Recovery of Hydrogen from Impurities Using a Palladium Membrane Reactor

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ABSTRACT

One of the important steps in processing the exhaust from a fusion reactor is recovering tritium which is incorporated into molecules such as water and methane. One device which may prove to be very effective for this purpose is a *palladium membrane reactor*. This is a reactor which incorporates a Pd/Ag membrane in the reactor geometry. Reactions such as water gas shift, steam reforming and methane cracking can be carried out over the reactor catalyst, and the product hydrogen can be simultaneously removed from the reacting mixture. Because product is removed, greater than usual conversions can be obtained. In addition ultrapure hydrogen is produced, eliminating the need for an additional processing step. A palladium membrane reactor has been built and tested with three different catalysts. Initial results with a Ni-based catalyst show that it is very effective at promoting all three reactions listed above. Under the proper conditions, hydrogen recoveries approaching 100% have been observed. This study serves to experimentally validate the palladium membrane reactor as a potentially important tool for fusion fuel processing.

INTRODUCTION

One of the more daunting problems in fusion fuel processing is the recovery of tritium from fusion fuel (D-T) impurities such as water and methane. This is difficult because of the relative stability of these species. Various methods have been used or proposed for this purpose [1], but most suffer from problems such as waste generation, unreliability and complexity.

As will be shown in this paper, one device which is proving to be quite effective for this purpose is a membrane reactor. This is a combined reactor/permeator. Membrane reactors have been examined for various applications since the late 1960's. They typically consist of a plug-flow catalytic reactor with walls composed of a membrane material. The membrane walls facilitate the addition of reactants or the removal of products along the length of the reactor. This is particularly useful for reversible reactions which are limited by thermodynamic equilibrium. Products can be removed as the reaction proceeds and, with a proper membrane, reactions can be taken to 100% conversion.

Membrane reactors have been considered for applications such as hydrogenation and dehydrogenation reactions [2,3,4,5], the water gas shift reaction [6], and steam reforming [7]. A number of theoretical treatments of this problem have also been presented [8,9,10] and a review has been given by Armor [11].

Specifically for recovering hydrogen isotopes from fusion fuel impurities, it is a *palladium membrane reactor* (PMR) that is most interesting. Using shift catalysts, hydrogen can be moved from the impurities to the free hydrogen form. Examples of these reactions are:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \text{Water Gas Shift}$$

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad \text{Steam Reforming}$$
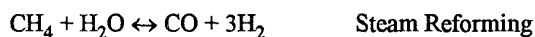
Both of these reactions are reversible and are limited by thermodynamic equilibrium. By including in the reactor a membrane which selectively removes H_2 from the reacting system, the reactions can be brought to completion. Non-porous Pd/Ag meets the need for this highly selective membrane as Pd/Ag is permeable only to hydrogen isotopes.

The staged use of shift reactions for processing impurities has been discussed [12,13,14,15]. The specific use of a palladium membrane reactor for this purpose has been proposed [1,16]. To demonstrate the palladium membrane reactor concept for fusion fuel processing applications, a reactor and test stand has been constructed at the Tritium Systems Test Assembly (TSTA) which is part of Los Alamos National Laboratory (LANL). This paper will describe the palladium membrane reactor and test stand, and report on initial experience and data collected.

EXPERIMENTAL DESCRIPTION

A. The Palladium Membrane Reactor

Figure 1 is a scale drawing of the palladium membrane reactor that has been constructed at TSTA. The central tube is made of 75%Pd/25%Ag and was obtained from Rosemont GmbH & Co., Hanau, Germany. Its dimensions are 530 mm long (including its 11.9 mm flange), 5 mm outer diameter and 0.2 mm wall thickness. It is mounted in an MDC Corp. "Del-Seal" flange, 2.12" dia. x 0.470" thick, 304 stainless steel. This flange facilitates easy removal of the tube from the reactor shell.

The reactor shell is constructed of 0.065" wall thickness 304 stainless. Its inside length is 26" measured between the flange surfaces. The shell outer diameter is 1". Thermowells are included to measure the membrane surface temperature at three points as shown. The annular space between the
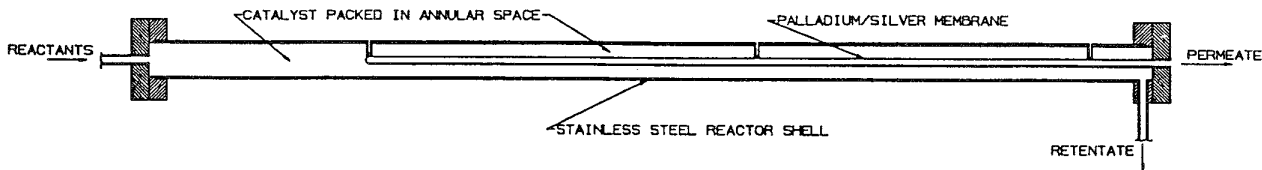
Figure 1 TSTA's Palladium Membrane Reactor

membrane and the reactor shell is packed with catalyst. The use of demountable flanges as shown allows for relatively easy access to the inside of the shell for changing catalyst.

Reactant gases are fed to the assembly through a 1/4" tube welded into the flange shown at the left. As reactions occur over the catalyst, H_2 is extracted from the annular space via permeation through the Pd/Ag membrane by pumping the inside of the membrane. For a practical application of the PMR, it is this ultrapure H_2 permeate that would be, for example, sent to the cryogenic isotope separation system. That which does not permeate, the retentate, is exhausted through a 1/4" tube which has been welded into a radial bore in the shell's flange as shown on the right.

Catalyst is typically packed to within about 1" from either end. The remaining spaces are filled with stainless steel wool.

The entire assembly is heated by enclosing it in a split-hinge tube furnace. The furnace is mounted vertically and employs three independently controlled heaters to maintain uniform temperature along the length of the reactor.

B. Test Stand

Figure 2 shows the experimental test stand which has been built to test the PMR. Up to three gases can be mixed with flowrates between 0 and 500 sccm. To this mixture, water can be added via a syringe pump which injects into a heated line to make steam. The retentate diagnostics include humidity, flowrate, pressure and gas composition using an

MTI gas chromatograph. For the permeate, pressure and flowrate are measured. Pumping for the permeate is provided by a Normetex 15 scroll pump backed by a metal bellows pump.

A personal computer is used for data acquisition and control. It displays and archives measured values, and sets control valve settings. A separate personal computer is used to operate the gas chromatograph and analyze its data.

RESULTS AND DISCUSSION

A. Water Gas Shift using an Iron Catalyst

The first catalyst chosen for testing was an iron-based catalyst with a Cr stabilizer from United Catalyst (type C12-3-05, crushed to between 14 mesh and 1/8"). This is commonly referred to as a high-temperature water gas shift catalyst. After activating the catalyst (treatment with H_2 to remove oxygen from the catalyst as water), the PMR was fed with H_2O and CO. The water was successfully converted to hydrogen, of which substantial quantities were recovered in the permeate. Tests were conducted at temperatures ranging from 350-450 °C. After a few days of experiments performance degraded and a large pressure drop was observed over the catalyst. Opening the reactor showed that about the first 1" of catalyst had formed a plug which had to be chipped out; the rest of the catalyst poured out of the shell easily. Using a slightly different activation procedure, this experience was repeated a second time with the same plugging result.
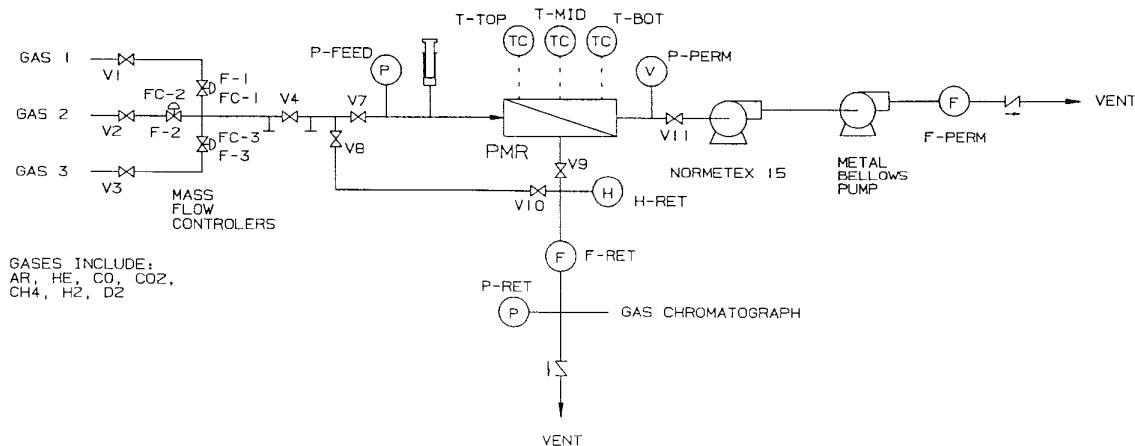

Figure 2 Schematic of the Palladium Membrane Reactor Experimental Test Stand

In industrial practice Fe catalysts are only partially reduced and are used in reactions with excess water. In our case an excess of CO was used to ensure complete conversion of water. This environment apparently reduced the iron oxide all the way to elemental Fe. It is believed that the elemental Fe further reacted with CO to form iron carbide, resulting in the plugging that was observed. Though a catalyst similar to ours was used by [6] they did not see this behavior. This is probably because [6] was concerned with maximizing CO conversion and so ran with excess water rather than excess CO as in our study. Because of the plugging with fusion fuel relevant conditions (excess CO), iron-based catalysts are believed to be inappropriate for this application.

B. Water Gas Shift using a Copper/Zinc Catalyst

The next catalyst tested was a copper/zinc-based catalyst from United Catalyst (type C18HC, 3/16" x 3/32" tablets). This is commonly referred to as a low-temperature water gas shift catalyst.

The first series of runs with this catalyst fed the reactor with H_2O and CO as before, and temperatures ranging from 310-430°C were used. This series of runs lasted for a period of about one month. Again substantial H_2 was recovered in the permeate resulting from the water gas shift reaction. However, over time a decrease in PMR performance was observed as indicated by increasing humidity in the retentate and decreasing permeate flowrate. This is believed to be due to operating the catalyst at too high a temperature. This catalyst is designed to be operated between 200-250°C. Evidently operation at higher temperatures eventually deactivated the catalyst.

The next series of runs, beginning with a new charge of catalyst, was conducted at 310°C. This temperature was chosen to be high enough to prevent the formation of β phase Pd, but low enough to prevent the degradation of the catalyst. CO and steam were fed to the PMR in the ratio 1.61:1 at various flowrates. A summary of the feed conditions and resulting permeate and retentate measurements for these runs is presented in Table 1. The first half of the table shows data that were all collected on one day. Then the same set of conditions were repeated, but the PMR was allowed to run at steady state for >7 hours before measurements were recorded.

Table 1 Summary of 310°C Runs Over Cu/Zn at Various Flowrates

Date & Time	Feed CO sccm	Feed Steam sccm	Feed Pressure torr	Permeate Flowrate sccm	Permeate Pressure torr	Retentate Humidity °C Dew Pnt	Retentate H2 %	Retentate CO %	Retentate CO2 %	Recovery %
2/8/93 9:44	480.0	298.7	614	102.9	0.86	-2	24.75	25.48	44.32	34.4
2/8/93 10:31	299.4	186.7	604	95.7	0.81	-6	19.65	27.81	48.29	51.3
2/8/93 11:05	200.0	124.4	600	89.0	0.76	-8	14.02	27.98	54.25	71.5
2/8/93 11:32	100.0	62.2	596	63.2	0.54	-28	1.79	31.67	65.14	101.5
2/8/93 12:49	50.1	31.1	594	32.4	0.27	-43	0.14	31.11	66.93	104.1
2/8/93 13:38	26.0	16.2	593	17.2	0.15	-46	0.09	30.31	68.38	106.4
2/8/93 14:45	16.1	10.0	593	9.5	0.05	-49	0.07	31.20	66.85	95.3
Data above were collected all in one day. Runs below were run for at least 7 hr. at steady state before recording data										
2/12/93 15:11	26.0	16.2	595	16.2	0.17	-59	0.05	32.76	65.19	100.0
2/16/93 15:44	49.9	31.1	594	30.9	0.22	-59	0.09	33.94	64.86	99.4
2/18/93 16:00	100.0	62.2	598	61.1	0.49	-33	1.86	31.76	64.10	98.2
2/19/93 16:12	199.8	124.4	599	87.9	0.78	-9	13.68	27.34	54.95	70.6
2/22/93 15:36	299.9	186.7	602	95.8	0.83	-5	20.45	25.21	48.63	51.3
2/23/93 19:42	480.0	298.7	613	100.0	0.98	-4	24.66	23.92	43.80	33.5
2/25/93 19:37	16.0	10.0	594	10.1	0.24	-58	0.04	32.59	65.49	101.1

The last column in Table 1 represents the percentage of H_2 that was recovered, i.e. Recovery = Permeate Flowrate / Steam Feed Flowrate * 100%. The recovery is plotted versus total feed flowrate in Figure 3. Recovery approaches 100% up to a total flowrate of about 160 sccm.

Also shown on the figure is a line representing the thermodynamic equilibrium conversion for the feed conditions. This value of 96% represents the ultimate conversion of H_2O to H_2 that would occur at 310°C with a $CO:H_2O$ ratio of 1.61:1 without a permeator to upset the equilibrium. It is observed that at the lower flowrates, recoveries exceed 96% indicating that the removal of H_2 via the permeator is promoting conversion beyond what would be possible without the permeator. Further, it important to recognize that the recovery includes separation (usually a separate processing step) as well as reaction with the product being ultrapure hydrogen.

At higher flowrates the recovery drops substantially. Primarily this indicates that there is not sufficient residence time in the PMR for the hydrogen resulting from the reaction to permeate. Rather, much of the hydrogen is being exhausted with the retentate as listed in Table 1.
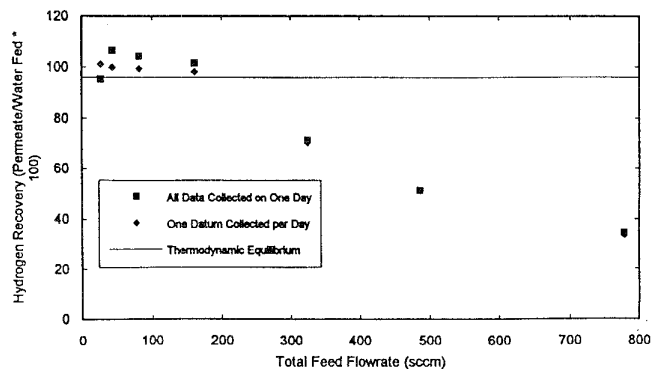

Figure 3 Recoveries for 310°C Runs Over Cu/Zn at Various Flowrates

The next tests were oriented toward examining the longer term behavior of this system. Runs were conducted at 310°C with 200 sccm CO and 124 sccm steam over a period of 12 days (shut down at night and on weekend, but held at temperature with Ar purge). The permeation flowrate data from this series is plotted versus cumulative run time (downtime eliminated) in figure 4. Over the first 70 hours of operation it is observed that the flowrate dropped from about 84 sccm to about 80. Though the evidence is not conclusive, it is suspected that this slow decrease is indicative of a degradation of the Cu/Zn catalyst. The temperature used is 60-110°C hotter that is normal for this catalyst

After the run which ended at about 70 hours, the water was turned off, but a CO purge rather than the normal Ar purge was left on over night. Thereafter, the flowrate dropped to about 74 sccm. It was suspected that this decrease was due to coking. Coking is the deposition of elemental carbon inside the reactor and can interfere with catalyst activity and/or the membrane's permeability. A series of treatments were tried to bring the permeate flowrate up to its former levels. These included flowing on separate occasions H_2, CO_2, and 13% O_2 in He over the bed. Subsequent water gas shift experiments after each of these treatments reveals that none of these procedures enabled the bed to perform as it had before.

While Cu/Zn certainly does a good job of promoting the water gas shift reaction, it is unclear how stable it would be at temperatures high enough to make permeation practical. It is apparent that further work would be necessary to demonstrate that it is ready for practical use. Other related catalysts such as Cu/Cr may be more stable and better suited for further testing of this catalyst system.

C. Water Gas Shift using a Ni Catalyst

Only recently have tests on a United Catalyst Ni-based catalyst begun (type C150-4-03, 1/4" pellets). This is usually marketed as a steam reforming catalyst. Various forms of Ni reforming catalyst are sold which are intended for use at temperatures ranging from ~500°C ("pre-reforming" catalyst) to ~900°C. The "pre-reforming" catalyst which was used in
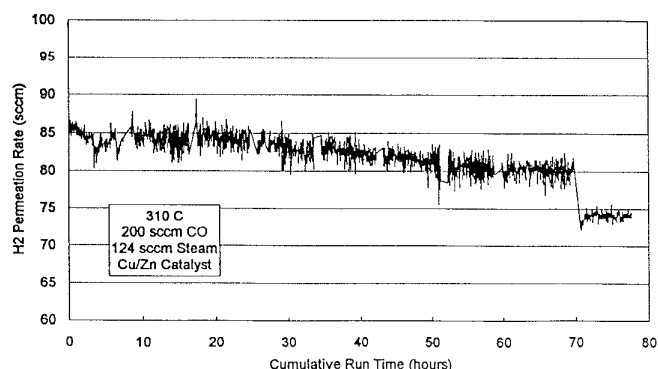
this study has a very high Ni content (co-precipitated with alumina) to maximize its activity. Preliminary results are available for water gas shift, steam reforming and methane cracking reactions (discussed below).

Ni catalyst is not usually used for water gas shift because it only becomes active at temperatures which are too high for thermodynamic equilibrium for this reaction to be maximized (lower temperatures increase conversion). However, using a membrane reactor, overall H_2 recovery is not limited by thermodynamic equilibrium.

Tests were conducted at 500°C with a feed containing CO:water ratios of 1.0, 1.2 and 1.6. The results are summarized on figure 5. Recoveries approach 100% up to total flowrates of about 110 sccm. Also included on this plot are solid lines showing the thermodynamic maximum conversions of water to H_2 at the various CO:water ratios (similar to the solid line on figure 3). Because of the higher temperature for this series of runs, these lines are lower than the line on figure 3. This series makes the PMR's ability to produce recoveries greater than thermodynamic equilibrium quite striking. Recoveries approach 100% when conversions without a membrane present would have been limited to 65-83%.

D. Steam Reforming using a Ni Catalyst

A series of runs were conducted with a CH_4 and H_2O feed at 450 and 500°C. Various amounts of Ar and CO were included in some of the feed mixtures. The results are summarized on figures 6 and 7. At 450°C the maximum recoveries observed are about 98% at total feed rates of about 50 sccm. At 500°C results are better with recoveries approaching 100% at flowrates up to about 70 sccm. There is insufficient data to draw definitive conclusions regarding the effects of varying CH_4:water ratios and the presence of CO or Ar in the feed, but apparently effects on recoveries, if any, are small.
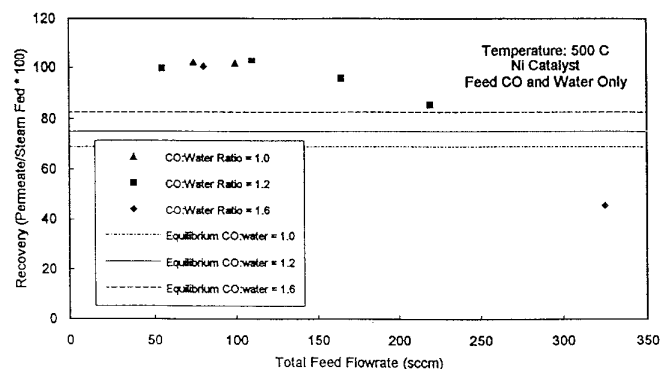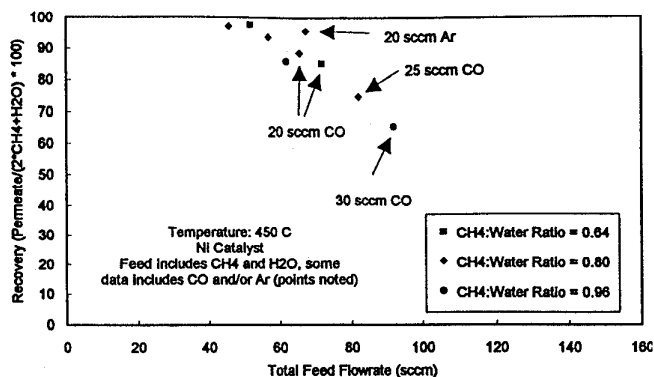

Figure 4 Extended Cu/Zn Run Permeation Rate

Figure 5 Water Gas Shift over Ni at 500°C

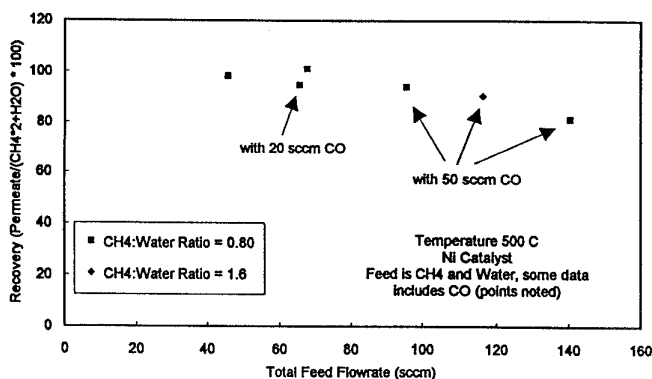Figure 6 Steam Reforming at 450°C

Figure 7 Steam Reforming at 500°C

Figure 8 Methane Cracking at 500°C

E. Methane Cracking using a Ni Catalyst

The methane cracking reaction, $CH_4 \leftrightarrow C + 2H_2$ was studied at 500°C using feeds of CH_4 with either Ar or CO. These results are summarized on figure 8. The maximum recoveries observed were about 94% at total flowrates of about 50 sccm. These are the lowest recoveries observed for the three classes of reactions studied over Ni, so this appears to be the most difficult reaction.

Also plotted on figure 8 is the thermodynamic equilibrium conversion that would be expected for the CH_4/Ar data without the membrane. These values were obtained using SOLGAS [17]. (The curvature of this equilibrium line stems from the combination of two conditions: for this reaction there is a difference in the total number of product and reactant moles, and an inert with varying concentration is being used.) Particularly at the lower flowrates, the dramatic difference between the PMR recoveries and the thermodynamic equilibrium is a striking display of the utility of the PMR.

Of course, CH_4 cannot be cracked over this catalyst indefinitely without excessive coking problems. Preliminary testing has shown that it is possible to remove the carbon from the bed subsequent to CH_4 cracking by treatment with H_2 (running the cracking reaction in reverse) or CO_2

$(C + CO_2 \leftrightarrow 2CO)$. Treatment with pure or diluted oxygen would also be expected to prove effective.

CONCLUSIONS

For water processing it has been shown that iron-based catalysts are inappropriate for the PMR due to rapid degradation probably due to carbide formation. The copper-based catalyst worked well, but limited data indicate that the Cu/Zn catalyst tested here may slowly deactivate at temperatures required for the permeator to operate.

Early data for the Ni-based catalyst is very encouraging. This single catalyst is capable of effectively promoting water gas shift, steam reforming and methane cracking reactions. Further, this catalyst is known to be very robust and is not expected to suffer from deactivation problems. More data will be required to confirm this. Striking results were observed with the Ni catalyst showing that the PMR is capable of producing conversions much greater than thermodynamic limits which apply to typical reactors. This is because the PMR continuously removes product, thus upsetting the equilibrium.

In one processing step, the palladium membrane reactor has shown that it can remove hydrogen from impurities and separate that hydrogen from the remaining reaction products. The H_2 product needs no further treatment before being sent, for instance, to a cryogenic isotope separation system.

This study has shown that a palladium membrane reactor is very effective at recovering H_2 from both water and methane. Further study of the PMR, including tritium testing, is planned at TSTA. Data collected to date lead to the expectation that the PMR will become a useful and valued component in fusion fuel processing.

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