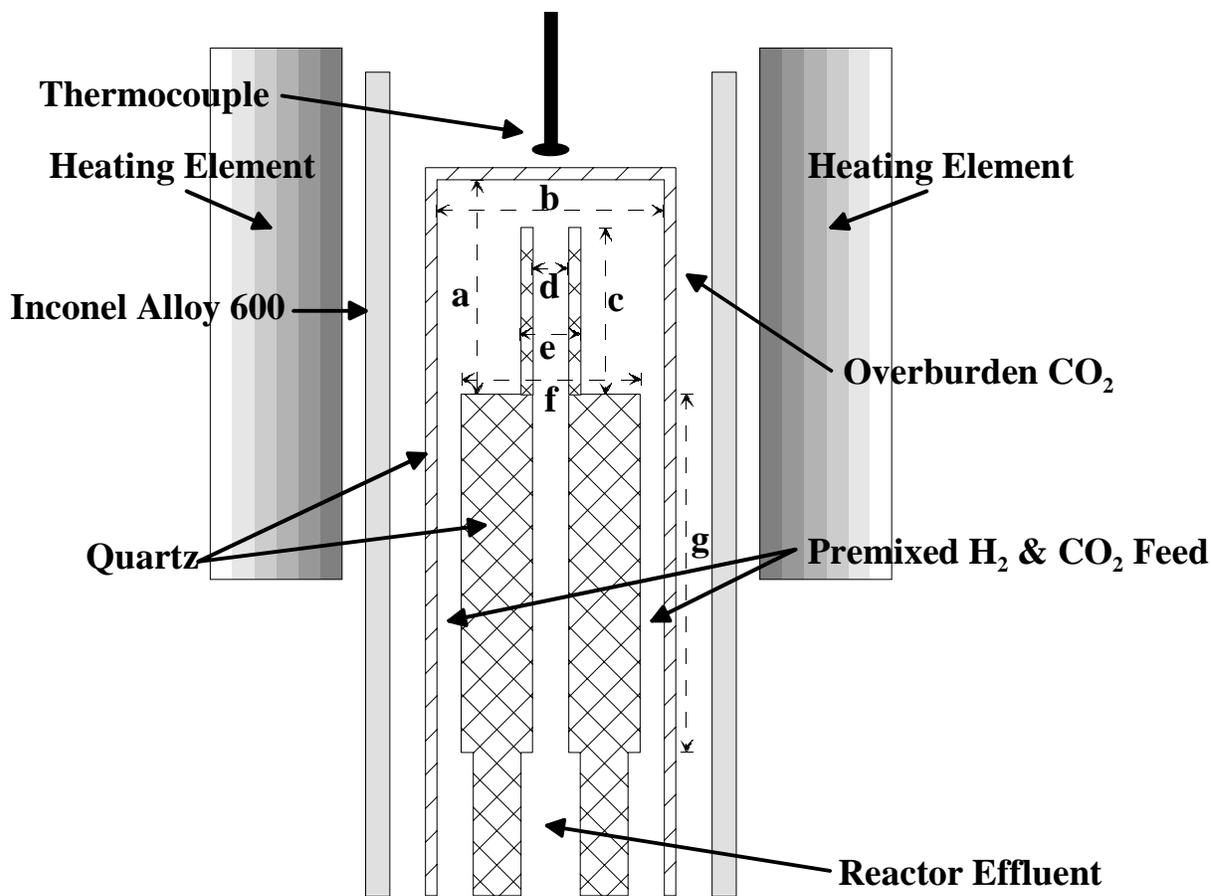


Figure 2. Details of the quartz and Inconel reactors.

The reacting gases then flowed downward through the inner tube and exited the reaction zone. The reaction products were rapidly cooled as they flowed toward the reactor effluent line. The temperature of the tubing was maintained at 573 - 673 K, which was hot enough to prevent condensation of water produced by the reverse WGS reaction but cold enough to prevent further conversion of the reactants.

The effluent of the reactor was analyzed with a gas chromatograph equipped with a TCD detector. Argon was used as carrier gas. The GC column, HayeSep® D, allowed the

quantification of H₂, CO, CO₂ and H₂O in the range of concentrations of interest. Concentrations of oxygen in the product remained below the detection limit of about 1 ppm.

Membrane Tests – Palladium-copper alloy foils, 99.9% purity, 0.1 mm thick, were fabricated by ACI Alloys, San Jose, California. Palladium foil, 99.9%, 0.1 mm thick, and copper foil, 99.9%, 1.0 mm thick, were obtained from Alfa Aesar. Membranes were fabricated by hand-cutting roughly circular pieces from the as-received foil sheets. The foil disks were cleaned and mounted in a specially designed membrane test unit at the National Energy Technology Laboratory (NETL). The resulting mounted membranes had an active hydrogen permeation area of 56.7 mm².

The hydrogen membrane test (HMT) unit, fabricated at the NETL, was designed to evaluate membrane performance at high-pressures and temperatures via steady-state hydrogen flux testing and has been described previously[26]. The apparatus was designed to operate at temperatures and pressures up to 1173 K and 3 MPa, respectively. The membrane was placed within the HMT apparatus to allow the feed gases to axially enter the apparatus, contact the membrane surface, and axially exit. A 90% hydrogen-10% helium mixture was fed to the unit on the retentate side and ultra-high purity argon sweep gas was supplied to the permeate side. The flow rates were controlled in such a manner that the concentration of hydrogen in the permeate did not exceed 4.0 mol-%, which was monitored by an online HP5890 Series II gas chromatograph. Although the HMT unit has the capability of operating at total pressure differentials in excess of 3.0 MPa, testing was conducted with a maximum total pressure gradient of 0.14 MPa, with hydrogen partial pressure gradients as high as 2.6 MPa.

RESULTS AND DISCUSSION

Equimolar feeds of CO₂ and H₂ were introduced both at a total pressure of 0.101 MPa and 1.6 MPa. The Arrhenius representation of the reaction rate data for the reverse WGS reaction over the 1148 – 1198 K temperature range is shown in Figure 3. Table 2 provides the corresponding activation energy and pre-exponential constant along with literature values. The power law exponents of the H₂ and CO₂ were assumed to be 0.5 and 1.0, respectively.

Table 2. Kinetic expressions for the reverse WGS reaction in quartz reactors.

Reference	Mat.	Temp. K	Press. MPa	α	β	E kcal/mol	k_0 (mol/l) ^{$\alpha+\beta-1$} s ⁻¹
Graven and Long [27]	Q	1148-1323	0.1	0.5	1.0	56	2.9x10 ⁹
Kochubei and Moin [28]	Q	1023-1523	0.1	0.5	1.0	78	6.4x10 ¹²
Tingey [29]	Q	1073-1323	0.1	0.5	1.0	76	1.2x10 ¹³
Tingey [29]	Q	673-1073	0.1	0.333	1.0	39	7.6x10 ⁴
Mohindra and Karim [30]	FS	<2400	0.1	0.5	1.0	95	2.3x10 ¹⁶
Kaskan and Browne [31]	FS	873-1323	0.1	0.5	1.0	80	5.1x10 ¹³
NETL	Q	1148-1198	0.1	0.5	1.0	47	8.32x10 ⁷
NETL	Q	1148-1198	1.6	0.5	1.0	52	8.69x10 ⁸

$$r = k[\text{H}_2]^\alpha[\text{CO}_2]^\beta = k_0 \exp(-E/RT)[\text{H}_2]^\alpha[\text{CO}_2]^\beta, R = 1.987 \cdot 10^{-3} \text{ kcal/mol K},$$

Q = quartz, FS = flame study.

For the low-pressure tests the calculated reverse WGS reaction rate constant was approximately 25% greater than that reported by Graven and Long[27]. The activation energy of 47 kcal/mol was slightly less than the value of 56 kcal/mol reported by Graven and Long. As shown in Figure 3, our reaction rate constant values were roughly much greater than those reported by Tingey[29] and Karim and Mohindra[30]. Therefore, our low-pressure results exhibited closest agreement with the results of Graven and Long.

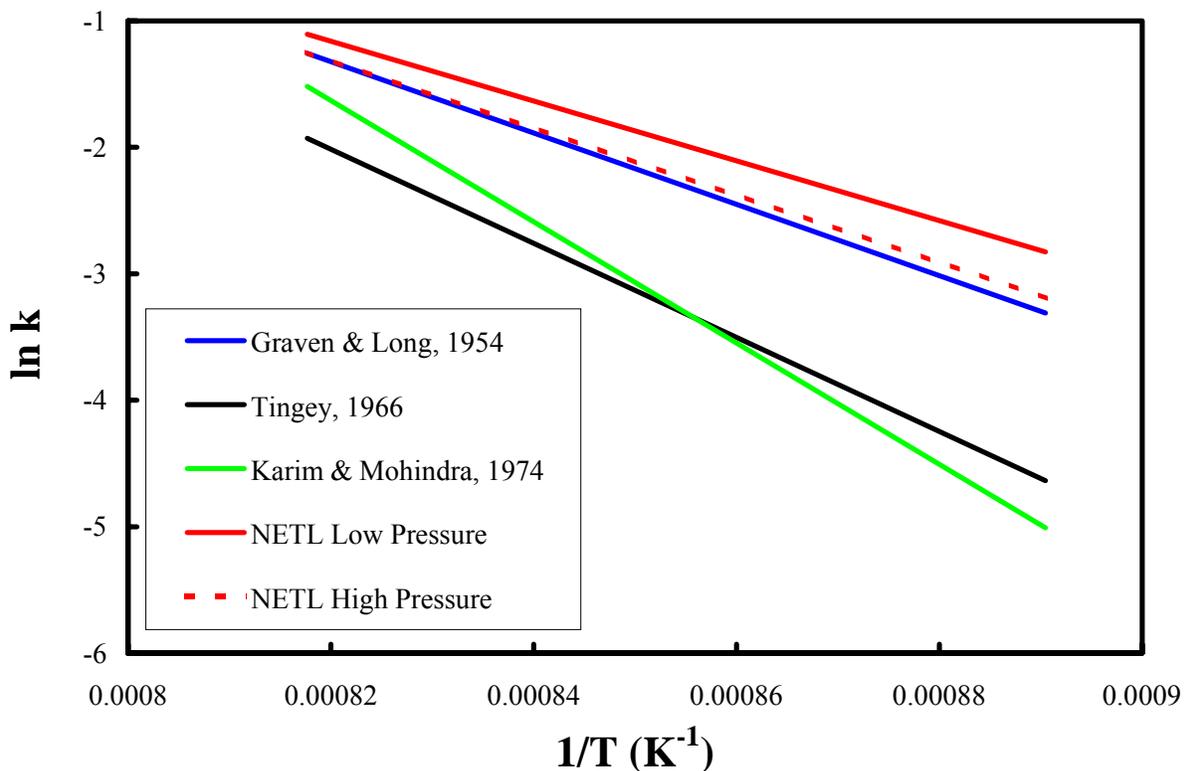


Figure 3. Reverse WGS rate constant (k) results for the quartz reactor tests.

For the high-pressure tests, the activation energy of 52 kcal/mol was slightly greater than the low pressure result of 47 kcal/mol, and the reaction rate constant was approximately 10% greater than that reported by Graven and Long. Again, our high-pressure results were also in very good agreement with the Graven and Long finding.

Rates of reactions in quartz vessels provide an understanding of the intrinsic kinetics of the reverse WGS reaction. However, the industrial application of this technology will occur in vessels composed of metal surfaces. Therefore, the catalytic effect of the wall on the rate of reaction were evaluated for empty and packed Inconel reactors at 1173 K and 0.1 MPa using an equimolar feed of CO_2 and H_2 . The results are shown in Figure 4. Conversions were very high (10-40%), given the short residence time (< 0.5 s) and the equilibrium limitation of 55%. These levels of conversion were much greater than those observed using the quartz reactor, which were

less than 0.1% under the same experimental conditions. This implies that the metal walls of the Inconel reactor catalyzed the reaction. An increase in the Inconel surface area was achieved by packing the reactor with Inconel rings and, as shown in Figure 4, the resulting conversions were roughly twice of those observed with the empty Inconel reactor.

The reverse WGS reaction was also conducted at high-pressure conditions in an Inconel reactor over a wide temperature range using equimolar feeds of CO_2 and H_2 . Longer residence times (8-10 sec.) resulted because of increased gas density and limitations on the maximum flow rate of the reactor effluent through the GC back-pressure regulator. The high-pressure results from the Inconel reactor experiments are presented in Figure 5 along with results obtained using the quartz reactor. The rate of reaction in the Inconel reactor was significantly greater than that attained in the quartz reactor, especially at low temperatures. Near-equilibrium conversions were attained at temperatures greater than 873 K in the Inconel reactor. These results further support the observations obtained at low-pressure conditions that the Inconel surfaces catalyze the reverse WGS reaction. Levels of conversion were so high that accurate kinetic expressions could not be derived for the reverse WGS reaction in an Inconel reactor.

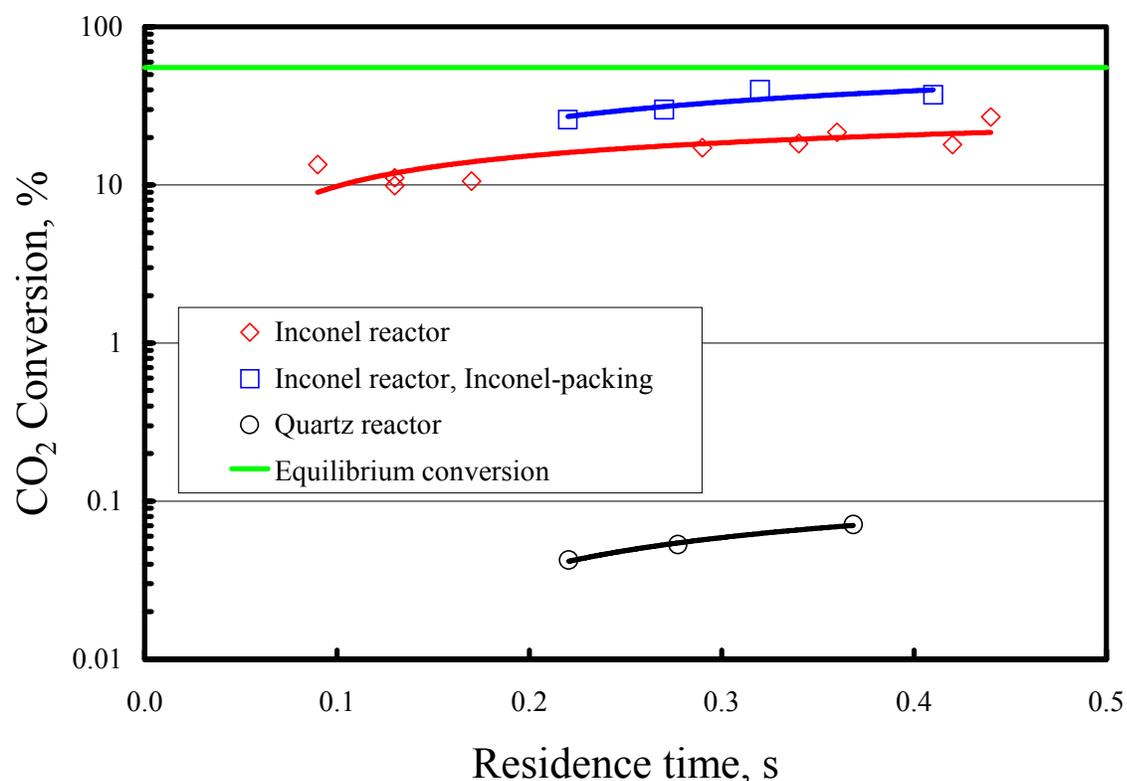


Figure 4. Reverse WGS reaction in an Inconel reactor. 1173 K, 0.101 MPa, $[\text{H}_2]_0 = [\text{CO}_2]_0$. Equilibrium conversion at these conditions is 55%.

Both the low-pressure and high-pressure results indicated that the Inconel 600 catalyzed the reverse WGS reaction. Two rings of the Inconel 600 packing (72% Ni, 17% Cr, and 10% Fe) were

analyzed using SEM-EDS before and after their use in the low-pressure reactor. Significant loss of Ni and/or enrichment of Cr occurred in the Inconel surface after exposure of the Inconel to the reverse WGS reaction environment.

Membrane Study - The second part of this study focused on quantifying the permeance of various palladium–copper membranes. The hydrogen flux through the tested membranes was forced to be proportional to the difference of the square root of the hydrogen partial pressures on the retentate and permeate sides. Thus, Equations 2 and 3 were used to quantify the performance of the membrane in terms of permeability, k , and permeance, k' , respectively.

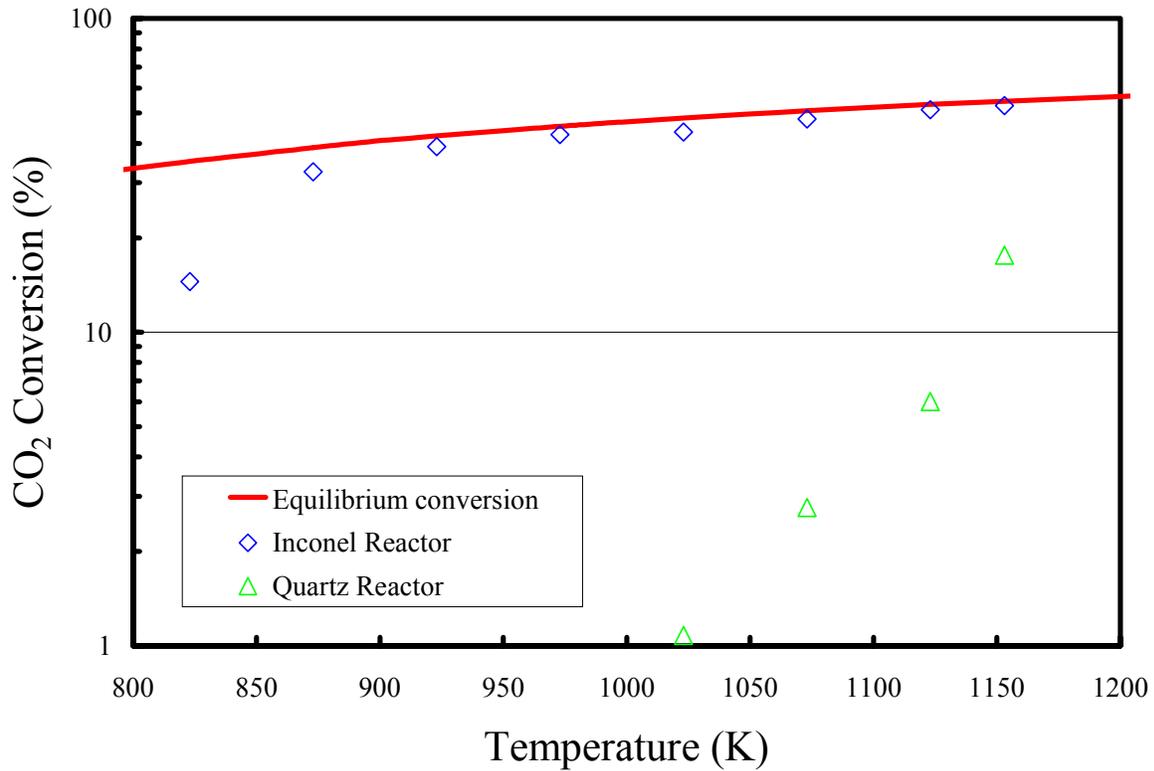


Figure 5. Reverse WGS reaction in an Inconel reactor. 1.6 MPa, $[H_2]_o=[CO_2]_o$. Conversions in the quartz reactor were from our high-pressure kinetic results. Residence times were 8-10 s.

$$N_{H_2} = -k \frac{(P_{H_2,ret}^{0.5} - P_{H_2,perm}^{0.5})}{X_M} \quad 2$$

$$N_{H_2} = -k' (P_{H_2,ret}^{0.5} - P_{H_2,perm}^{0.5}) \quad 3$$

Where, N_{H_2} = flux of H_2 , $P_{H_2,perm}$ = hydrogen partial pressure in the permeate, $P_{H_2,ret}$ = hydrogen partial pressure in the retentate, k = permeability, k' = permeance, X_M = membrane thickness.

The permeance results for the 53%Pd-47%Cu, 60%Pd-40%Cu and 80%Pd-20%Cu membranes, along with the permeance values of the palladium and copper membranes, are presented in Figure 6 as a function of inverse absolute temperature. All the membranes were completely selective for hydrogen. The number associated with each data point corresponds to the sequential order of the membrane's temperature history and these conditions are also represented on Figure 7. The data point number for each permeance value is referred to parenthetically in the text that follows.

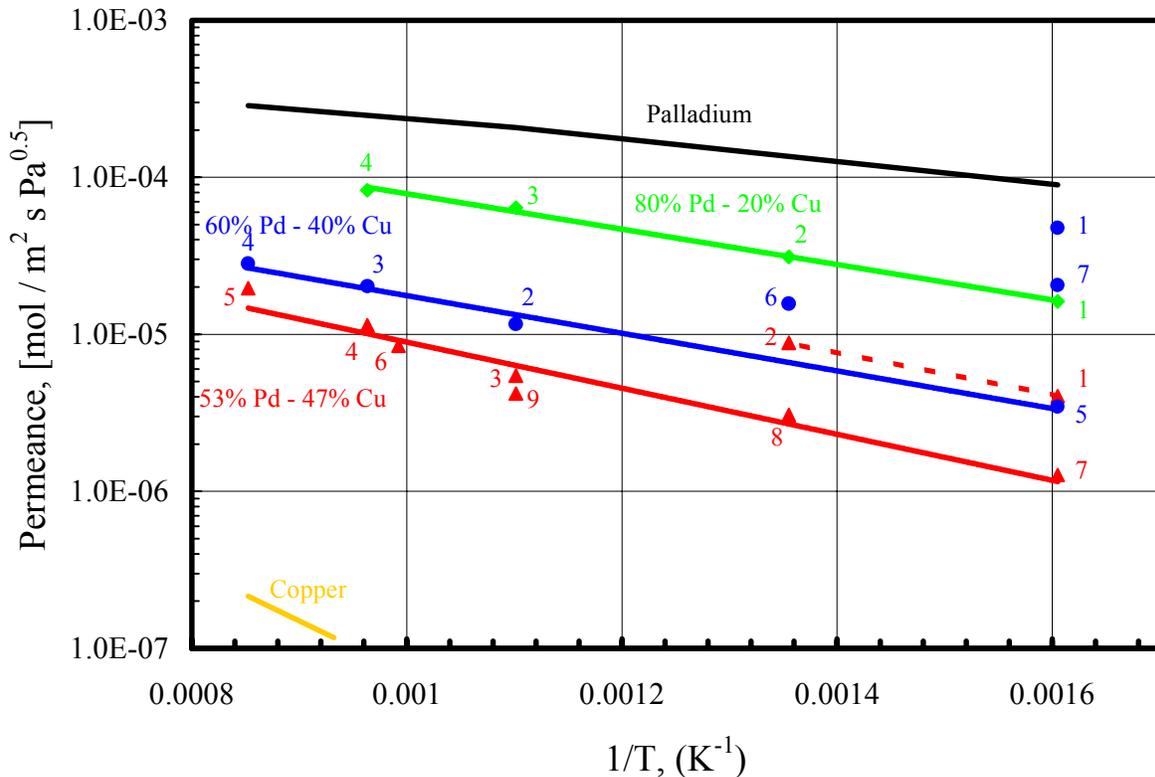


Figure 6. Permeance of Pd, Pd-Cu alloys and Copper.

The 53%Pd-47%Cu alloy permeance was initially measured at 623 K (1) and then at 738 K (2). This alloy composition corresponds to the middle of the β region shown in Figure 6, which has a bcc to fcc transition temperature of about 870 K. Therefore, these permeance values (1,2) are expected to correspond to the bcc structure (dashed line). Nonetheless they were more than an order-of-magnitude less than that of pure Pd. When the membrane was heated to 908 K (3), the permeance diminished because of the transition from the bcc phase to the less permeable fcc phase. The membrane exhibited fcc permeance values (solid line) as the membrane was heated to higher temperatures of 1038 K (4) and 1173 K (5), and then cooled to 1008 K (6) and 623 K (7) before being heated again to 738 K (8) and 908 K (9). The membrane was not permitted to remain at 623 K for an extended period of time, thus not allowing transition back to the bcc phase(1,2).

The 60%Pd-40%Cu alloy initially exhibited a much higher permeance at 623 K (1) than the 53%Pd-47%Cu alloy while in the bcc region; approximately half of the permeance of pure Pd. The permeance diminished when temperature was increased to 908 K (2), 1038 K (3), and 1173 K (4) prior to being cooled to 623 K (5). These permeance values (2,3,4,5) were well correlated by an Arrhenius type equation and corresponded to fcc phase permeance values that were one-tenth that of pure Pd. The membrane was heated to 738 K and maintained at this temperature for 74 hours (6) and the permeance increased to a value greater than that indicated by the line correlating the fcc phase results. The membrane was then cooled to 623 K (7) and maintained at this temperature for 22 hours. The permeance (7) was greater than that observed at condition (5) but less than that of the first measurement at this temperature (1). The elevated permeance values associated with conditions (6) and (7) indicate that the membrane was slowly reverting to the bcc phase because the temperature was being maintained at values less than the phase transition temperature for an extended period of time.

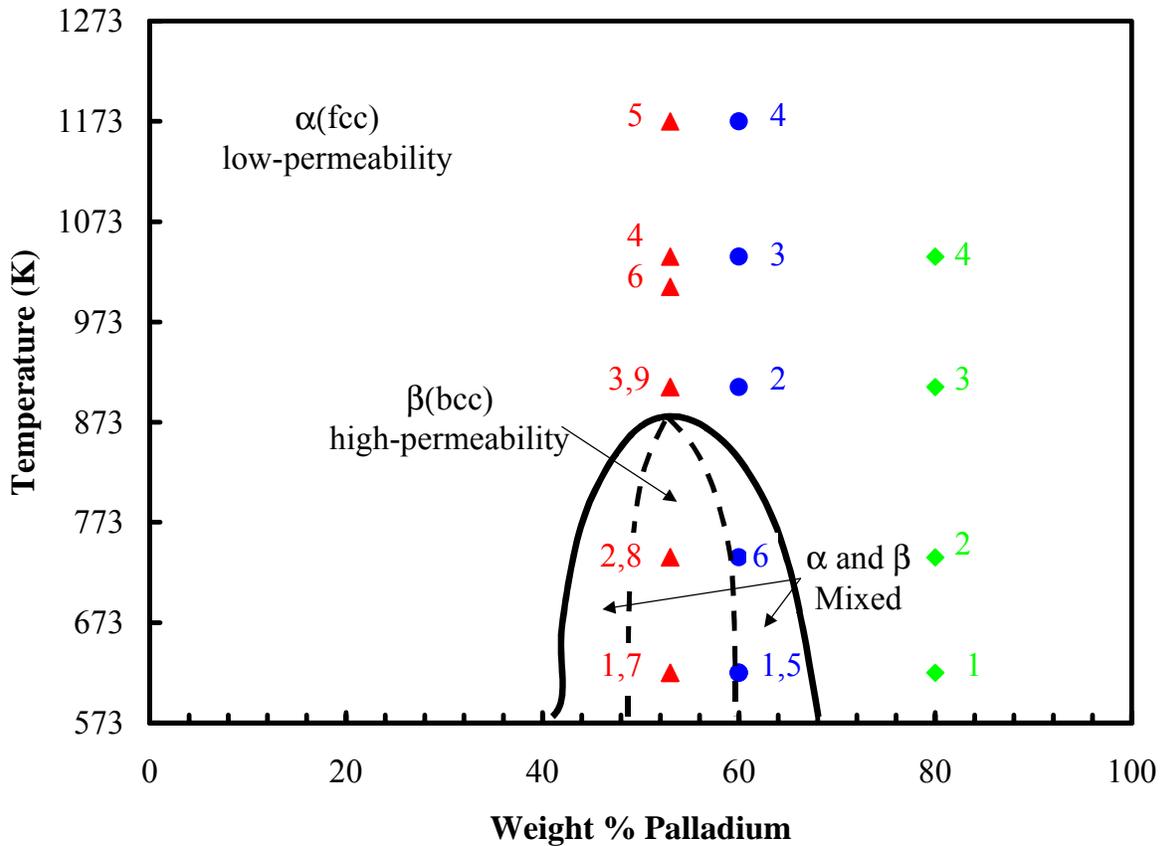


Figure 7. Phase Diagram of Pd – Cu alloys[24].

According to the phase diagram, the 80%Pd-20%Cu alloy should be in the fcc phase over the entire temperature range examined. As shown in Figure 6, this alloy exhibited permeance values roughly one fourth of pure Pd over the 623 – 1173 K temperature range. An Arrhenius correlation fit all of the permeance values indicating there were no phase changes over the tested temperature range. Although the 80%Pd-20%Cu alloy was less permeable than the 60%Pd-

40%Cu alloy at 623 K, it exceeded the permeance of the 60%Pd-40%Cu alloy at temperatures greater than 623 K. Also the 80%Pd-20%Cu alloy exhibited higher permeance values than the 53%Pd-47%Cu alloy at all temperatures.

CONCLUSIONS

The rate of reaction of the homogeneous, reverse WGS reaction was evaluated in a quartz reactor at elevated temperature (973-1198 K), low pressure (0.1 MPa) and high pressure (1.6 MPa) conditions in the absence of a diluent gas. The results were consistent with the previously published, low-pressure rate expression of Graven and Long.

A pressure-equilibrated quartz reactor was used to study the homogeneous rate of reaction for the first time at high temperature, high-pressure conditions (up to 1.6 MPa). The rate of reaction correlated by the low pressure and high pressure Arrhenius expressions were in good agreement over the 1148 – 1198 K temperature range indicating there was no significant effect of elevated pressure on the rate of reaction.

Conversions attained in an Inconel reactor at 1173 K and 0.1 MPa were approximately two orders-of-magnitude greater than those attained in the quartz reactor for residence times of 0.1 – 0.5 seconds. High conversions were also observed when the Inconel reactor was operated at high pressure, with near-equilibrium conversions at temperatures as low as 873 K for residence times of 8-10 s. This large conversion in the presence of Inconel suggested that the Inconel surfaces catalyzed the reverse WGS reaction.

Pd-Cu alloys exhibited hydrogen permeability values intermediate to palladium and copper over the 623 – 1173 K temperature range and 0.1 – 2.6 MPa pressure range. The 53%Pd and 60%Pd alloys exhibited relatively high permeance values at temperatures corresponding to bcc crystal structure. The 53%Pd alloy exhibited bcc permeance values over a wider range of temperature than the 60%Pd alloy consistent with the phase diagram. However the 60%Pd alloy exhibited the highest permeance value (relative to pure Pd) at 623 K. The permeance of the 60%Pd alloy dropped markedly at higher temperatures due to the transition of the Pd-Cu crystal structure from bcc to fcc. The 60%Pd membrane retained low permeance values even when initially cooled, however the alloy slowly increased in permeability as the membrane was maintained at 623 K due to the transition from fcc phase to bcc phase. Although the permeance of the 80%Pd alloy was less than that of the 60%Pd alloy at 623 K, the 80%Pd alloy exhibited greater permeance values at temperatures greater than or equal to 738 K.

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