Methanol Steam Reforming and Ethanol Steam Reforming in Membrane Reactors: Experimental Study

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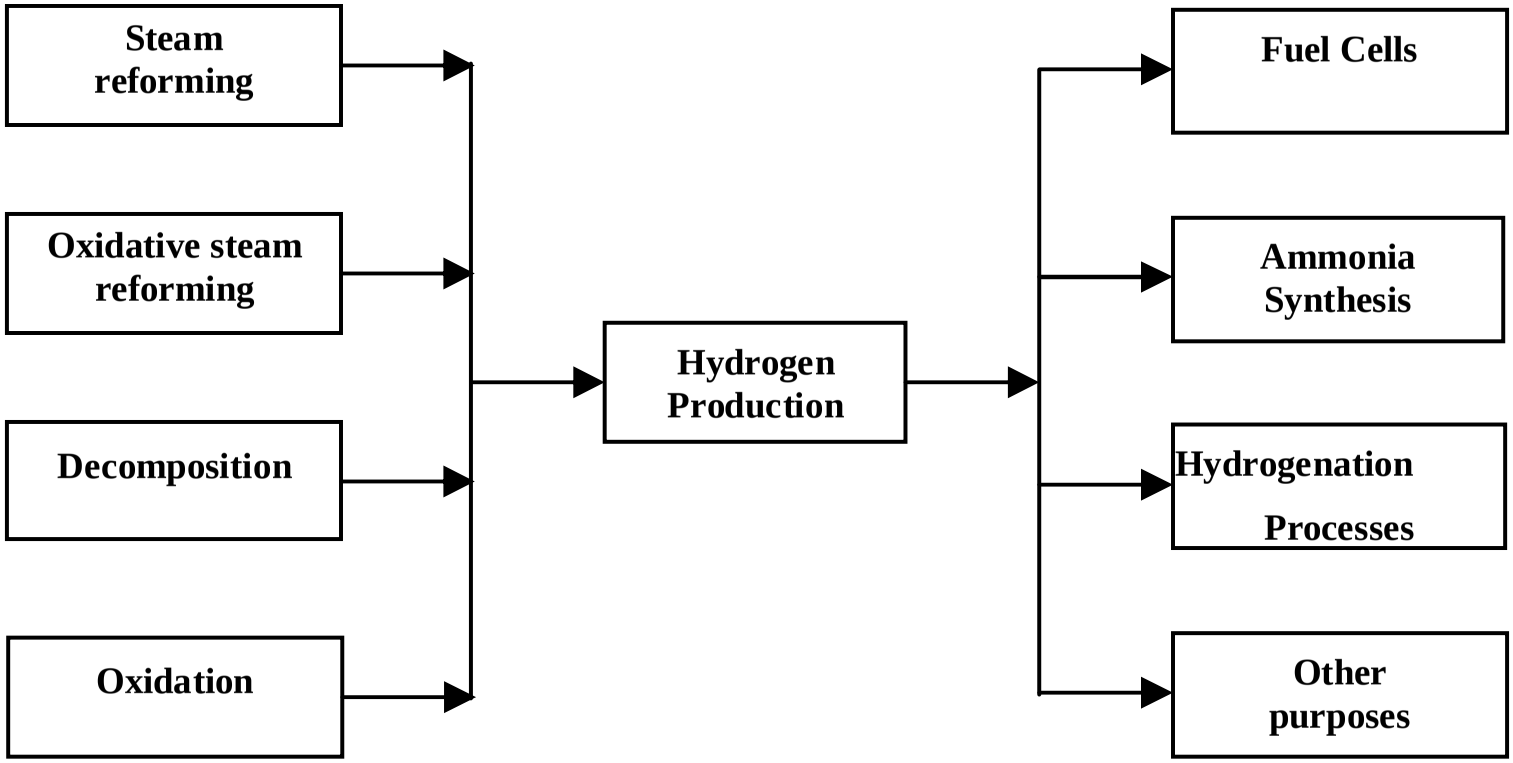
Outline

- **Introduction**

  Hydrogen production by steam reforming reaction

- **Objectives**
- **Membrane reactors**
- **Results and discussion**
- **Conclusion**


Steam reforming
Oxidative steam reforming
Decomposition
Oxidation
Hydrogen Production
Fuel Cells
Ammonia Synthesis
Hydrogenation Processes
Other purposes

Methanol steam reforming : literature

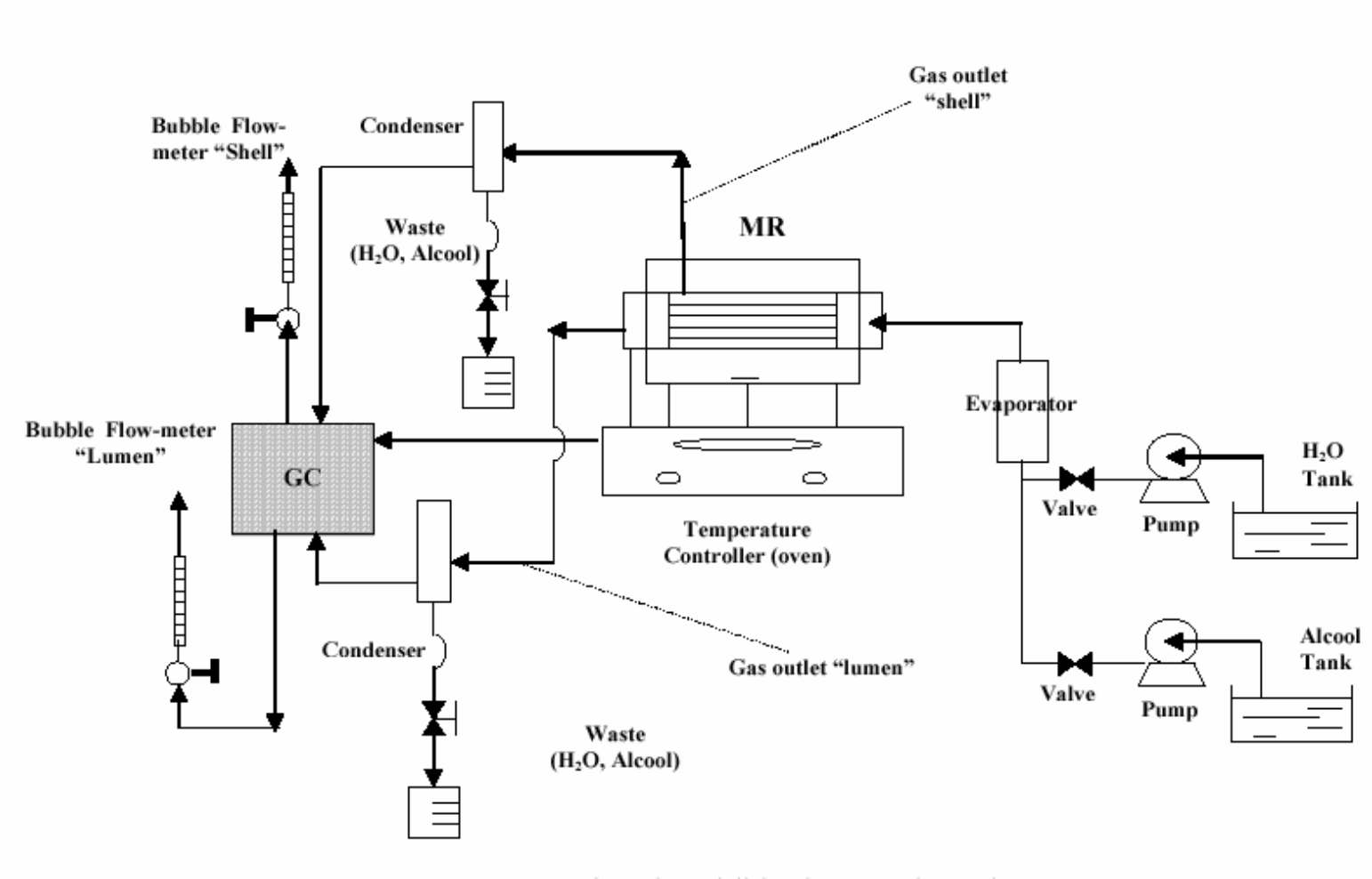
$$CH_3OH + H_2O \Leftrightarrow CO_2 + 3H_2 \qquad \Delta H^\circ_{298\ K} = 49.4\ kJ \cdot mol^{-1}$$

- Optimal conditions:
  - **High T (200 - 500°C)**
  - **Low p (1- 2 atm)**
- Catalysts:
  - **Cu- based: $Cu/ZnO/Al_2O_3$, Cu/CeO_2, Cu/Cr, Cu/Zr, $Al_{63}Cu_{25}Fe_{12}$**
  - **Amorphous alloys: Cu-Zr-Pt, Cu-Zr-Au**
  - **Ni/ZnO, Co/ZnO, Pt/ZnO, Ru, Mg/Al, Ni/Al, Co/Al**
- Membranes (Pd-based):
  - **Pd/V/Pd**
  - **$Pd_{75}Ag_{25}$**
  - **$Pd_{60}Cu_{40}$**

Ethanol steam reforming : literature

$$C_2H_5OH + 3H_2O \Leftrightarrow 2CO_2 + 6H_2 \quad \Delta H^\circ_{298\,K} = 173.1\ kJ\cdot mol^{-1}$$

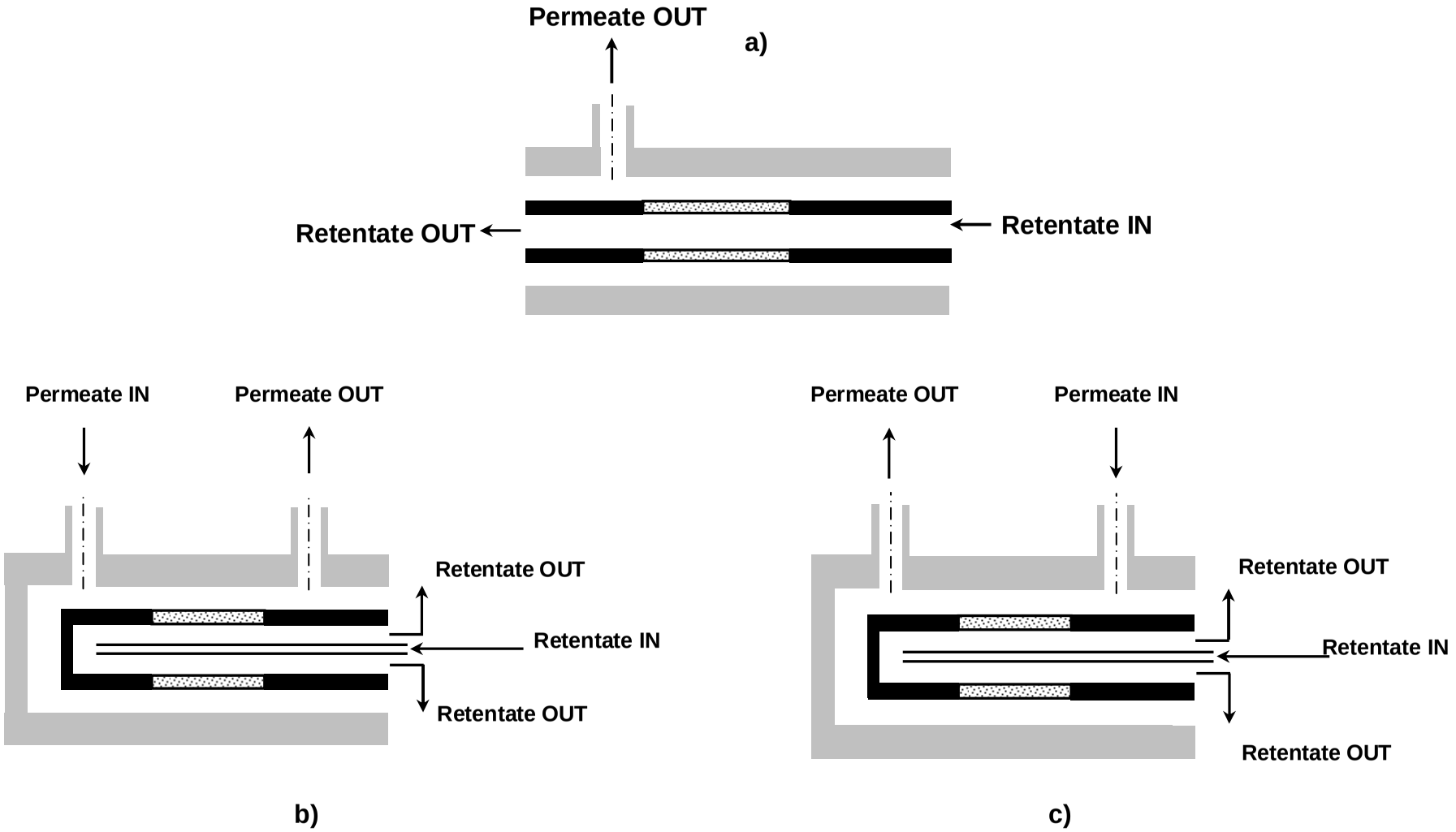
- Optimal conditions:
  - **High T (350 - 650°C)**
  - **Low p (1- 2 atm)**
- Catalysts:
  - **Rh, Ru, Pd, Pt, Ni, Co and Cu supported on Al_2O_3, SiO_2, MgO, and La_2O_3**
- Membranes (Pd-based):
  - **Not yet**


Gas outlet
"shell"
Bubble Flow-
meter "Shell"
Condenser
Waste
(H_2O, Alcool)
MR
Evaporator
Bubble Flow-meter
"Lumen"
GC
Valve
Pump
H_2O
Tank
Temperature
Controller (oven)
Condenser
Gas outlet "lumen"
Valve
Pump
Alcool
Tank
Waste
(H_2O, Alcool)

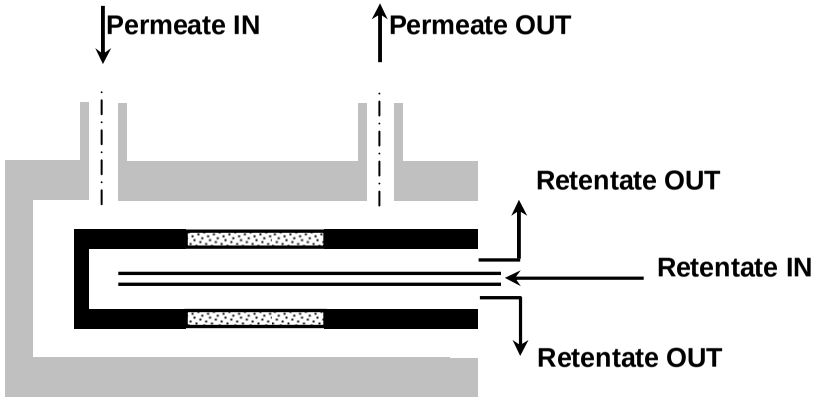
Membrane reactors

In this study, three different membranes are used in membrane reactors:

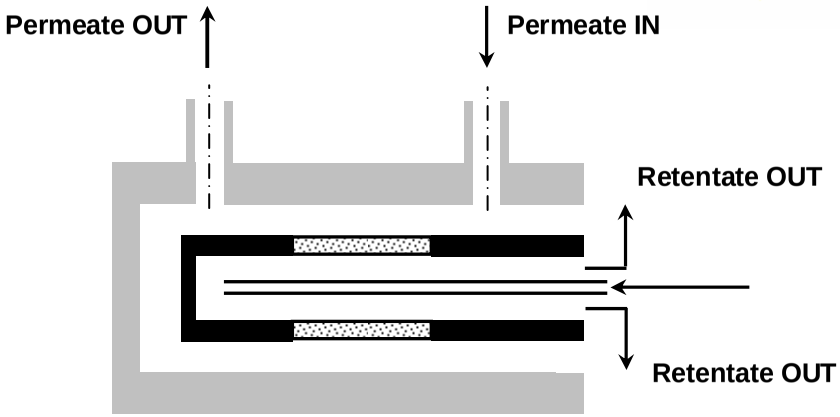
1) **The first membrane is a TiO_2-Al_2O_3 asymmetric porous commercial membrane (Inoceramic) produced at the CNR-CSMSOA laboratories (Pisa, Italy) by depositing Pd and Ag on the TiO_2-Al_2O_3 asymmetric support;**
2) **The second one is also an asymmetric porous ceramic membrane produced at the University of Genova laboratories by depositing Pd and Ag on the ceramic asymmetric support with a different technique respect to the first one;**
3) **The third one is a pine-hole free Pd-Ag thin wall membrane tube permeable only to hydrogen produced by a cold-rolling and diffusion welding technique in ENEA laboratories (Frascati, Italy);**

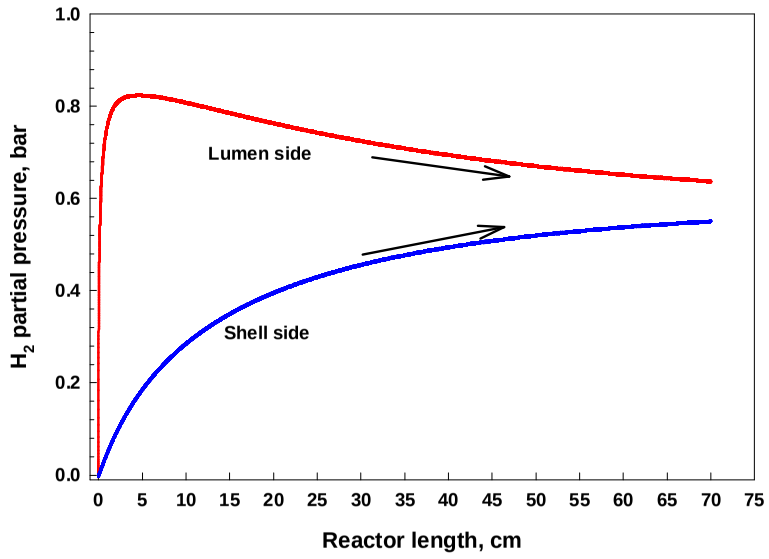

Permeate OUT
a)
Retentate OUT
Retentate IN
Permeate IN
Permeate OUT
Retentate OUT
Retentate IN
Retentate OUT
b)
Permeate OUT
Permeate IN
Retentate OUT
Retentate IN
Retentate OUT
c)

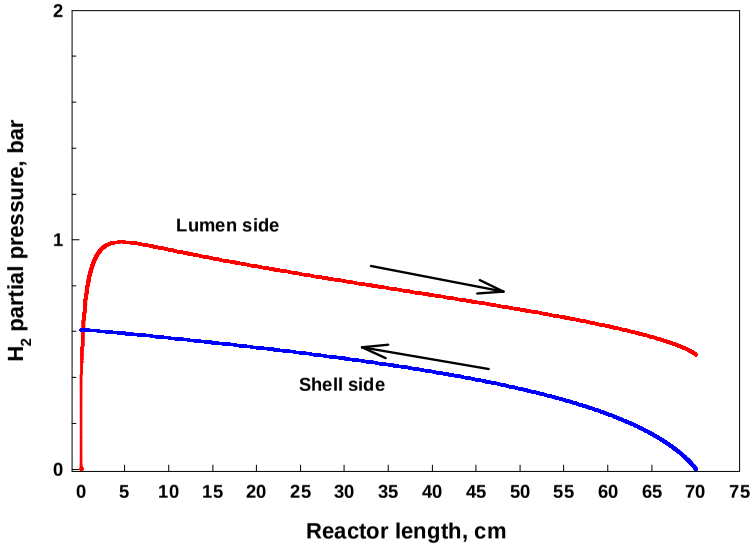
Past, Present and Future Uses of Absorption and Membrane Processes In Hydrogen Production

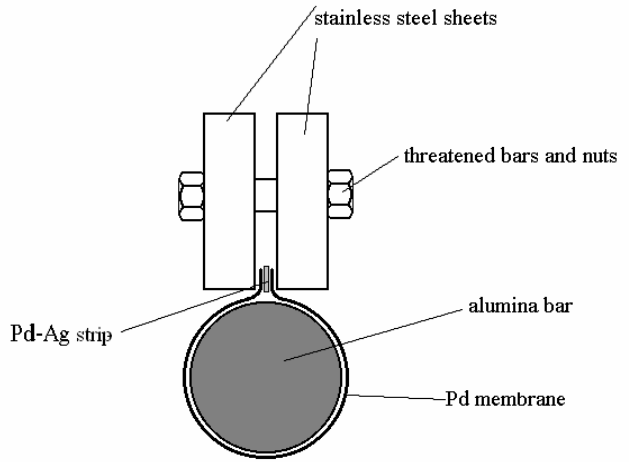


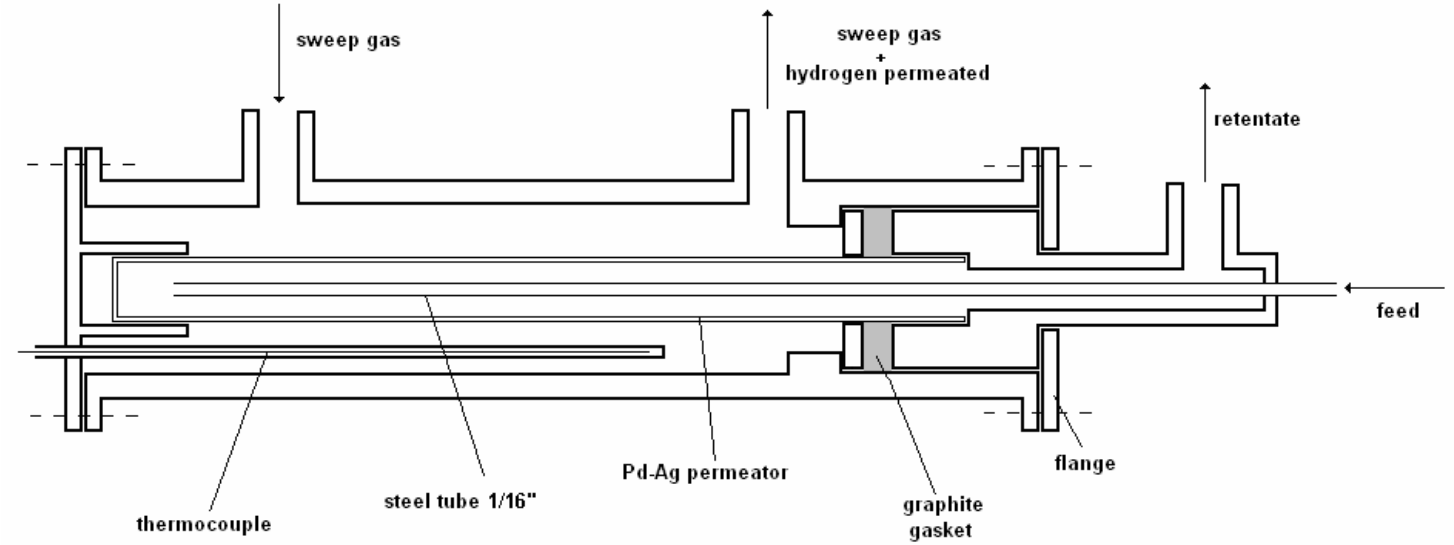
Co-current mode

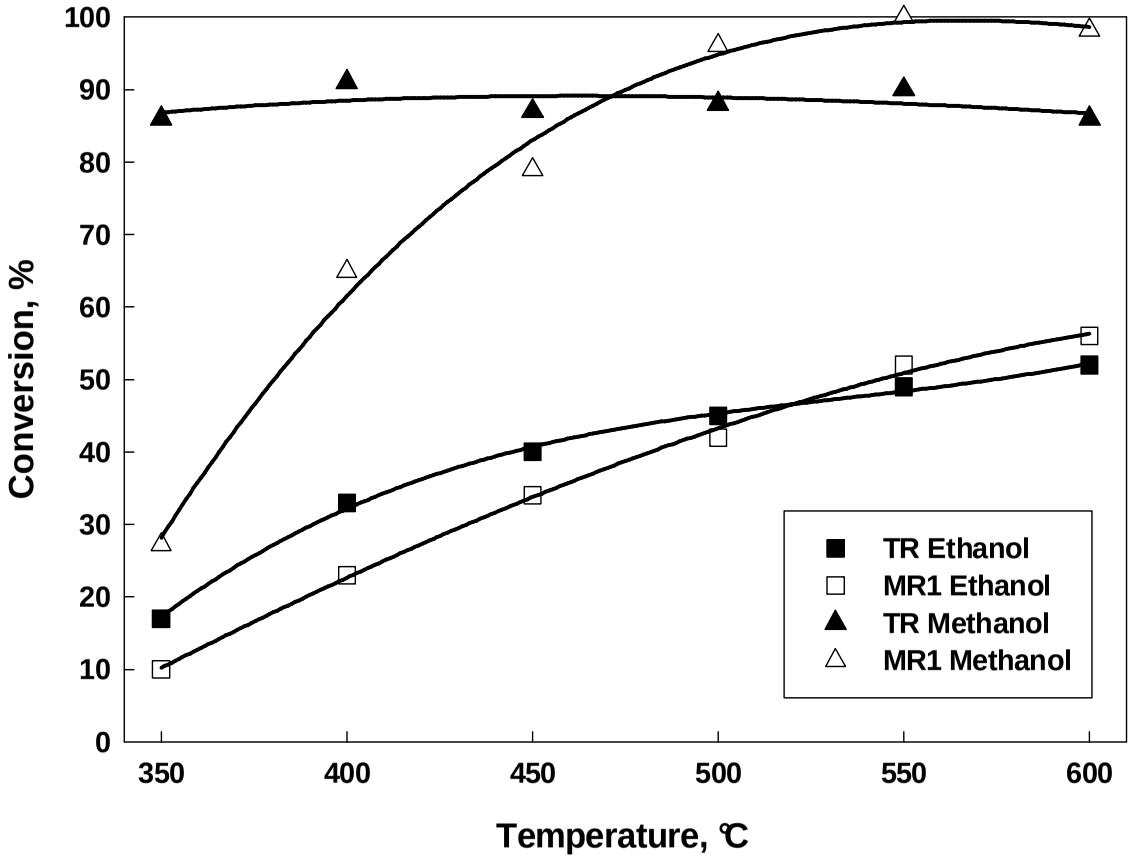







stainless steel sheets
threatened bars and nuts
Pd-Ag strip
alumina bar
Pd membrane


sweep gas
sweep gas
+
hydrogen permeated
retentate
feed
thermocouple
steel tube 1/16"
Pd-Ag permeator
graphite
gasket
flange

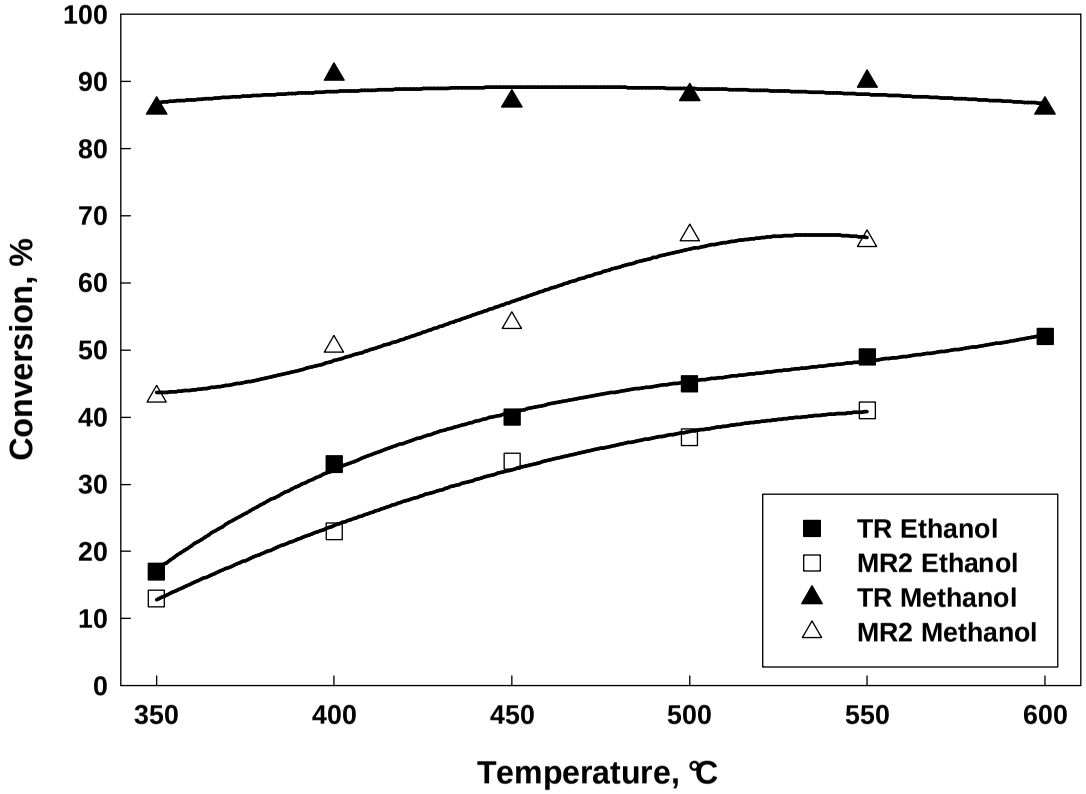


Methanol and Ethanol conversion versus temperature in MR1 and TR, H2O/Alcool = 4.5/1, plumen=1.3 bar, pshell = 1 bar (for MR)

	MR1		TR	
	ESR	MSR	ESR	MSR
T [°C]	S_{H2} [%]	S_{H2} [%]	S_{H2} [%]	S_{H2} [%]
350	75.00	67.60	43.20	60.30
400	75.50	65.70	55.10	61.10
450	76.70	66.20	64.70	63.90
500	77.10	66.30	68.60	65.30
550	80.10	68.70	69.20	65.80
600	80.10	69.20	70.30	68.90

Hydrogen selectivity by ESR and MSR in MR1 and TR

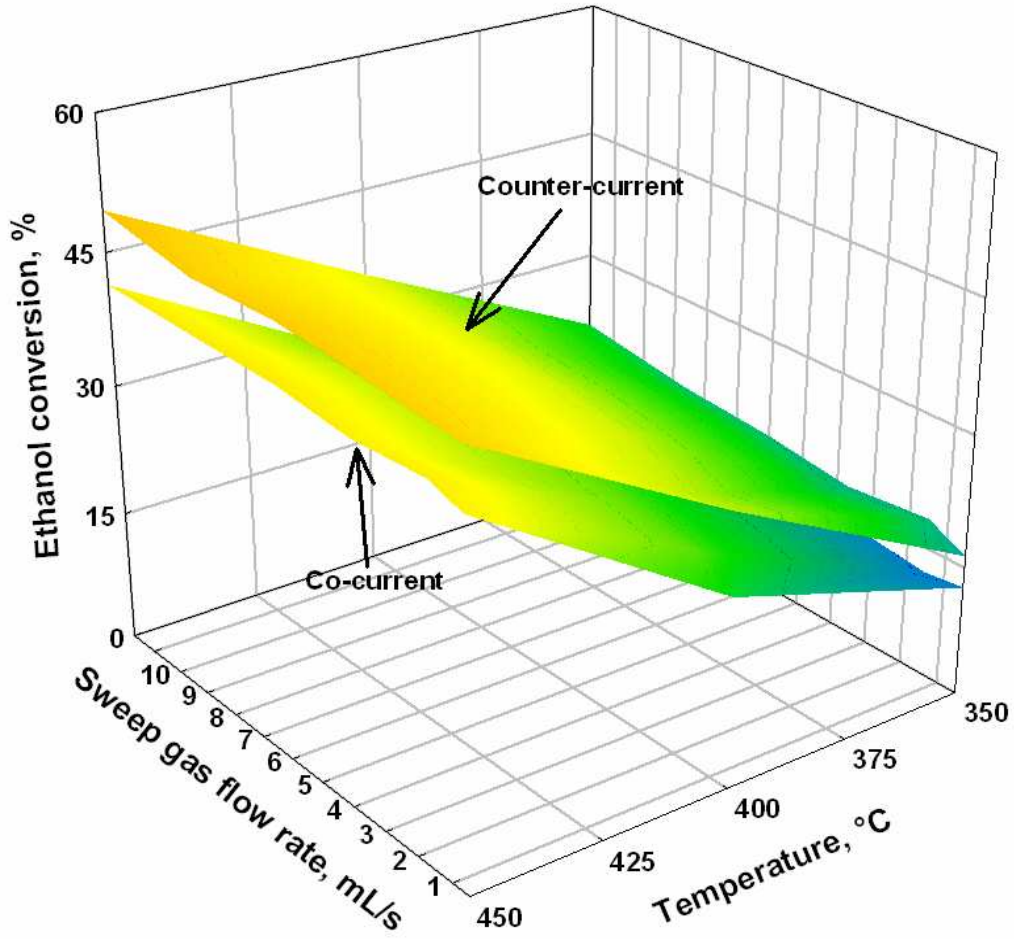
Past, Present and Future Uses of Absorption and Membrane Processes In Hydrogen Production



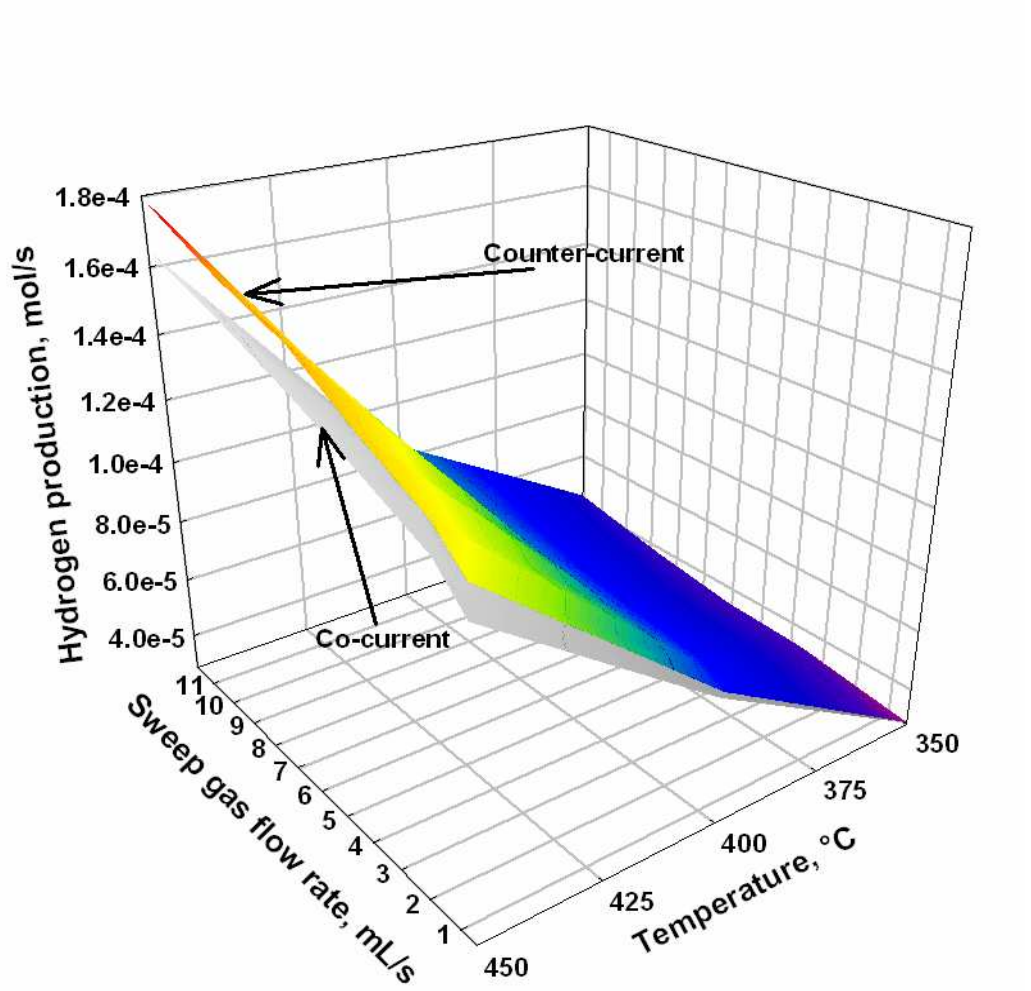
Methanol and Ethanol conversion versus temperature in MR2 and TR, H2O/Alcool = 4.5/1, plumen=1.3 bar, pshell = 1 bar (for MR)

	ESR – MR1	ESR – MR2	ESR – TR
T [°C]	Carbon [mol/s]	Carbon [mol/s]	Carbon [mol/s]
350	2.18E-05	2.54E-05	4.63E-05
400	2.85E-05	3.33E-05	4.93E-05
450	3.76E-05	4.33E-05	4.66E-05
500	4.27E-05	5.07E-05	4.75E-05
550	6.36E-05	5.59E-05	4.88E-05
600	6.84E-05		4.97E-05

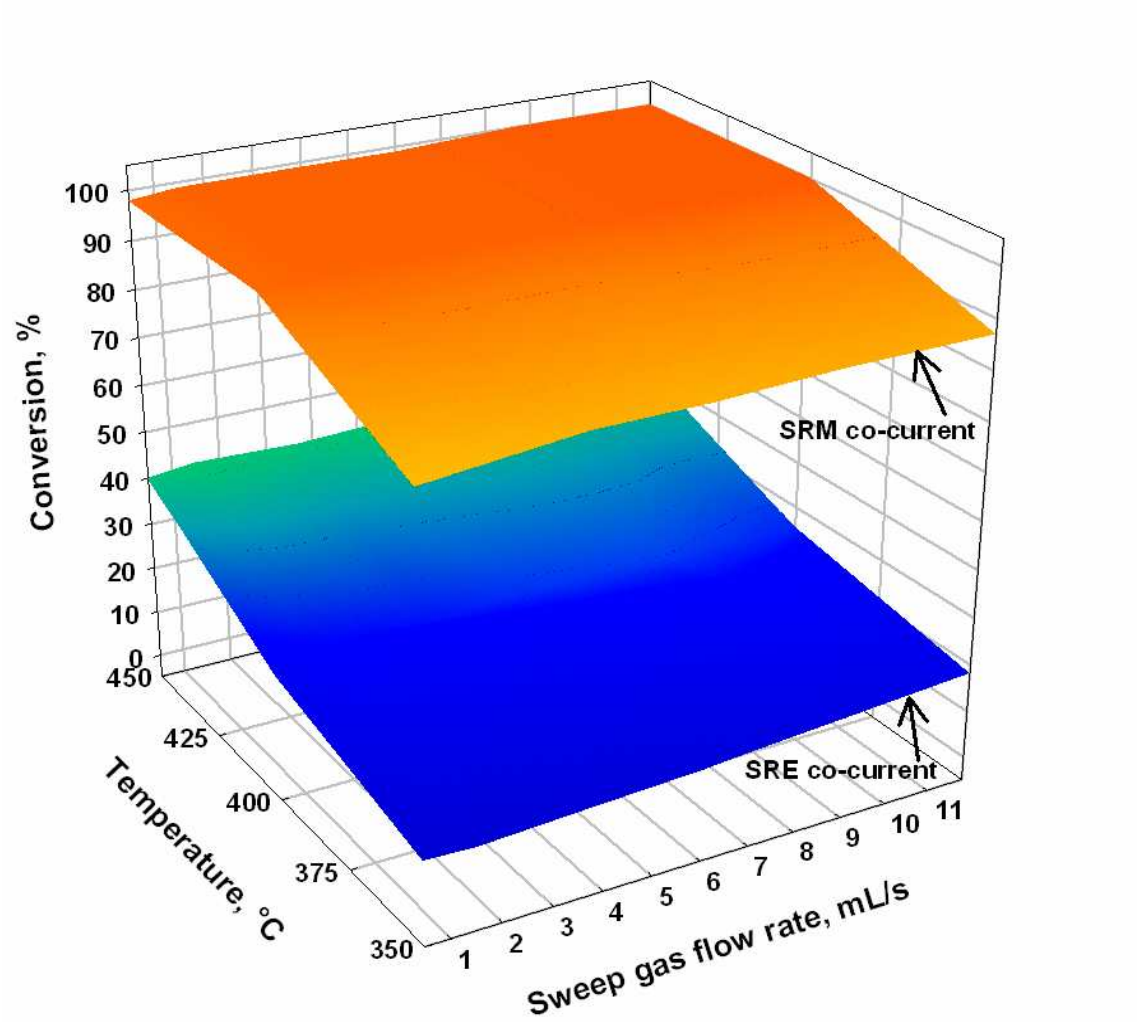
Carbon deposition during ESR in MR1, MR2 and TR



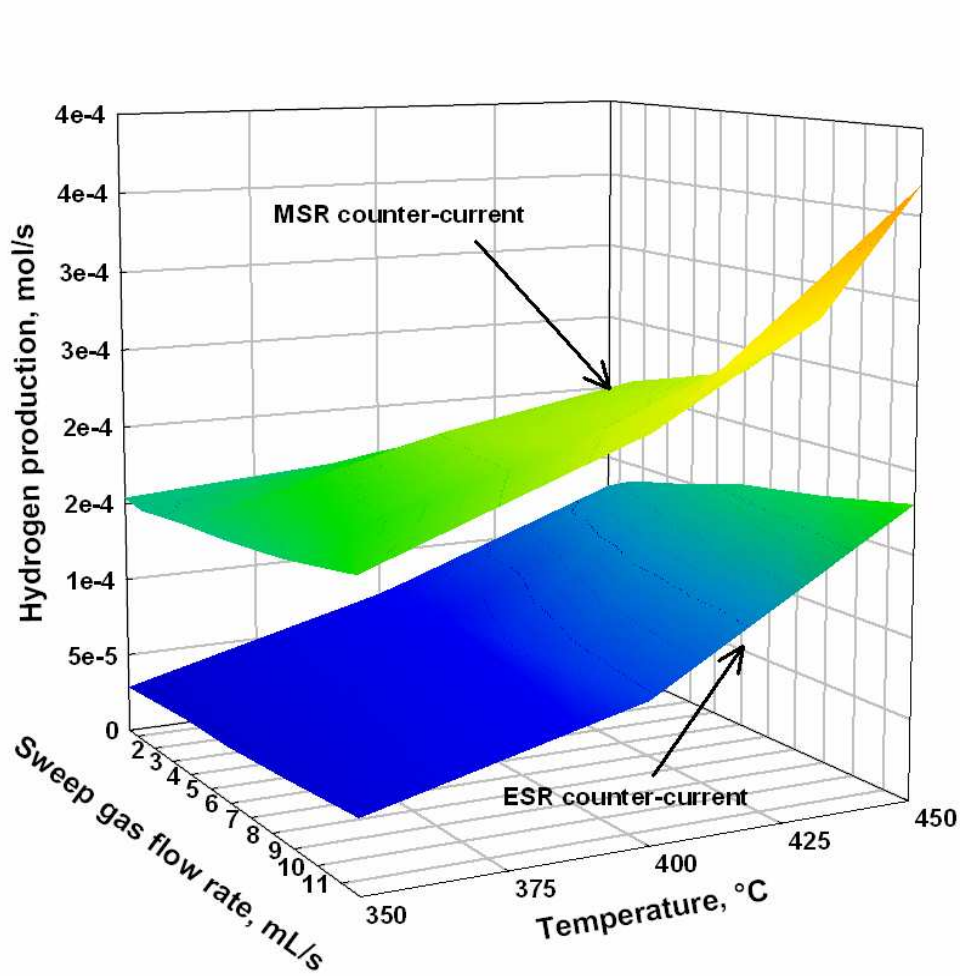
Ethanol conversion versus temperature and versus sweep gas flow rate in MR3.
Co-current and Counter current mode, H2O/Alcool = 4.5/1, plumen=1.3 bar, pshell = 1 bar



Hydrogen production versus temperature and versus sweep gas flow rate during ESR in MR3. Co-current and Counter current mode, H2O/Alcool = 4.5/1, plumen=1.3 bar, pshell = 1 bar



Ethanol and methanol conversion versus temperature and versus sweep gas flow rate in MR3. Co-current mode, H2O/Alcool = 4.5/1, plumen=1.3 bar, pshell = 1 bar



Hydrogen production versus temperature and versus sweep gas flow rate during ESR and MSR in MR3. Counter-current mode, H2O/Alcool = 4.5/1, plumen=1.3 bar, pshell = 1 bar

Conclusions

For MSR, the highest conversion is achieved in MR3 where, already at T = 400℃, in counter-current mode and sweep gas flow r ate equal to 11.8 mL/s, 100% conversion is reached

For ESR, the highest conversion is achieved in MR3 at T = 450℃, in counter-current mode and sweep gas flow rate 11.8 mL/s, and it is equal to 50%.

By using Ru-Al2O3 5% as a catalyst, ESR shows coke deposition with consequent deactivation of the catalyst. Finally, we can conclude that, in the conditions investigated in this work, the MSR reaction is much suitable than the ESR for producing hydrogen.