Power+Energy™
Fueling the Hydrogen Economy

Abstract

- Good agreement between measured H_2 separation efficiency and theoretical model calculations for a very compact palladium alloy micro-channel membrane separator/reactor.
- Close to 100% WGS conversion capability demonstrated for micro-channel catalytic membrane reactor.
- Technology extendable to lower cost / higher power densities enabling widespread, point of use hydrogen generation from carbon based fuels including renewables.

Context, State of the Art

- "In order to realize the vision of extraction of hydrogen from fossil fuels, more efficient gas separation methods are needed that are better integrated with the gasification infrastructure. Membrane separation would be ideal, if materials can be found to survive and function in the fossil fuel gasification environment."
- "The best possible solution to the separation issue would be a *membrane reactor*. An appropriately designed reactor could combine the shift and separation steps into one, realizing a significant leap forward in efficiency and lowered cost of hydrogen produced."
- "However, because of its multiple functions, a membrane reactor must be able to tolerate more divergent conditions than a membrane that only has to separate hydrogen and carbon dioxide that has already been pre-cleaned to a given specification."

Citations from Oct. 13, 05 NETL/DOE study: Kurt S. Rothenberger et al., Palladium-copper Alloy Membrane Performance under Continuous H_2S Exposure, ref. 1.

Introduction

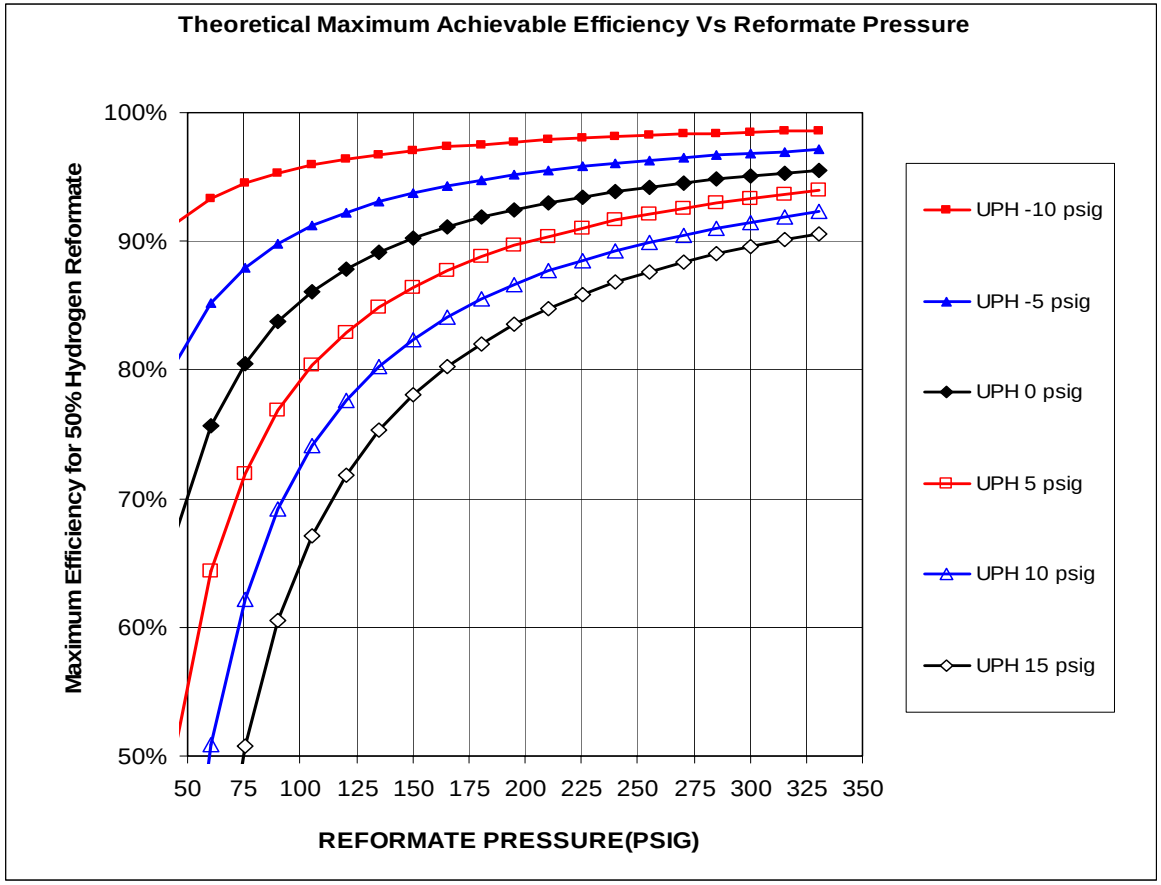
- Palladium alloy membranes effectively separate H_2 from reformate gas delivering consistently high purity H_2 streams free of fuel cell catalyst poisons. Compared to pressure-swing absorption separation, Pd membranes are much more compact and require minimal maintenance.
- A membrane reactor integrates reformer, WGS and separator components resulting in a significantly less complex and highly efficient single stage hydrocarbon fuel processing system. Such a system is capable of accepting a wide range of hydrocarbon and alcohol based fuels, including renewables, with only the water to carbon ratio to adjust.
- Power and Energy, a major supplier of hydrogen purifiers for the compound semiconductor industry, has developed a next generation of thin palladium membranes and the corresponding separator/reactor modules.

Separator Theory

- The mechanism for hydrogen transport through a heated palladium membrane consists of H_2 dissociating into atomic hydrogen at the wall of a heated palladium membrane. The resulting hydrogen atoms travel through the membrane and recombine into molecular hydrogen at the outlet wall. Since this transport is only possible for hydrogen (not for any other gases) makes a palladium membrane highly suitable for producing ultra pure hydrogen.

- The input of a purifier consists of a flow of contaminated H_2 that basically dead ends against the membrane wall while a relatively small bleed stream removes the contamination. The partial H_2 pressure in a purifier can be treated as basically constant. In contrast, a separator processes a reformate stream with high concentrations of other gaseous species. The partial pressure H_2 of changes significantly as the reformate passes along the membrane.

- The mathematical equations describing a membrane separator are somewhat similar to those describing a counter-current heat exchanger. One difference is that the flux through the membrane is proportional to the difference between the partial pressure of H_2 to a power p (typically close to 0.5) upstream and downstream of the membrane. Another difference is that radial diffusion of H_2 through the non-H_2 components in the reformate impedes the obtainable efficiency of the separator. The developed mathematical numerical model calculates separator performance as efficiency and purified H_2 flow rate based on input design geometry parameters, physical properties and operating conditions. The model links a delivered wattage to a membrane area and thickness enabling the calculation of the physical size and shape of an actual device.



Theoretical maximum achievable efficiency values for various pressure combinations of the upstream and downstream pressure of the separator membrane, in absence of any radial diffusion effects. The used analytical expression takes the “compression” of the matrix gas into account as H_2 is removed while the reformate travels along the membrane.

Fuel Processing Theory

- Steam reforming (SR) is favored over ATR and POX when using a pressure-driven H_2 separation method, see reference 2.
- The SR reactor, the WGS reactor and the separator can be integrated into a single membrane reactor. A single membrane reactor allows running a combination of processes to completion, while operating at conditions not necessarily favorable for any of the individual processes. The operating conditions can now be based on other considerations such as a high power density.
- The numerous advantages of membrane reactor based H_2 generation, for a wide range of carbon-based fuels, are pointed out in numerous articles, see ref. 3-6. Advantages include higher efficiency, reduced part count, simplicity and possible optimization for minimal catalyst use. Killmeyer in reference 8 looked into a high temperature, pressure membrane reactor operating without WGS catalyst.

In absence of suitable membranes, however, applications for membrane reactors in fuel reforming remain very limited. P&E has such membrane and has published some of its earlier work on its use in a membrane reactor for the WGS reaction, ref. 7.

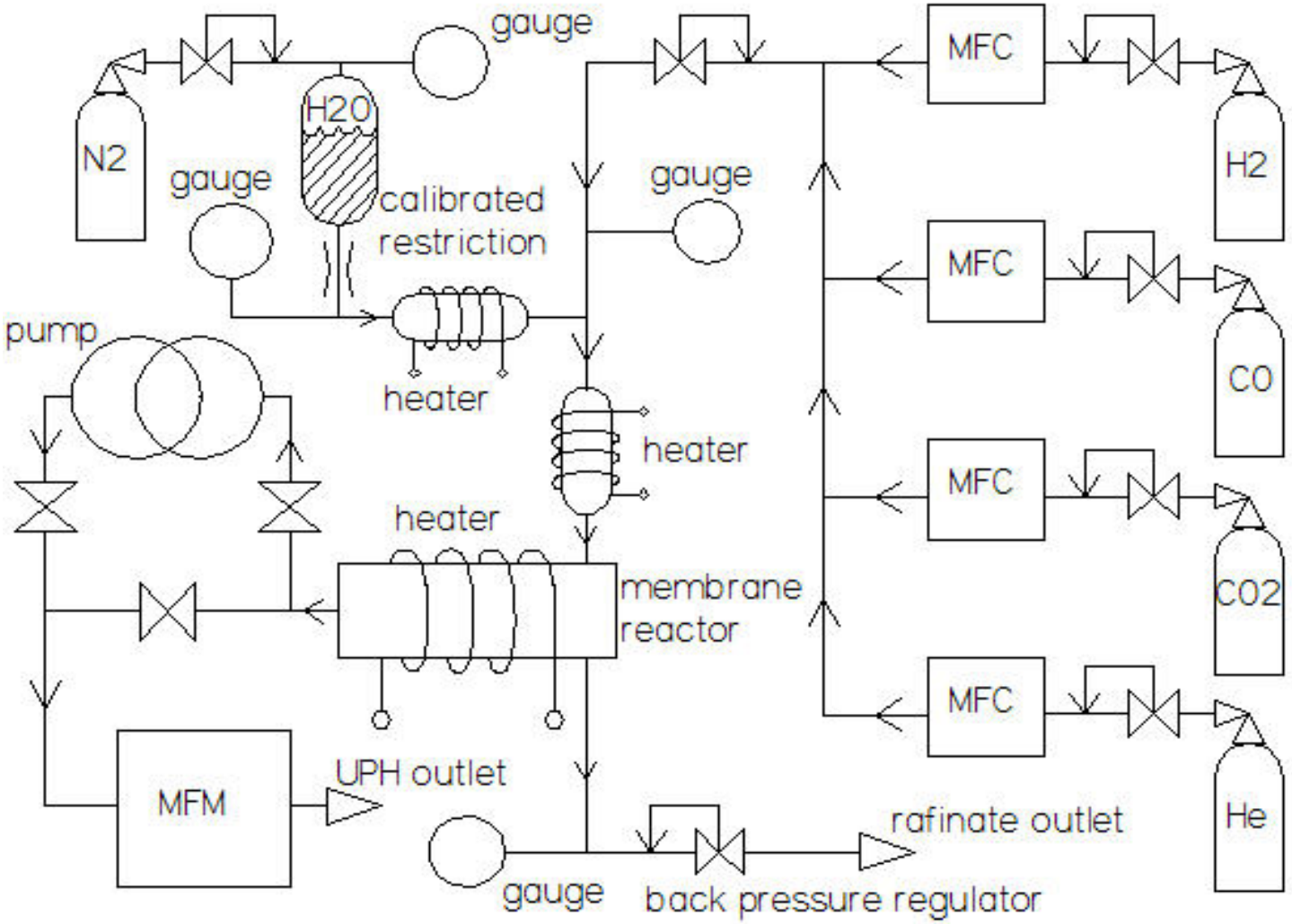
Chemistry

$$\mathbf{C_nH_m} + n\mathbf{H_2O} \leftrightarrow n\mathbf{CO} + (n+m/2)\mathbf{H_2}$$

$$\mathbf{CO} + \mathbf{H_2O} \leftrightarrow \mathbf{CO_2} + \mathbf{H_2}$$

Excess water and selective H_2 removal shift both reactions toward generating more H_2

Experimental Setup



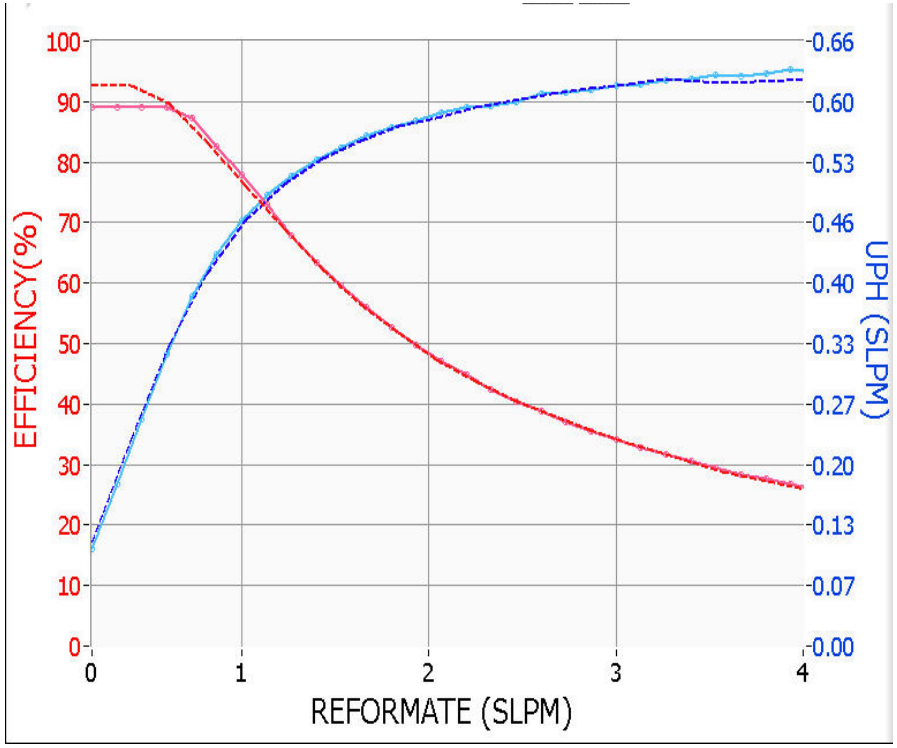
Experimental Setup

- Synthesized reformate mixture is created by blending up to four streams of gas (H_2, carbon monoxide, carbon dioxide and helium or argon) using a high precision mass flow controller (MFC). MFC specification: one percent of reading accuracy from 20% to 100% full-scale and 0.2% of full scale below 20% of full-scale settings. The separated ultra-pure H_2 stream was also measured by a mass flow meter.

- Pressures were measured with transducers with a 250 psia range and 0-5V output. All pressure sensors were calibrated against a NIST-traceable precision gauge with 0-300 psia range and a 1 psi sub-divided scale.

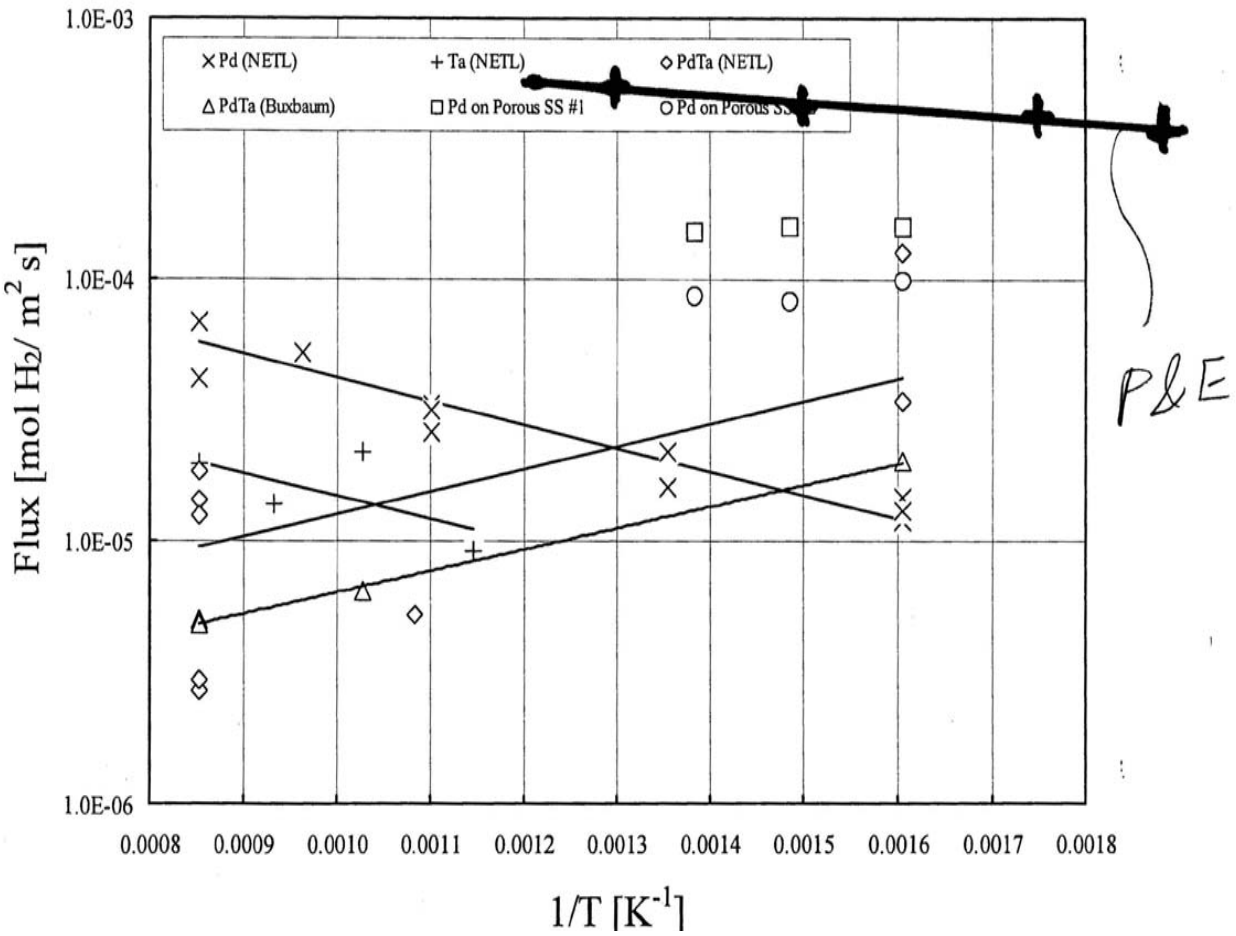
- Steam was added to the mixture through a calibrated capillary by creating a pressure difference over a vessel containing liquid water. The separator/reactor and preheat coil were heated with band heaters controlled by thermocouples and P&E proprietary control electronics.

Measured data (solid lines) and computer model calculation (dashed lines)



Measured efficiencies for a 60% hydrogen mixture, plotted with computer model calculated efficiency (red lines) versus total reformate flow rate, where the efficiency is based on the ratio of generated ultra pure H2, UPH, flow rate (blue lines) and the hydrogen flow rate in the reformate.

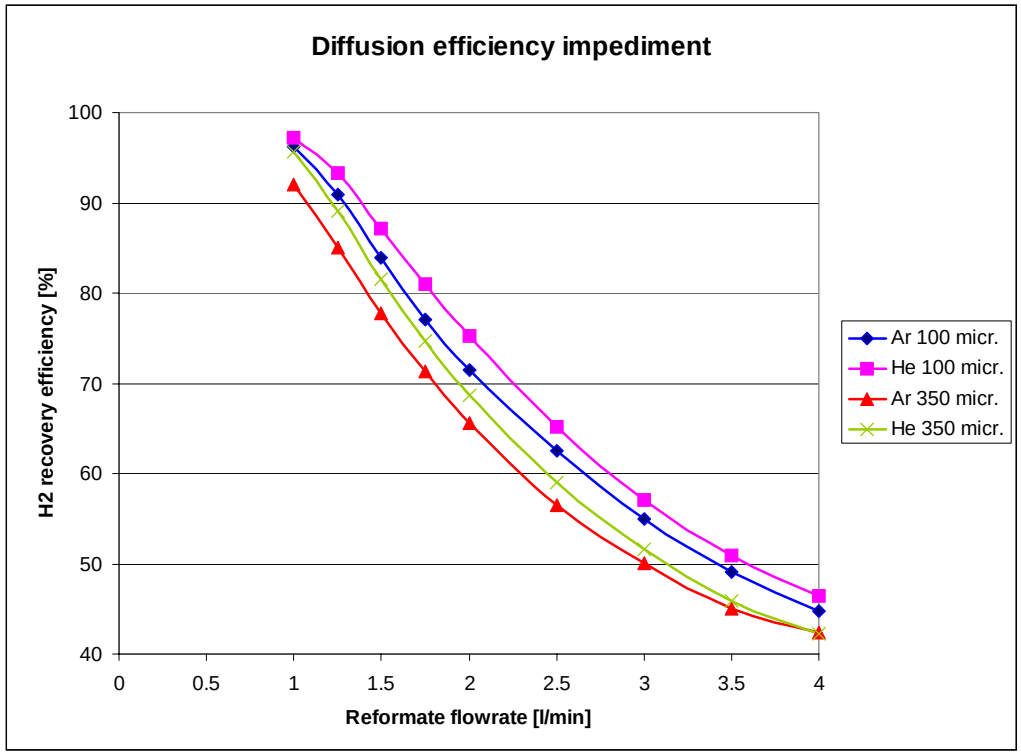
Results: membrane flux comparison



P&E

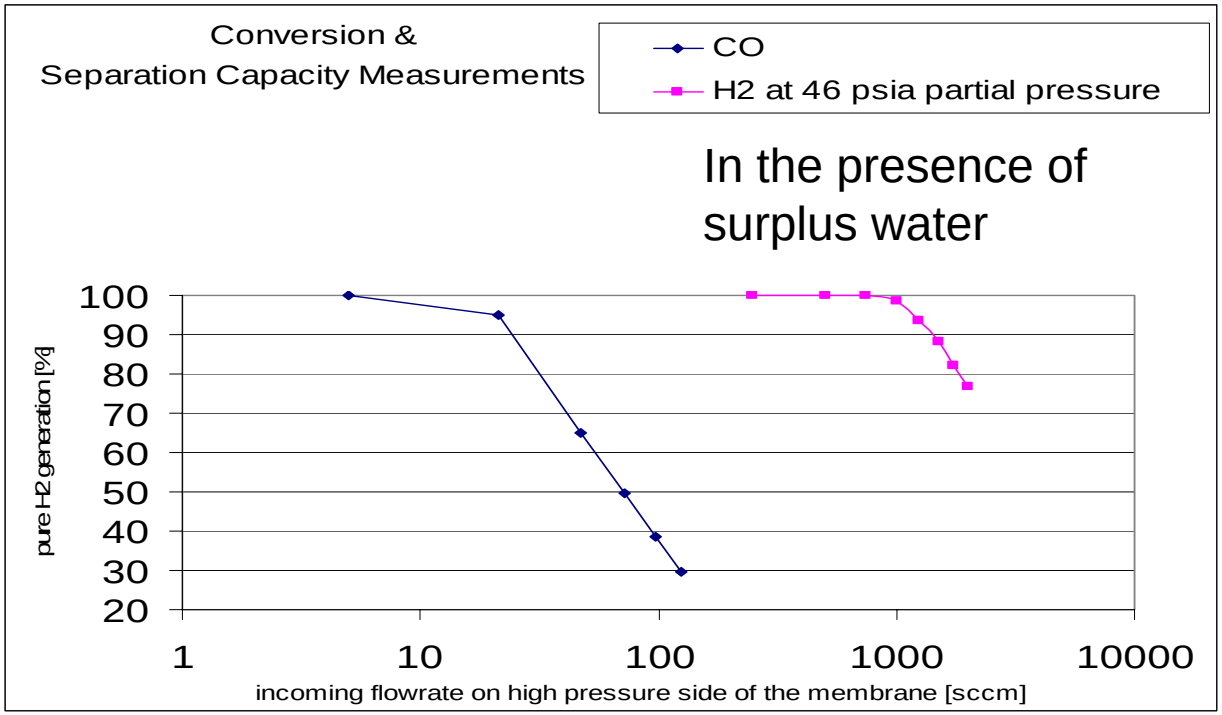
P+E membrane measured flux plotted with fluxes for state of the art membranes, using data from: NETL, reference 9.

H2 diffusion efficiency impediment in Ar and He matrices, same membrane with 100 and 350 micron gap distances, 400 °C, 50/50 mix. Note that H_2 diffuses 81% easier through He than Ar.



P&E's patented design forces reformate to reside in a very narrow micro-channel neighboring the membrane. This limits the distance H2 has to diffuse through a non-hydrogen matrix to reach the membrane.

Membrane Reactor



Membrane hydrogen separation and WGS conversion capacity, in absence of any catalyst. The reformate stream consists of equal fractions of inert gas, steam and H2. Small flows of CO were added to this mixture according to the x-axis indication. The CO conversion is independent of H2 in the reformate. This was confirmed by testing a reformate mixture with no H2.

50 kW, 500 & 100 Watt separators with power densities up to 15 kW/liter.

Conclusion and Outlook

- Performance of a small robust H2 separator/purifier was tested and results were found to agree with mathematical modeling.
- Optimized membrane reactor modules operating at higher pressure and temperature (favoring kinetics) enable conversion capacities much closer to the separation capacity. This allows the integration of a complete fuel processor into a single, simple, compact device.
- Further reduction of membrane thickness with composite membranes will enable both increased flux rates and reduced palladium cost. P&E has proprietary composite membrane structures which eliminates substrate blockage. a major bottleneck issue in creating composite membranes.

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References

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