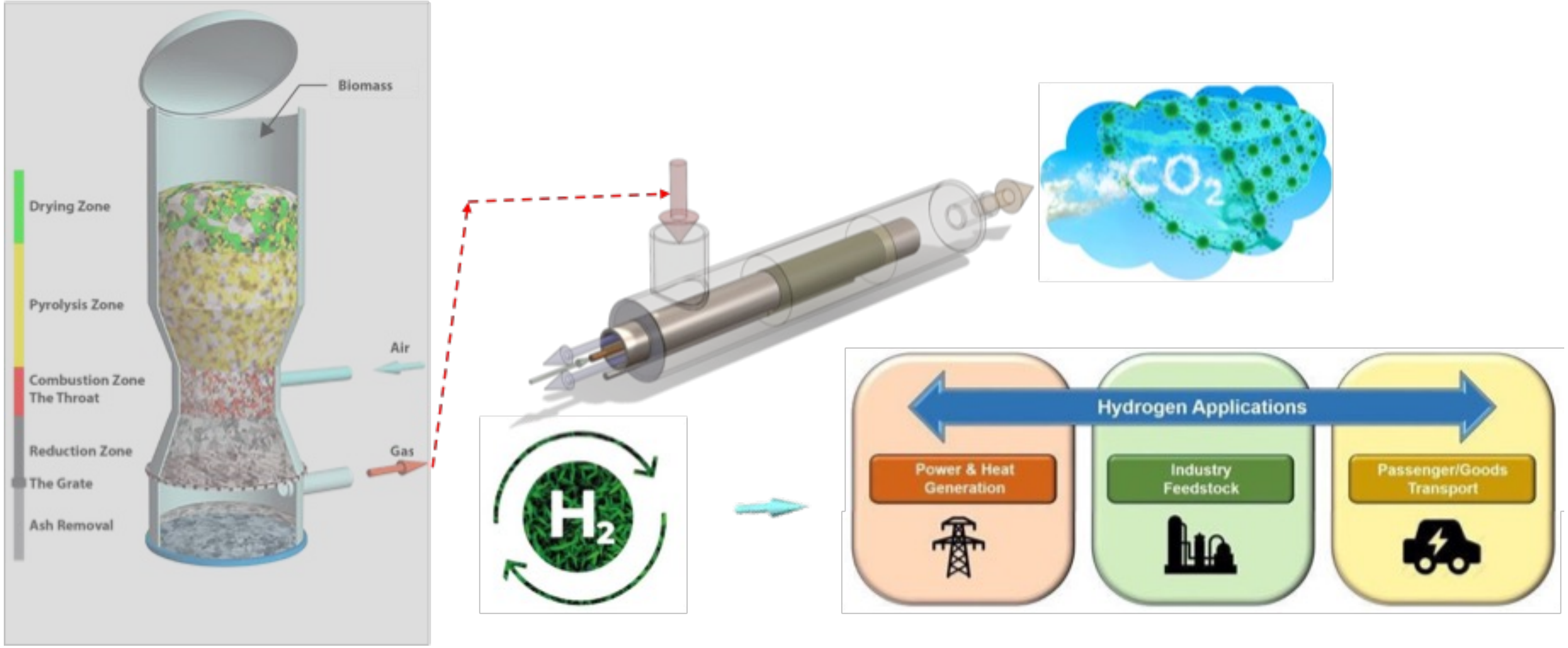
Metallic Membrane Reactors: An Intensified Process to Transforming the Production of Carbon-Neutral Hydrogen (DE-FE0032205)

Simona Liguori



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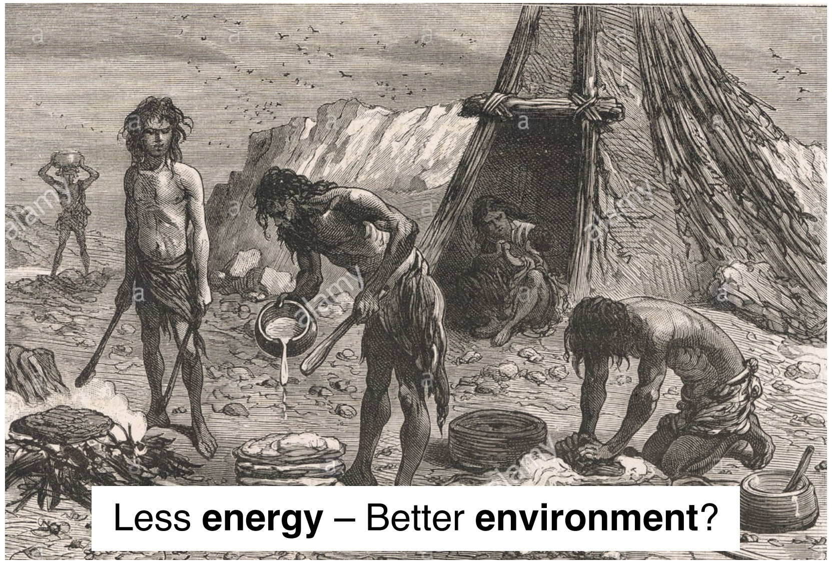
Clarkson University

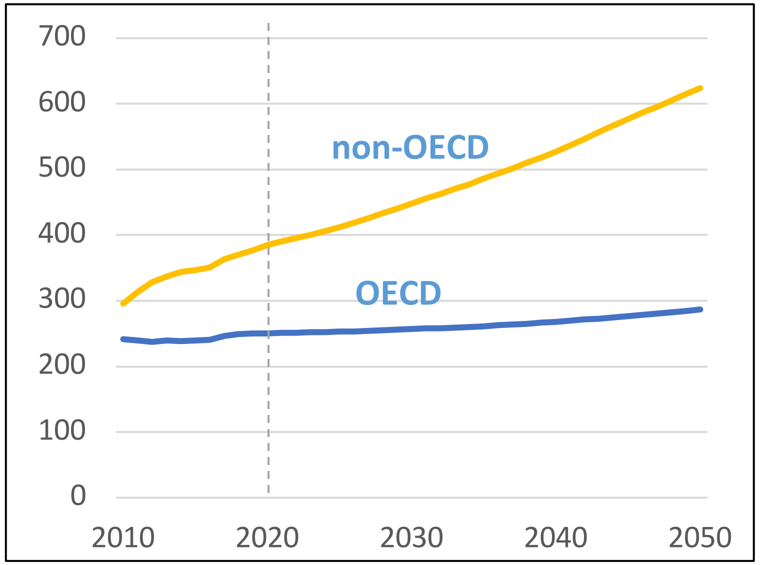
Background: Clean Hydrogen – Biomass Gasification

Energy Dilemma

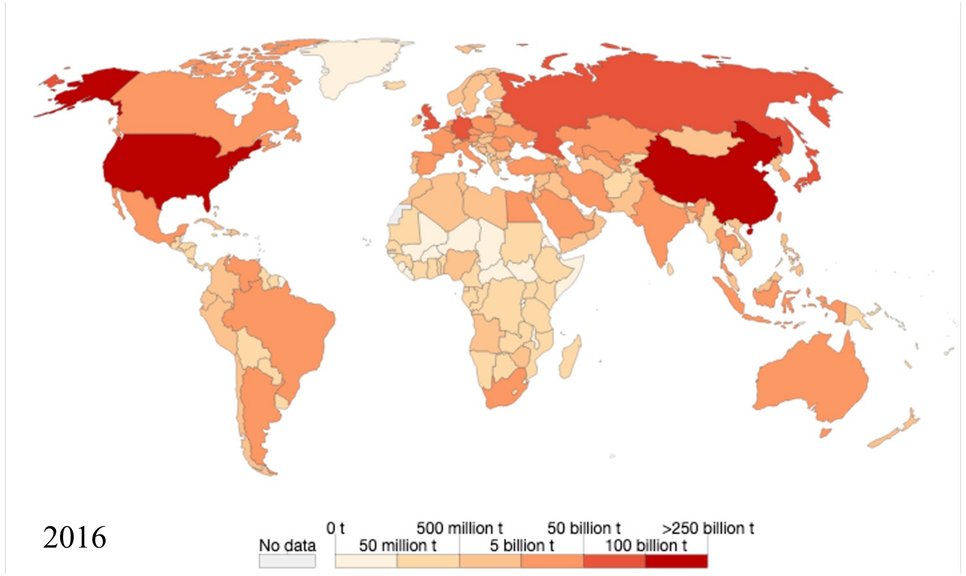


Energy Consumption and CO_2 emissions

World energy consumption [quadrillion BTU]



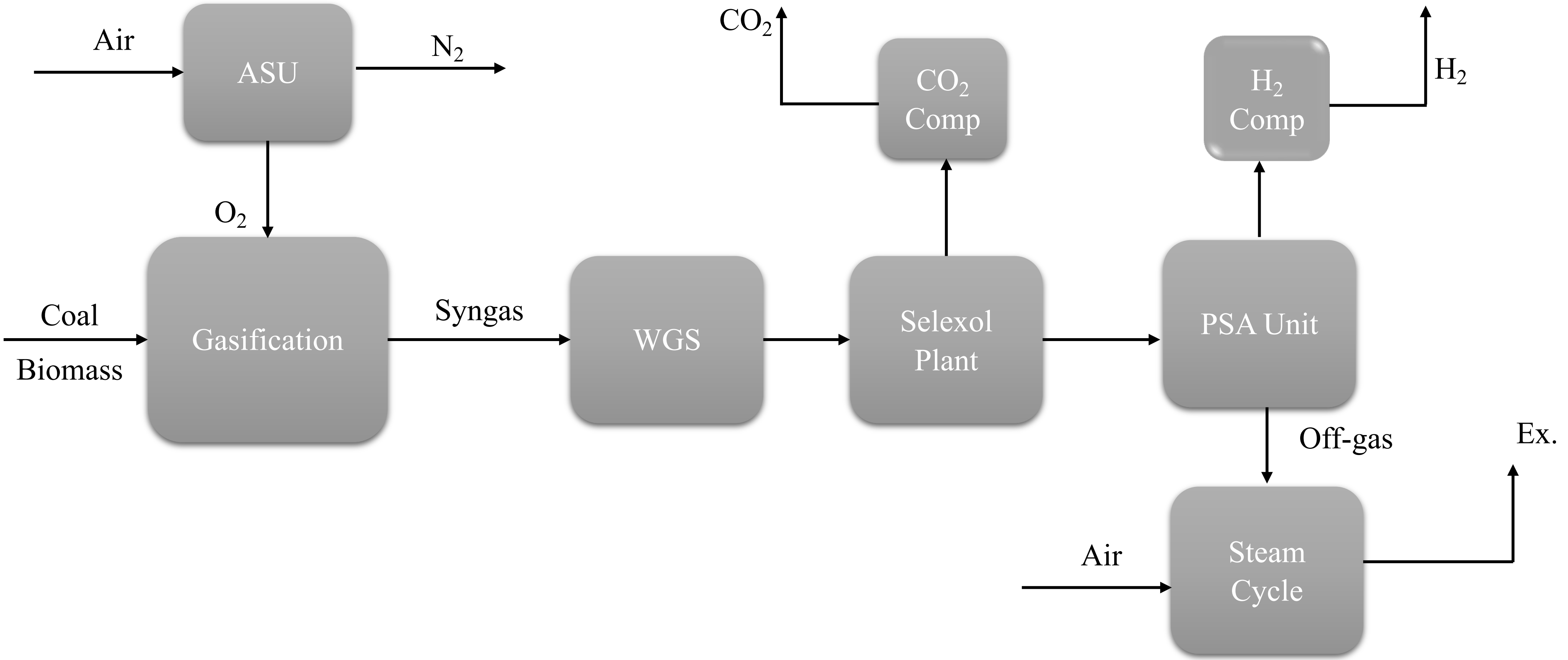
Cumulative CO_2 emissions, from 1751 to 2016



https://www.eia.gov/todayinenergy/detail.php?id=41433

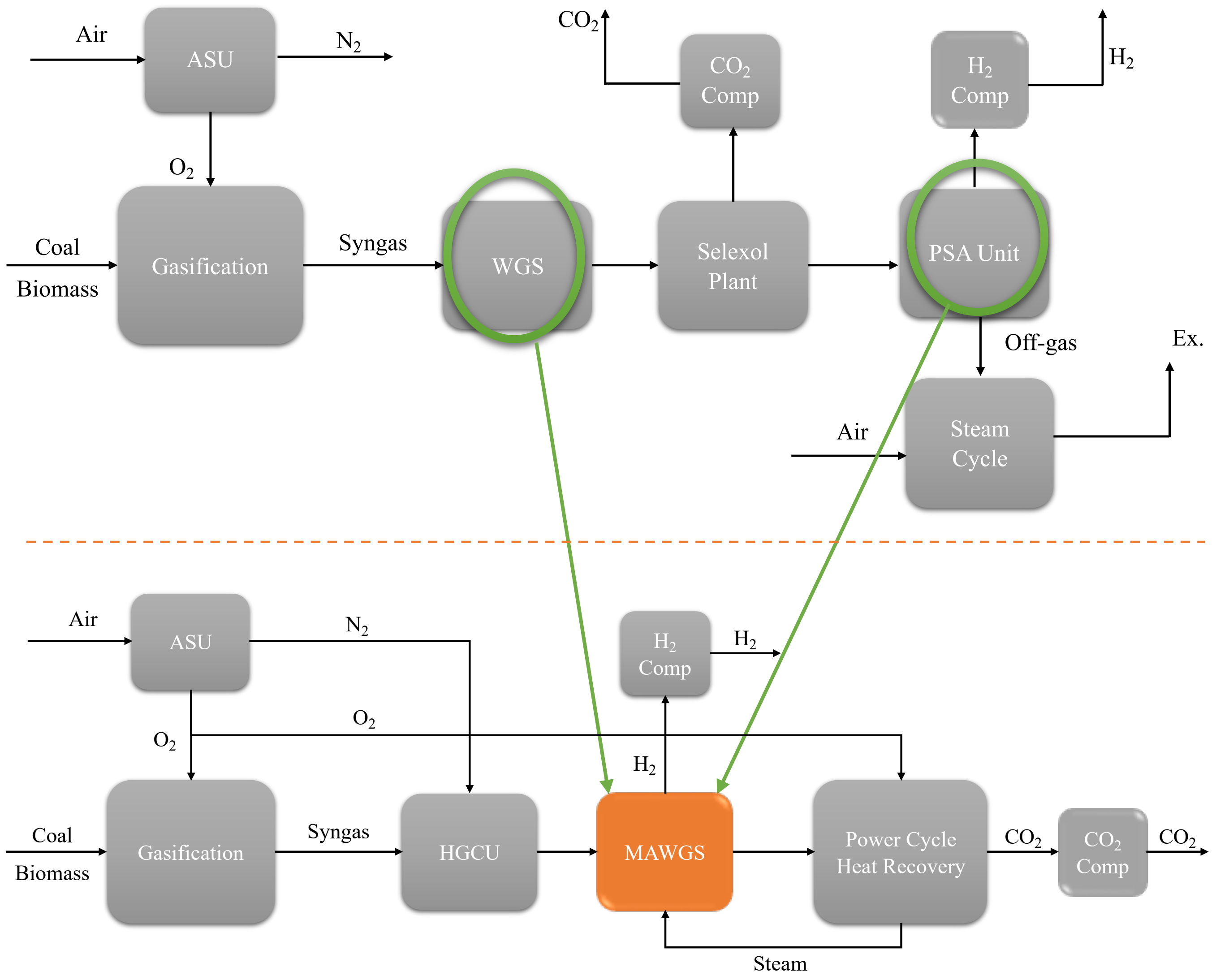
https://ourworldindata.org/co2-emissions

Background: Hydrogen – Biomass Gasification*



* IEAGHG CO. Capture at coal-based power and hydrogen plants, Report 2014/3; 2014. https://ieaghg.org/docs/General_Docs/Reports/2014-03.pdf

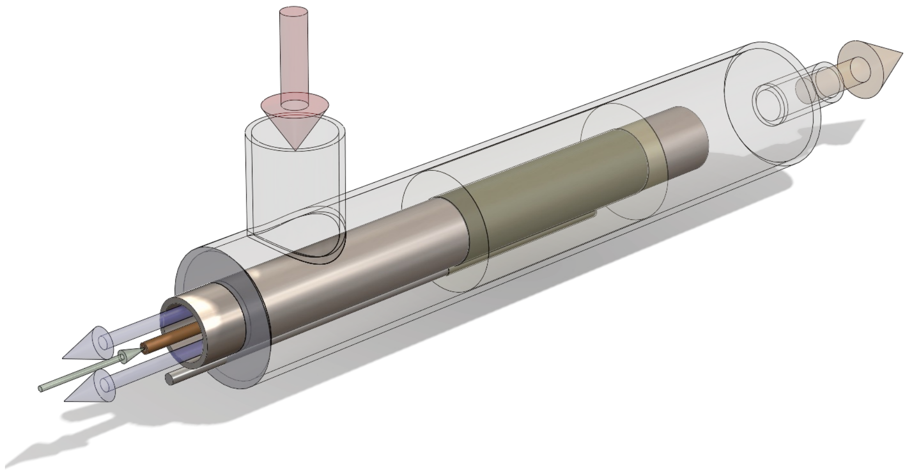
New Approach: Process Intensification



Intensify the biomass gasification process by the use an H_2-selective Membrane Assisted Water Gas Shift reactors (MAWGS).

H_2-selective Membrane Assisted Water Gas Shift reactors

The H_2-selective Membrane Assisted Water Gas Shift reactors is a tool where synergy is created through a combination of catalytic and separation technologies.



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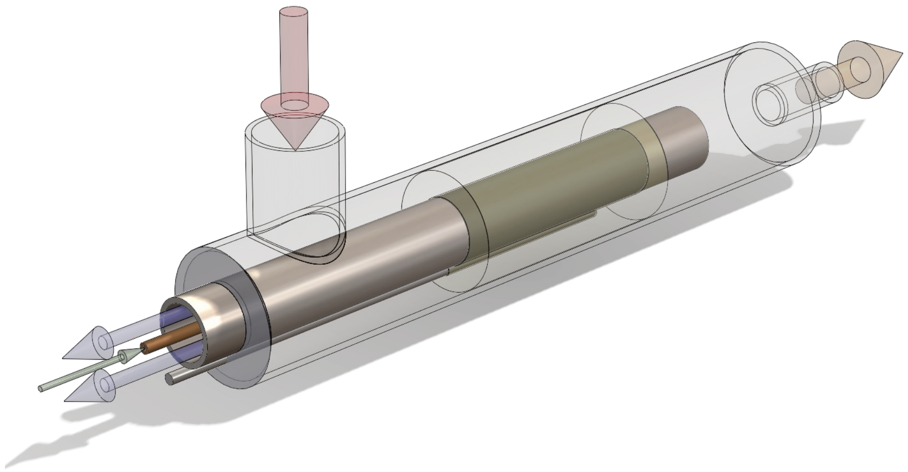

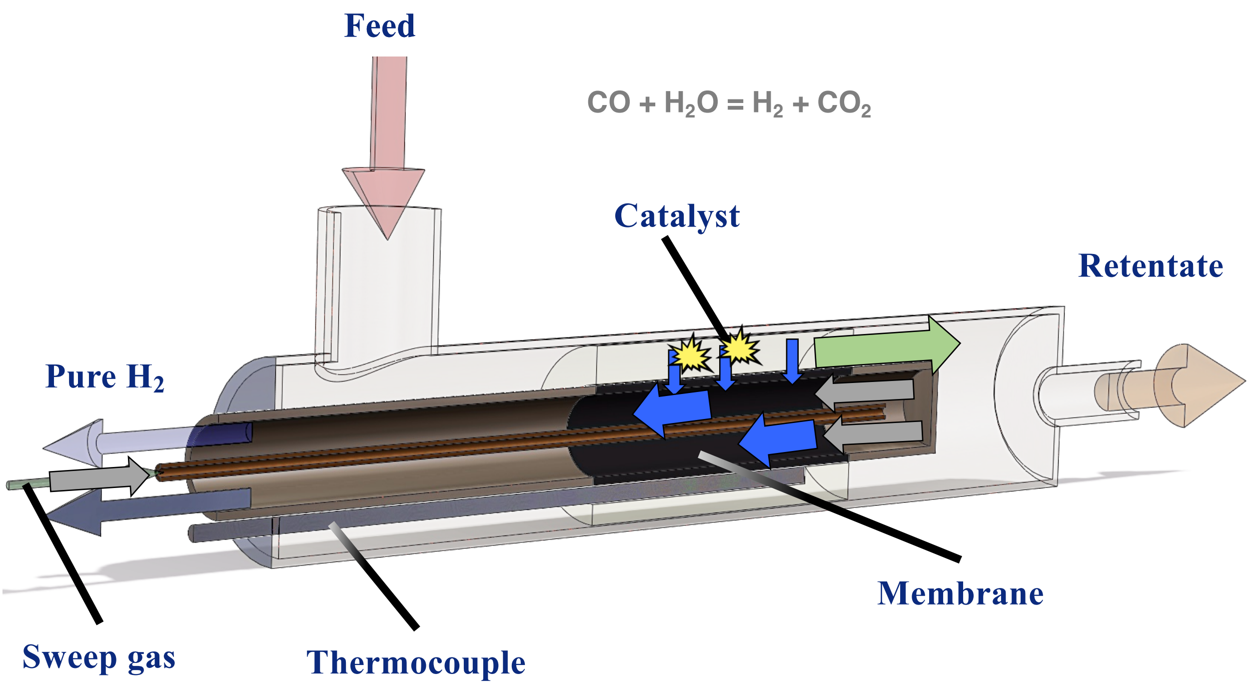

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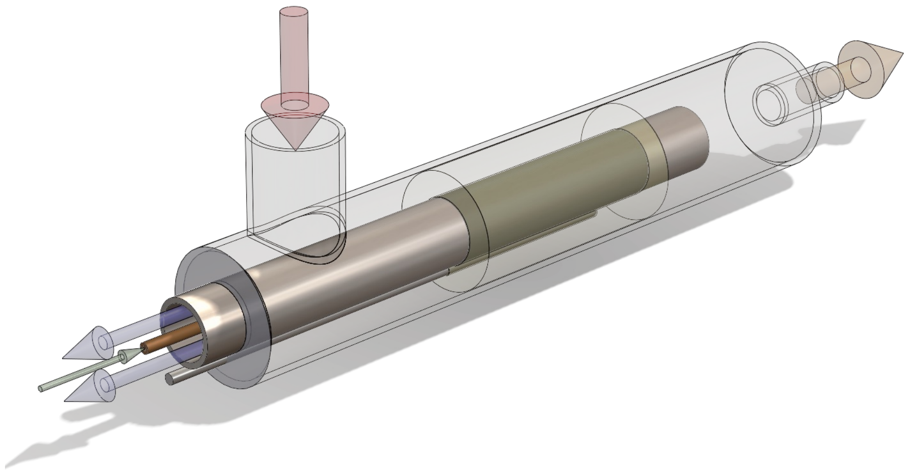

- No thermodynamic constraints (it is an open system)
- Higher conversions with respect conventional process at the same T
- Same conversions at lower T
- Two product streams
  - **Ultra pure hydrogen** production
  - Stream highly composed by CO_2
- Clear example of process intensification[1]

[1]A Basile, A Iulianelli, **S Liguori**, Process intensification in the chemical and petrochemical industry, in: Sustainable Development in Chemical Engineering, V Piemonte, M De Falco, A Basile (Eds), Wiley, pp. 119-151, (2013), ISBN: 9781119953524

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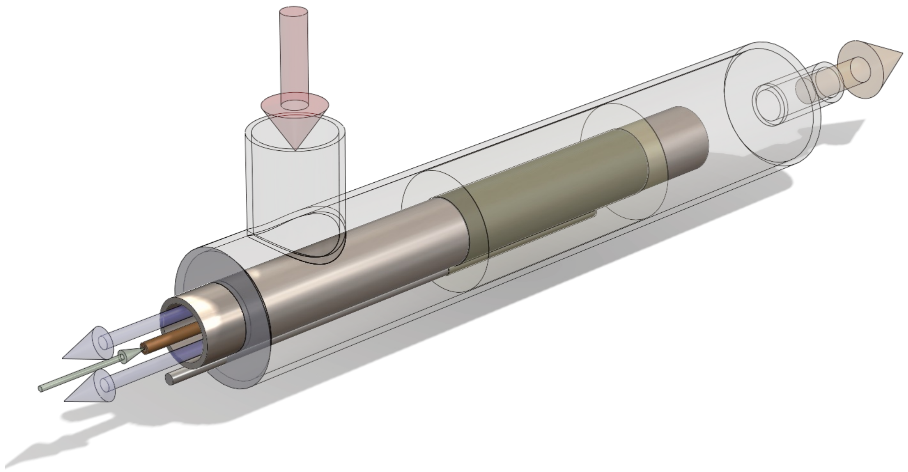

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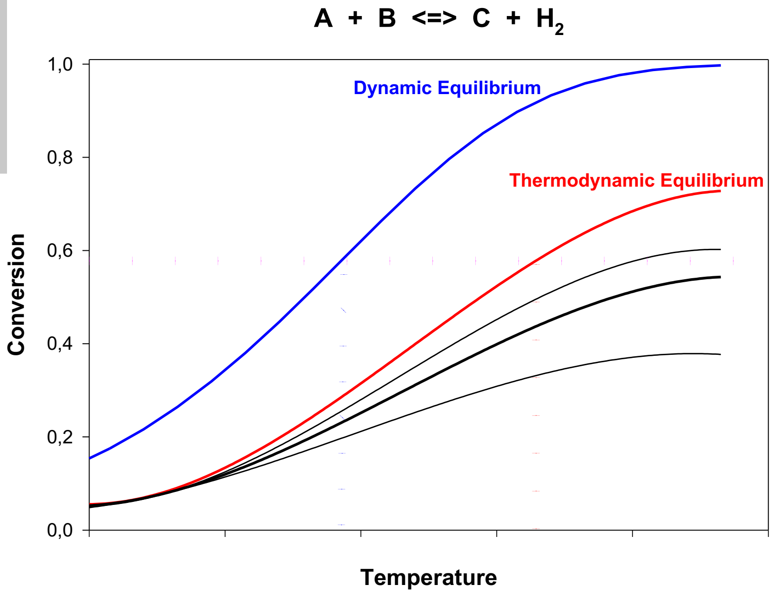
Better performance?

Pure H_2?



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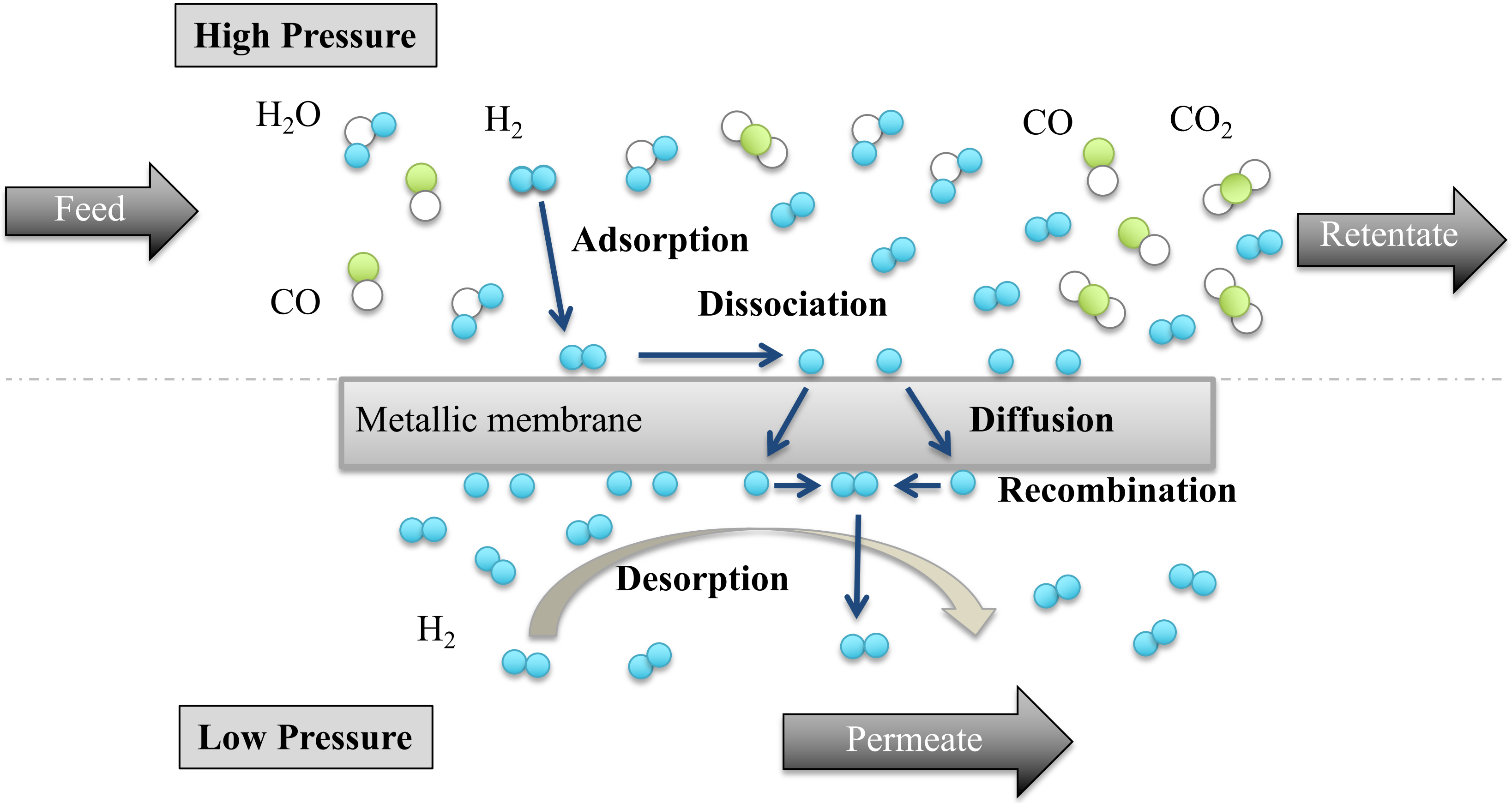
H_2-selective Membrane Assisted Water Gas Shift reactors



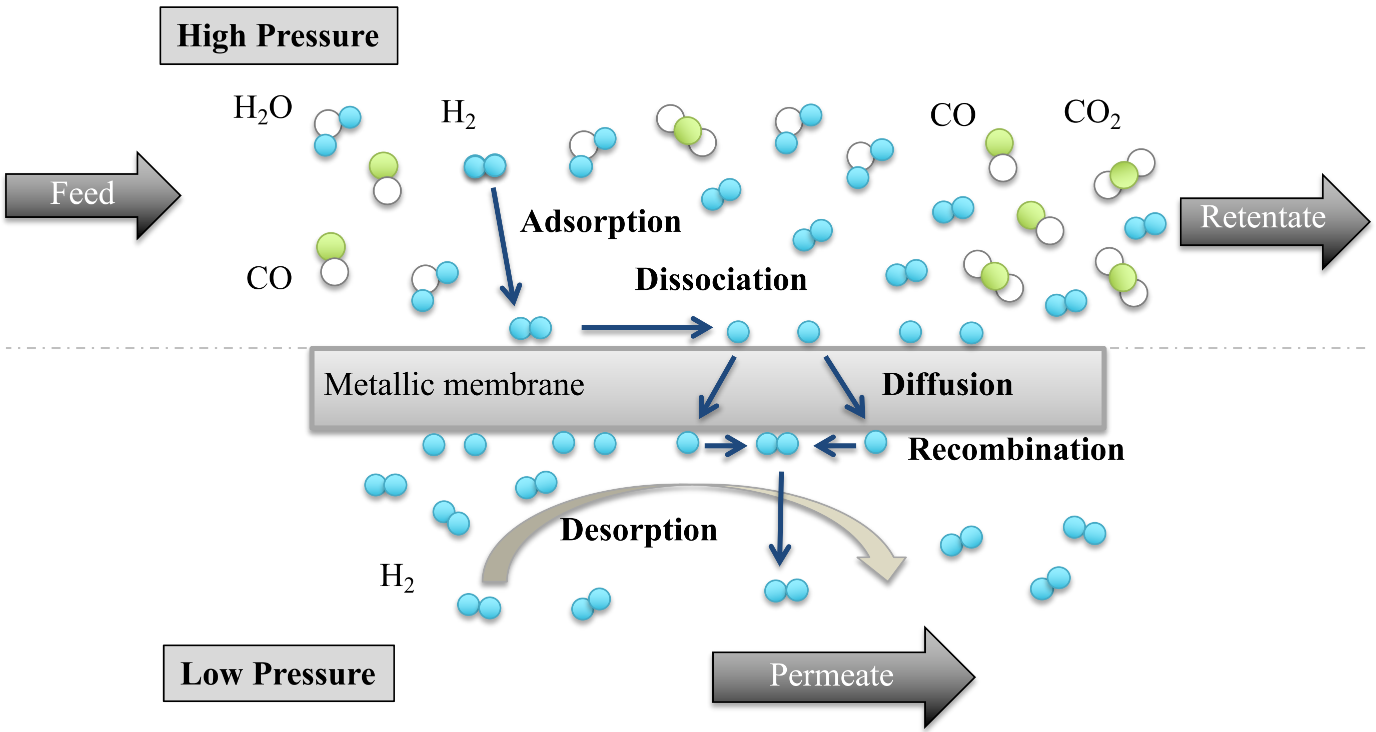
$$J_{H2} = \frac{Pe}{\delta} \cdot (p^{0.5}_{H2-retentate} - p^{0.5}_{H2-permeate})$$

Sieverts' law @ T constant

$$J_{H2} = \frac{Pe_0 \cdot exp(-E_a / RT)}{\delta} \cdot (p^{0.5}_{H2-retentate} - p^{0.5}_{H2-permeate})$$

Richardson's law

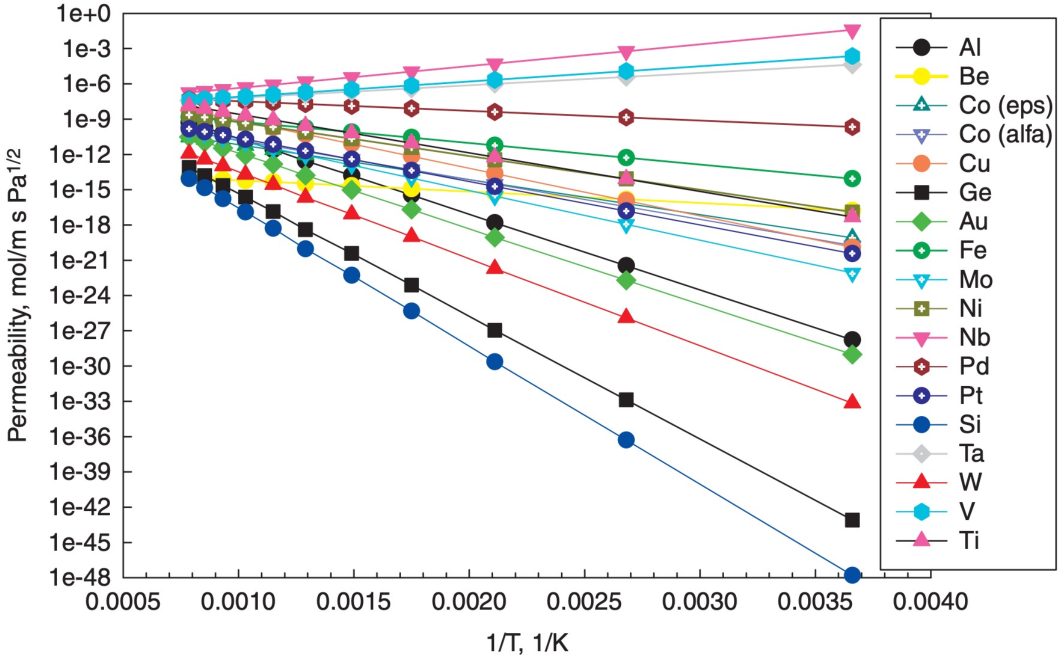
H_2-selective Membrane Assisted Water Gas Shift reactors



$$J_{H2} = \frac{Pe}{\delta} \cdot (p^{0.5}_{H2-retentate} - p^{0.5}_{H2-permeate})$$ Sieverts' law @ T constant

$$J_{H2} = \frac{Pe_0 \cdot exp(-E_a / RT)}{\delta} \cdot (p^{0.5}_{H2-retentate} - p^{0.5}_{H2-permeate})$$ Richardson's law

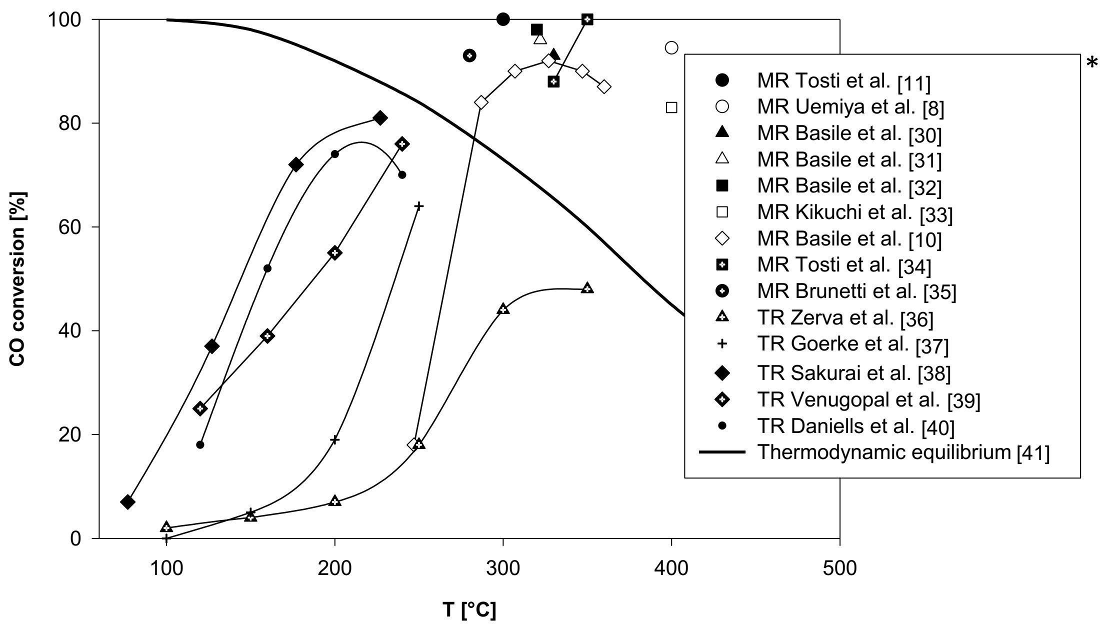
How to choose the Metallic Membrane



Hydrogen permeability through various metals at different temperature.*

- Basile A et al., Synthesis, Characterization, and Applications of Palladium Membranes, 255–323, 2008. doi:10.1016/S0927-5193(07)13008-4

H_2-selective Membrane Assisted Water Gas Shift reactors



Hydrogen is ***constantly*** produced via WGS reaction and removed from the reaction zone through the H_2-selective membrane allowing for the equilibrium conversion of CO to CO_2 to proceed to near completion, while also separating the H_2 from the CO_2

Pure Pd membranes have shown great potential for their application to H_2 separation at high temperature. However, they are **affected**: by (i) embrittlement, (ii) deposition of carbonaceous impurities, and (iii) poisoning by CO and H_2S, which often result in a mechanical failure of the membrane and in low chemical stability

In addition, although they have shown hydrogen flux exceeding the 2015 flux targets set by US Department of Energy (~90 Nm^3 H_2/m^2h at 1.4 bar pressure difference), **their use is restricted by their relatively low microstructural stability, which leads to cracks and pinholes formation.**

A key to the realization and development of this promising technology is the synthesis of a reliable H_2-selective membrane material

*Mendes, D., Mendes, A., Madeira, L. M., Iulianelli, A., Sousa, J. M., & Basile, A. (2010). *Asia-Pacific Journal of Chemical Engineering, 5(1), 111–137.* doi:10.1002/apj.364

H_2-selective Membrane - Materials Selection Process and Methodology

Ternary Pd-Ag-Au improves poisoning resistance, avoids leak growth and enhances the long-thermal stability as well as hydrogen permeability.

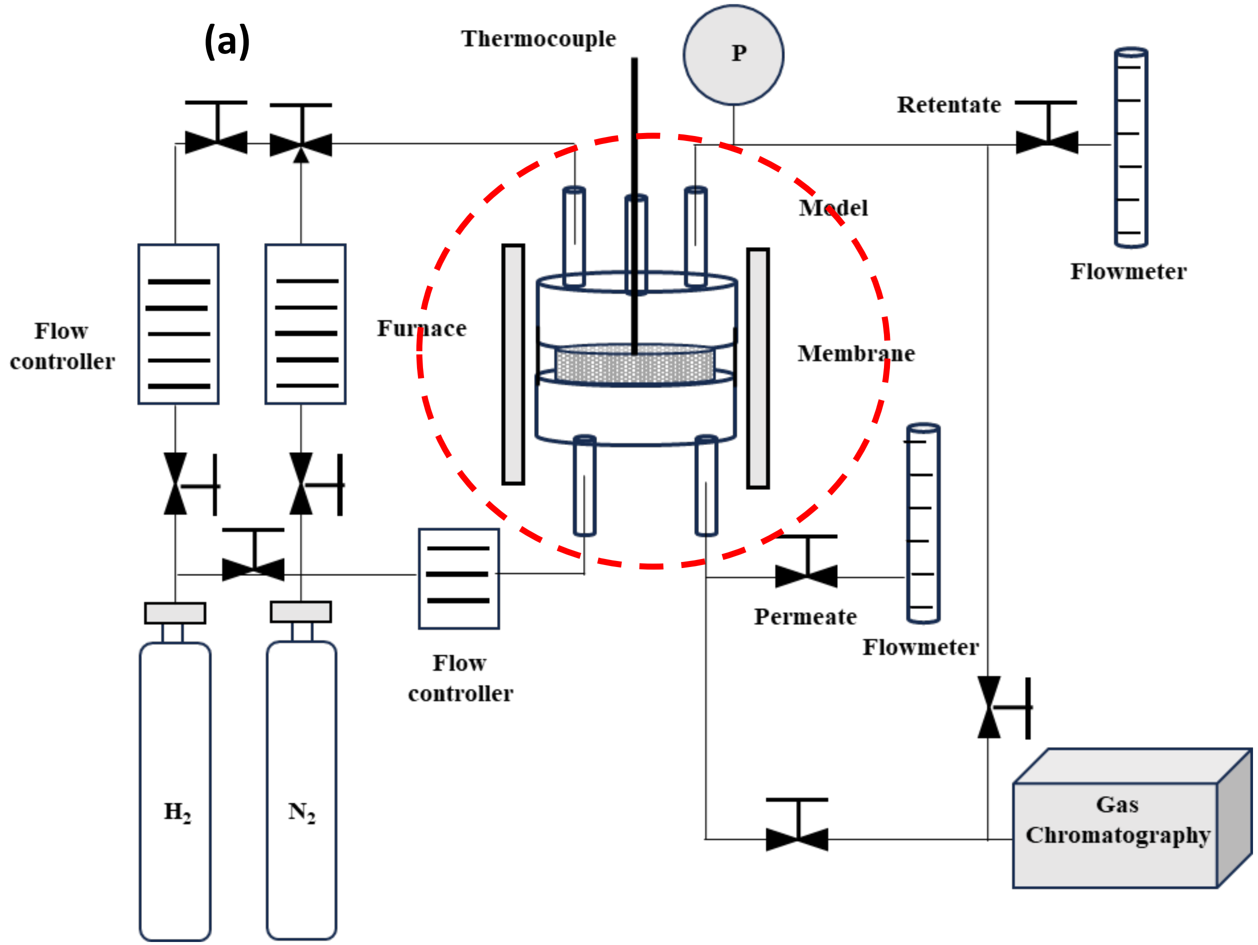
Compositions

Midrange Au compositions (15–25 wt%) are chosen because they represent **a balance between high H_2 permeability** (low Au compositions – less than 10 wt%) and **resistance to H_2S poisoning** (high Au compositions – 40 wt%).
Ag is added to one of the midranges Pd-Au membranes in order **to increase the permeability, decrease the membrane cost, and because the metals display good miscibility**.

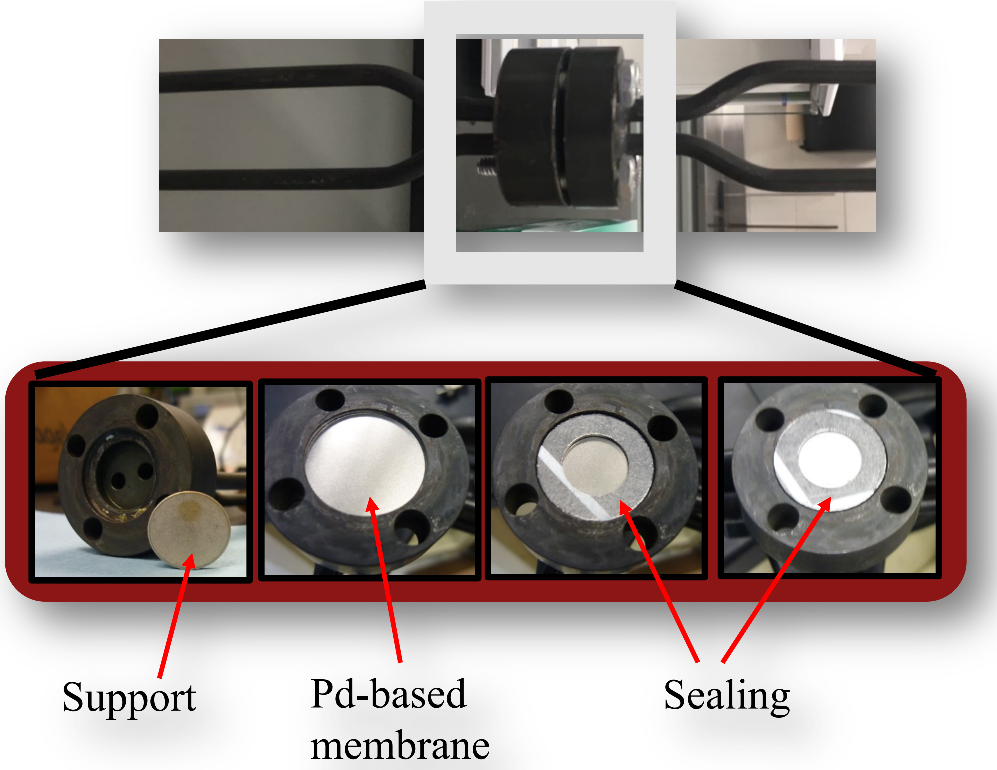
Selection and Modification of Porous Substrate –

Effect of the Porous Stainless-Steel support on the hydrogen permeation test

(a)



(b)



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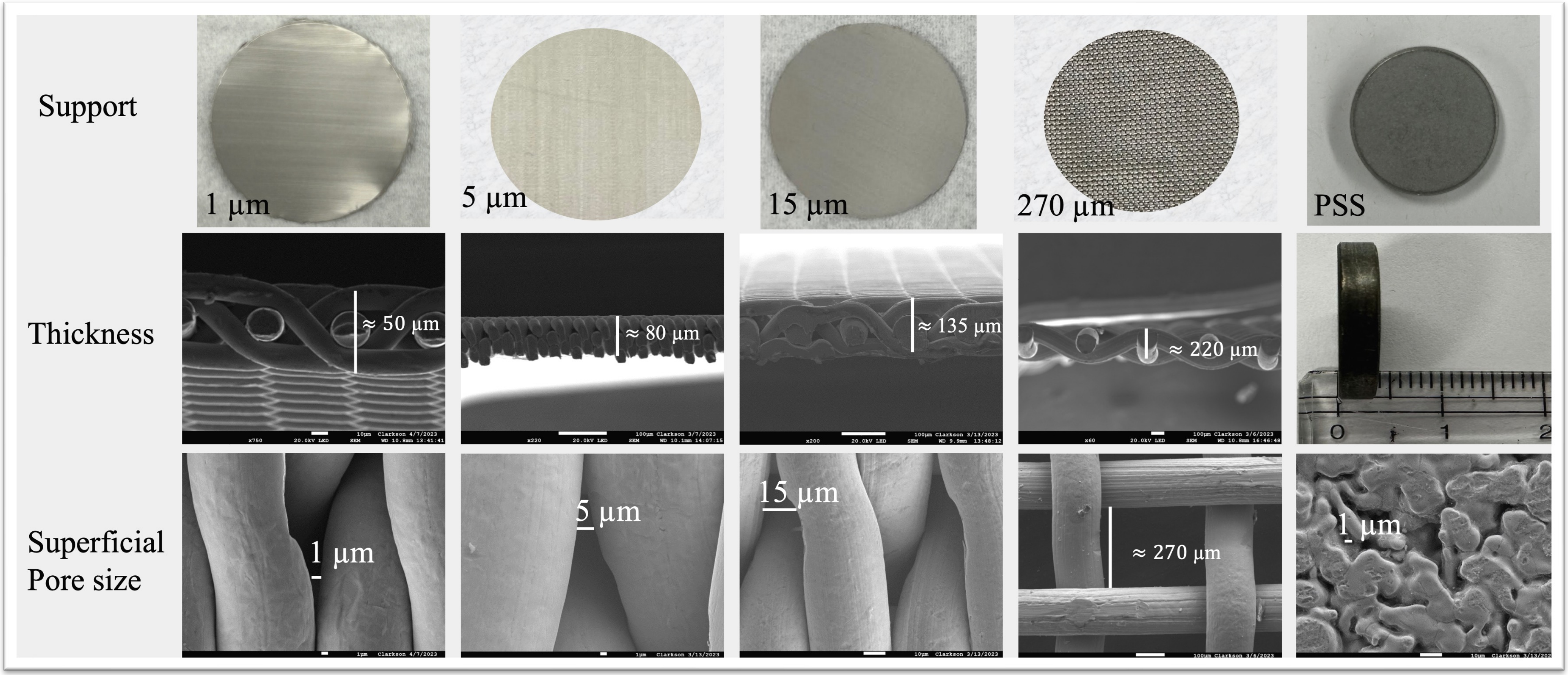


Selection and Modification of Porous Substrate –

Effect of the Porous Stainless-Steel support on the hydrogen permeation test

Operating conditions

T = 400 °C

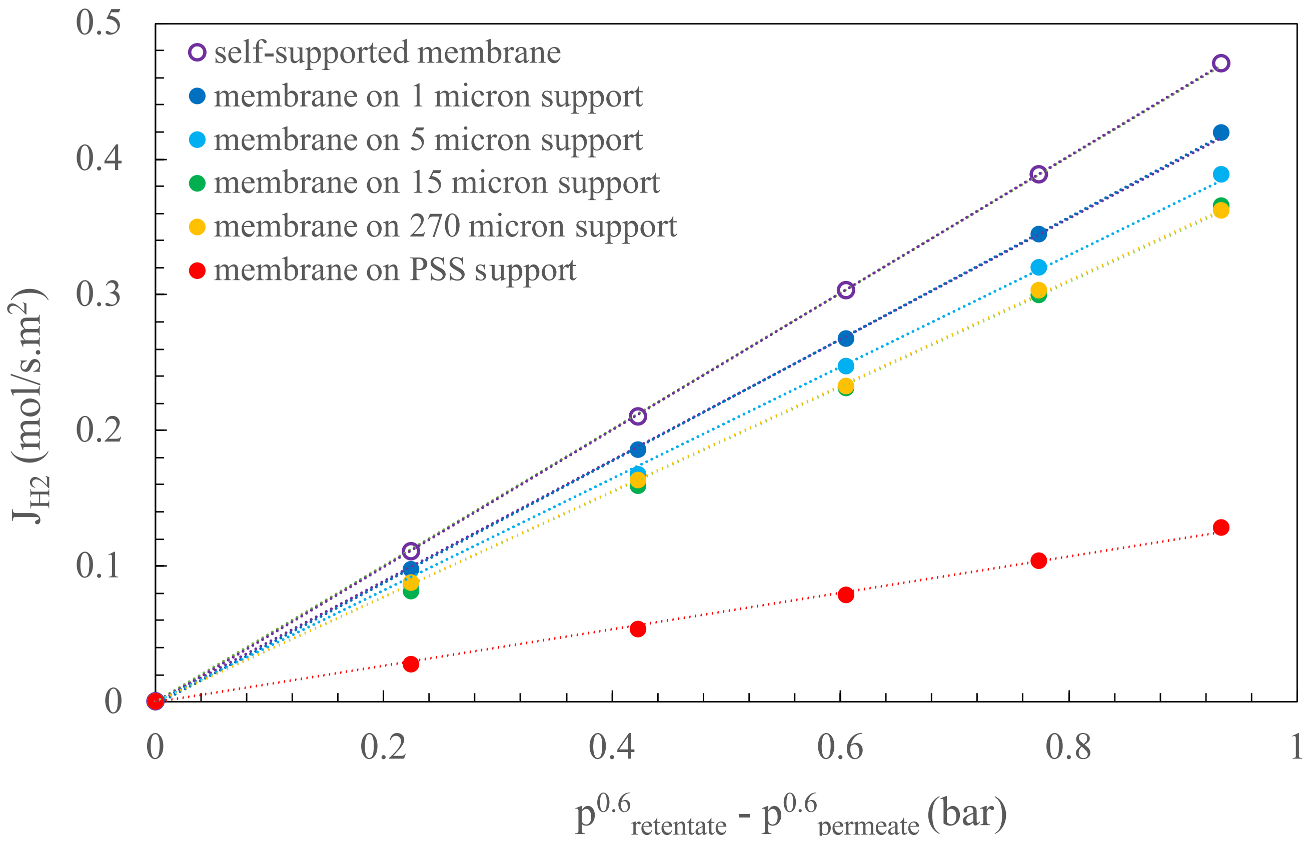
$P_{permeate}$ = 1 bar (abs)

$P_{retentate}$ = 1 – 3 bar (abs)

Self-supported membrane showed an n value of n=0.6, so the hydrogen permeation flux of the supported membrane was reported with an n value of 0.6

Supports affect the hydrogen permeation.

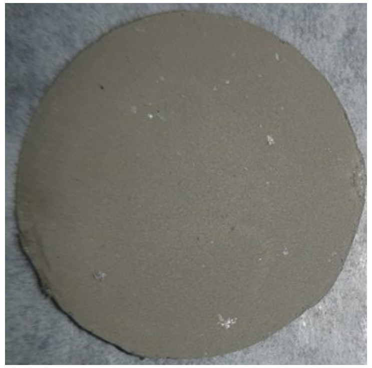
The influence is a combination of pore size and thickness of the support

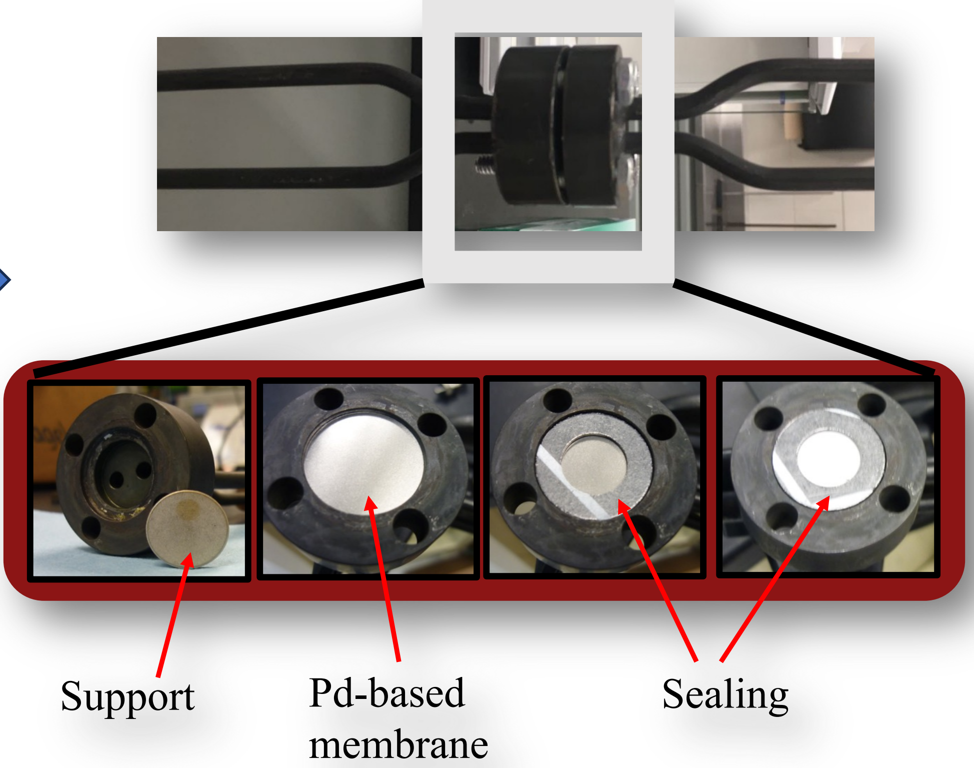


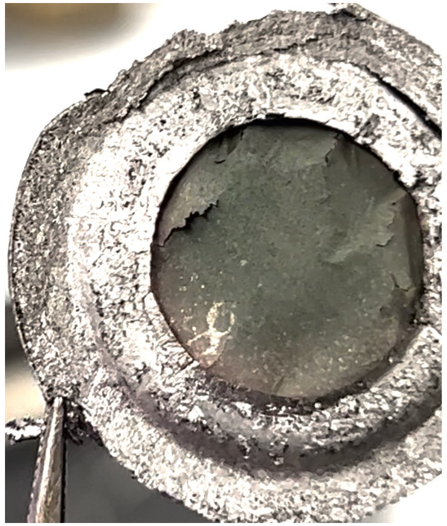
Fabrication and Evaluation of Disc Membranes

Fabrication of Alloyed Disc Membranes (1 μm support)

Synthesis of Pd-Au via ELP





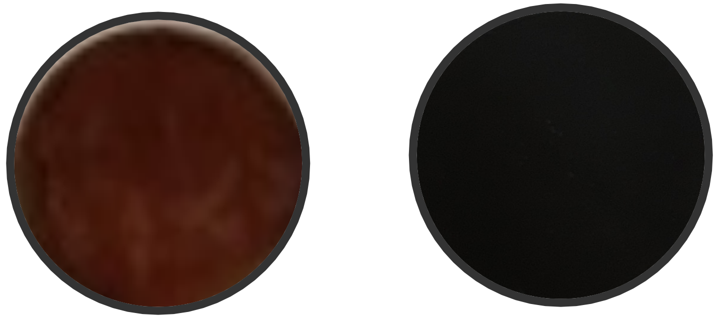


The Pd-Au membrane was selective at pressure up 1.5 bar and then the ideal selectivity dropped to 18

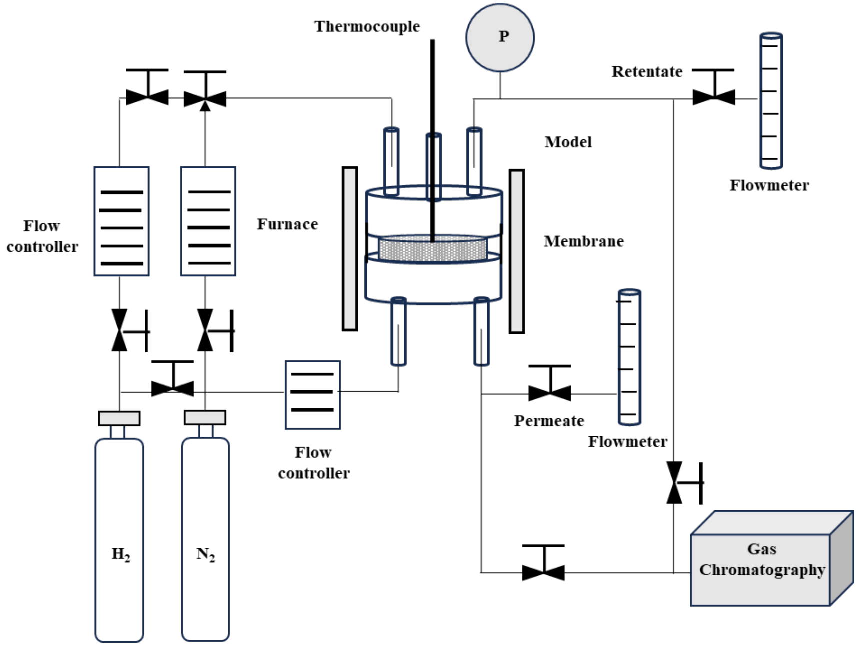
Fabrication and Evaluation of Disc Membranes *(Pd-PSS support)*

0.2M/PSS Disc | ***Intermediate layer***

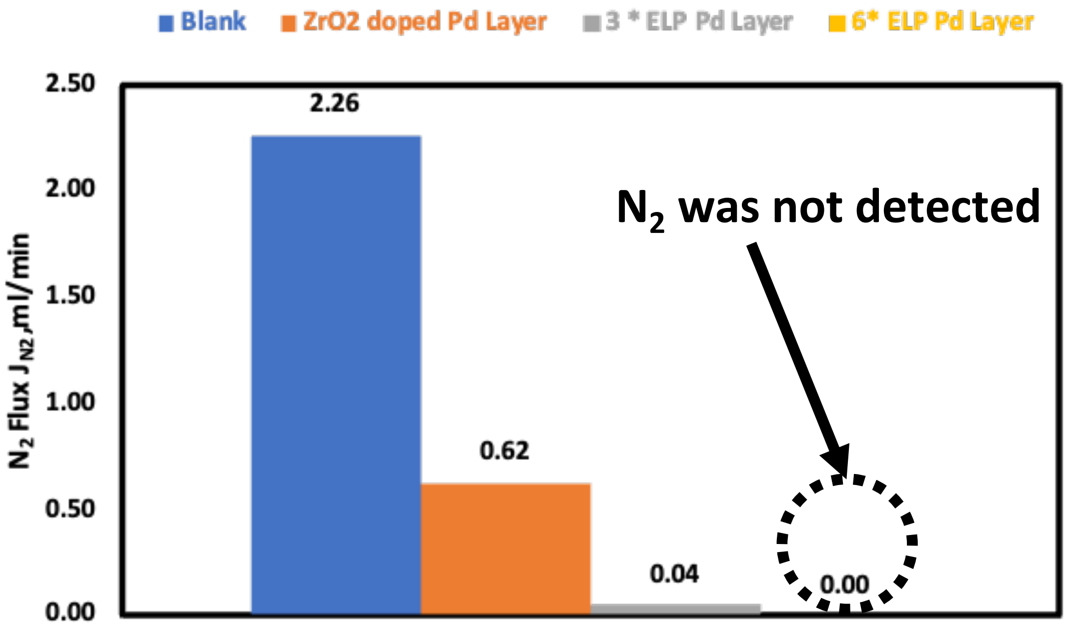
Activation layer – Pd seed formation



ELP Pd layer



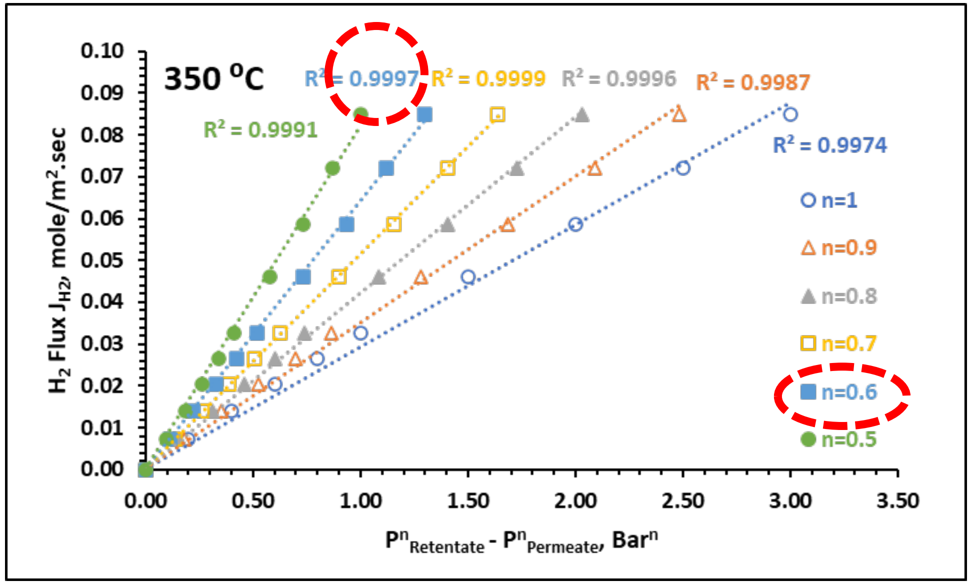
Experimental setup

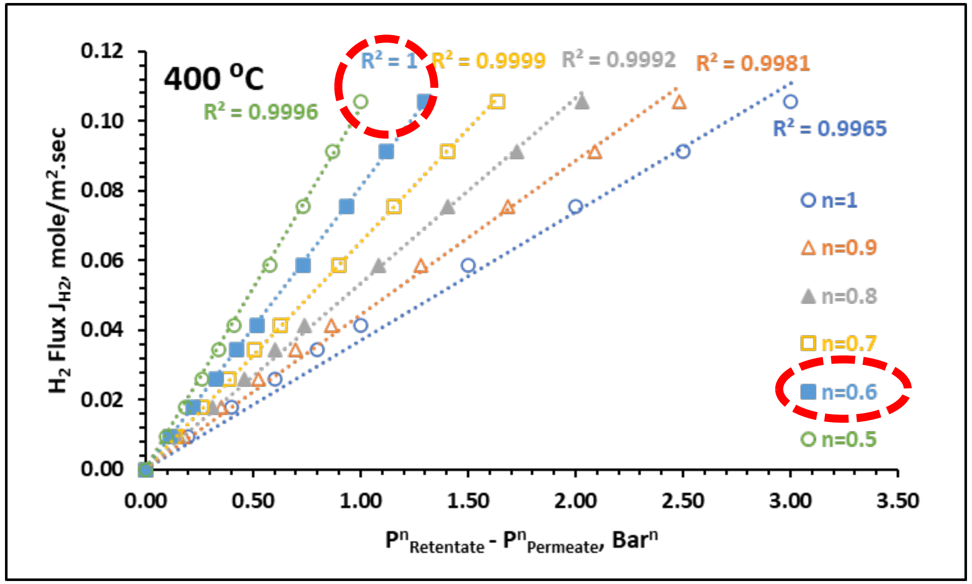


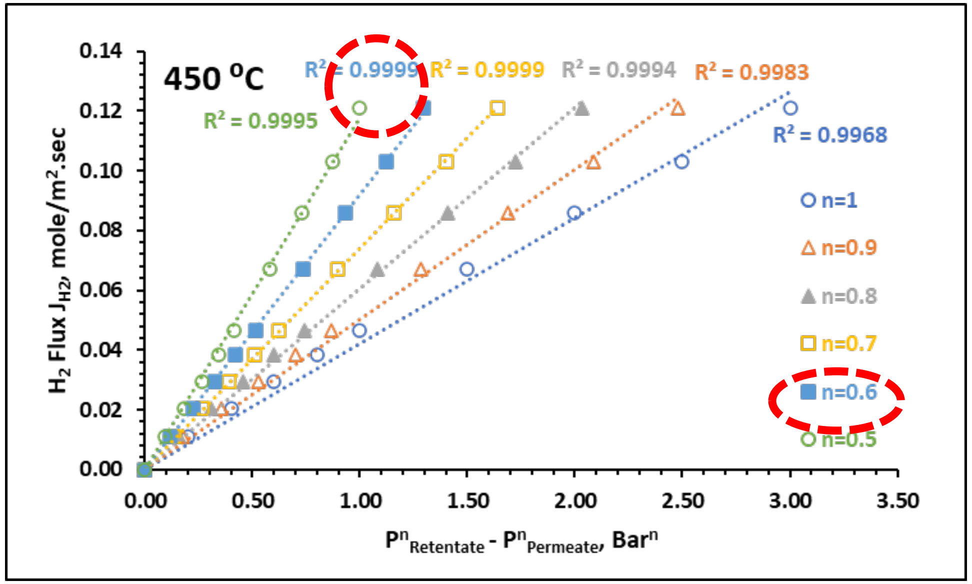
N_2 permeating at 25^oC and 1 Bar

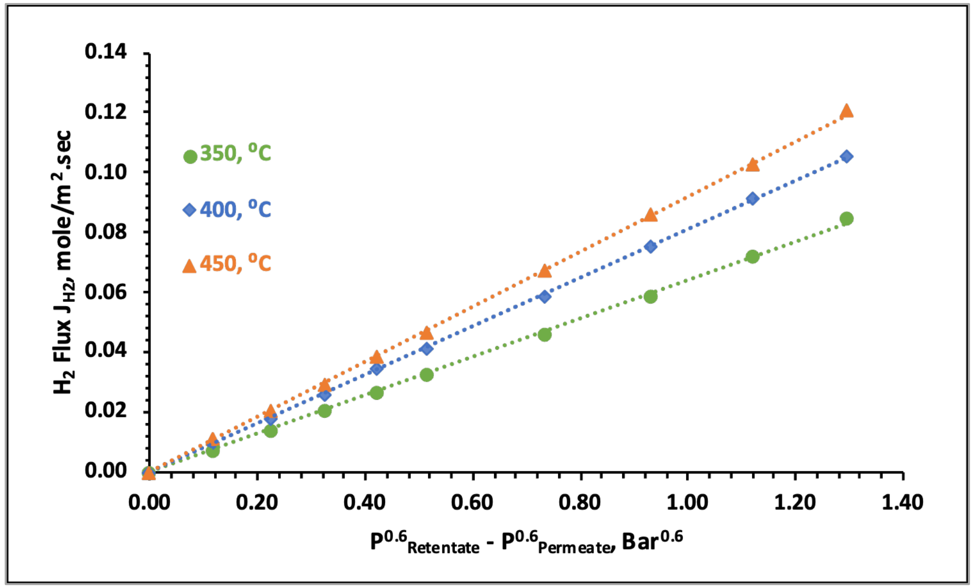
Fabrication and Evaluation of Disc Membranes *(Pd-PSS support)*

Hydrogen flux at different pressures and temperatures - Pure Pd





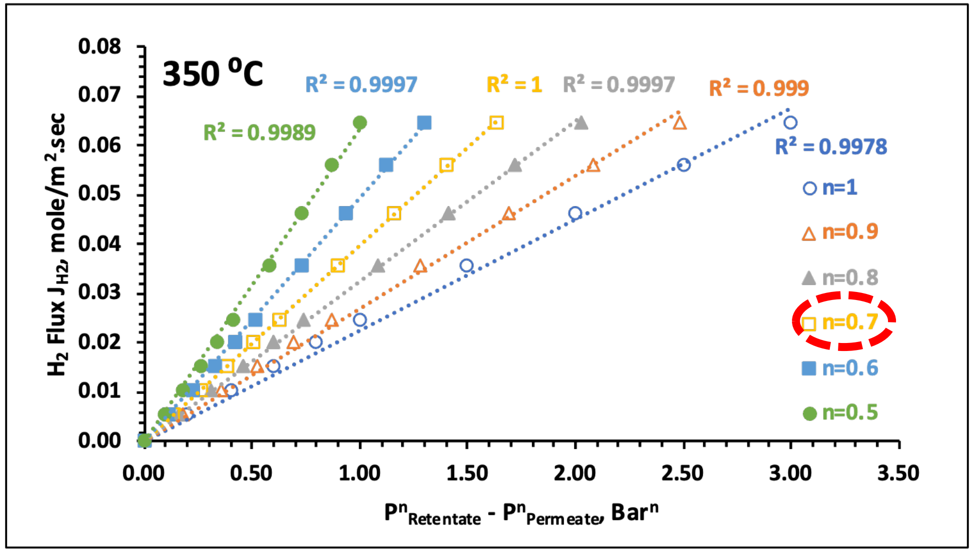


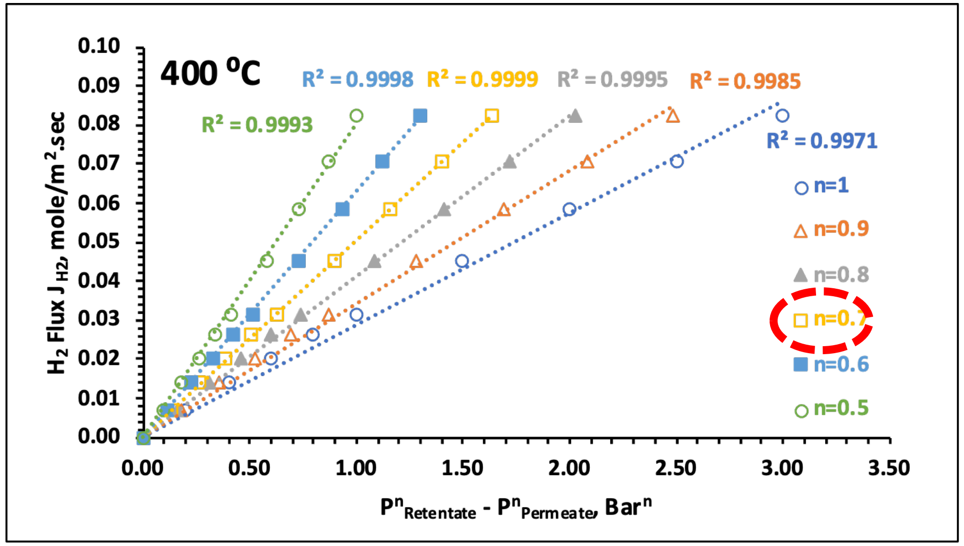


The membrane is fully selective to hydrogen permeation.

Fabrication and Evaluation of Disc Membranes *(Pd-Au (69-31 w/w%)-PSS support)*

Hydrogen flux at different pressures and temperatures - Pd-Au (69-31 w/w%)-PSS support





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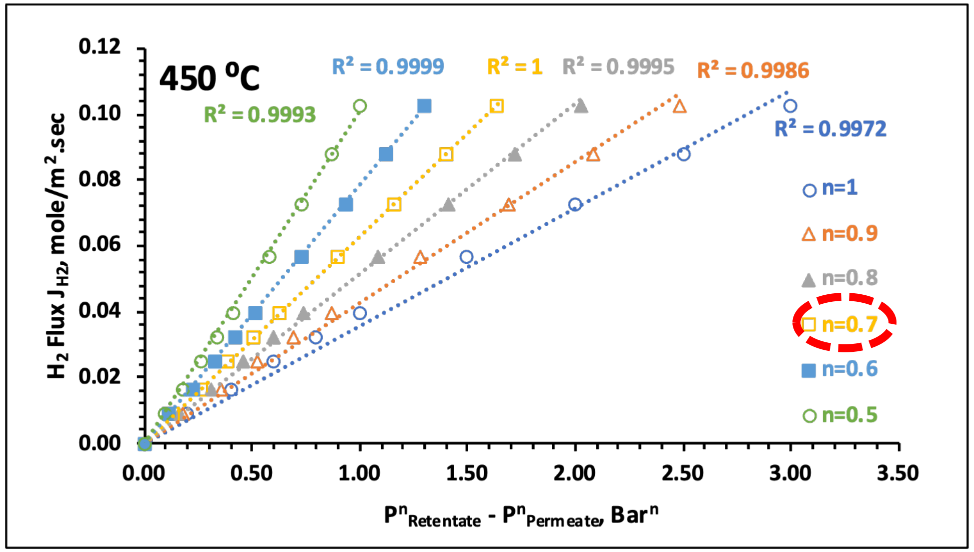
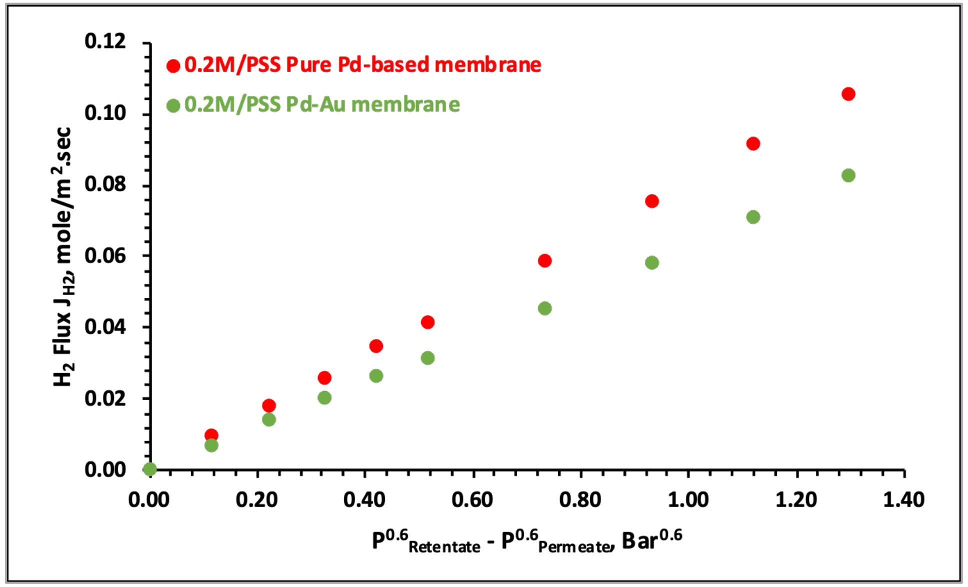
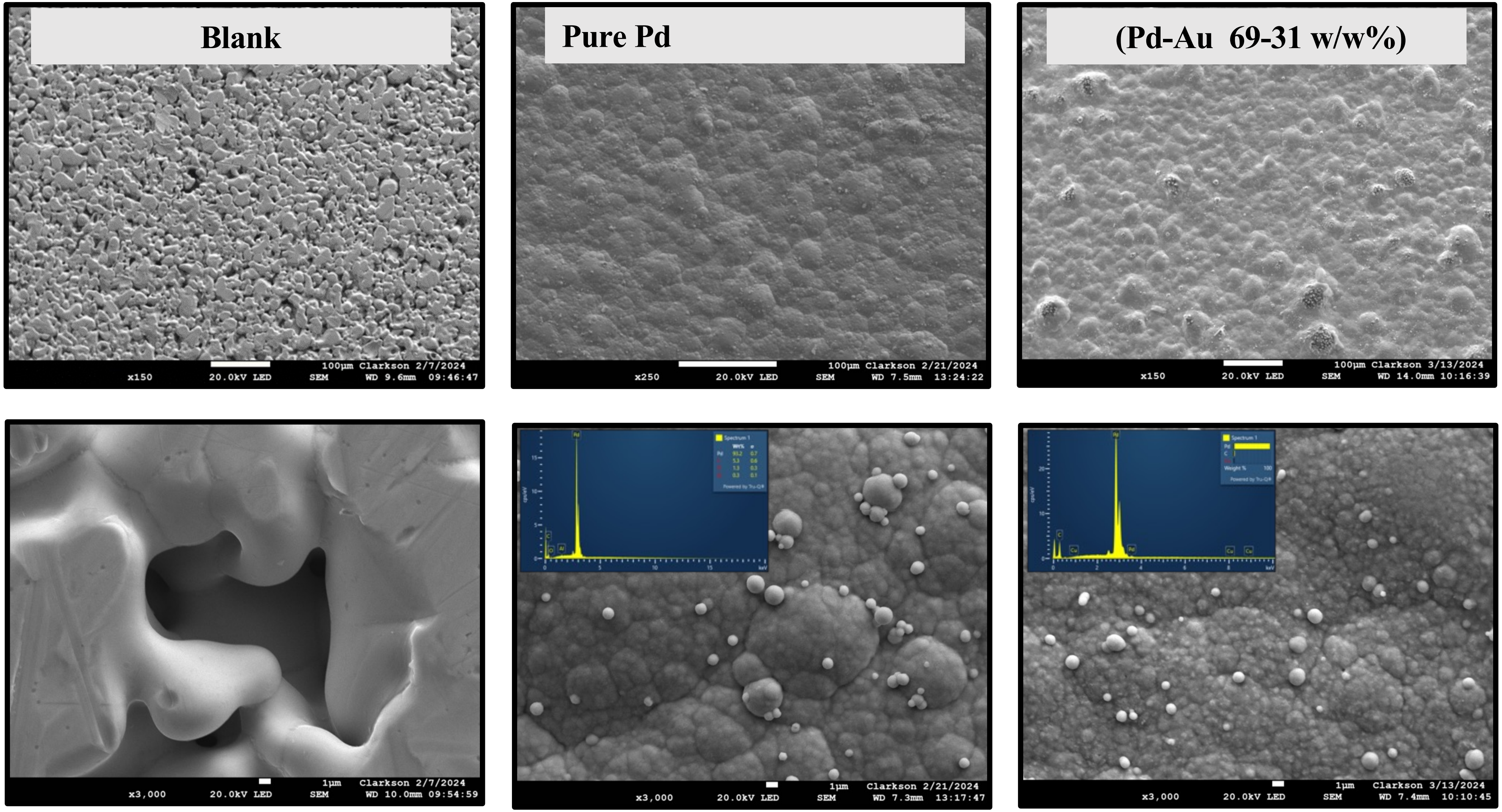




The addition of 31 wt.% of Au dropped the hydrogen flux

Membranes Characterization *(Pd-Au (69-31 w/w%)-PSS support)*



Reaction Test: Pd-Au-Ag (70-26-4 w/w%)-PSS support

The ternary alloy membrane was annealed at 500 °C.

It showed complete selectivity towards hydrogen permeation.

Reaction Tests

$CO + H_2O \rightarrow CO_2 + H_2$ $\Delta H^{\circ}_{298\,K} = -41.1$ kJ/mol

Operating conditions:

Reaction temperature = 300 °C

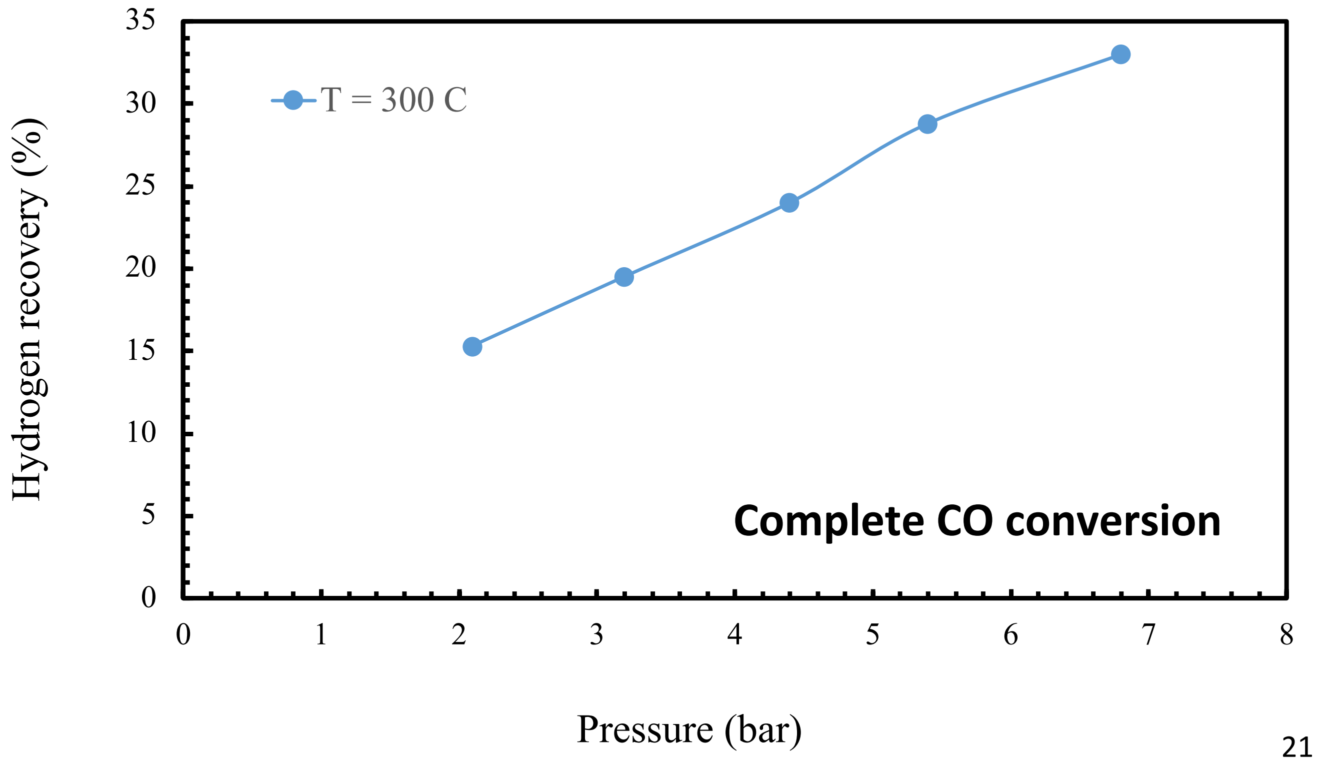
Permeate pressure = 1.0 bar

Retentate pressure = 2.0 – 6.8 bar

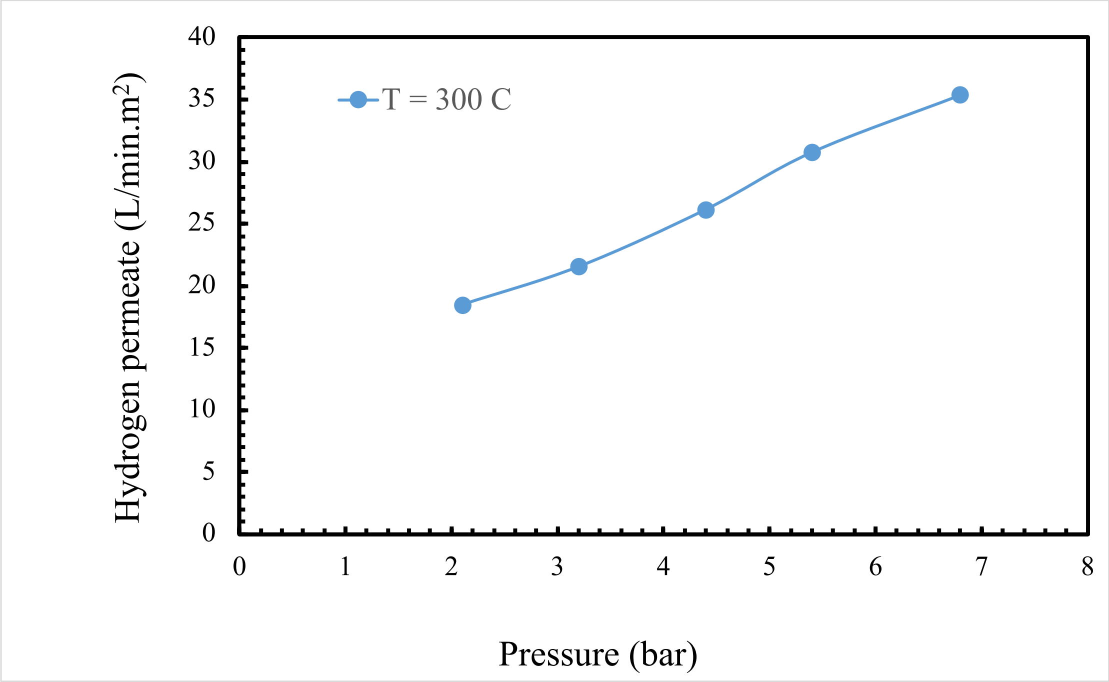
$H_2O/CO = 2/1$

$$CO\ Conversion\ (\%) = \frac{(CO)_{in} - (CO)_{out}}{(CO)_{in}} \cdot 100$$

$$H_2\ Recovery\ (\%) = \frac{H_{2,\ permeate}}{H_{2,\ permeate} + H_{2,\ retentate}} \cdot 100$$



Pure Hydrogen Produced: Pd-Au-Ag (70-26-4 w/w%)-PSS support



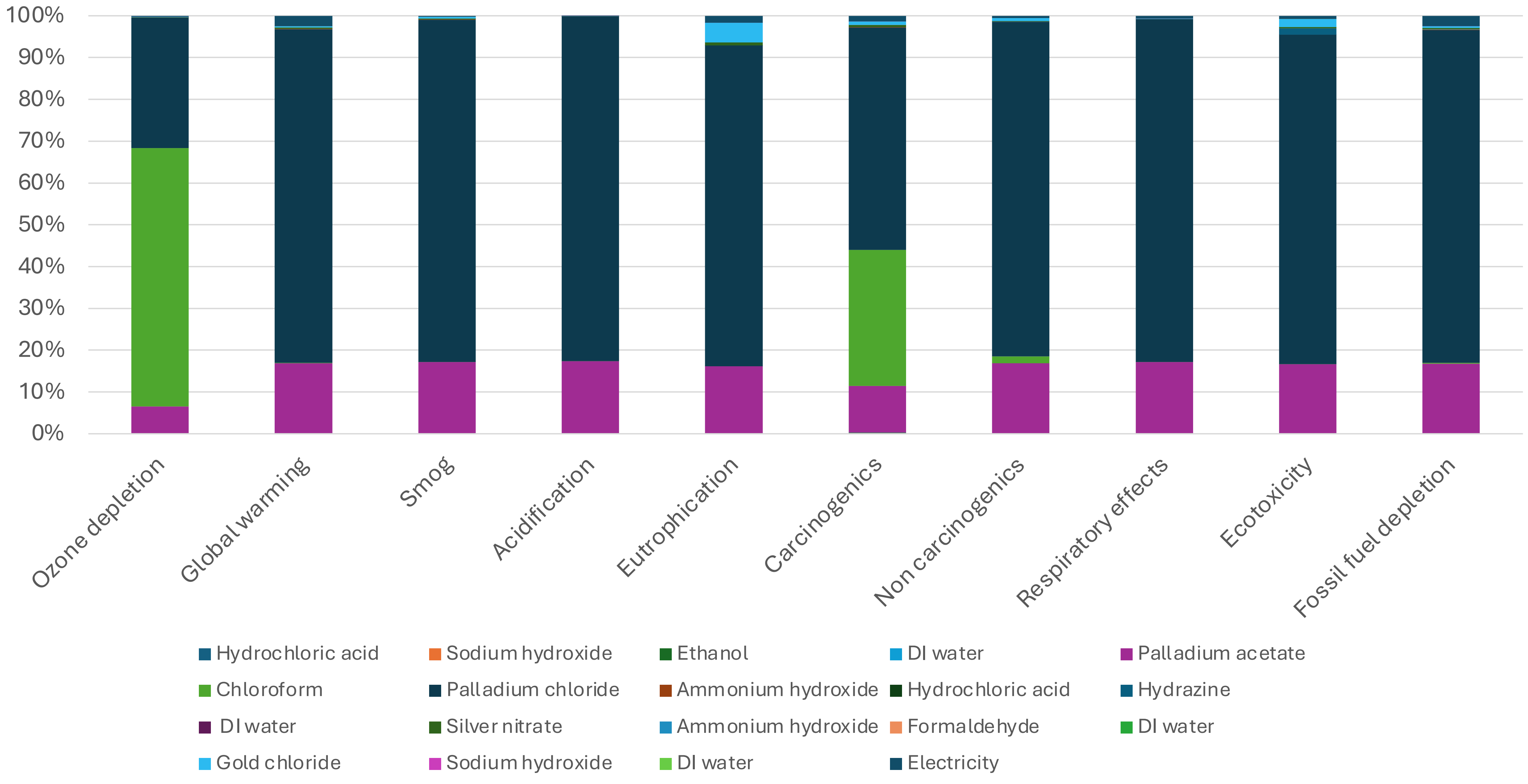
The membrane was exposed at several thermal cycles.

It is still stable and running at 400 °C

The CO has a little effect on H_2 permeation, reducing its permeation by ~9%.

Membrane	Permeance, mole/m^2.sec.Pa	Ideal Selectivity
Membrane 0.5M/PSS - 100% Pd	6.95E-07	1500 - 3700
Membrane 0.2M/PSS - 100% Pd	4.14E-07	> 10^7
Binary		
Membrane 0.5M/PSS - 99% Pd, 1% Au	5.49E-07	> 10^7
Membrane 0.2M/PSS - 68.6% Pd, 31.4% Au	3.14E-07	> 10^7
Ternary		
Membrane 0.5M/PSS - 86.8% Pd, 3.1% Ag, 10.1% Au	4.40E-07	> 10^7
Membrane 0.5M/PSS - 63.1% Pd, 23.9% Ag, 13% Au	6.68E-07	> 10^7
Membrane 0.2M/PSS - 70.3% Pd, 3.3% Ag, 26.4% Au	4.96E-07	> 10^7

Life Cycle Assessment – related to the Pd-Au-Ag membrane synthesis



Key Takeaways

- The ternary Pd-based membrane, Pd-Au-Ag (70-26-4 w/w%)-PSS support, shows good performance in terms of hydrogen permeation and ideal selectivity

- The membrane underwent several thermal cycle and it is still stable under reaction environment.

- Membrane reactor performs better than a traditional reactor.

- Regarding the LCA related to the chemicals of the membrane, palladium and chloroform are the big contributors across all of the impact categories by percentage.

ACKNOLEDGEMENT

Dr. Mohamed Elharati for membrane synthesis, characterization and reaction testing

Dr. Andrea Hicks for LCA and TEA

NATIONAL ENERGY TECHNOLOGY LABORATORY

Dr. Diane Madden

THANKS FOR YOUR KIND ATTENTION