

## PURE HYDROGEN PRODUCTION FROM OCTANE, ETHANOL, METHANOL, AND METHANE REFORMING USING A PALLADIUM MEMBRANE REACTOR

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### ABSTRACT

A palladium membrane reactor (PMR) has been used to convert hydrocarbons into pure hydrogen. This process has promise for generating hydrogen for use in PEM fuel cells and other applications. Ethanol, methanol and gasoline are being considered for fuel cell cars since they are liquids and therefore have high energy densities. Methane is being considered for terrestrial fuel cell applications. Each fuel was tested in the PMR at a range of inlet and operating conditions. Conversions to pure hydrogen approaching 100% were obtained for all of the fuels.

The PMR was loaded with either Cu/Zn-O, Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Ni/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, or Pt/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst, depending on the hydrocarbon being processed and the temperature of the experiment. The quantity of water injected into the reactor ranged from 50-100% of the stoichiometric requirement for complete conversion of the hydrocarbons. At 100% of the stoichiometric requirement, the retentate (outlet of reaction side) was mostly CO<sub>2</sub>. At less than the stoichiometric requirement, significant concentrations of CO, H<sub>2</sub>O, and CH<sub>4</sub> were observed. If the water injection was too low then carbon formation occurred in the reactor. The effect of injection rate on hydrogen recovery was measured. It was observed that higher percentages of hydrogen were recovered as the injection rate was decreased. Octane reforming worked well at 600°C. Methane reforming worked well at 450°C, but performance was poor at 400°C. Ethanol reforming worked well at 500 and 550°C. For methanol reforming, the performance was best at 300°C and decreased as the temperature was increased to 350°C. The decrease in hydrogen production in the permeate was caused by an increase in methane production in the retentate.

### INTRODUCTION

A palladium membrane reactor (PMR) has been used to convert hydrocarbons into pure hydrogen. This process has promise for generating hydrogen for use in PEM fuel cells and other applications. Ethanol, methanol, and gasoline are being considered for fuel cell cars since they are liquids and therefore

have high energy densities. Methane is being considered for terrestrial fuel cell applications. Each fuel was tested in the PMR at a range of inlet and operating conditions. Conversions to pure hydrogen approaching 100% were obtained for all of the fuels.

The PMR is a combined permeator and catalytic reactor. Catalysts are used to foster reactions such as methane steam reforming,  $\text{CH}_4 + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO}$ , and water-gas shift,  $\text{H}_2\text{O} + \text{CO} \rightarrow \text{H}_2 + \text{CO}_2$ . Due to thermodynamic limitations these reactions only proceed to partial completion. Thus, a Pd/Ag membrane, which is exclusively permeable to hydrogen, is incorporated into the reactor. By maintaining a hydrogen-partial-pressure gradient across the membrane, pure hydrogen is produced on the permeate side enabling the reactions to proceed toward completion.

The PMR converts fuel into pure hydrogen in a single stage. This is a significant simplification when compared to other fuel processing systems for fuel cell applications which typically have several stages in series and excess water addition. These multiple stages are required to reduce the CO concentration to <10 ppm so that the PEM fuel cell is not poisoned. Water addition in excess of the stoichiometric quantity is also required to get low CO levels. Use of excess water results in no hydrogen production and significantly decreases system efficiencies. The PMR can operate at or below the stoichiometric requirement for water injection and, therefore, is potentially a much simpler and more efficient method for producing hydrogen than systems using conventional reactors.

### EXPERIMENTAL APPARATUS

Figure 1 is a schematic of the PMR. The PMR has a Pd/Ag tube which is 61.0 cm long, 0.635 cm in outer diameter, and has a wall thickness of 0.0178 cm. The stainless steel shell is 66.0 cm long, 2.54 cm in outer diameter, and has a wall thickness of 0.165 cm. An approximately 1 torr vacuum was maintained on the permeate side of the reactor with a Normatex 15 scroll pump

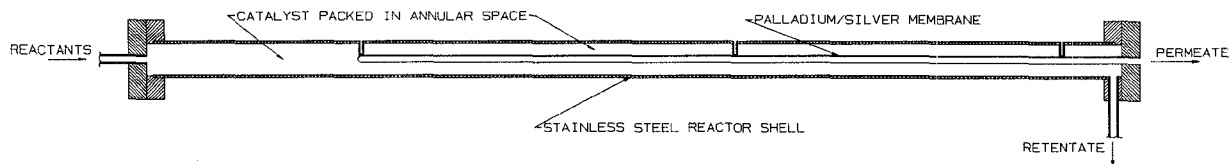


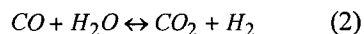
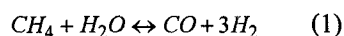
Figure 1. The Palladium Membrane Reactor.

backed by a Metal Bellows 601 pump. The PMR is oriented vertically in a tube furnace with the inlet at the top.

Gases were injected using Brooks 5850EM mass flow controllers. Water injection was made either by flowing a mixture of H<sub>2</sub> and O<sub>2</sub> over a Pt catalyst or by injection of liquid water with a Harvard Apparatus Model 22 syringe pump. Ethanol, methanol, and octane were also injected with the syringe pump. Retentate and permeate flow rate were measured with Brooks 5850EM mass flow meters. An MTI model M200 gas chromatograph was used to measure the performance of the PMR. The GC was calibrated to measure H<sub>2</sub>, CH<sub>4</sub>, CO and CO<sub>2</sub>. An Endress and Hauser trace humidity probe was used to measure the H<sub>2</sub>O concentration at the outlet for the methane, methanol, and ethanol experiments. The probes were calibrated from -80°C to 20°C dew point and have an accuracy of ±1°C dew point. An Endress and Hauser relative humidity probe was used to measure the H<sub>2</sub>O concentration at the outlet for the octane experiments. This probe could measure up to a 100°C dew point.

#### METHANE STEAM REFORMING

The PMR system at Los Alamos National Laboratory has 215 days of round-the-clock operation without failure. Most of this experience has been associated with the development of a PMR system for application in fusion-fuel processing (Willms and Birdsell, 1995, Birdsell and Willms, 1995, and Birdsell and Willms, 1997a). Fusion reactor exhaust contains tritiated water and tritiated methane, and the tritium in these impurities will need to be recovered for environmental and economic reasons. The PMR system recovers tritium by methane steam reforming



of the tritiated methane and water. Hydrogen is simultaneously removed via the Pd/Ag membrane while the steam reforming reactions are proceeding. This is the same process that could be

used to convert methane into hydrogen for, for example, PEM fuel cell applications.

Figure 2 shows the percentage of hydrogen recovered from the injected CH<sub>4</sub> and H<sub>2</sub>O as a function of the equivalent rate of H<sub>2</sub> (in the form of CH<sub>4</sub> and H<sub>2</sub>O) injected into the reactor. The injection H<sub>2</sub>O:CH<sub>4</sub>=1.25 for these experiments. 6.3% O<sub>2</sub> was added to prevent coking. Also, 30.8% of the inlet flow was Ar (Ar is an inert component that has significance for the fusion fuel application, but not to the hydrogen production application). Nearly all of the injected hydrogen is recovered as pure H<sub>2</sub> in the permeate stream at low injection rates. The recovery decreases as the injection rate increases. The maximum H<sub>2</sub> recovery in a conventional reactor is limited by thermodynamic equilibrium. Equilibrium was calculated with the SOLGAS code (Bessman, 1989) for the injection conditions of these experiments and the maximum H<sub>2</sub> recovery for a single, infinitely large conventional reactor was found to be approximately 37%.

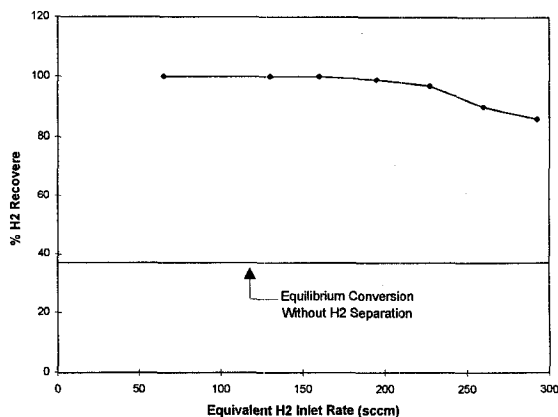


Figure 2. Methane steam reforming results at 500°C and inlet pressure of 0.78 atm. H<sub>2</sub>O:CH<sub>4</sub>=1.25 with 6.3% O<sub>2</sub> addition and Pt/α-Al<sub>2</sub>O<sub>3</sub> catalyst (Engelhard A-16825).

H<sub>2</sub> recovery has been tested at 400, 450, 500, 550 and 600°C. The H<sub>2</sub> recovery increases moderately with increasing

Table 1. Retentate Concentrations for Methane Reforming Experiments. H<sub>2</sub>O:CH<sub>4</sub>=1.25.

Equiv. H <sub>2</sub> Inlet Rate (sccm)	% H <sub>2</sub>	% CH <sub>4</sub>	% CO	% CO <sub>2</sub>	% H <sub>2</sub> O	% Ar	Permeate (sccm)
65	0.13	0.09	16	32	0.008	50	68
130	0.21	0.19	16	31	0.010	52	133
160	0.25	0.18	17	31	0.014	51	163
195	0.45	0.90	18	30	0.023	52	193
228	2.3	1.6	6.3	39	0.35	50	220
260	4.4	3.9	5.8	36	0.56	49	235
293	4.8	4.3	4.3	37	1.1	46	256

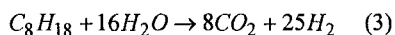
temperature between 450 and 600°C (Birdsell and Willms, 1997b). At 400°C, however, almost no H<sub>2</sub> recovery occurs. Conventional methane steam reforming plants operate at 800°C or higher (Twigg, 1989). The lower operating temperatures required by the PMR should add greatly to the efficiency of systems such as methane-fed PEM fuel cells.

The retentate compositions for the data shown in Figure 2 are given in Table 1. As the inlet rate increases, so does the breakthrough concentrations of H<sub>2</sub>, CH<sub>4</sub>, and H<sub>2</sub>O. The CO concentration decreases and the CO<sub>2</sub> concentration increases with increasing inlet rate. It can be seen from the water gas shift reaction (eq. 2) that, as the H<sub>2</sub>O concentration increases, the CO concentration should decrease.

Methane steam reforming experiments were done with 3 catalysts: Ni/γ-Al<sub>2</sub>O<sub>3</sub> catalyst (United Catalyst C150-8-01), Ni/α-Al<sub>2</sub>O<sub>3</sub> (United Catalyst C11-9-09 EW), and Pt/α-Al<sub>2</sub>O<sub>3</sub> catalyst (Engelhard A-16825). All 3 catalysts were demonstrated to achieve greater than 99% hydrogen recovery, but the Ni catalysts performed slightly better than the Pt catalyst. The Pt catalyst was a thin washcoat on alumina pellets, while the Ni catalysts were homogenous, thus providing more effective catalyst area. Although the data shown in Figure 2 are not in the coking regime, under coking conditions the Ni catalysts were observed to degrade into a fine powder, while the Pt catalyst has undergone many coking/decoking cycles without degradation.

## OCTANE STEAM REFORMING

Octane steam reforming



was used as a surrogate for gasoline steam reforming. The reverse reactions in eqs. (1) and (2) are also important in octane steam reforming. Reactions forming higher hydrocarbons are also possible, but equilibrium modeling with the SOLGAS code indicates that these reactions are not favored at steam reforming conditions. Figure 3 shows results at 600°C and inlet pressure of 0.78 atm. A constant octane injection rate of 3.71 sccm was used in these experiments. The inlet rate was increased by increasing the H<sub>2</sub>O:C<sub>8</sub>H<sub>18</sub>. At the equivalent H<sub>2</sub> inlet rate of 63 sccm, the H<sub>2</sub>O:C<sub>8</sub>H<sub>18</sub> is 8, or ½ of the stoichiometric requirement for complete conversion. At the equivalent H<sub>2</sub> inlet rate of 93 sccm, the H<sub>2</sub>O:C<sub>8</sub>H<sub>18</sub> is 16, which is the stoichiometric requirement for complete conversion. The figure shows that H<sub>2</sub> recovery increases with increasing H<sub>2</sub>O:C<sub>8</sub>H<sub>18</sub>.

Table 2 shows the results for these experiments. The C<sub>8</sub>H<sub>18</sub> concentration in this table is calculated from a carbon balance. As the H<sub>2</sub>O:C<sub>8</sub>H<sub>18</sub> increases, the H<sub>2</sub>, CH<sub>4</sub>, C<sub>8</sub>H<sub>18</sub>, and H<sub>2</sub>O outlet concentrations decrease, resulting in higher H<sub>2</sub> recoveries.

Table 2. Retentate Concentrations for Octane Reforming Experiments.

C <sub>8</sub> H <sub>18</sub> in (sccm)	H <sub>2</sub> O in (sccm)	% H <sub>2</sub>	% CH <sub>4</sub>	% CO	% CO <sub>2</sub>	% H <sub>2</sub> O	% C <sub>8</sub> H <sub>18</sub> (calc.)	Permeate (sccm)
3.71	30	7.3	25.6	20.	35	1.8	10.	40
3.71	40	7.8	14.8	23	44	3.2	7.2	59
3.71	50	10.	10.6	16	54	7.8	2.1	70
3.71	60	2.8	0	1.9	93	12	0.0	88

Coking could be forming at the lower H<sub>2</sub>O:C<sub>8</sub>H<sub>18</sub>, but cannot be quantified because of the absence of C<sub>8</sub>H<sub>18</sub> analysis.

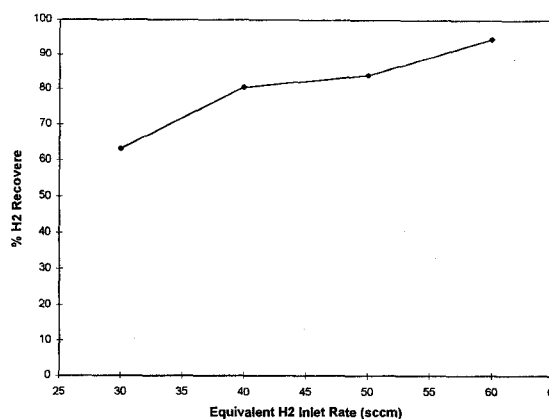
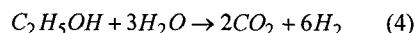


Figure 3. Octane steam reforming results at 600°C and inlet pressure of 0.78 atm. H<sub>2</sub>O:C<sub>8</sub>H<sub>18</sub> ranges from 8 (at an inlet rate of 63 sccm) to 16 (at an inlet rate of 93 sccm). Pt/α-Al<sub>2</sub>O<sub>3</sub> catalyst (Engelhard A-16825).

## ETHANOL STEAM REFORMING

Ethanol steam reforming



experiments were done at H<sub>2</sub>O:C<sub>2</sub>H<sub>5</sub>OH of 2.0, 2.5, and 3.0. Figure 4 shows results at 550°C and 0.78 atm. The H<sub>2</sub> recovery is not significantly different for H<sub>2</sub>O:C<sub>2</sub>H<sub>5</sub>OH=2.0 or 2.5, but increases at H<sub>2</sub>O:C<sub>2</sub>H<sub>5</sub>OH=3.0, which is the stoichiometric requirement for complete conversion. Ethanol steam reforming also involves the reverse of reactions (1) and (2). Similar to methane and octane reforming, the H<sub>2</sub>, CH<sub>4</sub>, and H<sub>2</sub>O concentrations decrease with decreasing inlet rate or increasing H<sub>2</sub>O:C<sub>2</sub>H<sub>5</sub>OH.

A single data point was recorded at H<sub>2</sub>O:C<sub>2</sub>H<sub>5</sub>OH=2.5 and 500°C (not shown on Figure 4). The H<sub>2</sub> recovery was 100% at these conditions (the same as in the 550°C). Conventional ethanol steam reforming is done at 700°C for fuel cell applications (Saini, and Cheng, 1993). Therefore, ethanol reforming, like methanol reforming, can be done at significantly lower temperatures in a PMR than in conventional reactors.

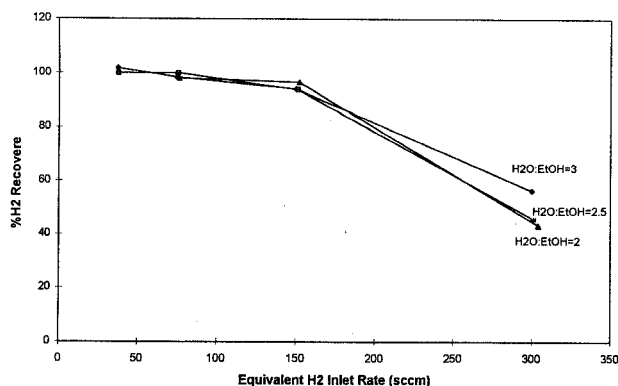
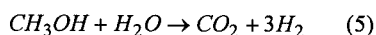


Figure 4. Ethanol steam reforming results at 550°C and inlet pressure of 0.78 atm. Pt/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst (Engelhard A-16825).

### METHANOL STEAM REFORMING

Methanol steam reforming



experiments were done at an inlet H<sub>2</sub>O:CH<sub>3</sub>OH=1.0 and T=300, 325, and 350°C (Figure 5). At 300°C, the H<sub>2</sub> recovery decreases with increasing inlet rate, as is expected. However, at 325 and 350°C, the H<sub>2</sub> recovery goes through a maximum at an equivalent H<sub>2</sub> inlet rate of 120 sccm. This is due to a large percentage of methane forming in the reactor at low inlet rates. At higher temperatures, higher percentages of CH<sub>4</sub> are formed and the H<sub>2</sub> recovery decreases. It is anticipated that reducing the temperature below 300°C will result in even higher H<sub>2</sub> recoveries.

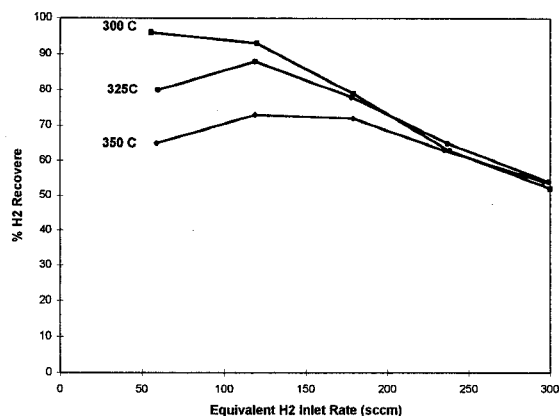


Figure 5. Methanol steam reforming results at 300, 325, and 350°C and inlet pressure of 0.78 atm. H<sub>2</sub>O:CH<sub>3</sub>OH=1.0. United Catalyst C18HC copper/zinc oxide catalyst.

For methanol reforming experiments, the PMR annulus was packed with United Catalyst C18HC copper/zinc oxide catalyst. This is generally marketed as a "low-temperature shift" catalyst and has been determined to be one of the best methanol reforming catalysts (Amphlett et al., 1992).

### DISCUSSION

PMRs have significant advantages in efficiency over other fuel processing systems being investigated for use in fuel cell applications (see Creveling, 1993 for a discussion of a methanol reforming system and Saini and Cheng, 1993 for a discussion of an ethanol reforming system). In conventional steam reforming systems, several reactors such as reformers, shifters and preferential oxidizers are required. These components require heat exchange and water or air injection equipment and control can be difficult. In addition, a 25-100% excess of water is needed to keep CO and hydrocarbon concentrations below levels that are poisonous to the fuel cell. The excess water requirements can drastically reduce system efficiencies. With a PMR system only one reactor is required. The PMR operates at a lower, more efficient temperature than conventional reformers and requires no excess water injection. Also, fuel cells can operate more efficiently on the pure hydrogen generated with a PMR than on reformate. Although membrane reactors hold the promise of more efficient hydrocarbon reforming systems for fuel cell applications, their costs are high. Development of thinner Pd/Ag membranes or alternative, less expensive materials are required.

The Pd/Ag membranes used in these experiments were tubes with a wall thickness of 178  $\mu\text{m}$ . This is far too much Pd to be cost effective in a fuel cell system. Some advances have been made recently in achieving thinner membranes. For example, Peachey, et al. (1996) have developed a membrane that has Pd thickness as small as 0.5  $\mu\text{m}$ . These membranes also have high H<sub>2</sub> fluxes.

A vacuum pumping system capable of evacuation to around 1 torr was used on the permeate stream for these experiments. Pumping to this low pressure would not be practical for a fuel cell system. The pumping system would be too large, expensive, and inefficient. Pumping technology appropriate for use in fuel cell systems needs to be identified. The PMR would then need to be tested to determine performance at the higher permeate pressures. Also, pumping power requirements will have a negative impact on the efficiency of a fuel cell system. Pumps could be powered by electricity or expanders. In order to compare the overall efficiency of a fuel cell system with a PMR to that of a conventional reformer, a detailed system efficiency analysis will be required.

### CONCLUSIONS

A palladium membrane reactor was used to reform octane, ethanol, methanol, and methane into pure hydrogen. Conversions approaching 100% were achieved for each of the hydrocarbons.

The effect of injection rate on hydrogen recovery was measured. It was observed that higher percentages of hydrogen were recovered from the hydrocarbons as the injection rate was decreased. The effect of hydrocarbon-to-water inlet ratio was also measured for octane and ethanol. It was observed that higher percentages of hydrogen were recovered from the hydrocarbons as the hydrocarbon-to-water inlet ratio was increased.

Octane reforming worked well at 600°C. Methane reforming worked well at 450°C, but performance was poor at 400°C. The required temperature for efficient methane reforming in a PMR is much less than the 800°C temperature used in conventional methane reforming applications. Ethanol reforming worked well

at 500 and 550°C. These temperatures compare to temperature requirements for conventional ethanol reforming of 700°C. For methanol reforming, the performance was best at 300°C and decreased as the temperature was increased to 350°C. The decrease in hydrogen production in the permeate was caused by an increase in methane production in the retentate. It is anticipated that performance of the PMR will continue to improve as temperatures are dropped below 300°C.

PMR systems may provide an efficient alternative to conventional reforming systems for hydrogen production in fuel cell applications. However, inexpensive Pd membranes and pumping systems will be needed before PMRs will be cost effective.

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