Inorganic Membranes & Membrane Reactors

EINDHOVEN UNIVERSITY OF TECHNOLOGY

Membrane Reactors for Hydrogen production

Fausto Gallucci, Inorganic Membranes and Membrane Reactors

AndreaH

Clean Hydrogen Partnership

Funded by the European Union

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Outlook

- Who we are
- Why integrated reactors
- Hydrogen
- Ammonia
- Next steps

Our Lab(s)

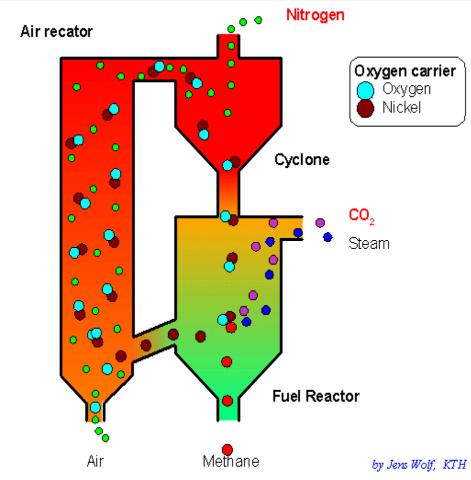
tecnalia
MEMBER OF BASQUE RESEARCH & TECHNOLOGY ALLIANCE

Research themes - SIR

Novel intensified reactor concepts via:

- Integration reaction and separation
  (membrane reactors, chemical looping)

- Integration reaction and heat/energy management
  (endo/exothermic, plasma systems)



- **Research approach:** combination experimental PoC and modelling

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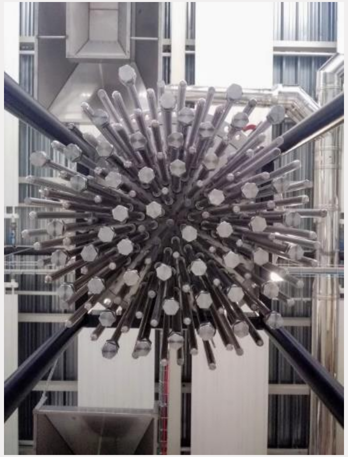
Research themes - SIR

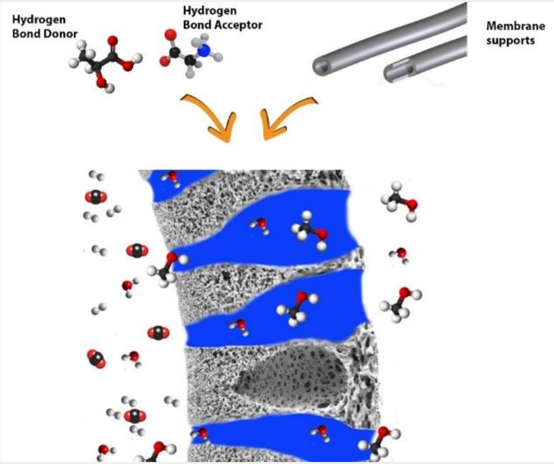
Integration reaction + separation

Packed bed and fluidized bed membrane reactors

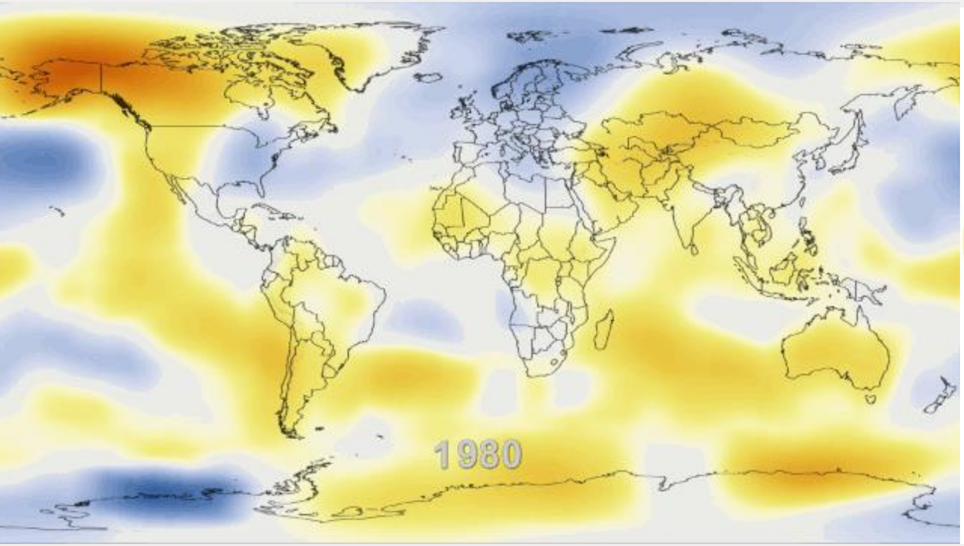
(H_2, syngas, oxidative dehydrogenations, partial oxidations)

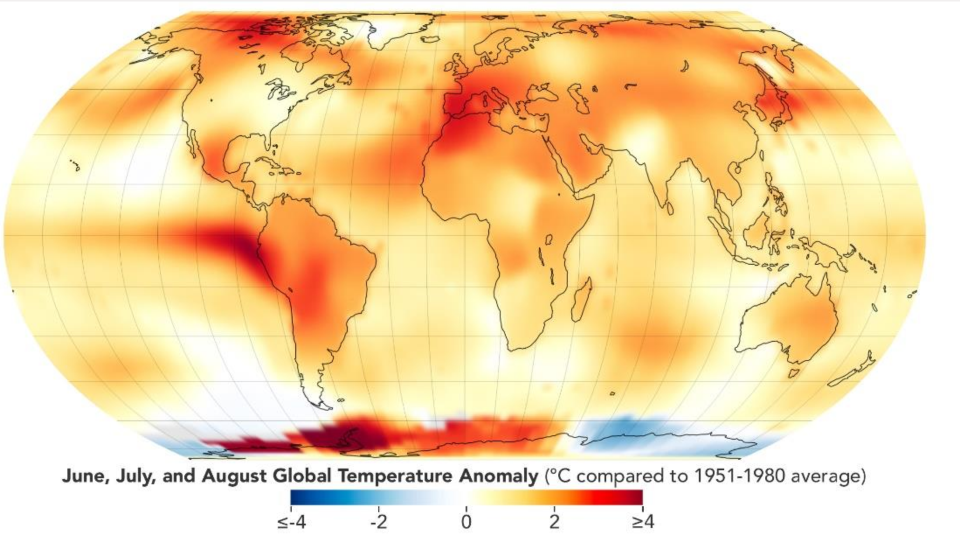
- Use membranes to improve fluidization and fluidization to improve membrane flux
- Liquid supported membranes





One of our challenges





https://kaiserscience.wordpress.com/2019/06/24/the-discovery-of-global-warming/

https://climate.nasa.gov/news/3282/nasa-announces-summer-2023-hottest-on-record/

Earth = 4,54 By   Homo sapiens = 300000 y   Industrial revolution = 100 y

Solutions

1) **Reduce the number of people;**

2) **Reduce the fossil energy use (by use of renewables and improved efficiency)**

3) **Capture the CO_2 (at the production point but also from the atmosphere)**

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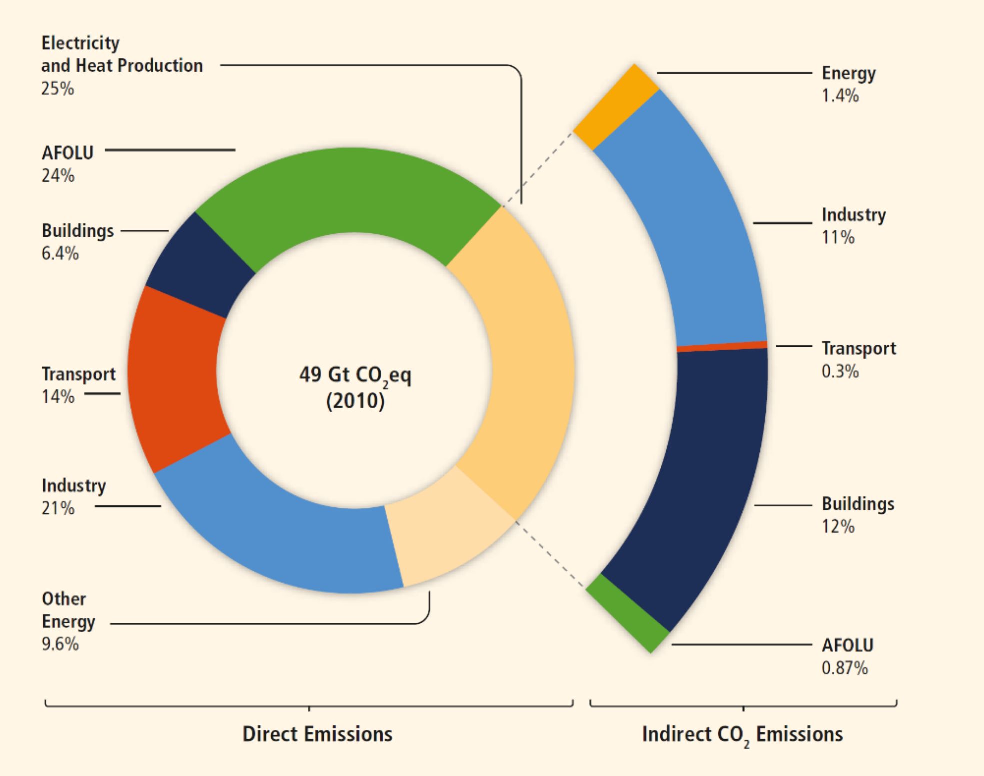
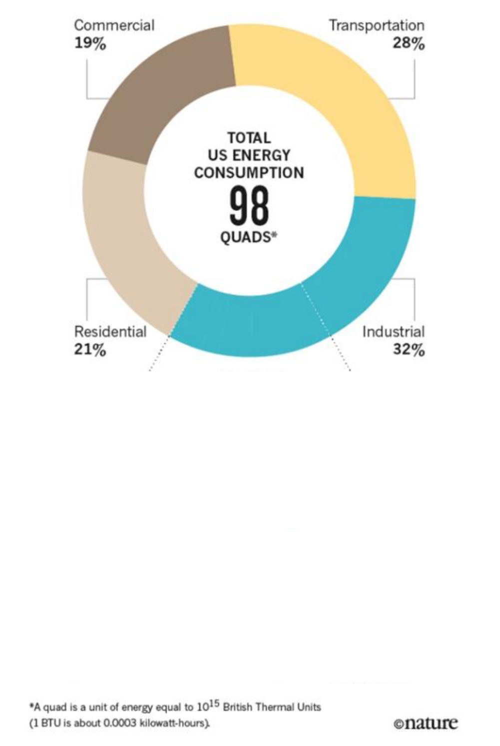
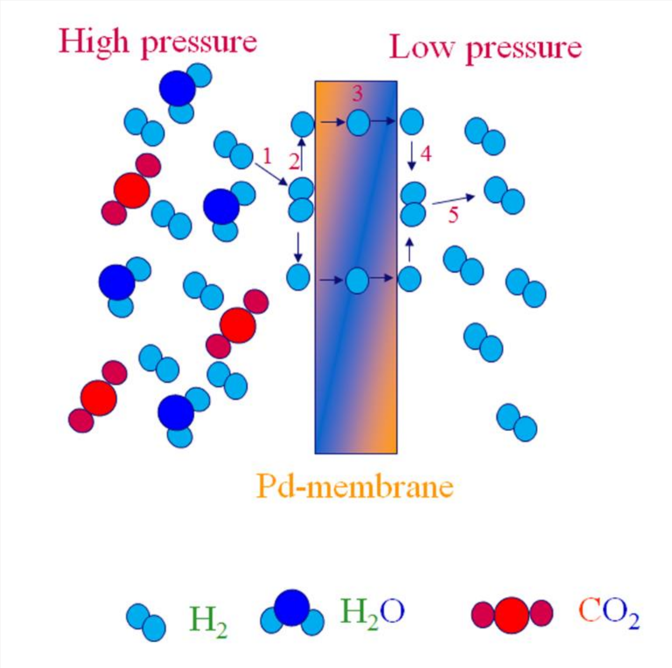
Who is responsible



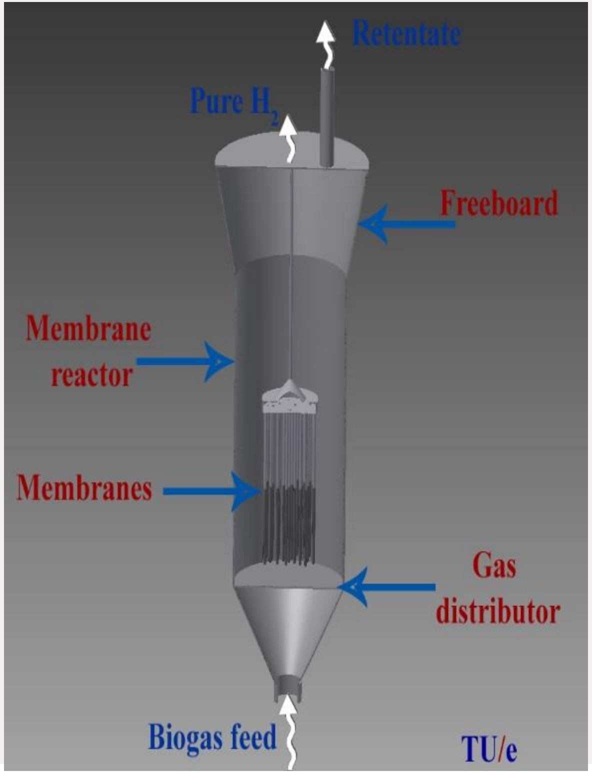
IPCC report

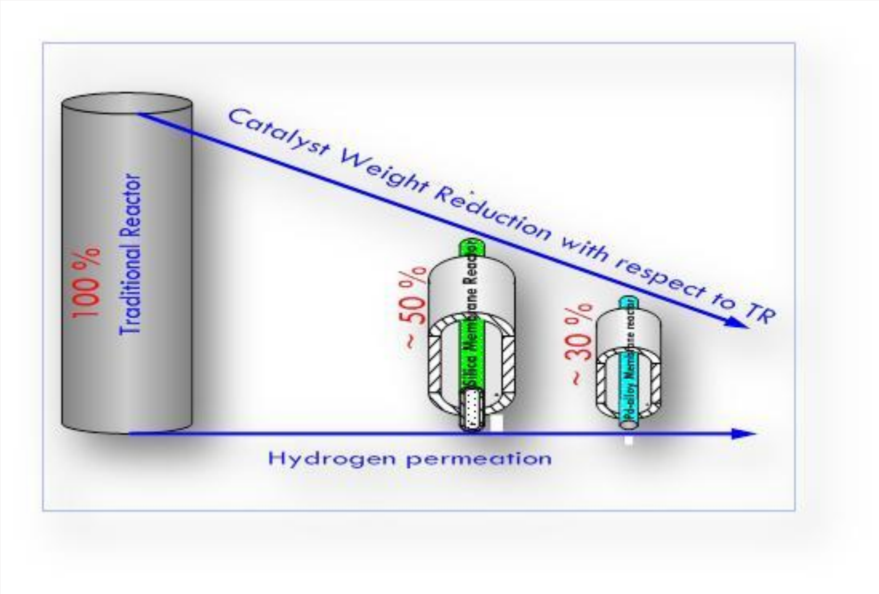
A possible solution





A membrane reactor

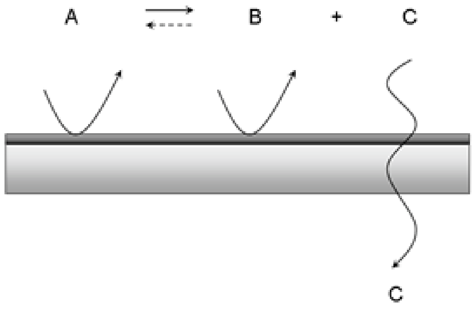


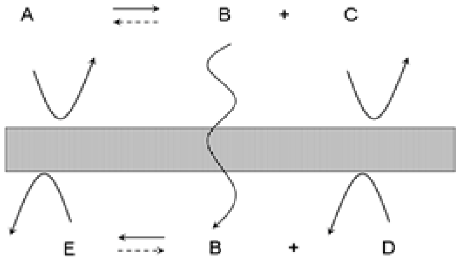


Brunetti A.; Caravella C.; Barbieri G.; Drioli E.; "Simulation study of water gas shift in a membrane reactor", *J. Membr. Sci.*, 2007, 306(1-2), 329-340

Why a membrane reactor?

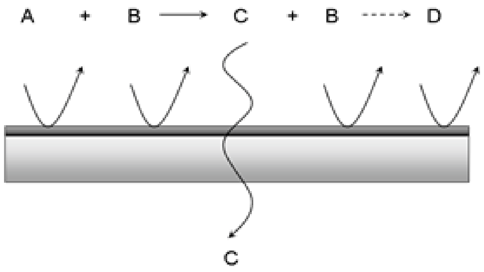
conversion enhancement by selective permeation of a reactant product of an equilibrium limited reaction

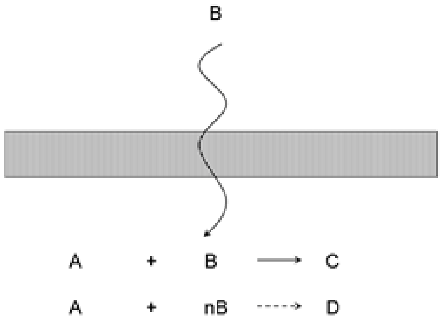




conversion enhancement by coupling of reactions

selectivity enhancement by selective permeation of an intermediate product

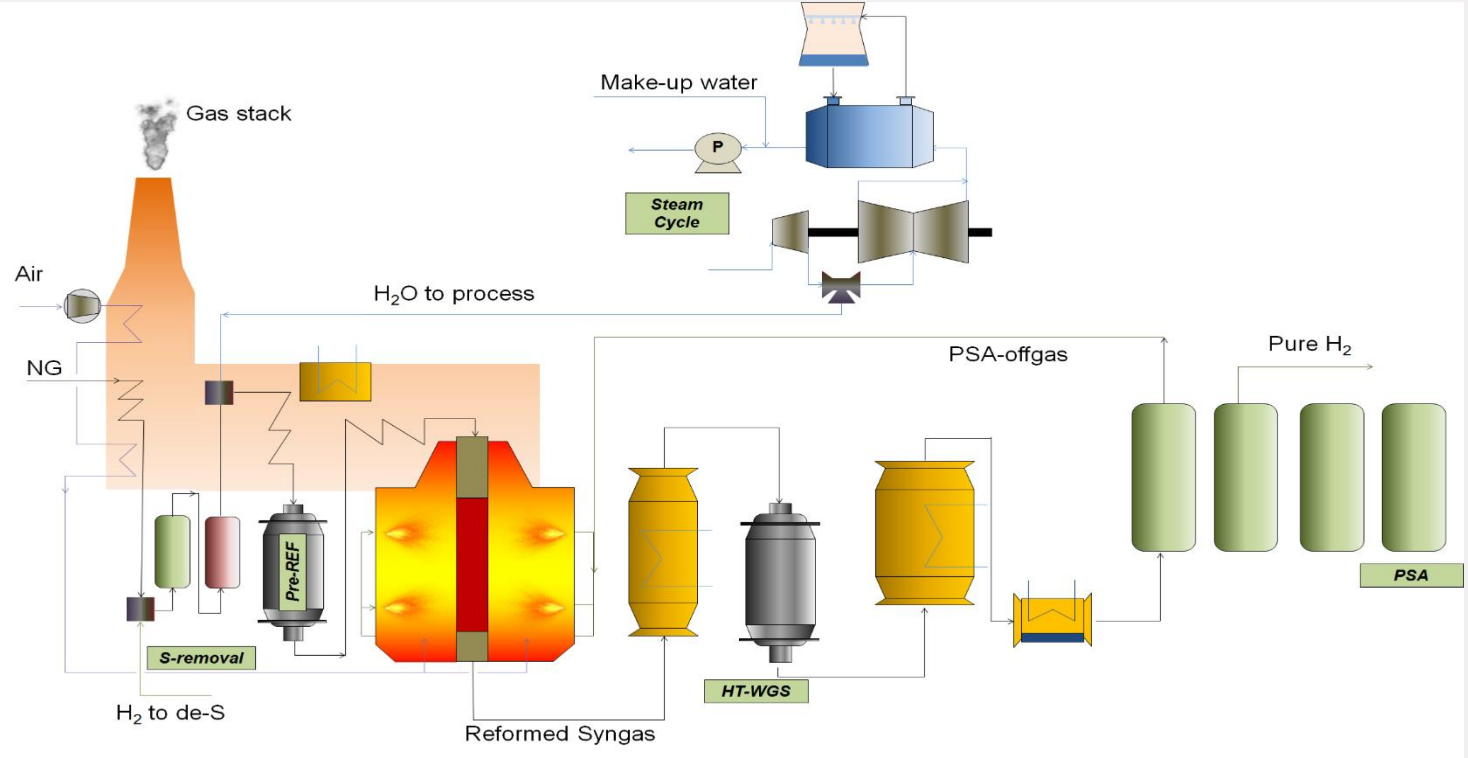




selectivity enhancement by dosing a reactant through the membrane

Examples: Hydrogen

Hydrogen production



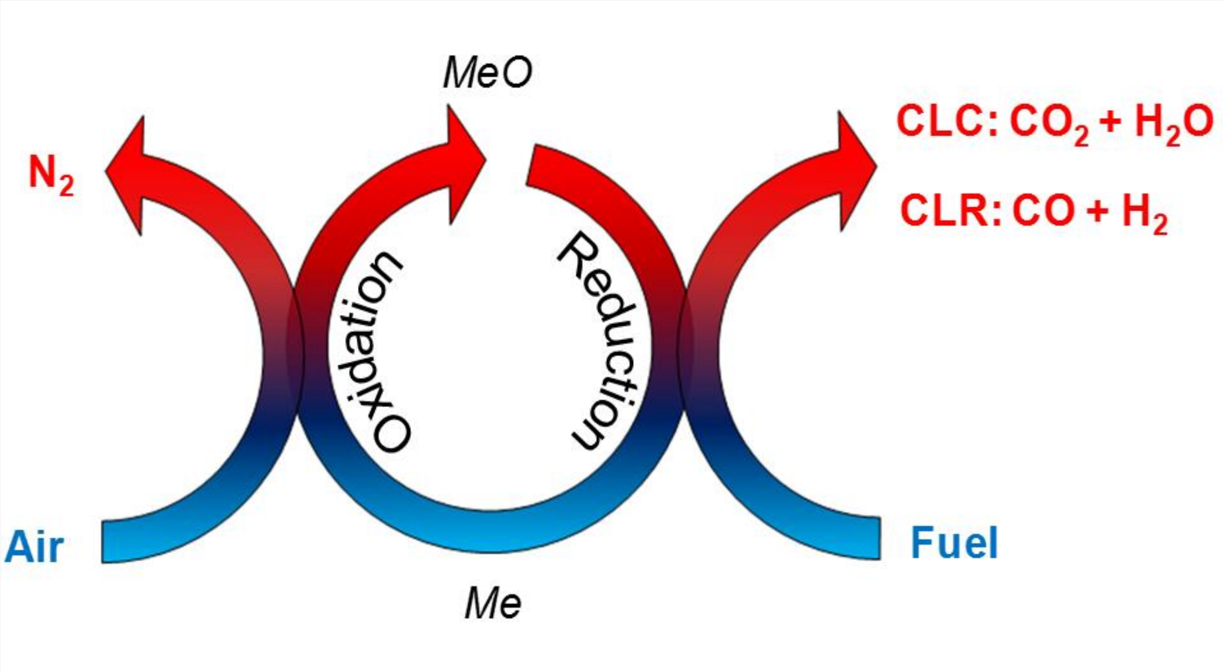
Hydrogen production - chemistry

Membrane reactors

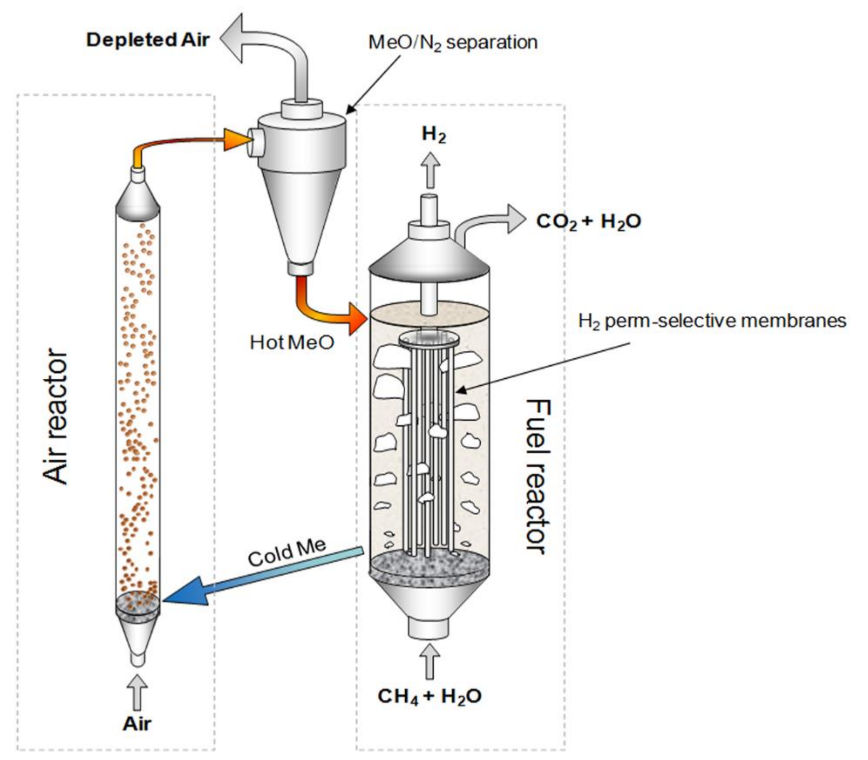
$$CH_4 + 2\,H_2O \Leftrightarrow CO_2 + 4\,H_2 \qquad \Delta H = 165\ \text{kJ/mol}$$

Sorption enhanced reactors

Interesting technologies to improve reforming with CO_2 capture



Integrate Membranes and CLC



NWO
Netherlands Organisation for Scientific Research

VIDI - 12365

2012 – TRL1

2017 – TRL4/5

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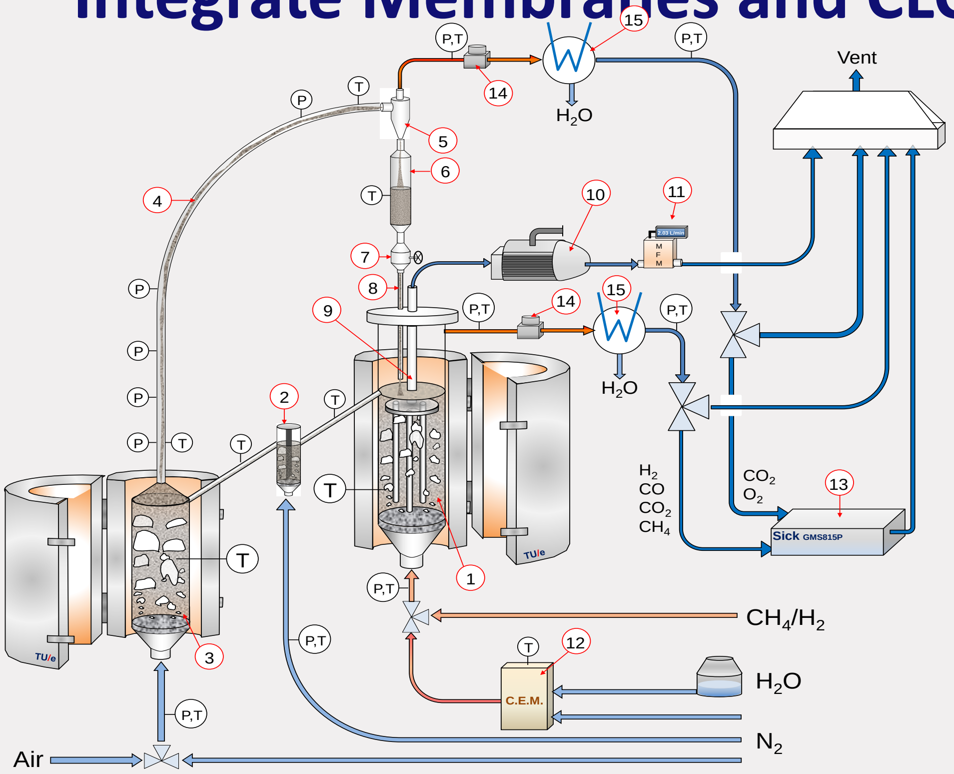
Integrate Membranes and CLC



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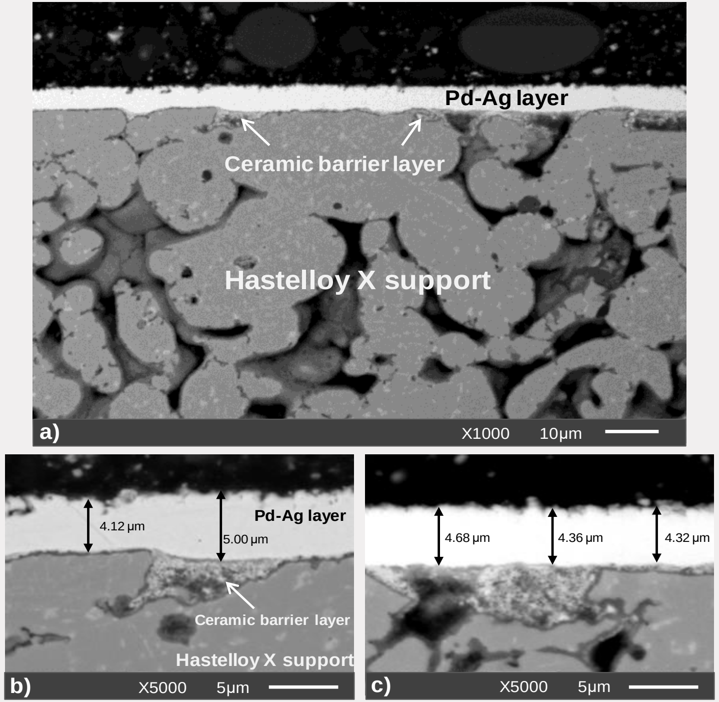
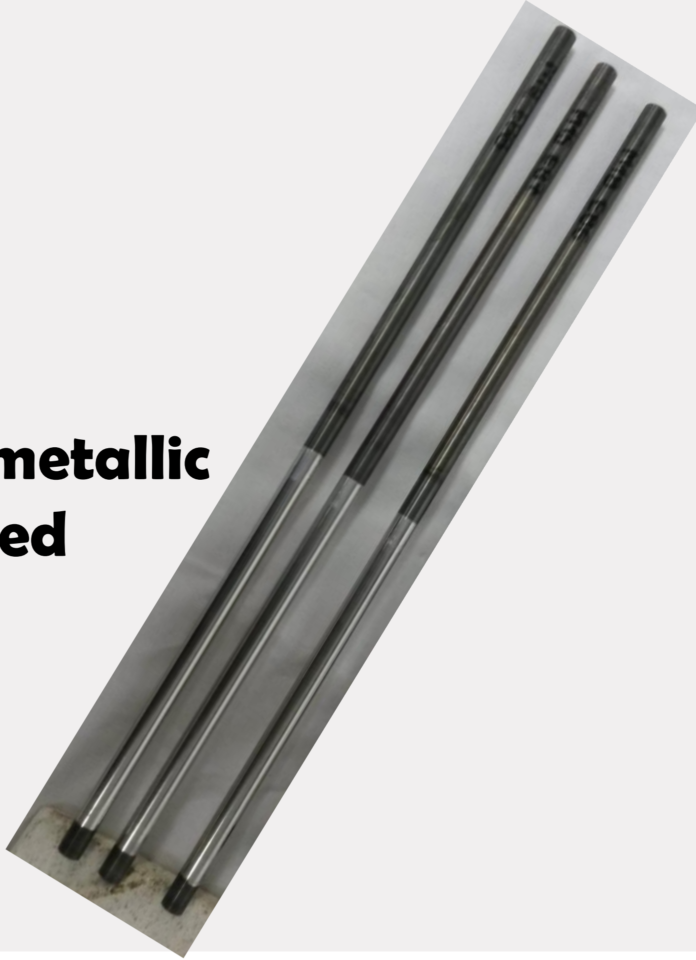
Integrate Membranes and CLC

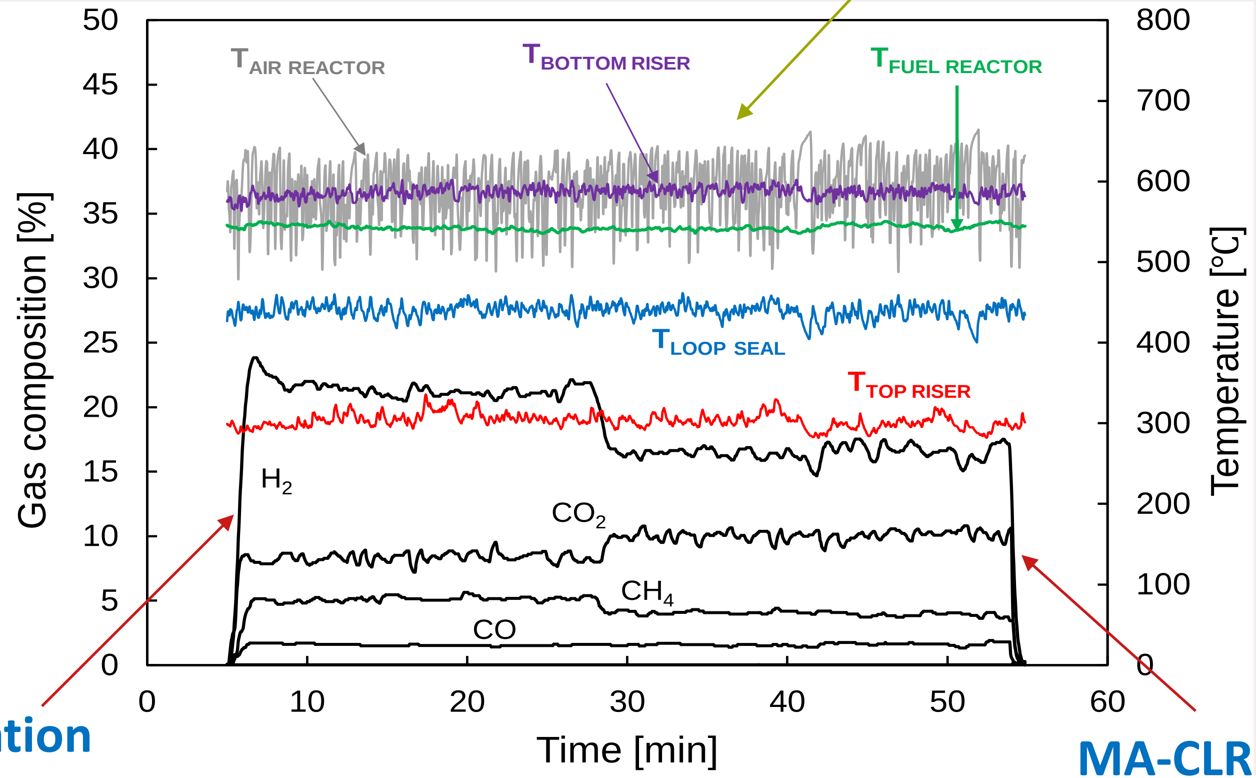


Pd-Ag metallic supported



Integrate Membranes and CLC

Oscillations in temperature indicate solids movement



CLR configuration

MA-CLR configuration

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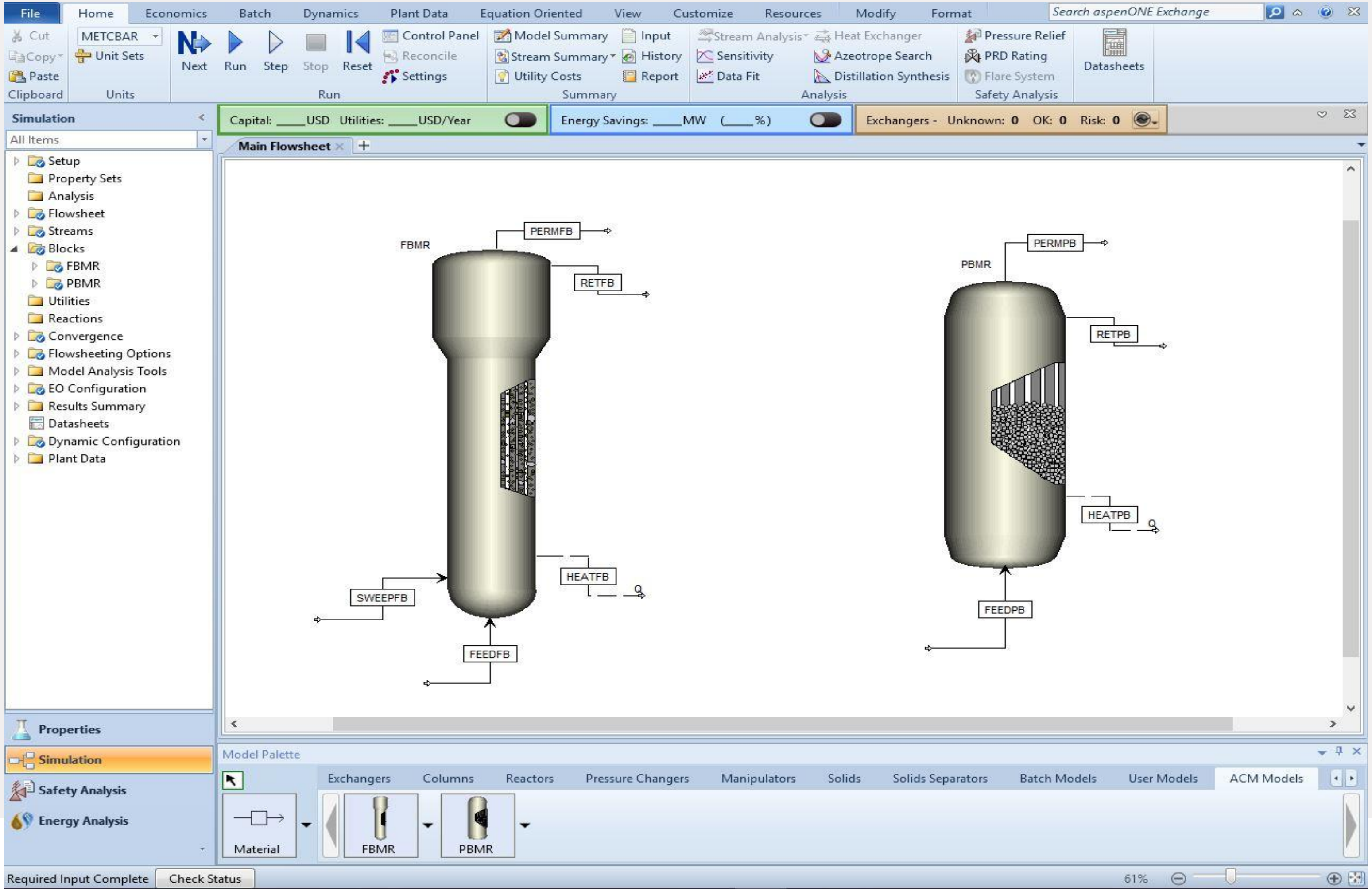
File
Home
Economics
Batch
Dynamics
Plant Data
Equation Oriented
View
Customize
Resources
Modify
Format
Search aspenONE Exchange
Simulation
All Items
Setup
Property Sets
Analysis
Flowsheet
Streams
Blocks
FBMR
PBMR
Utilities
Reactions
Convergence
Flowsheeting Options
Model Analysis Tools
EO Configuration
Results Summary
Datasheets
Dynamic Configuration
Plant Data
Main Flowsheet
FBMR
PERMFB
RETFB
HEATFB
SWEEPFB
FEEDFB
PBMR
PERMPB
RETPB
HEATPB
FEEDPB
Properties
Simulation
Safety Analysis
Energy Analysis
Model Palette
Exchangers
Columns
Reactors
Pressure Changers
Manipulators
Solids
Solids Separators
Batch Models
User Models
ACM Models
Material
FBMR
PBMR
Required Input Complete
Check Status

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MODELTA

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an official spin-off

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MACBETH
Membranes And Catalysts Beyond Economic and Technological Hurdles

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MA

Is MA-CLR really interesting?

	Conventional NO CO_2 capture	Conventional WITH CO_2 capture	MA-CLR concept
Efficiency (%)	81	67	82
CO_2 avoided (%)	-	74	91
Cost of H_2 (€/m³)	0.216	0.282	0.213

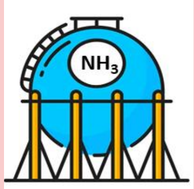
Examples: Ammonia

Ammonia as an energy carrier

RENEWABLE ENERGY GENERATION

GREEN AMMONIA SYNTHESIS

GREEN AMMONIA STORAGE

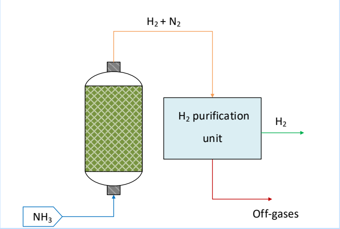


GREEN AMMONIA TRANSPORTATION

GREEN AMMONIA UTILIZATION

- Direct utilization (ICE for mobility or NH_3 solid oxide fuel cells)

- NH_3 decomposition for H_2 production



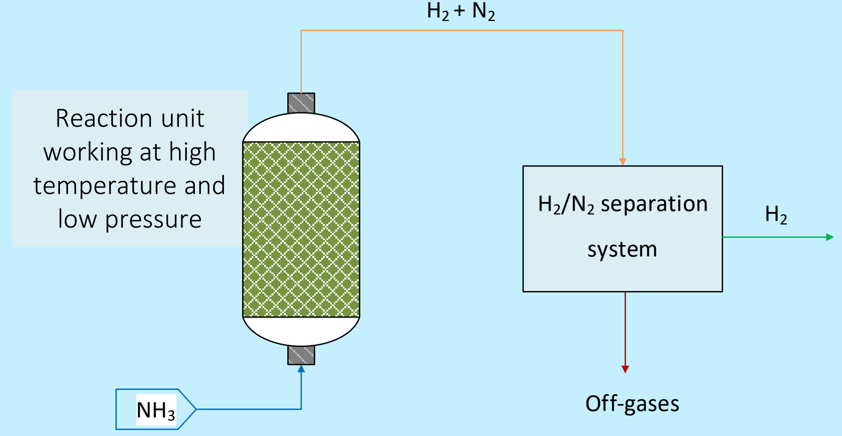
H_2 production from NH_3 decomposition

$$\mathbf{NH_3 \leftrightarrow 0.5\ N_2 + 1.5\ H_2}$$

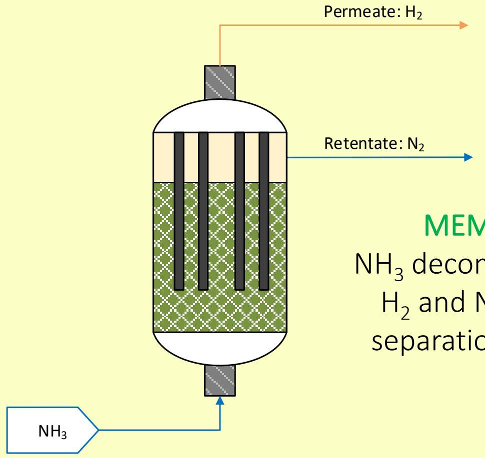
$$\Delta H_f^o = 45.9\ {}^{kJ}/_{mol}$$

NH_3 decomposition is favored at
low pressure and high temperature

Conventional system

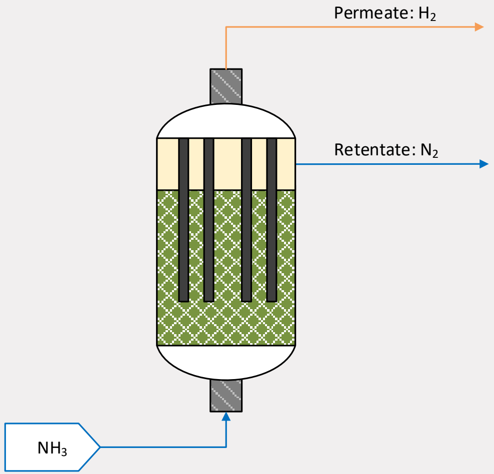


Novel technology

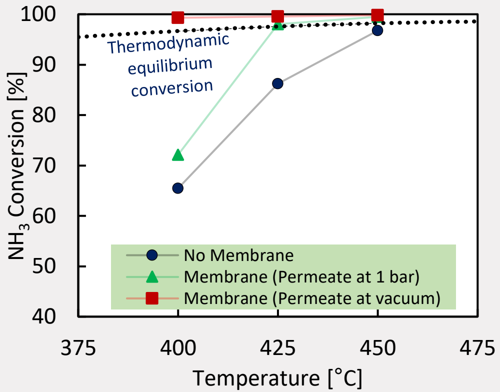


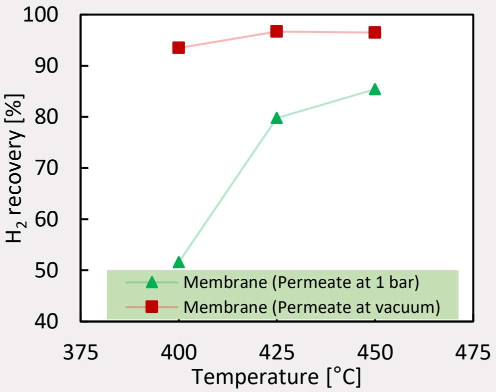
MEMBRANE REACTOR
NH_3 decomposition reaction into H_2 and N_2 and high-purity H_2 separation are simultaneously performed

H_2 production from NH_3 in a membrane reactor



Experimental conditions	
ΔP [bar]	3
Permeate pressure [bar]	0.01-1
Feed flow rate [L_N/min]	0.5
Membrane	Double-skinned Pd-Ag
Thickness selective layer [μm]	~4.61



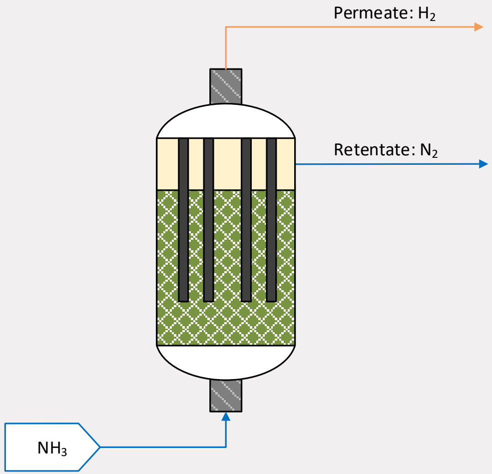


Compared to conventional systems, in a membrane reactor:

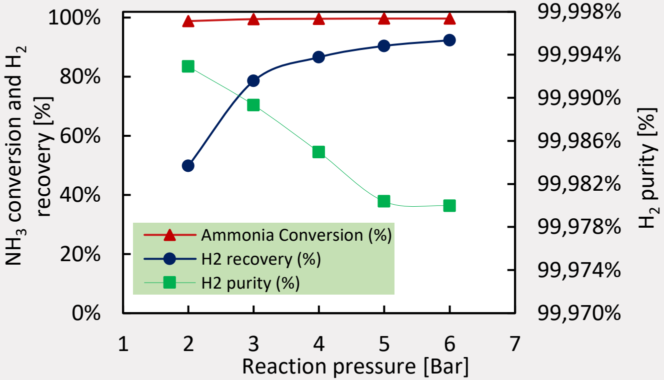
- ❑ Higher NH_3 conversion can be achieved at lower temperature (higher efficiencies)
- ❑ High-purity H_2 is recovered
- ❑ the footprint of the technology is reduced

V. Cechetto, L. Di Felice, J. A. Medrano, C. Makhloufi, J. Zuniga, and F. Gallucci, "H_2 production via ammonia decomposition in a catalytic membrane reactor," *Fuel Process. Technol.*, vol. 216, p. 106772, 2021, doi: https://doi.org/10.1016/j.fuproc.2021.106772.

H_2 production from NH_3 in a membrane reactor



Experimental conditions	
T [°C]	450
Permeate pressure [bar]	0.01-1
Feed flow rate [L_N/min]	0.5
Membrane	Double-skinned Pd-Ag
Thickness selective layer [µm]	~4.61



Reaction pressure [bar]	NH_3 conversion [%]	H_2 recovery [%]	H_2 purity [%]
2	98.8	49.8	99.993
3	99.5	78.6	99.989
4	99.6	86.6	99.985
5	99.7	90.5	99.980
6	99.7	92.4	99.980

V. Cechetto, L. Di Felice, J. A. Medrano, C. Makhloufi, J. Zuniga, and F. Gallucci, "H_2 production via ammonia decomposition in a catalytic membrane reactor," *Fuel Process. Technol.*, vol. 216, p. 106772, 2021, doi: https://doi.org/10.1016/j.fuproc.2021.106772.

Hydrogen purification from ammonia

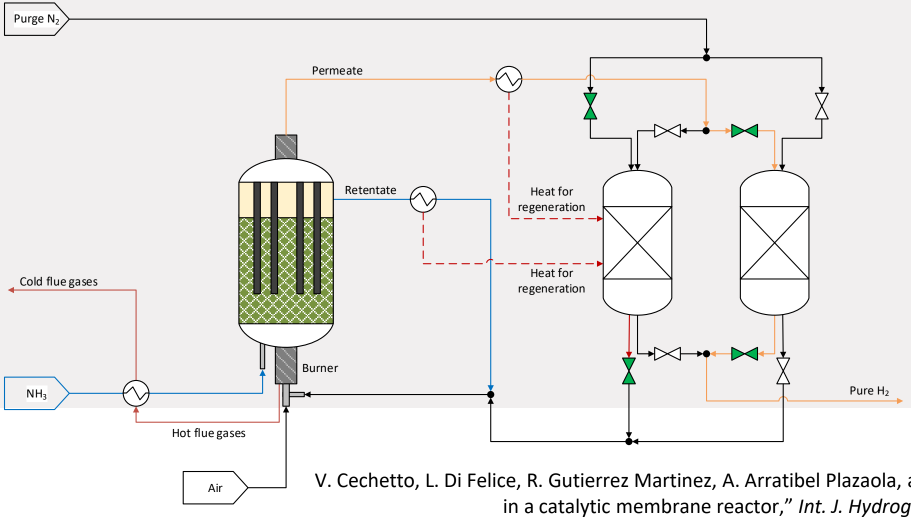
Strategy 1: Increase of the membrane selective layer thickness

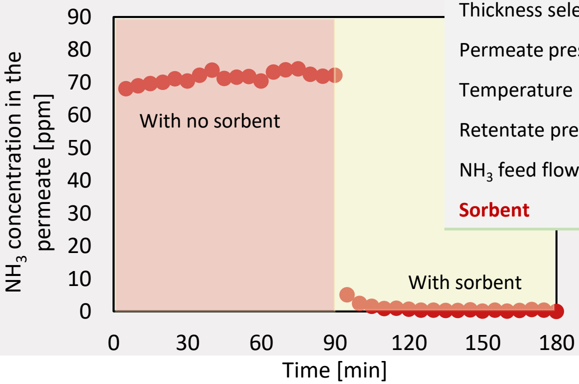
PEMFC specifications requires residual NH_3 concentration in the H_2 feed < 0.1 ppm.

Membrane code	Thickness selective layer [µm]			NH_3 concentration in the permeate [ppm]
Arenha-2	~ 1	5210	93.2	47 (±2.1)
Arenha-3	~ 6 – 8	68960	84.8	< 0.75

Reaction temperature = 500 C, reaction pressure = 4 bar(a), ammonia feed flow rate = 0.5 L_N/min.

Strategy 2: Addition of a H_2 purification stage downstream the membrane reactor





Experimental conditions	
Thickness selective layer [µm]	1
Permeate pressure [bar]	1
Temperature [°C]	450
Retentate pressure [bar]	3
NH_3 feed flow rate [L_N/min]	0.5
Sorbent	**Zeolite 13X**

V. Cechetto, L. Di Felice, R. Gutierrez Martinez, A. Arratibel Plazaola, and F. Gallucci, "Ultra-pure hydrogen production via ammonia decomposition in a catalytic membrane reactor," *Int. J. Hydrogen Energy*, 2022, https://doi.org/10.1016/j.ijhydene.2022.04.240.

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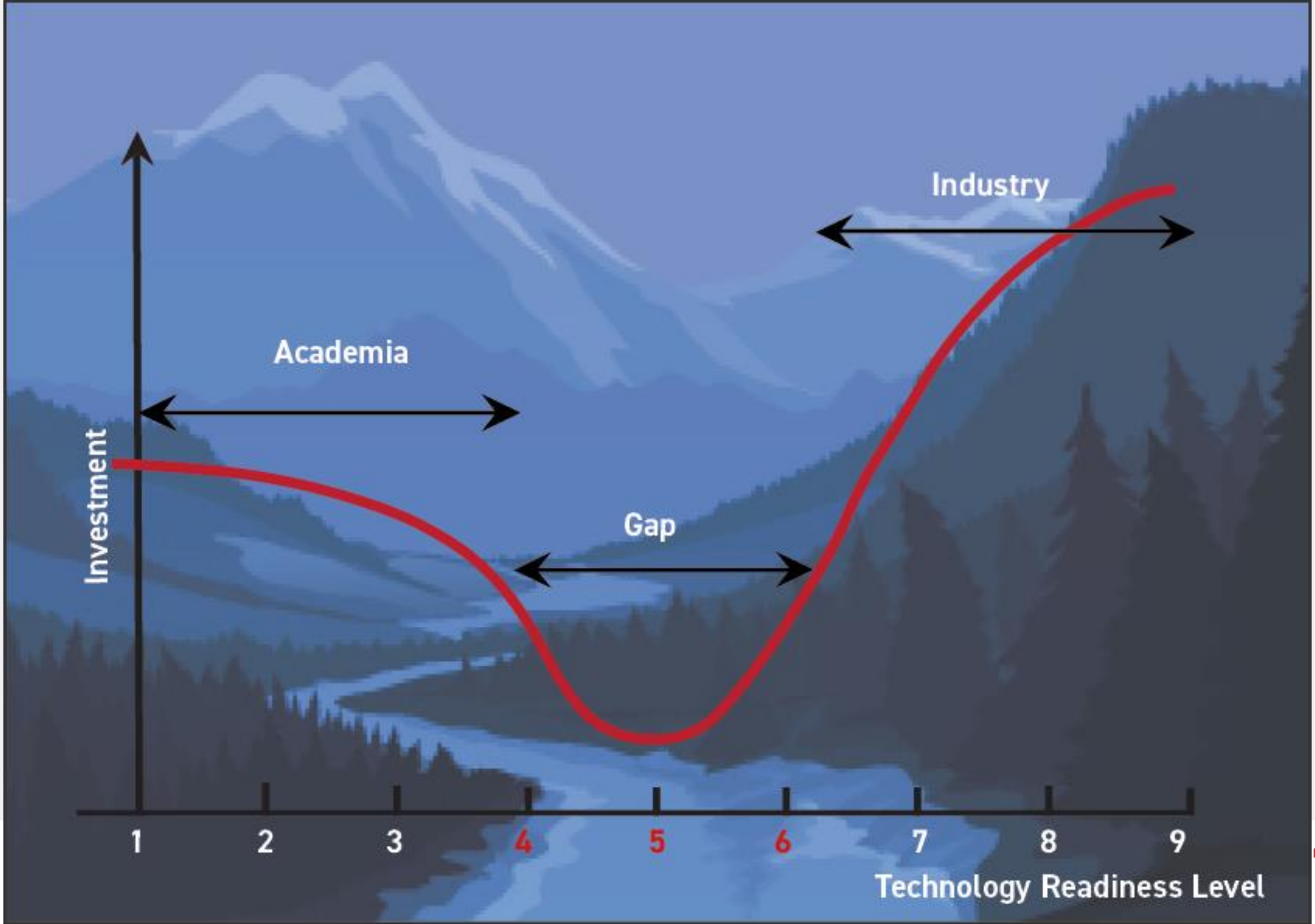
Industry
Academia
Gap
Investment
1
2
3
4
5
6
7
8
9
Technology Readiness Level

Scale-up steps

2018

2016

2014

2012

2010

H2 SITE
Membrane reactors for H2 generation

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MEMBER OF BASQUE RESEARCH & TECHNOLOGY ALLIANCE

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CATART PROJECT

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Membranes And Catalysts Beyond Economic and Technological Hurdles

$areNH_3a$

AMBHER

GICO2
Gasification Integrated with CO2 capture and conversion

MEASURED

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