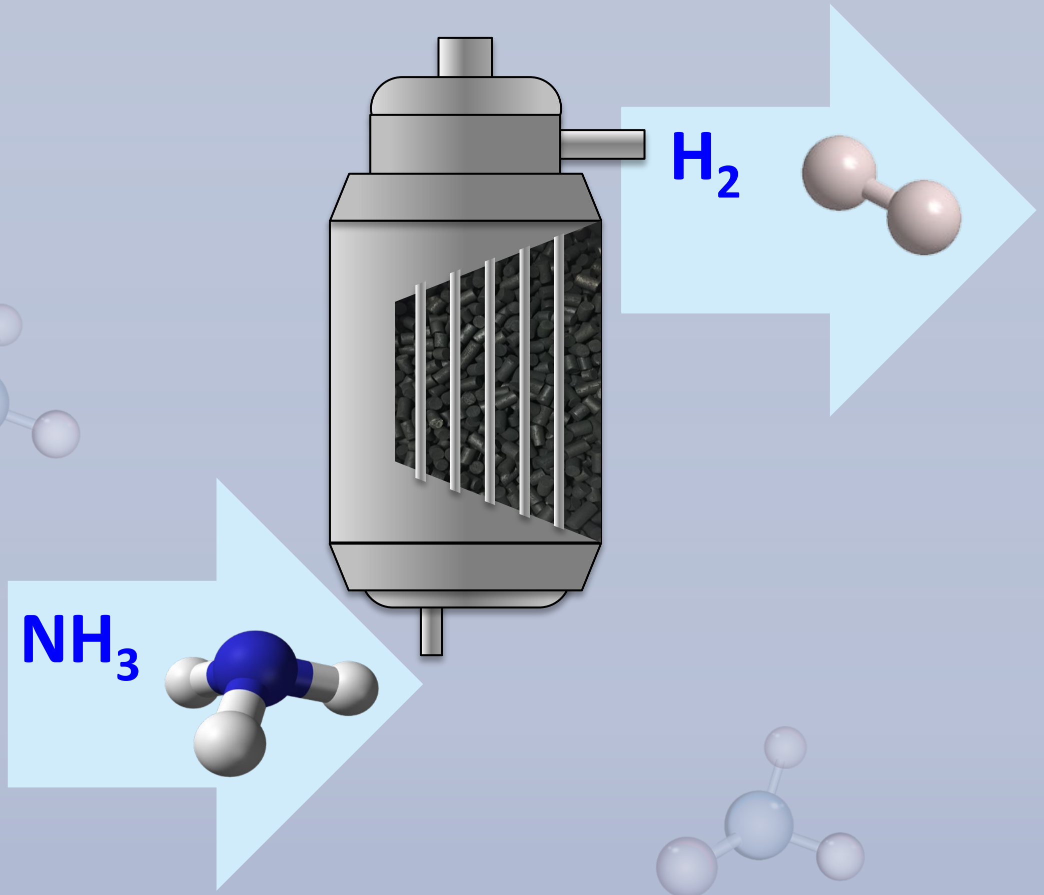
Hydrogen production via ammonia decomposition in membrane reactors

Dr. Valentina Cechetto



AndreaH

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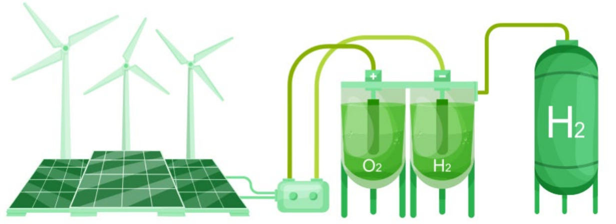
Why ammonia?

RENEWABLE ENERGY

Intermittency

Energy storage in the form of dispatchable energy carriers

H_2 Ideal energy carrier

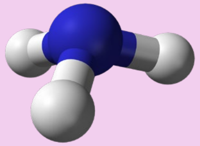


- ✓ Carbon free
- ➢ Low volumetric energy density
- ➢ Low boiling point

Challenging storage and handling

H_2 storage in
liquid carrier compounds

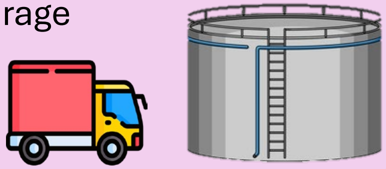
- ✓ Easy transport over long distances
- ✓ Easy storage for long time
- ✓ Possible in-situ decomposition to produce H_2 when required



NH_3

- ✓ Existing infrastructure for transport
- ✓ Existing infrastructure for storage
- ✓ Carbon free

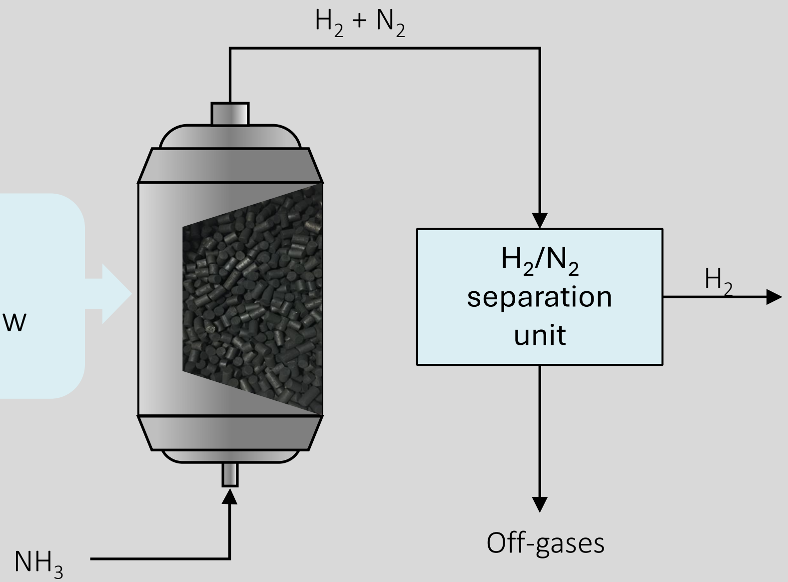
CO₂ FREE



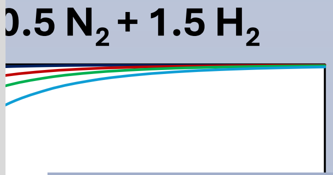
Suitable for carbon sensitive applications
PEM fuel cell

Ammonia decomposition

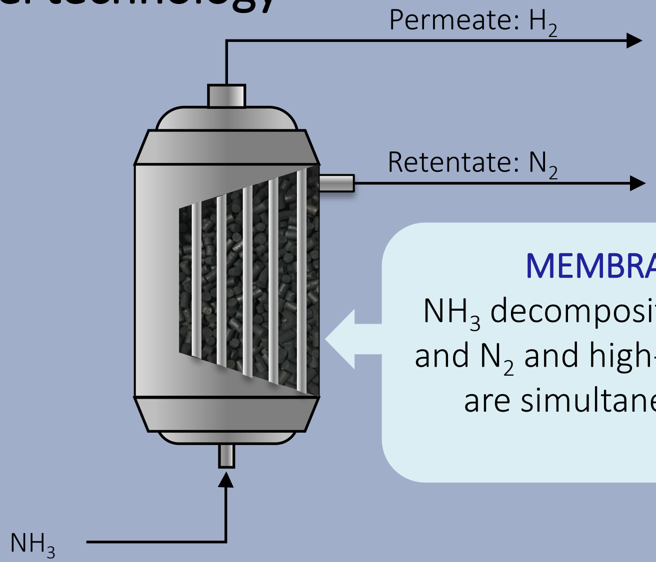
Conventional system



Reaction unit working at high temperature and low pressure



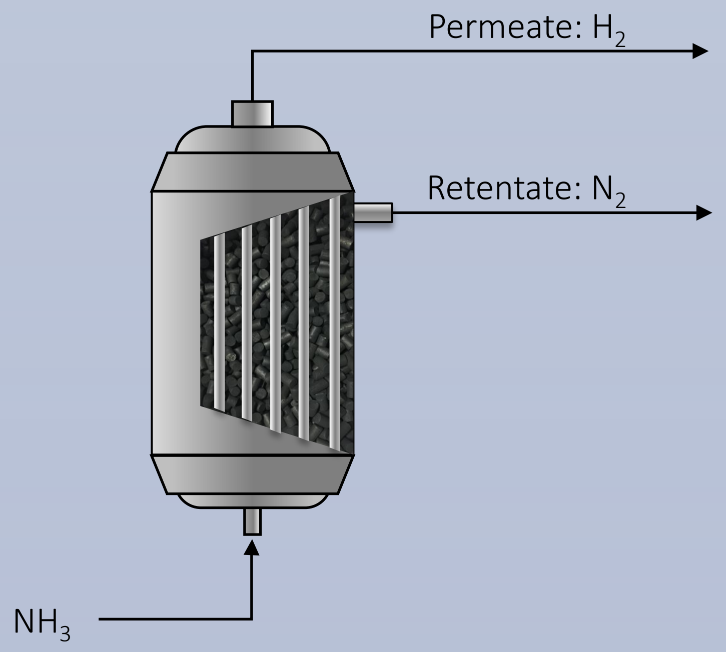
Novel technology

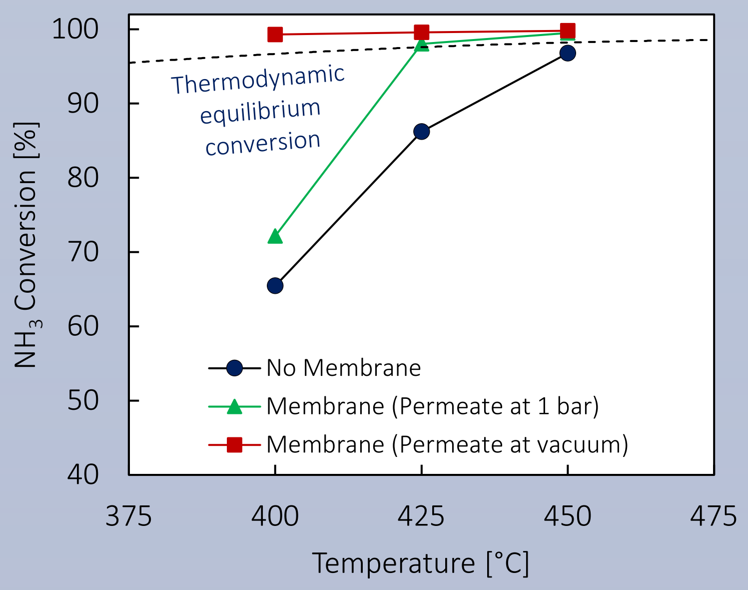


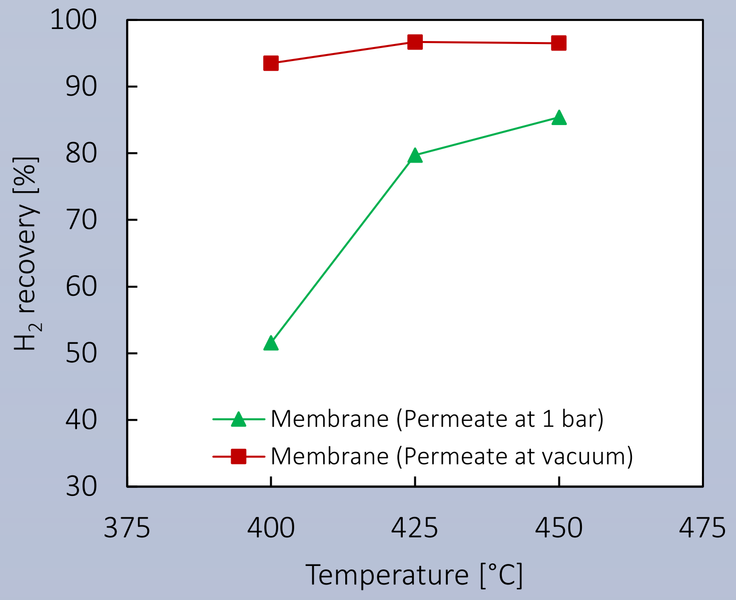
MEMBRANE REACTOR

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

Proof of concept







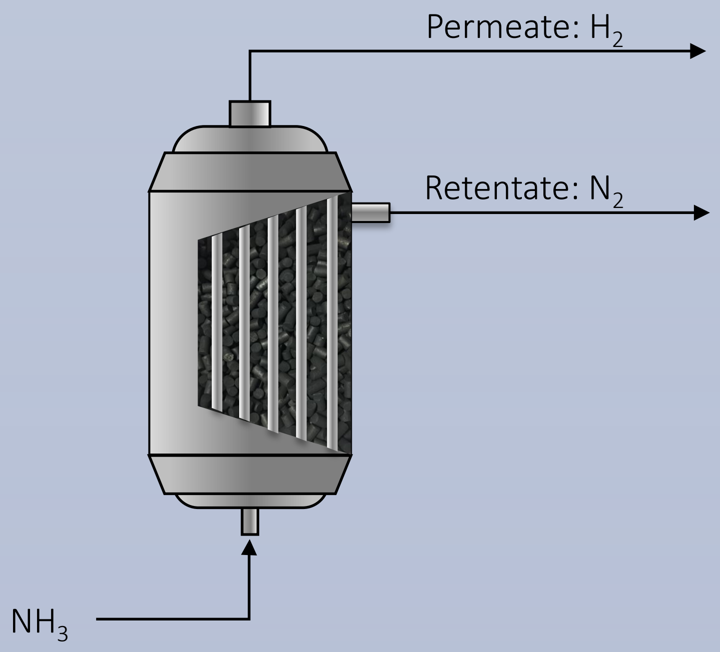
Experimental conditions	
ΔP [bar]	3
Permeate pressure [bar]	0.01-1
Feed flow rate [L_N/min]	0.5
Membrane	Double-skinned Pd-Ag
Thickness selective layer [μm]	~4.61

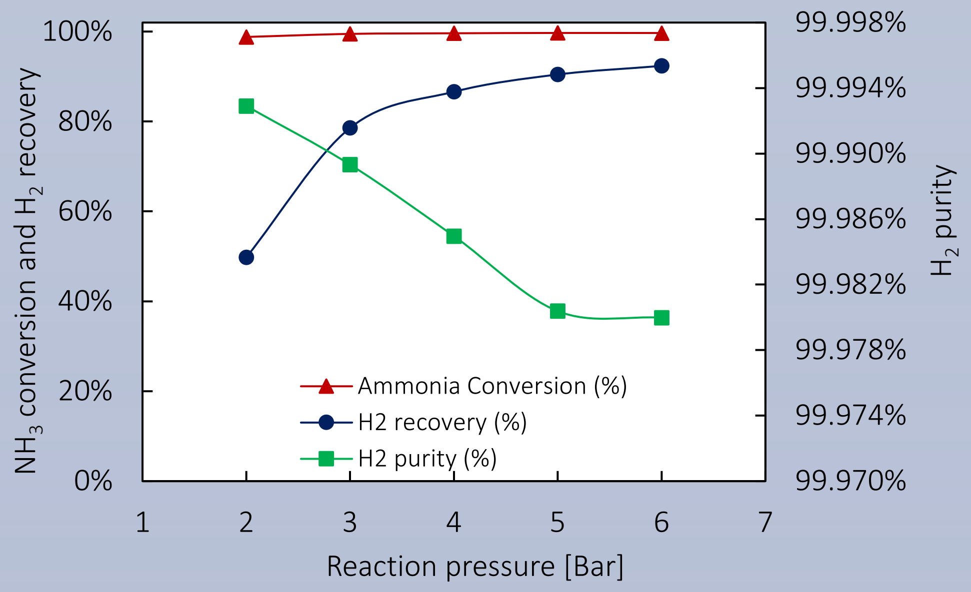
Compared to conventional systems, in a membrane reactor:

- ☐ Comparable or higher NH_3 conversion can be achieved at lower temperature (higher efficiencies)
- ☐ High-purity H_2 is recovered

Cechetto, V.; Di Felice, L.; Medrano, J.A.; Makhloufi, C.; Zuniga, J.; Gallucci, F. H_2 production via ammonia decomposition in a catalytic membrane reactor, *Fuel Processing Technology*, **2021**, Volume 216, 106772, https://doi.org/10.1016/j.fuproc.2021.106772.

Proof of concept





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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 similar pressures (higher compactness)
- ❑ Lower purities of H_2 recovered

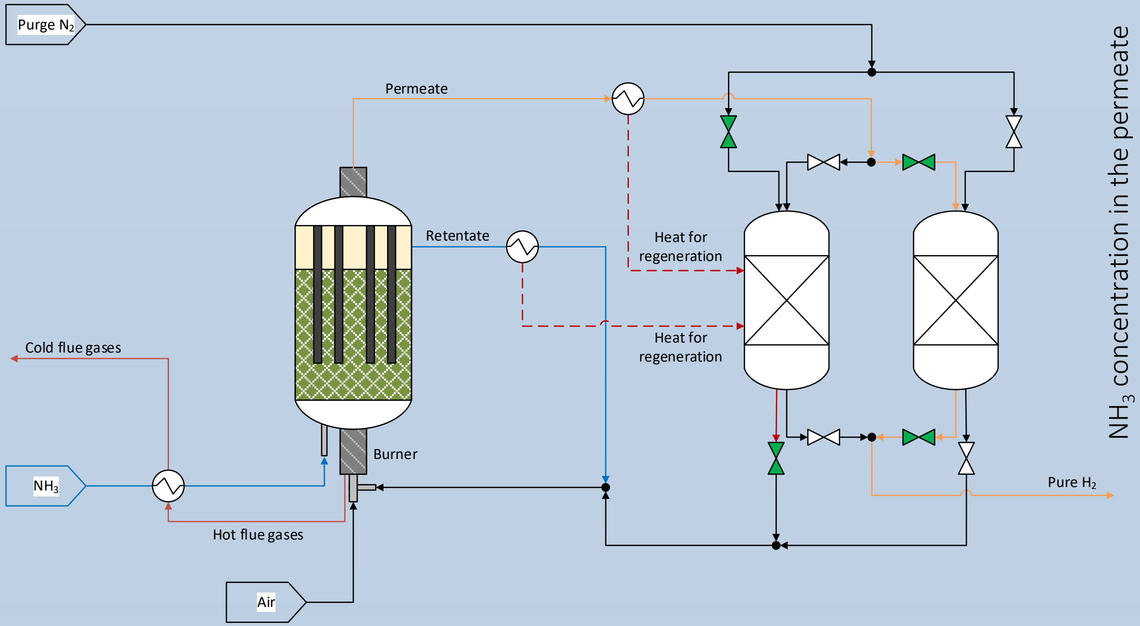
Cechetto, V.; Di Felice, L.; Medrano, J.A.; Makhloufi, C.; Zuniga, J.; Gallucci, F. H_2 production via ammonia decomposition in a catalytic membrane reactor, *Fuel Processing Technology*, **2021**, Volume 216, 106772, https://doi.org/10.1016/j.fuproc.2021.106772.

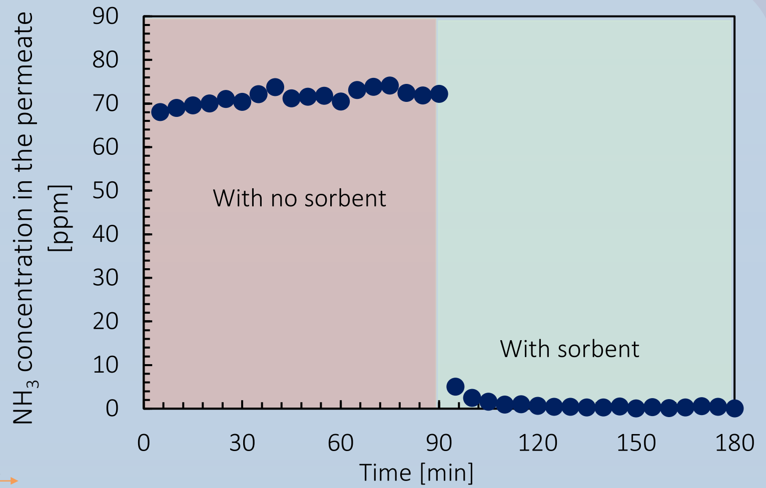
The challenge of H_2 purity

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

Strategy 1: increase of membrane selectivity by increasing the membrane thickness

Strategy 2: implementation of a cleanup unit downstream of the MR implementing thin membranes





T= 450°C, P=3 bar, NH_3 feed flow rate =0.5 L_N/min
Thickness selective layer ~ 1µm
Sorbent: zeolite 13X

Both the strategies are technically feasible

Strategy 2 is more economically viable

The reactor can be operated at lower temperatures with higher residual NH_3 concentration

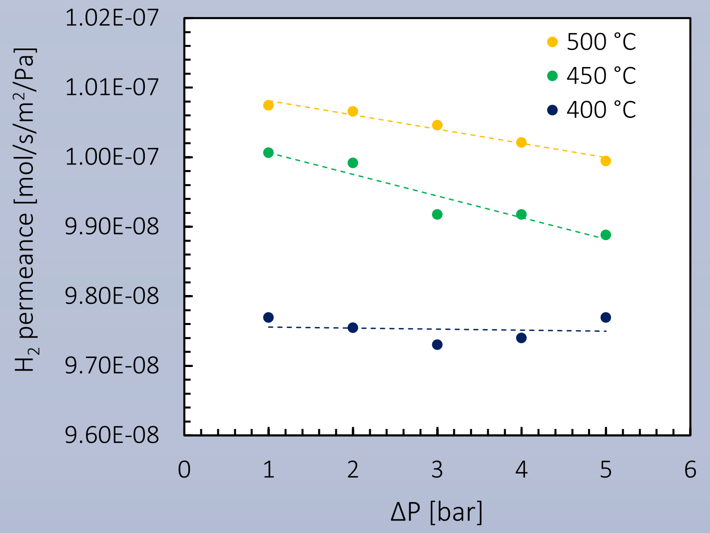
- ✓ Higher energy efficiency
- ✓ Less selective membranes can be implemented

Cechetto, V.; Gutierrez Martinez, R.; Di Felice, L.; Gallucci, F.; Ultra-pure hydrogen production via ammonia decomposition in packed bed membrane reactors, *International Journal of Hydrogen Energy*, **2022,** Volume 47, https://doi.org/10.1016/j.ijhydene.2022.04.240.

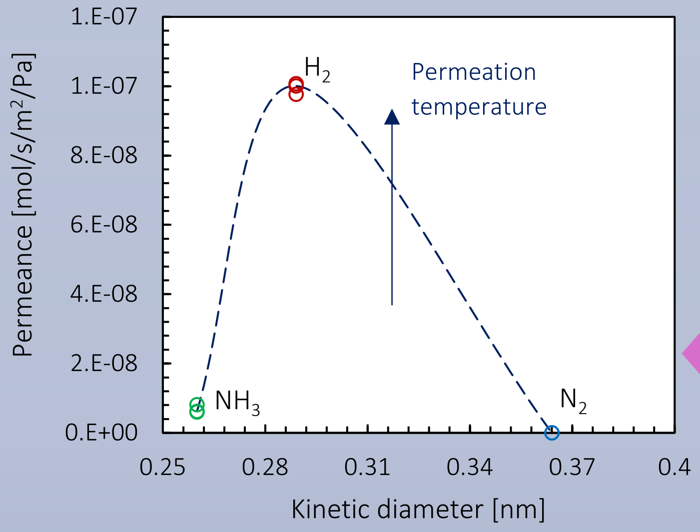
Carbon molecular sieve membranes for H_2 recovery from NH_3

Membrane preparation

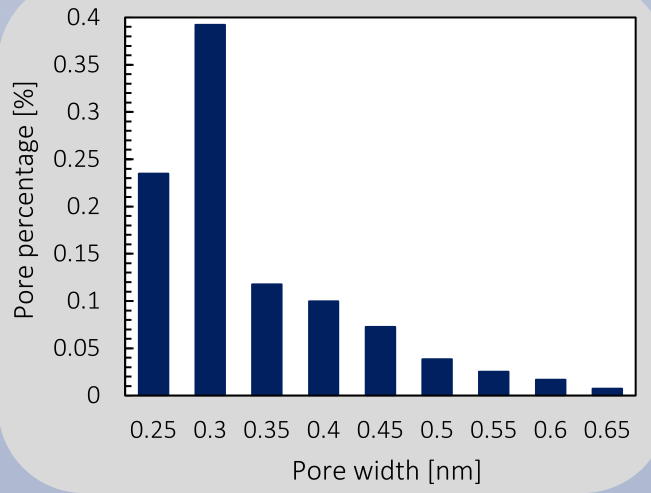
- Support preparation
- Polymeric precursor synthesis
- Dipping solution preparation
- Dip Coating
- Drying and polymerization
- Carbonization



Molecular sieving and/or adsorption diffusion are the main transport mechanisms

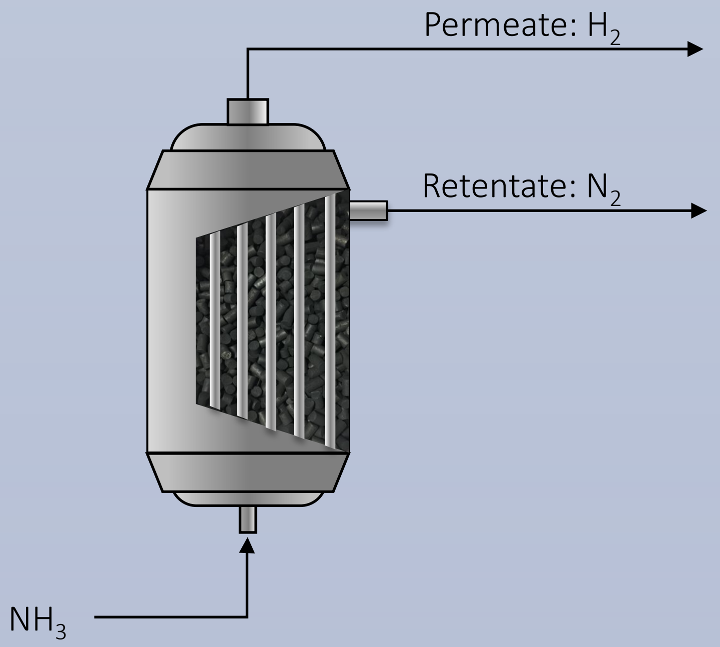


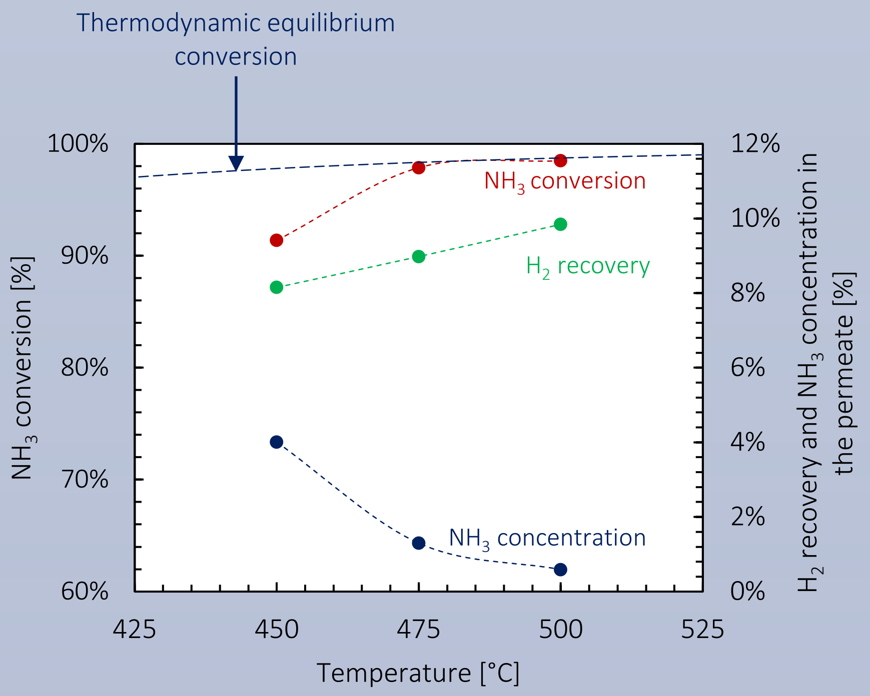
H_2-selective membrane



Cechetto, V.; Anello, G.; Rahimalimamaghani, A.; Gallucci, F. Carbon Molecular Sieve Membrane Reactors for Ammonia Cracking. *Processes* **2024**, *12*, 1168. https://doi.org/10.3390/pr12061168

Carbon molecular sieve membranes for H_2 recovery from NH_3





Experimental conditions	
ΔP [bar]	5
Permeate pressure [bar]	1
Feed flow rate [L_N/min]	0.5
Membrane	CMSM

PEMFC grade H_2 was not achieved at the reactor's outlet

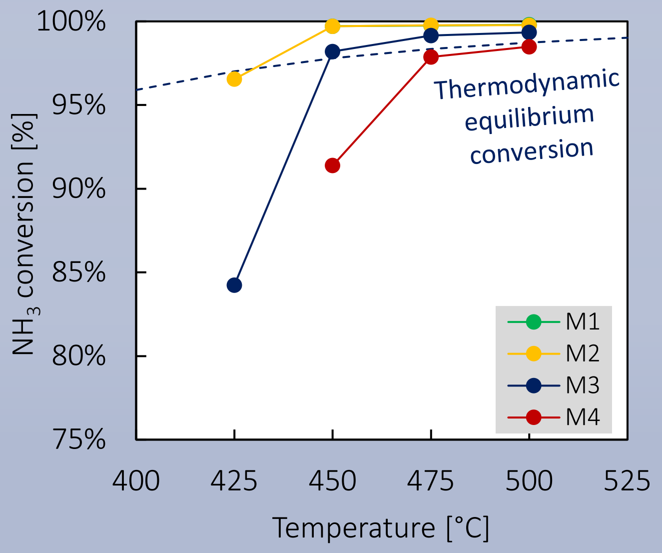
NH_3 concentration in the permeate <0.75 ppm was achieved through the implementation of a sorption unit downstream of the reactor.

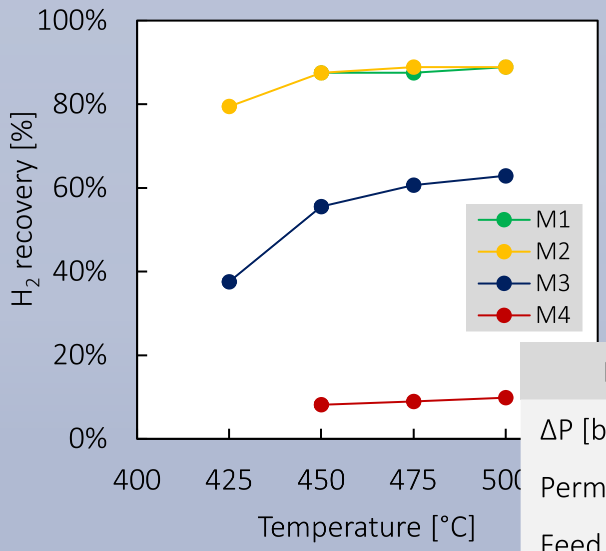
Cechetto, V.; Anello, G.; Rahimalimamaghani, A.; Gallucci, F. Carbon Molecular Sieve Membrane Reactors for Ammonia Cracking. *Processes* **2024**, *12*, 1168. https://doi.org/10.3390/pr12061168

Effect of membranes' separation properties on the performance of a MR for NH_3 decomposition

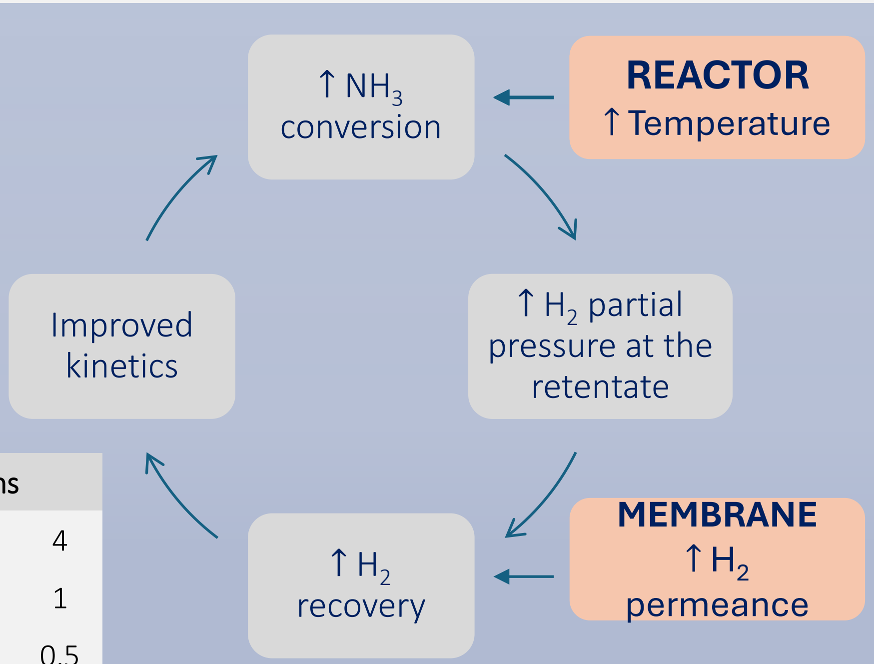
Membrane	Selective layer composition	Selective layer thickness [µm]	Membrane area [m^2]	Membrane configuration	Type of support	H_2 permeance [$mol/s/m^2/Pa$]	N_2 permeance [$mol/s/m^2/Pa$]	H_2/N_2 perm-selectivity [-]
M1	Pd-Ag	~ 4–5	$5.9\cdot10^{-3}$	Supported tubular DS	Ceramic	$1.64\cdot10^{-6}$	$3.47\cdot10^{-11}$	47080
M2	Pd-Ag	~ 6–8	$8.6\cdot10^{-3}$	Supported tubular DS	Ceramic	$1.15\cdot10^{-6}$	$1.66\cdot10^{-11}$	68960
M3	Pd-Ag	~ 6–8	$4.0\cdot10^{-3}$	Supported tubular conventional	Metallic	$6.57\cdot10^{-7}$	$1.12\cdot10^{-10}$	5890
M4	CMSM	~ 3–5	$2.5\cdot10^{-3}$	Supported tubular conventional	Ceramic	$1.01\cdot10^{-7}$	$3.85\cdot10^{-9}$	26

DS = Double -skinned





Experimental conditions	
ΔP [bar]	4
Permeate pressure [bar]	1
Feed flow rate [L_N/min]	0.5



REACTOR
↑ Temperature

↑ NH_3 conversion

↑ H_2 partial pressure at the retentate

↑ H_2 recovery

MEMBRANE
↑ H_2 permeance

Improved kinetics

Cechetto, V.; Agnolin, S.; Di Felice, L.; Pacheco Tanaka, A.; Llosa Tanco, M.; Gallucci, F. Metallic Supported Pd-Ag Membranes for Simultaneous Ammonia Decomposition and H_2 Separation in a Membrane Reactor: Experimental Proof of Concept. *Catalysts* **2023**, *13*, 920. https://doi.org/10.3390/catal13060920

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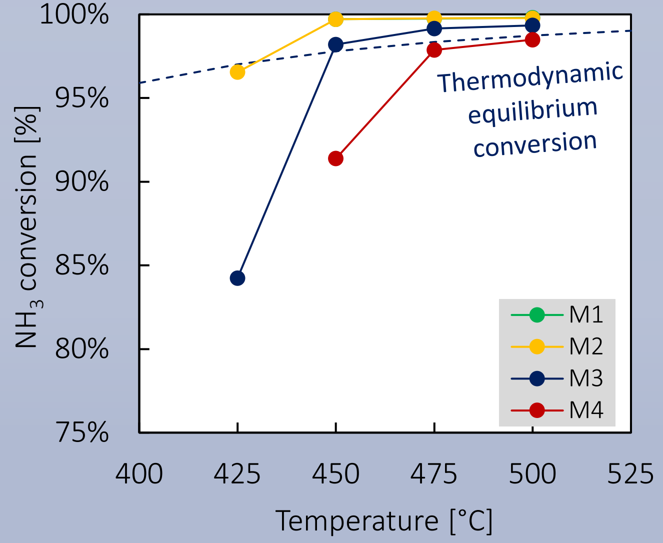
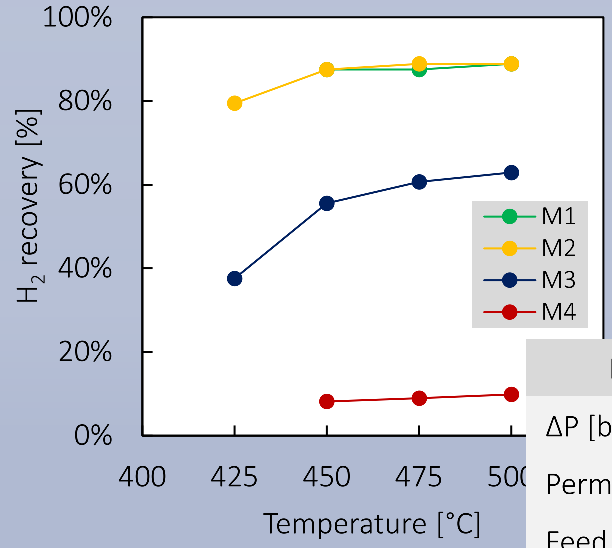




Experimental conditions	
ΔP [bar]	4
Permeate pressure [bar]	1
Feed flow rate [L_N/min]	0.5

The reactor's performance is optimized by tuning:

- ☐ membrane separation performance
- ☐ installed membrane area
- ☐ reactor operating conditions

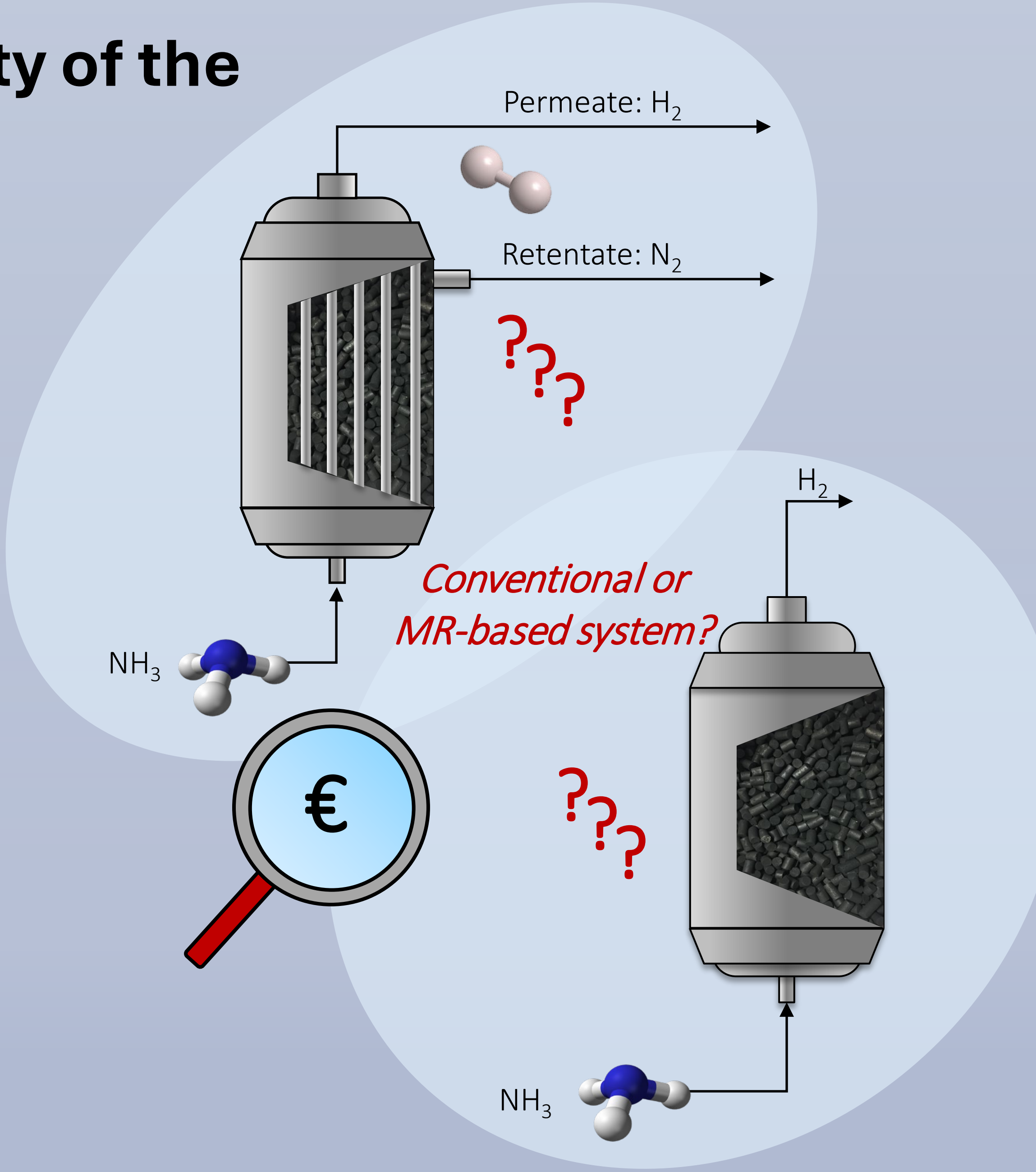
Cechetto, V.; Agnolin, S.; Di Felice, L.; Pacheco Tanaka, A.; Llosa Tanco, M.; Gallucci, F. Metallic Supported Pd-Ag Membranes for Simultaneous Ammonia Decomposition and H_2 Separation in a Membrane Reactor: Experimental Proof of Concept. *Catalysts* **2023**, *13*, 920. https://doi.org/10.3390/catal13060920

What about the economic feasibility of the process?

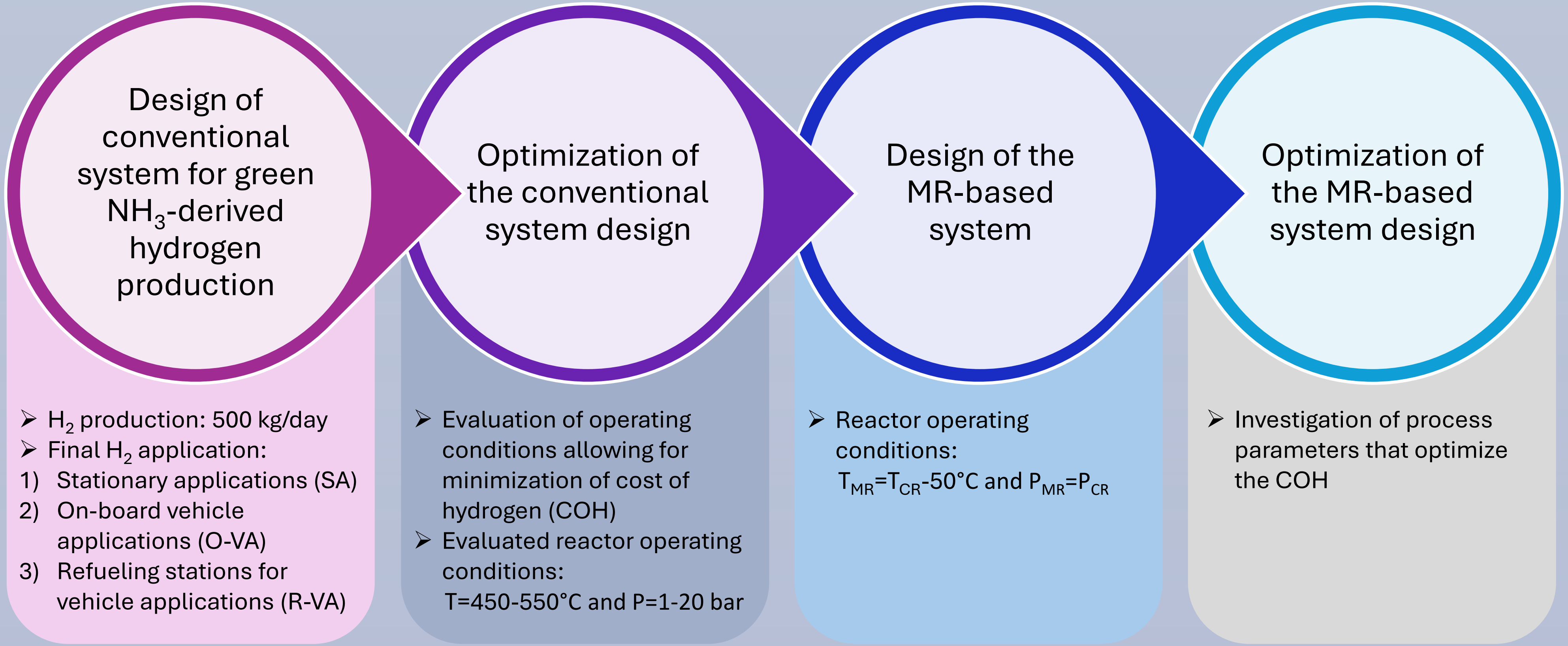
Is the membrane reactor-based system economically competitive compared to a conventional system?

- Studies available in literature calculated the costs of hydrogen production, but a comparative study addressing a techno-economic assessment at different plant capacities and system configurations is not available.

This work:
Techno-economic assessment of a decentralized plant for hydrogen production from ammonia decomposition
- H_2 for direct use in PEM fuel cells
- Applications: stationary applications (a), on-board vehicle applications (b), and refuelling stations (c)



Methods



Design of conventional system for green NH_3-derived hydrogen production

- ➢ H_2 production: 500 kg/day
- ➢ Final H_2 application:

1) Stationary applications (SA)
2) On-board vehicle applications (O-VA)
3) Refueling stations for vehicle applications (R-VA)

Optimization of the conventional system design

- ➢ Evaluation of operating conditions allowing for minimization of cost of hydrogen (COH)
- ➢ Evaluated reactor operating conditions: T=450-550°C and P=1-20 bar

Design of the MR-based system

- ➢ Reactor operating conditions: $T_{MR}=T_{CR}-50°C$ and $P_{MR}=P_{CR}$

Optimization of the MR-based system design

- ➢ Investigation of process parameters that optimize the COH

Methods: economic assessment

$$COH = \frac{(TOC \cdot CCF) + C_{O\&M,fixed} + C_{O\&M,variable}}{Capacity \cdot Plant\ availability}$$

Plant Component	Cost [k€]
Component W	A
Component X	B
Component Y	C
Component Z	D
Bare Erected Cost [BEC]	A+B+C+D
Direct costs as percentage of BEC	
Total Installation Costs [TIC]	80% BEC
Total Direct Plant Cost [TDPC]	BEC+TIC
Indirect Costs [IC]	14% TDPC
Engineering procurement and construction [EPC]	TDPC+IC
Contingencies and owner’s costs	
Contingency	10% EPC
Owner’s cost	5% EPC
Total contingencies & OC [C&OC]	15% EPC
Total Overnight Cost [TOC]	EPC+C&OC

$$C_i = C_0 \cdot \left(\frac{S_i}{S_0}\right)^n \cdot F_p \cdot F_m \cdot F_T \cdot \frac{CEPCI}{CEPCI_{reference\ year}}$$

Cost O&M fixed	
Maintenance	2.5% TOC
Insurance	2% TOC
Labor	27991 €/year/pp[1]

COST O&M variable	
Green NH_3	853.92 €/ton [2]
Electricity	0.085 €/kWh [3]
Catalyst	143 €/kg [3]
Zeolite 13X	43.7 €/kg [4]
Membrane	6000 €/m [3]

Assumptions	
Plant availability	90%
Plant lifetime (n)	25 years [3]
Catalyst lifetime	5 years [3]
Lifetime Zeolite 13X	5 years
Membrane lifetime	5 years
Discount factor (i)	8% [3]

$$CCF = \frac{(i+1)^n}{((i+1)^n - 1)}$$

[1] https://www.payscale.com/research/NL/Job=Chemical_Process_Operator/Salary

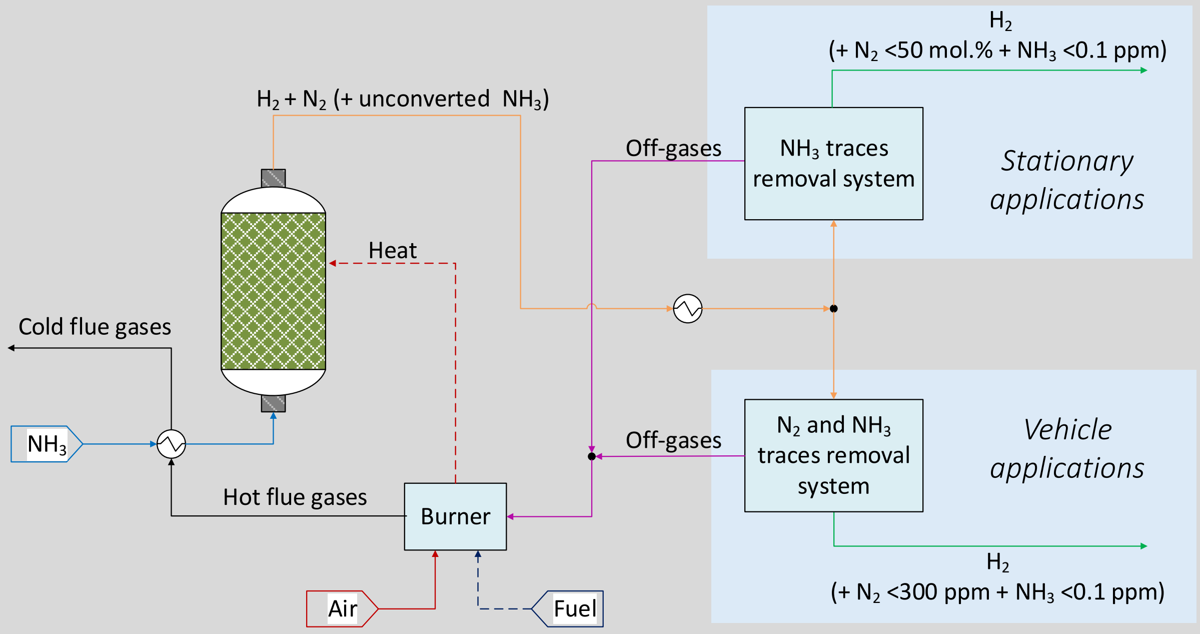
[2] https://www.iea.org/reports/global-hydrogen-review-2021/executive-summary

[3] S. Richard, A. Ramirez Santos, and F. Gallucci, “PEM genset using membrane reactors technologies An economic comparison among different e-fuels”, International Journal of Hydrogen Energy

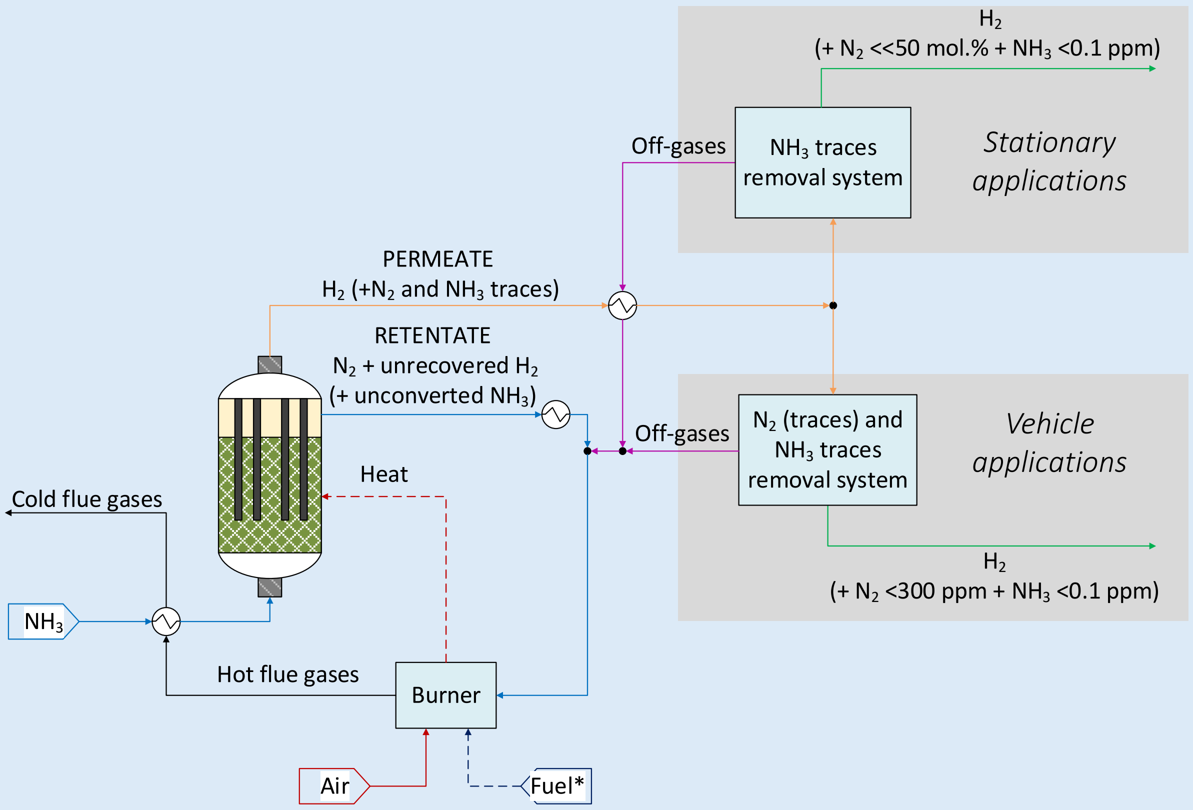
[4] https://www.msesupplies.com/products/1kg-molecular-sieves-13x-pellets-spheres?variant=31758805205050

H_2 production from NH_3: the conventional and the MR-based systems

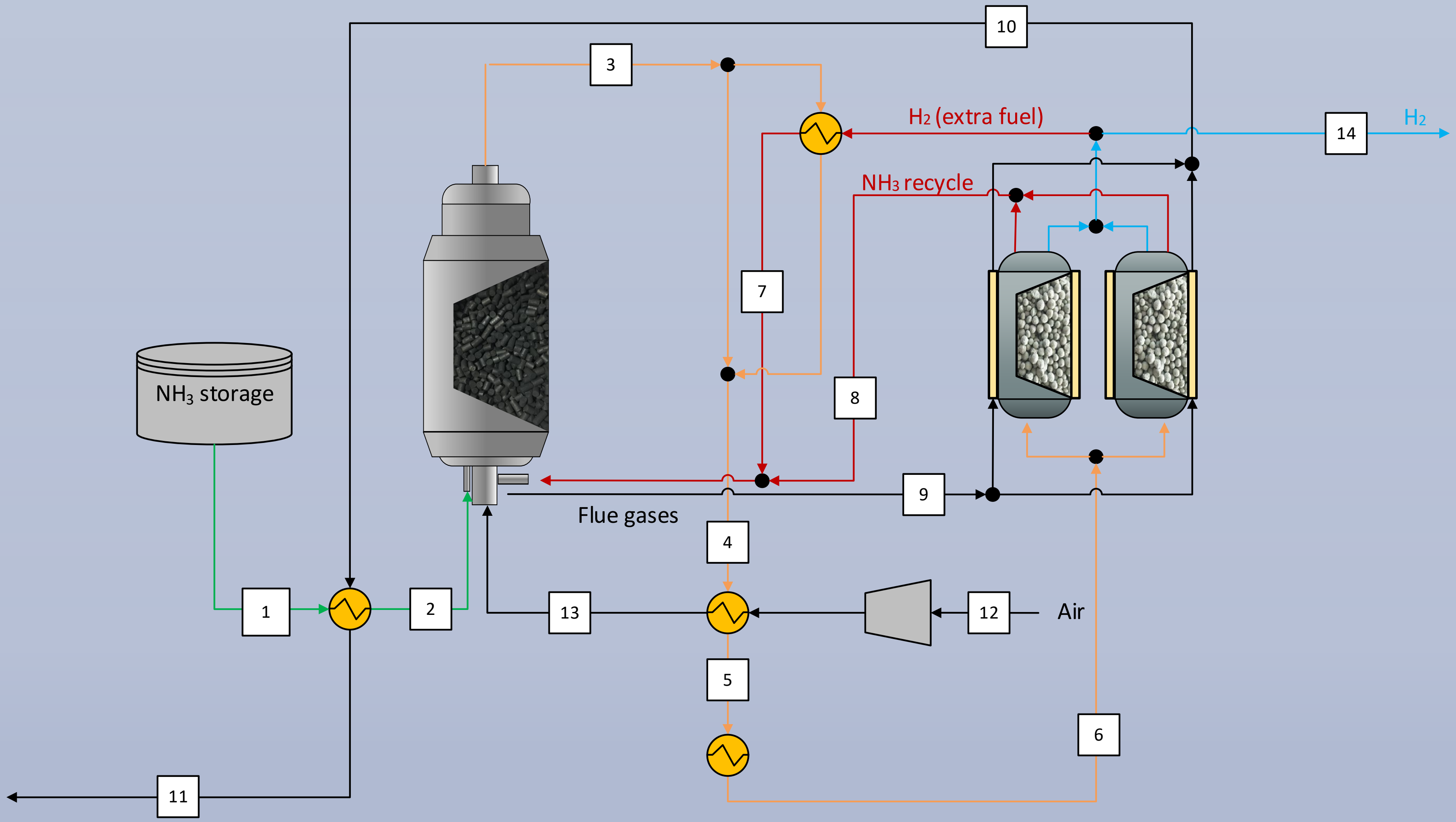
Conventional system



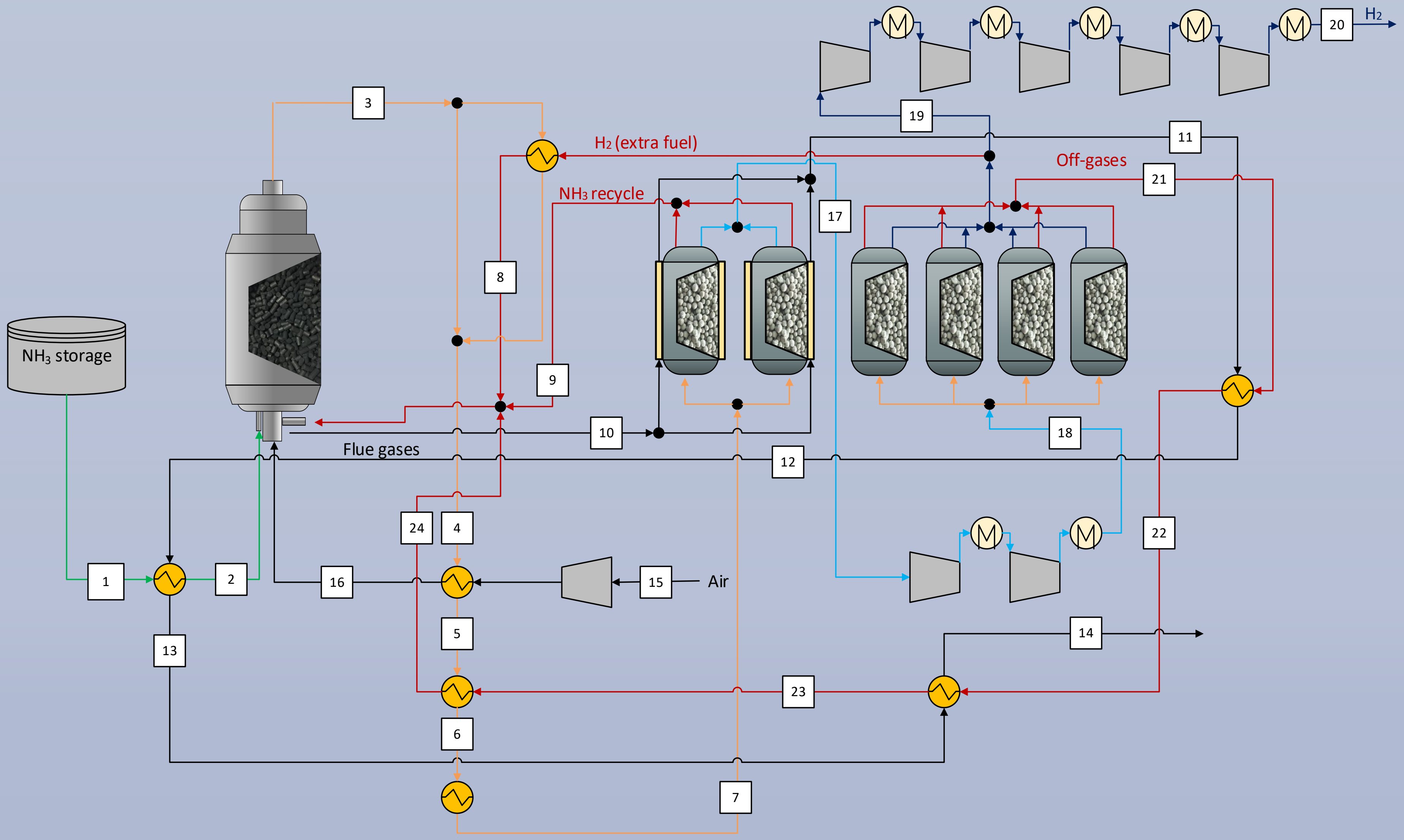
Membrane reactor-based system



Design of the conventional process for SA

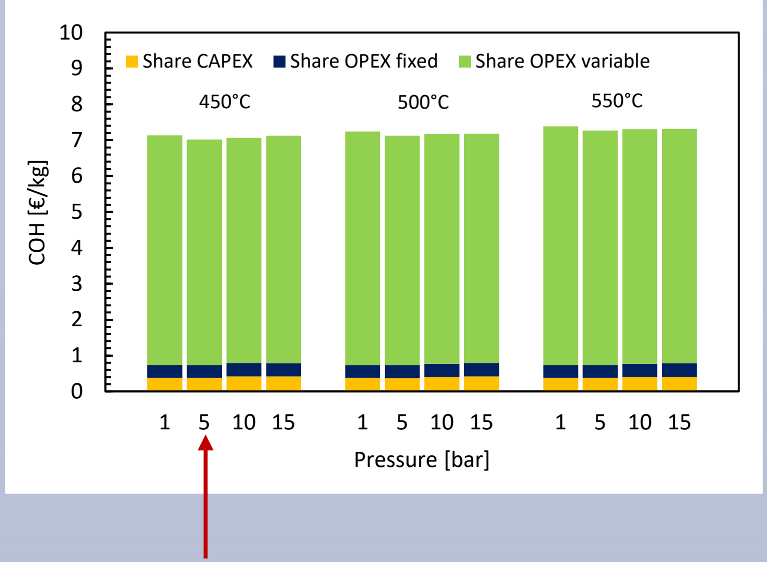


Design of the conventional process for VA

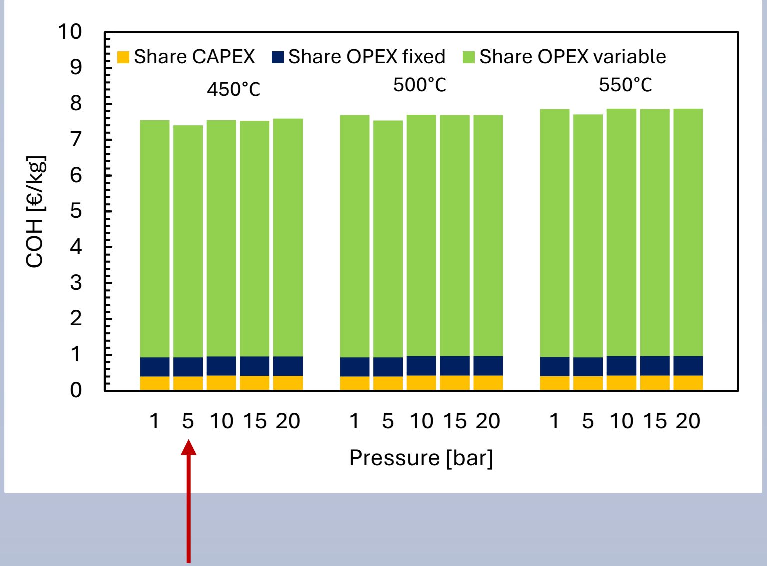


Optimization of the conventional system

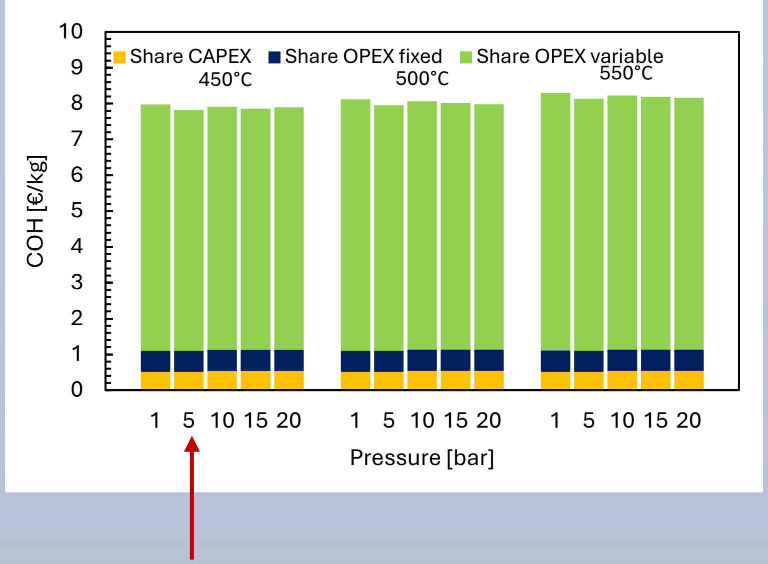
Stationary applications (SA)



On-board vehicle applications (O-VA)

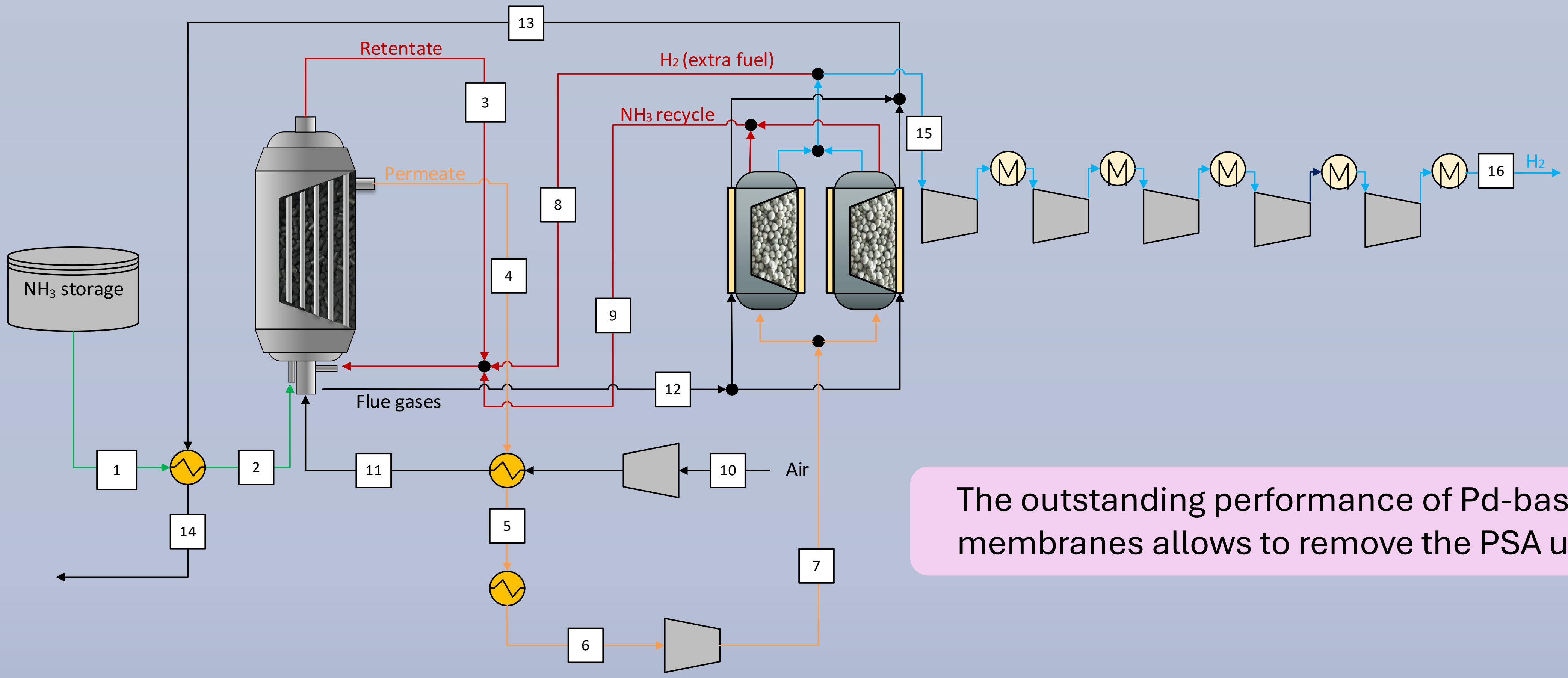


Refueling stations for vehicle applications (R-VA)



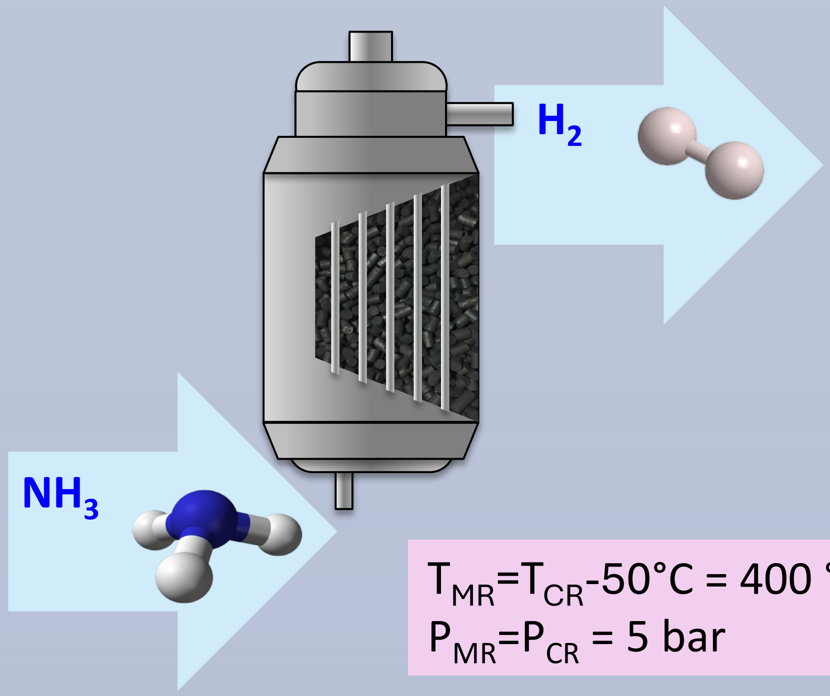
- ➢ COH in the conventional system is minimized with the reactor operated at T=450 °C and 5 bar
- ➢ The process is OPEX-intensive with the cost of the NH_3 feedstock being the main contributor to COH

Design of the MR-assisted process for SA/VA



The outstanding performance of Pd-based membranes allows to remove the PSA unit

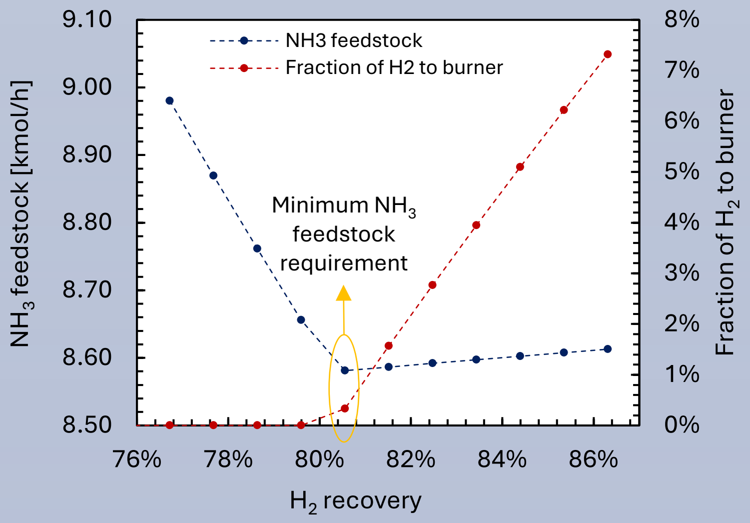
Optimization of MR-based system



$T_{MR}=T_{CR}-50°C = 400\ °C$
$P_{MR}=P_{CR} = 5\ bar$

The cost of NH_3 feedstock is the main contributor to COH

Objective
Minimization of the NH_3 feedstock



Reactor optimization ≠ Process optimization

A higher recovery reduces the available heat from the combustion of the retentate, which leads to an increased quantity of fuel that must be burned to sustain the NH_3 decomposition reaction and that, in turn, implies a greater flow rate of NH_3 to be processed.

Economic assessment

Is the packed bed MR technology competitive compared to the packed bed conventional technology?

Scenario 1: stationary applications

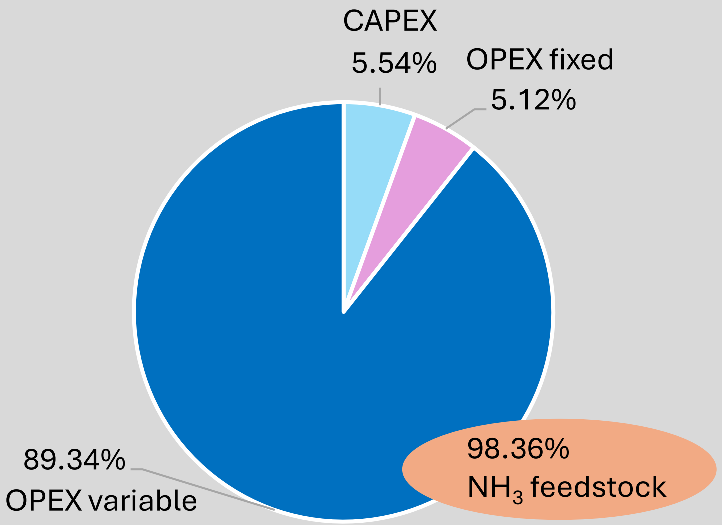
Both in the conventional and in the MR-based systems the COH is 6.95 €/kg

No economic advantage from utilization of the packed bed MR technology

Scenario 2.1: on-board vehicle applications

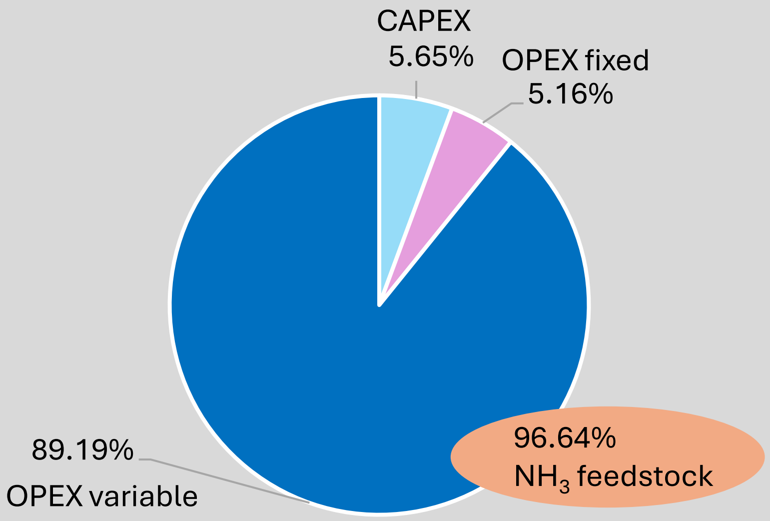
Conventional system

COH = 7.15 €/kg



MR-assisted system

COH = 6.95 €/kg

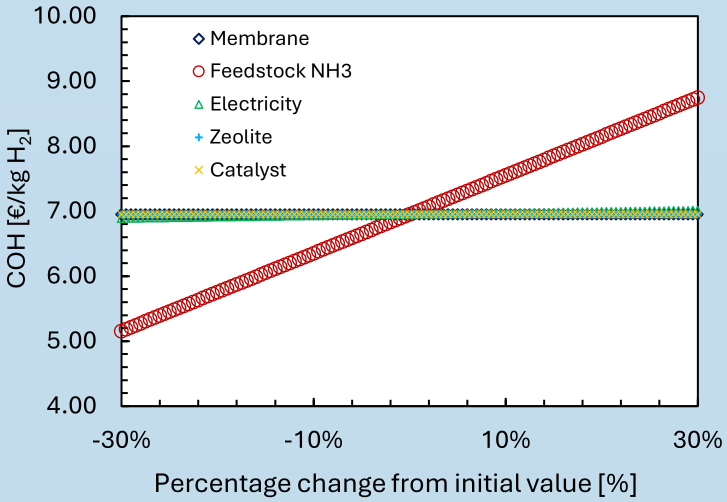


Scenario 2.2: refueling stations for vehicle applications

Similar conclusions to scenario 2.1 with $COH_{conventional}$=7.57 €/kg and $COH_{MR\text{-}assisted}$=7.38 €/kg

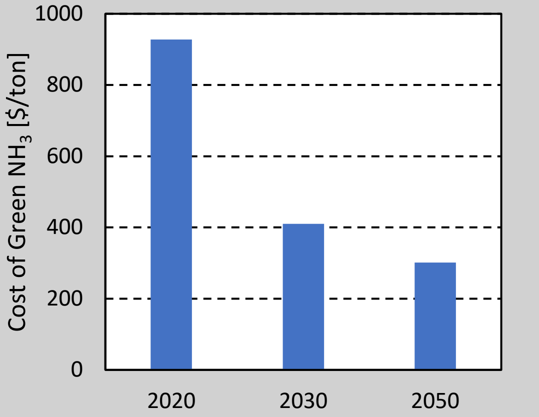
Economic assessment

Sensitivity analysis



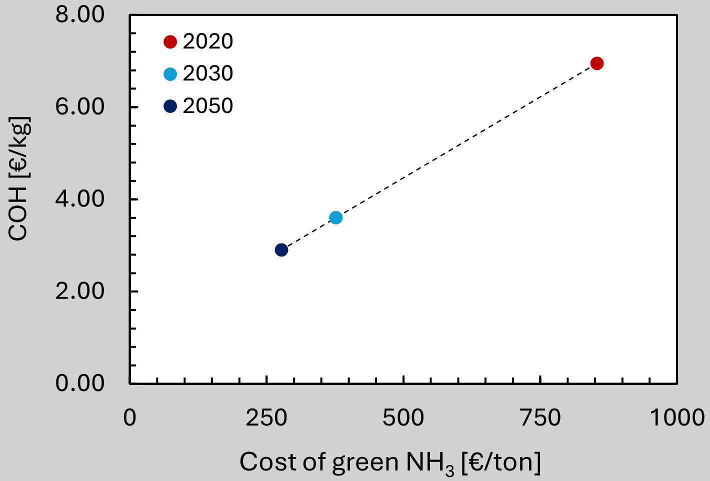
The process is OPEX-intensive and green NH_3 is the main cost driver

Forecasting



https://www.iea.org/reports/global-hydrogen-review-2021/executive-summary

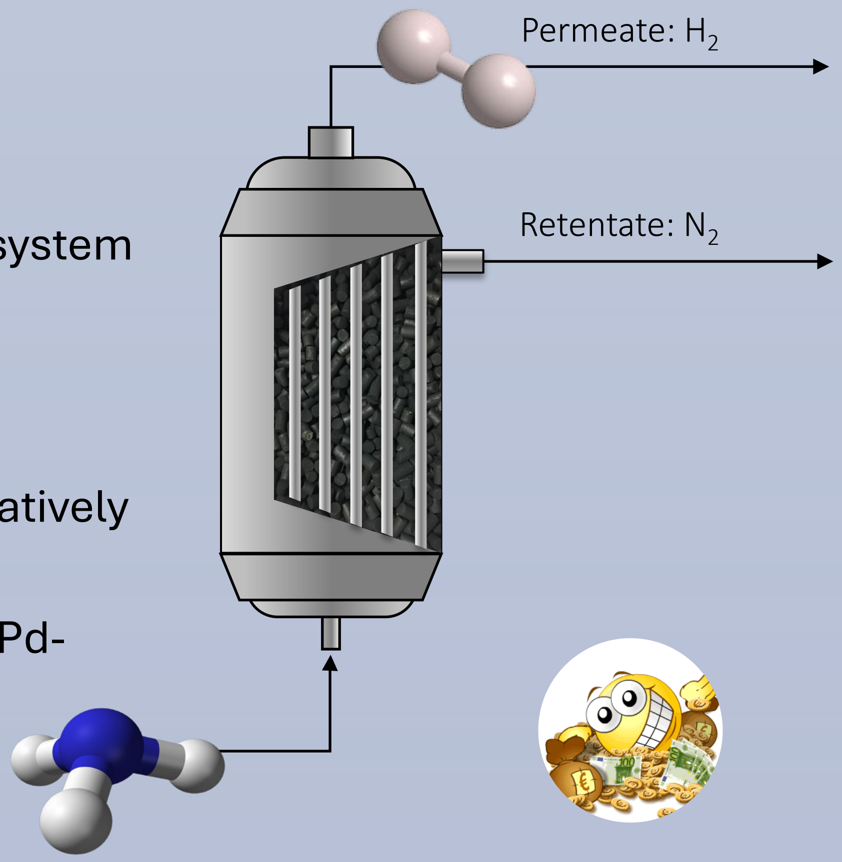
Year	Cost of NH_3 [€/ton]	COH [€/kg]
2020	853.92	6.95
2030	377.07	3.60
2050	277.30	2.90



Conclusions

In a membrane reactor for H_2 production from NH_3:

- Higher efficiency and compactness compared to a conventional system are achieved
- Optimization is possible by tuning the membrane separation performance, the membrane area and the operating conditions
- Fuel cell-grade H_2 production is possible with the addition of a relatively inexpensive sorption unit downstream of the reactor.
- Carbon membranes can be regarded a competitive alternative to Pd-based membranes



From an economic point of view, the recovery of H_2 from green NH_3 using MRs can be achieved at lower costs compared to the benchmark technology.

The MR technology holds significant potential in advancing the decarbonization of the current energy system.

Thank you for your attention