Effect of Inlet Conditions on the Performance
of a Palladium Membrane Reactor

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Abstract — Palladium membrane reactors (PMR) are used to remove tritium and other hydrogen isotopes from impurities such as tritiated methane and tritiated water. This paper investigates the effect of inlet conditions on the performance of a PMR. A set of experiments were run to determine, independently, the effect of inlet compositions and residence time on performance. Also, the experiments were designed to determine if the injected form of hydrogen (CH_4 or H_2O) effects performance. Results show that the PMR operates at optimal hydrogen recovery with a broad range of inlet compositions and performance is shown to increase with increased residence time. PMR performance is shown to be independent of whether hydrogen is injected in the form of CH_4 or H_2O.

I. INTRODUCTION

A process to recover tritium from simulated fusion fuels and tritiated water has been successfully demonstrated at the Tritium Systems Test Assembly at Los Alamos National Laboratory. The International Thermonuclear Experimental Reactor exhaust will contain tritiated impurities such as water and methane. Tritium will need to be recovered from these impurities for environmental and economic reasons. The PMR is a combined permeator and catalytic reactor. Catalysts are used to foster reactions such as water-gas shift,

$$Q_2O + CO \rightarrow Q_2 + CO_2, \qquad (1)$$

and methane steam reforming,

$$CQ_4 + Q_2O \rightarrow 3Q_2 + CO \qquad (2)$$

where Q represents the hydrogen isotopes H, D, and T. Due to thermodynamic limitations these reactions only proceed to partial completion. Thus, a Pd/Ag membrane, which is exclusively permeable to hydrogen isotopes, is incorporated into the reactor. By maintaining a vacuum on the permeate side of the membrane, product hydrogen isotopes are removed, enabling the reactions to proceed toward completion.

In addition to fusion-fuel processing, the PMR system can be used to recover tritium from tritiated water. A large quantity of tritiated water waste exists worldwide because the predominant method of cleaning up tritiated streams is to oxidize tritium to tritiated water. The tritiated water is then stored on molecular sieve with the ultimate intention of disposal by burial. The PMR provides a means to recover this tritium rather than dispose of it.

In the water-processing application, only HTO and CO are injected into the PMR and it might be expected that only reaction (1) would be of importance. However, near the inlet of the PMR, some CQ_4 is formed by the reverse of reaction (2). Therefore, performance of the PMR system at water-

processing conditions is similar to that of fusion-fuel processing conditions.

Membrane reactors using various membrane materials, catalysts and geometries have been examined for diverse applications since the 1960s. Such applications have been cited previously [1]. None of these applications were in the field of tritium. Also, other processes for recovering tritium from tritiated water have been investigated. Hot metal beds, electrolysis, catalytic exchange, and water-gas shift followed by permeation are discussed in [2]. The PMR has significant advantages in simplicity, reliability, and cost.

Results of our single-stage palladium-membrane reactor have been reported in previous papers. Simulated fusion fuels were processed with a PMR [1], but these early experiments contained no tritium. References [3 and 4] reported on tritium experiments with a single-stage PMR system and [5] reported on tritium experiments with a two-stage PMR system. The experiments were conducted at ITER relevant conditions and were found to have a 1st stage decontamination factor (DF=inlet hydrogen isotopes/retentate hydrogen isotopes) in the 150-400 range for the 1st stage alone and up to 3×10^6 for the 2nd stage alone. Reference [6] reported on a two-stage system for tritiated-water processing. Performance was similar to that of the fusion-fuel processing experiments.

The present study was done to determine the effect of the inlet compositions of methane, water, hydrogen, oxygen, and inerts on the performance of PMR systems. Determination of the effect of inlet composition not only leads to optimal performance of PMR systems, but also leads to the development of control strategies.

II. EXPERIMENTAL APPARATUS

Figure 1 shows a schematic drawing of the PMR. This PMR has a Pd/Ag tube 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. The annular space around the Pd/Ag tube is filled with 297 g of $Pt/\alpha-Al_2O_3$ catalyst (Engelhard A-16825). The PMR is oriented vertically in a tube furnace with the inlet at the top.

Feed gases are injected using Brooks 5850EM mass flow controllers. Outlet flow rates (retentate and permeate) are measured with Brooks 5850EM mass flow meters. Water is injected into the PMR by flowing a mixture of H_2 and O_2 over a Pt catalyst. CO, Ar, and CH_4 are mixed with the H_2O before injection into the PMR. The ~1 mb vacuum on the permeate side is generated by a Normetex PV-12 scroll pump backed by a Metal Bellows 601 pump. The inlet pressure is 590 torr and pressure drop between the inlet and retentate is
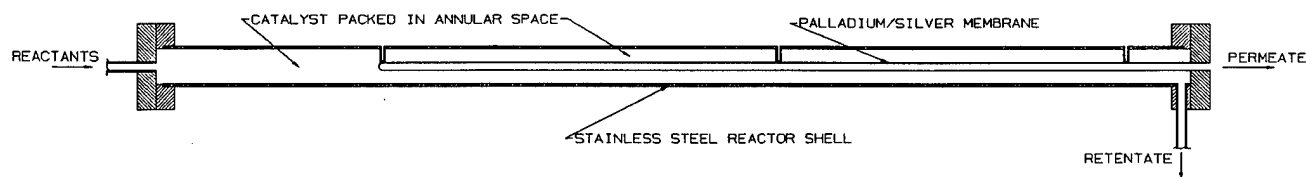
Fig. 1. Schematic of PMR.

negligible. The reactor temperature was held at 525°C for the data shown in this paper. An MTI model M200 gas chromatograph is used to measure the outlet stream (retentate) of the PMR. The GC has a sensitivity of approximately 0.01% for CH_4 and H_2 and can measure CO and CO_2 in the 1-100% range. An Endress and Hauser model 2850 humidity probe is used to measure the H_2O concentration at the outlet. The probe was calibrated from -80°C to 20°C dew point and has an accuracy of ±1°C dew point.

III. CARBON-TO-OXYGEN RATIO

Reactions (1) and (2) show that only 3 species are of interest in this work. Of these 3, only C and O remain at the outlet of the reactor since essentially all of the hydrogen isotopes are removed by permeation. Therefore, performance of the reactor, at a given inlet rate, can be determined by a single parameter: the carbon-to-oxygen ratio (C:O).

Fig. 2 shows decontamination factor versus C:O for a series of water-processing experiments. DF is large and independent of C:O at the lowest inlet rate. As the inlet rate increases, an optimum DF occurs in the range of 0.52 < C:O < 0.56 and good performance is obtained for a considerably larger range. If C:O < 0.52, not enough carbon is available to bond with the available oxygen and H_2O will exit the reactor in increased concentrations causing decreased performance (Fig. 3).
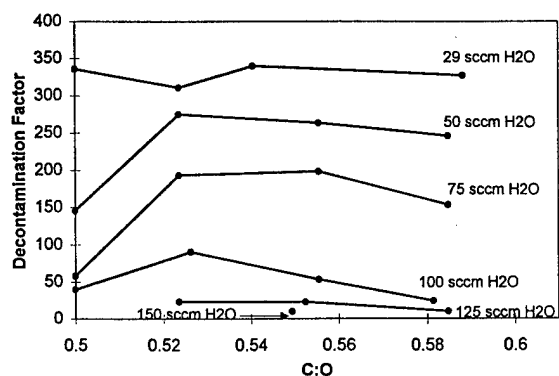

Fig. 2. DF v. C:O for water-processing experiments. These experiments are discussed in detail in [6].

If C:O > 0.56, two effects combine to cause decreased performance. At these higher C:O ratios, too much C is available and H combines with it to form higher concentrations of CH_4 at the outlet of the reactor (Fig. 4). In addition, since only CO and H_2O are injected, to increase the

C:O the CO injection fraction has to be increased significantly which decreases the residence time in the reactor. This decreased residence time also causes decreased performance.
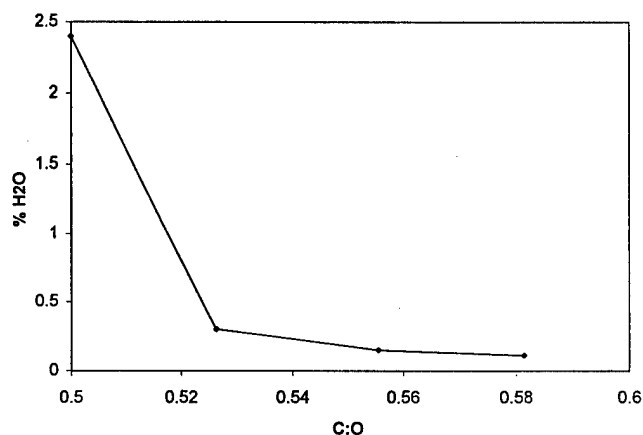

Fig. 3. Outlet H_2O concentration for the 100 sccm H_2O case of Fig. 2.

A set of experiments were designed to determine the independent effects of C:O and residence time on DF. Also, the experiments were designed to determine if the injected form of hydrogen (CH_4 or H_2O) effects PMR performance. Total hydrogen injection (in the form of CH_4 or H_2O) was held constant at an equivalent rate of 75 std. cm^3/min (sccm) H_2 so that hydrogen permeation effects were approximately equivalent for each experiment. C:O could be varied at a constant residence time by injecting a mixture of CO, O_2, Ar, H_2O, and CH_4. The percentage of injected H injected in the form of CH_4 ranged from 0-100%.
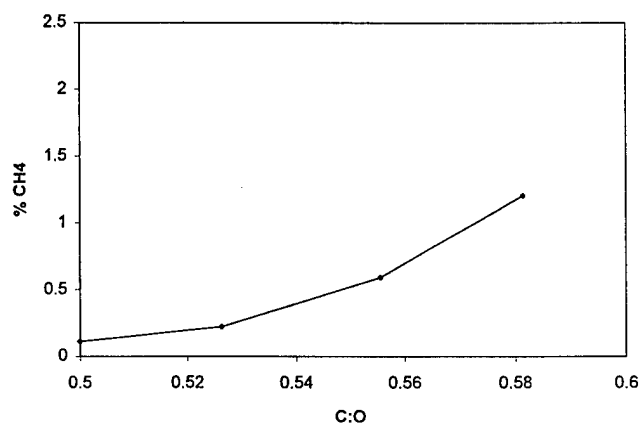

Fig. 4. Outlet CH_4 concentration for the 100 sccm H_2O case of Fig. 2.

Fig. 5 shows the results of these experiments. The flow rates shown on the figure are the averages of the inlet and outlet rates. The compositions shown on the figure are the percentages of total hydrogen injected that was injected as CH_4 (the balance was injected as H_2O). The chart shows that DF increases as residence time increases (i.e., inlet rate decreases). Comparison of the point at 0% CH_4 and 126 sccm to the curve of 40% CH_4 and 127.5 sccm, which have approximately equivalent inlet rates, shows that the PMR performs the same whether hydrogen is injected in the form of CH_4 or as H_2O. Only one point is shown for the 0% CH_4 case because this is water processing and, thus, the C:O and residence time effects cannot be separated.
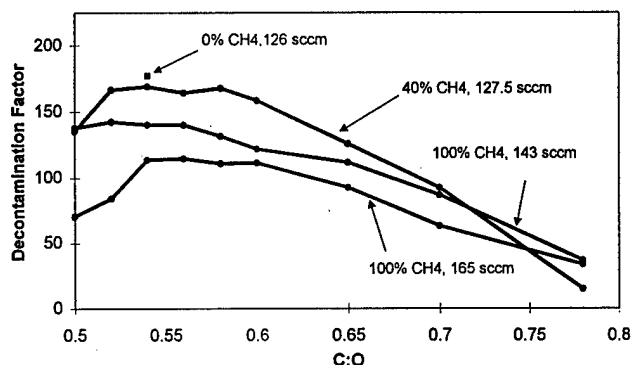

Fig. 5. DF v. C:O for experiments designed to separate the effects of C:O, residence time, and inlet form of hydrogen (i.e., CH_4 or H_2O). Equivalent H_2 injection is 75 sccm for all cases.

The optimum C:O is in the 0.52 < C:O < 0.60 range and good performance is obtained for a considerably larger range. This is a larger optimal range than the water processing case because the effect of decreased residence time with increased C:O occurs in water processing. From the perspective of PMR operation and control, this is a wide optimum since C:O ratio can be measured to an accuracy of ±0.002 using common gas chromatography and can be mixed to within ±0.005 using common mass flow controllers. Performance decreases as the C:O decreases below 0.52 or increases above 0.60 for the same reasons as in water processing. That is, H_2O breakthrough occurs at low C:O (Fig. 3) and CH_4 breakthrough occurs at high C:O (Fig. 4).

IV. CONCLUSIONS

A set of PMR experiments were run to determine, independently, the effects of carbon-to-oxygen ratio (C:O) and residence time on decontamination factor. Also, the experiments were designed to determine if the injected form of hydrogen (CH_4 or H_2O) effects performance. C:O could be varied at a constant residence time by injecting a mixture of CO, O_2, Ar, H_2O, and CH_4. The percentage of injected H injected in the form of CH_4 ranged from 0-100%. Conclusions from these experiments are as follows:

- The optimum C:O is in the 0.52 < C:O < 0.60 range and good performance is obtained for a considerably larger range. Performance decreases for the same reasons as in water processing. That is, H_2O breakthrough occurs at low C:O and CH_4 breakthrough occurs at high C:O. This

is a wide optimum from the perspective of PMR operation and control.

- Performance increases as the residence time in the PMR increases.

- PMR performance is independent of whether hydrogen is injected in the form of CH_4 or H_2O.

- During water processing (i.e., no CH_4 injection), increasing the C:O causes an increase in residence time. This combined effect limits the optimum C:O to 0.52 < C:O < 0.56.

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