

# METHANOL STEAM REFORMING & AMMONIA DECOMPOSITION IN PD-BASED MEMBRANE REACTORS: EXPERIMENTS & MODELING

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## Summary

Modular, single-step Pd membrane reactor technology is evaluated for generating high purity hydrogen from common feedstocks. A combination of bench-scale reactor experiments and modeling of methanol steam reforming and ammonia decomposition are carried out to assess reactor performance. The first part studies the inhibition of H<sub>2</sub> permeabilities of Pd-based nanopore membranes by reactant and product species. The second part involves performance studies of a single-fiber Pd membrane. Parameters obtained from the two parts are used to develop a 3-D model to simulate multi-fiber membrane reactors in order to understand the effect of various design parameters on hydrogen productivities and recoveries.

## Keywords

Membrane reactors; Hydrogen production; Process intensification

## Introduction

Hydrogen permselective membrane reactors couple reaction and separation to generate high purity hydrogen. In so doing, these intensify the process and achieve a higher reactant conversion if the reaction is equilibrium limited or kinetically inhibited due to the presence of hydrogen [1].

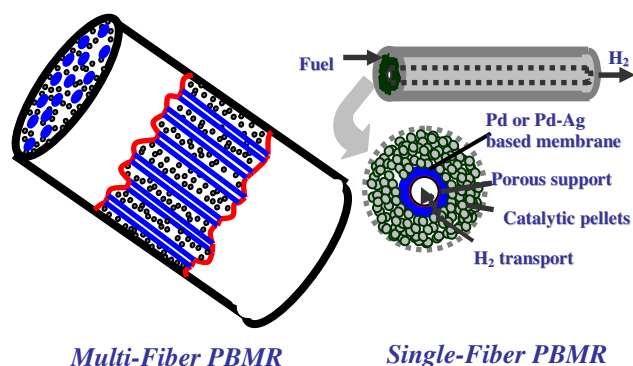


Figure 1- The membrane fuel processor involves feed of fuel to catalytic zone with hydrogen removal at atmospheric pressure for direct feed into fuel cell.

In the current study methanol steam reforming (MSR),  
 $\text{CH}_3\text{OH} + \text{H}_2\text{O} \leftrightarrow 3\text{H}_2 + \text{CO}_2$   $\Delta H = +49.4$  kJ/mol  
 $\text{CH}_3\text{OH} \leftrightarrow 2\text{H}_2 + \text{CO}$   $\Delta H = +90.5$  kJ/mol  
 $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{H}_2 + \text{CO}_2$   $\Delta H = -41.1$  kJ/mol  
and ammonia decomposition (AD),  
 $\text{NH}_3 \leftrightarrow 0.5 \text{N}_2 + 1.5 \text{H}_2$   $\Delta H = +46.2$  kJ/mol  
were evaluated in both packed bed reactors (PBRs) and packed bed membrane reactors (PBMRs).

## Effect of reactant and product species on permeability

The reactants and products of the AD reaction do not affect the permeability of palladium membranes [2]. But the various reactants and products of the MSR reaction (CH<sub>3</sub>OH, H<sub>2</sub>O, CO<sub>2</sub> and CO) can reduce the H<sub>2</sub> flux through the membrane. It is essential to quantify and understand the effect of these species on membrane permeability. A 3.4 micron Pd-Ag (23 wt% Ag) nanopore [3] membrane was used in a single fiber membrane separator apparatus. Initially pure H<sub>2</sub> was introduced into the shell side of the separator containing the Pd-Ag membrane and the flux through the membrane was measured at temperatures between 225 & 300 °C and at retentate pressures of 3 and 5 bars. Various concentrations of CH<sub>3</sub>OH, H<sub>2</sub>O, CO<sub>2</sub> and CO were introduced along with the H<sub>2</sub> and the resulting decrease in H<sub>2</sub> flux was measured. The three main causes for this decrease are lowering of the retentate side H<sub>2</sub> partial pressure, concentration polarization, and surface coverage effects (i.e. decrease in the surface area of the membrane). Langmuir type adsorption treatment was used to account for site blocking on the Pd-Ag membrane and was incorporated into a 2-dimensional reactor model. This model along with the experimental results (Figure 2) was used to estimate the coefficients of adsorption of the various gases on the membrane surface. These coefficients were then verified using independent experimental data.

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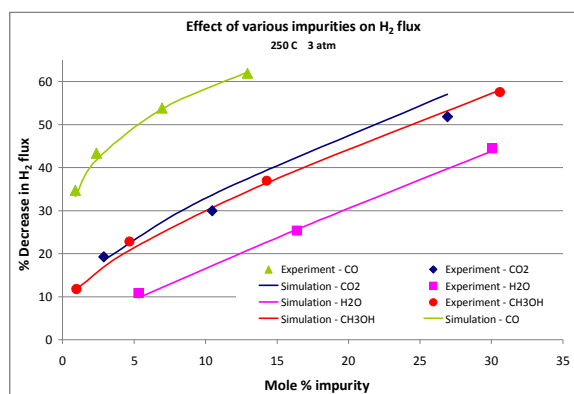


Figure 2 – Effect of various methanol reforming species on the permeate  $H_2$  flux at 250 °C, 3 bars.

## Single-fiber PBMR studies

In the second part of the study a comparison of AD [4] and MSR in PBRs versus in single-fiber PBMRs were carried out. The reactor diameter and catalyst loading of the PBMRs were varied in order to identify the rate determining step during the generation and purification of  $H_2$ .  $Cu/ZnO/Al_2O_3$  catalyst was used for MSR and  $Ni/Al_2O_3$  catalyst was used for AD. A 3.4 micron Pd-Ag nanopore (23 wt % Ag) and a 4 micron Pd nanopore membrane were utilized for the MSR and AD studies respectively. The conversion, hydrogen productivity, hydrogen utilization and outlet  $CO/CO_2$  ratio (for MSR) for the PBR and the PBMRs were compared at different pressures (3-5 bars) and temperatures (225-300 °C for MSR and 400-600 °C for AD). A 2-dimensional model was developed to simulate the results and to elucidate the rate limiting processes.

For the MSR reaction the results of the previous model (to determine effects of reactant and product species on membrane permeability) was incorporated in the PBMR model. It was determined that the rate limiting step in the MSR case is the permeability of the membrane whereas for AD it is the radial diffusion of  $H_2$ . For both reaction systems very good prediction of the component concentrations as a function of space velocity were obtained (Figure 3).

## Multi-fiber PBMR studies

The parameters obtained from the first two parts of this study were used to develop a 3-D model in order to simulate large scale multi-fiber PBMRs for design and scale-up. The effect of design parameters such as reactor diameter, reactor length, number of membrane fibers, the spacing between the fibers etc. on hydrogen productivity and recovery was investigated. An autothermal MSR reactor was also simulated using previously obtained results [5]. This was done by converting some of the Pd-Ag membranes into  $O_2$  inlet fibers. Figure 4 shows an example of the  $H_2$  distribution along the cross-section of a multi-fiber PBMR. The 3-D model is being used to optimize the number and location of the membrane tubes.

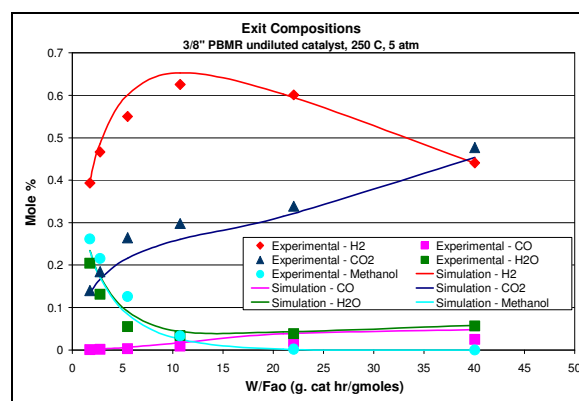


Figure 3 – Comparison of experimental and theoretical exit retentate compositions for a single-fiber 3/8" OD PBMR (MSR reaction; 250 °C; 3 bars)

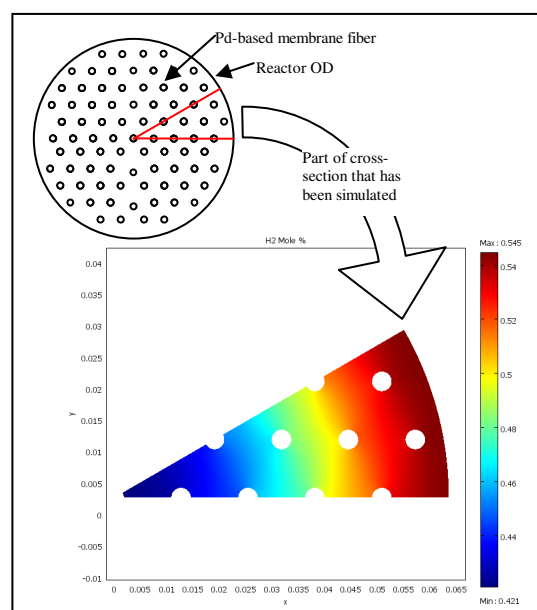


Figure 4 –  $H_2$  mole fraction at the cross-section of a multi-fiber PBMR (MSR reaction; 5" reactor ID; 3.7mm membrane OD; 0.5" triangular pitch; 250 °C; 3 bars)

## References

- (1) Paglieri, S.N., and Way, J.D., *Sep. Purif. Meth.*, 2002, 31, 1.
- (2) Sakaomoto, F., Kinari, Y., Chen, F.L., and Sakamoto, Y., *Int. J. Hydrogen Energy*, 1997, 22, 369.
- (3) Nair, B., and Harold, M.P., *J. Membrane Sci.*, 2007, 290, 182.
- (4) Israni, S.H., Nair, B.R., and Harold, M.P., *Catalysis Today*, 2009, 139, 299.
- (5) Lattner, J.R., and Harold M.P., *Catalysis Today*, 2007, 120, 78.