Steam Reforming of Ethanol at Elevated Pressures for Distributed Hydrogen Production

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Introduction Ethanol is an attractive renewable fuel because, as a liquid fuel, it has a high energy density, it is easy to transport, and it is environmentally more benign that petroleum-derived fuels. The hydrogen produced by reforming needs to be purified and compressed to the appropriate storage and dispensing pressures. Compressing hydrogen is energy intensive and can consume a significant fraction of the fuel's heating value. A promising option for producing hydrogen from ethanol is by conducting the ethanol steam reforming reaction at an elevated pressure, since injecting liquid feeds (ethanol and water) into a pressurized reactor requires very little energy. Also, producing hydrogen at elevated pressure offers flexibility in choosing an appropriate hydrogen purification/separation technology. Pressurized reforming is not without its challenges, however. Thermodynamic equilibrium calculations predict that reforming at elevated pressures will lead to a lower hydrogen and higher methane yield. Furthermore, pressurized operations favor the deposition of coke or carbonaceous products, leading to catalyst deactivation. These challenges may be overcome through a combination of preferred catalysts, higher temperatures and S/C molar ratios, and hydrogen separating membranes, etc. The objective of this work is to examine these options for the pressurized steam reforming of hydrated ethanol for distributed hydrogen production.

In past work, we have studied the effects of operating parameters, such as, temperature, steam-to-carbon (S/C) molar ratio, gas hourly space velocity (GHSV), and pressure, on the ethanol conversion and product gas yield of the catalytic steam reforming of ethanol in a laboratory-scale micro-reactor testing facility. Results of that work were presented at the 2006 Fuel Cell seminar. Our experimental work has now been extended to include the use a Pd membrane reactor to study the membrane's ability to improve the reaction kinetics and hydrogen yields. A membrane reactor has been designed and installed to allow the study of high-pressure ethanol steam reforming with and without hydrogen membrane separation concurrently. We are developing a mathematical model to define the important parameters for the performance of the membrane reactor for ethanol steam reforming. Initial data on hydrogen flux, combined with a thermodynamic model for the reaction kinetics, will provide an upper bound of the reactor performance and serve to explore limitations for the process and define preliminary optimal conditions.

Membrane Reactor Test Facility Figure 1 shows the schematic of the membrane reactor test facility used in this study. The ethanol-water solution is filtered and pumped to a vaporizer, along with a small amount of N_2 as an internal standard for product gas analysis. The vaporized mixture of ethanol and steam is fed into the membrane reactor that is heated by a clam-shell furnace. The reformate product gas from the membrane reactor flows through a cooler, a multiport valve, and a back-pressure regulator. The gaseous product is then analyzed by a micro-gas chromatograph. The pure hydrogen gas exiting from the membrane tube of the membrane reactor flows to a 3-way valve that allows for a batch sampling or directing to a mass flowmeter for measuring H_2 flow rates.

The membrane reactor, as shown in Fig. 2, is a 12.7-mm-ID x 25.4-mm-OD (0.5-in. ID x 1-in. OD) Hayne 230 high-temperature alloy; it is designed for the operation conditions up to 800^{o}C and 1500 psig. The membrane tube assembly (Fig. 3) consists of a catalyst basket and a membrane tube that is 3.175-mm OD (1/8-in. OD) stainless tube attached with a 25.4-mm long (1-in. long) membrane section. Powered catalyst, 150 -250 μm size, surrounds the membrane to a height to 35 mm and is packed between the membrane tube and the catalyst basket. At the end of the catalyst bed, a thin layer of alumina-silica paper is installed to hold up the catalyst bed and to prevent the reformate flow paths from being plugged up by the catalyst.

Characterization of Pd Membrane Tube with High-Purity Hydrogen The Pd-alloy membrane tube was purchased from REB Research & Consulting, MI. The membrane tube has 30-µm-thick Pd-alloy film supported on a 43-µm-thick support layer and is designed for test conditions up to 700°C and 1500 psig. The membrane tube assemblv was first installed with 0.45-g 4% Rh/La-Al_2O_3 catalyst (150 – 250 microns), the same catalyst used in our earlier ethanol reforming studies in the micro-reactor testing facility, and then tested with N_2 at 650°C and 1000 psig, the test conditions to be carried out for the ethanol reforming study. This test showed no N_2 flow in permeate, indicating that the Pd membrane is free of pinholes.

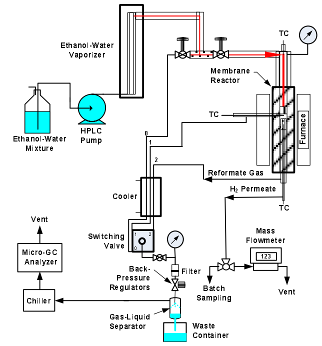

Fig. 1. Schematic of membrane reactor test facility

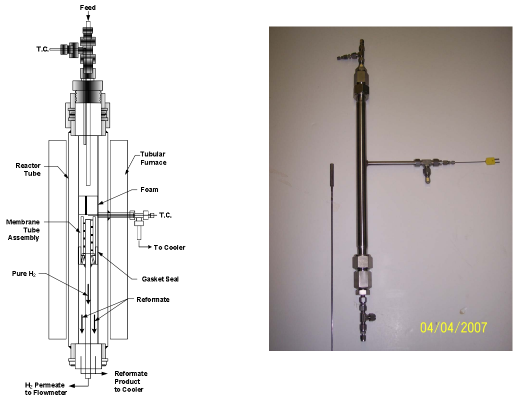

Fig. 2. Membrane reactor

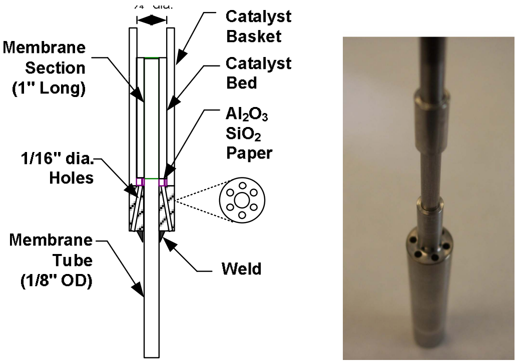

Fig. 3. Membrane tube assembly

To obtain the hydrogen separation flux characteristic of the Pd membrane tube, we also conducted a series of tests of the Pd membrane with 99.999% H_2 as functions of temperature varying from 250° to 650°C and pressure from 50 to 300 psig (the maximum hydrogen partial pressure expected in the catalytic reforming of the ethanol). The permeate side was maintained at ambient pressure. Fig. 4 shows the plots for the hydrogen flux functions of hydrogen pressure and temperature.

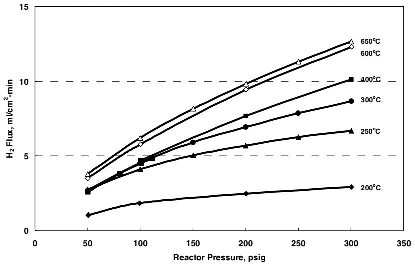

Fig. 4. H_2 flux as functions of pressure and temperature (Downstream pressure of the reactor = 0 psig)

These hydrogen flux data were then fitted with the Sievert and Arrhenius laws:

$$J = k\,[(P_{H2,hi})^{½} - (P_{H2,lo})^{½}\,] \qquad (1)$$

$$k = A_o\, e^{(-E/RT)} \qquad (2)$$

where J is the hydrogen transport rate (or flux), K is the rate constant, A_o is the frequency factor, and E is the apparent activation energy for rate of hydrogen transport through the Pd membrane. Figs. 5 and 6 show the Sievert plots and the Arrhenius plot, respectively.

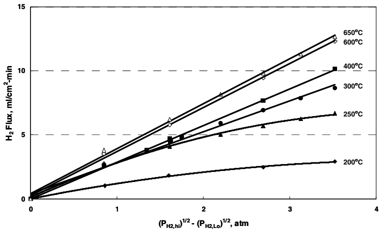

Fig. 5. Sievert plots

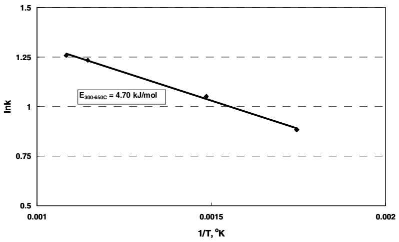

Fig. 6. Arrhenius plot

These plots clearly indicate that the hydrogen transport of the Pd-alloy membrane follows both Sievert and Arrhenius laws for the temperature region from 300° to 650°C, and the apparent activation energy for this region is calculated to be 4.70 kJ/mol. This activation energy is somewhat lower than those reported in the literature (12.5 - 48.5 kJ/mol for Pd/Ag type of membranes) [1]. The hydrogen permeation through a metal membrane is believed to follow 5-step gas transport mechanism [2]: 1) sorption of hydrogen molecules on the metal surface, 2) dissociation of hydrogen molecules into hydrogen atoms on the metal surface, 3) each hydrogen atom loses its election to the metal lattice and diffuses through the lattice as an ion, 4) Re-association of hydrogen atoms emerging at the permeate side of the membrane to form hydrogen molecules, and 5) desorption of hydrogen molecules from the metal surface to complete the permeation process. It has been reported [2] that at temperatures above 300°C, the surface sorption and dissociation of hydrogen molecules are fast and the hydrogen permeation rate is controlled by the diffusion of atomic hydrogen through metal lattice. Figs. 5 and 6 indicate that this rate can be characterized by both Sievert law (Eq. 1) and Arrhenius law (Eq. 2). At temperatures below 300°C, the sorption and dissociation of hydrogen molecules on the membrane surface control the transport mechanism, and the permeation characteristics of the membrane deviate from Sievert law, as shown in Fig. 5.

Mathematical Model A mathematical model of the membrane reactor is being developed to evaluate the beneficial effect of hydrogen extraction through membrane in the ethanol steam reforming reactor. The model was exercised to define the ideal case scenario, or upper bound limitation of the membrane reactor performance based on the membrane's permeation data obtained above (Fig. 4) and the assumptions of very fast reforming kinetics and no mass-transfer limitations in the reactor. Fig. 7 shows the hydrogen yields as a function of reactor volume for the reactor operated at 68 atm, 650°C and GHSV of 15,000 h^{-1} using a feed of ethanol/water mixture of S/C molar ratio of 6. The use of fast kinetics is reflected in the hydrogen yield of ~2.5 mol/(mol of ethanol) in the reffinate at the very near reactor inlet. The rest of the reactor essentially serves to permeate the hydrogen, which in turn leads to additional hydrogen production via methane reforming and water-gas shift reaction. For the permeation rates corresponding to current data (Jo) and under the conditions specified, 1.6 mols of hydrogen permeate across while ~ 2 mols leave with the reformate in the raffinate stream. A membrane with 5 times higher permeation rate would lead to the recovery of 5.5 mols of high purity hydrogen, from a theoretical maximum achievable of 6 mols per mol of ethanol ($C_2H_5OH + 3\ H_2O = 2\ CO_2 + 6\ H_2$).

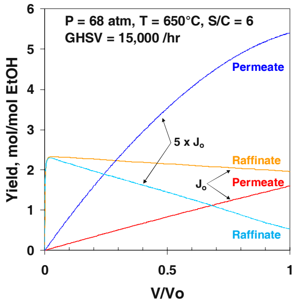

Fig. 7. Hydrogen yield as a function of reactor volume. Jo represents the flux based on the experimental data in Fig. 4. The curves for

Initial Test of Ethanol Steam Reforming An ethanol steam reforming test was conducted in the membrane reactor at 650°C, 68 atm (1000 psig), and GHSV = 14,700 h^{-1} using a feed of S/C = 6. The test was carried out both with and without membrane permeation as shown in the product yield plots of Fig. 8. The product yields agree with the equilibrium prediction, as shown in Table 1. Table 1 also clearly shows that in the hydrogen permeation mode, a higher total hydrogen yield was obtained, along with a higher COx selectivity, which is defined as the sum of CO and CO_2 yields as a percentage of total carbon in the feed, than reforming mode without permeation. These data indicate that the recovery of hydrogen through the membrane reactor provides an additional potential force for driving the reforming reaction toward right as predicted by the Principle of Le Chatelier. Under the test conditions, the permeated hydrogen yield was measured to be 0.28 mol (Fig. 8), which is significantly lower than the 1.6 mols as predicted by the model shown in Fig. 7. More studies are needed to understand this discrepancy.

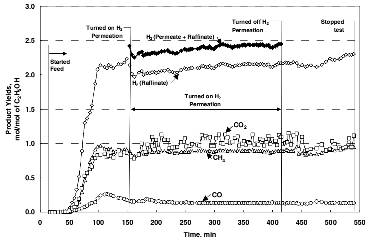

Fig. 8. Product yield over time for wt%Rh/ La-Al_2O_3 catalyst. Test conditions: S/C = 6, 650°C, 68 atm, and

Table 1. Comparison of experimental product yields with equilibrium

Catalyst Bed Temp., °C		650	650	650
Pressure, psig		1000	1000	1000
S/C Molar Ratio		6	6	6
GHSV, h^{-1}		14,700	14,700	15,000
		Exp. Test		Equilibrium
H_2 Permeation		No	Yes	No
Product Yields, mol/mol of EtOH				
	H_2	2.21	2.39	2.35
	CO	0.13	0.14	0.10
	CH_4	0.90	0.88	0.87
	CO_2	0.96	1.02	1.00
Carbon Conv., % (Based on C to gas)		101	103	
COx Selectivity, % [($CO + CO_2$)/C in C_2H_5OH]		55	58	

References

1. A. Basile, F. Gallucci, and L. Paturzo, "A Dense Pd/Ag Membrane Reactor for Methanol Steam Reforming: Experimental Study," Catalysis Today, 104 (2005) 244-250
2. R. W. Baker, Membrane Technology and Applications, McGraw-Hill, pp. 297-298 (2000)

Acknowledgement

This work was supported by the U.S. Department of Energy's Hydrogen, Fuel Cells, and Infrastructure Technologies Program. Argonne National Laboratory is operated for the U. S. Department of Energy by UChicago Argonne, LLC, under contract DE-AC-02-06CH11357.