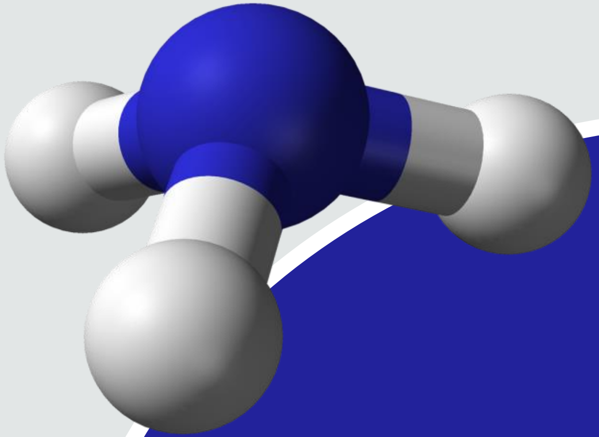
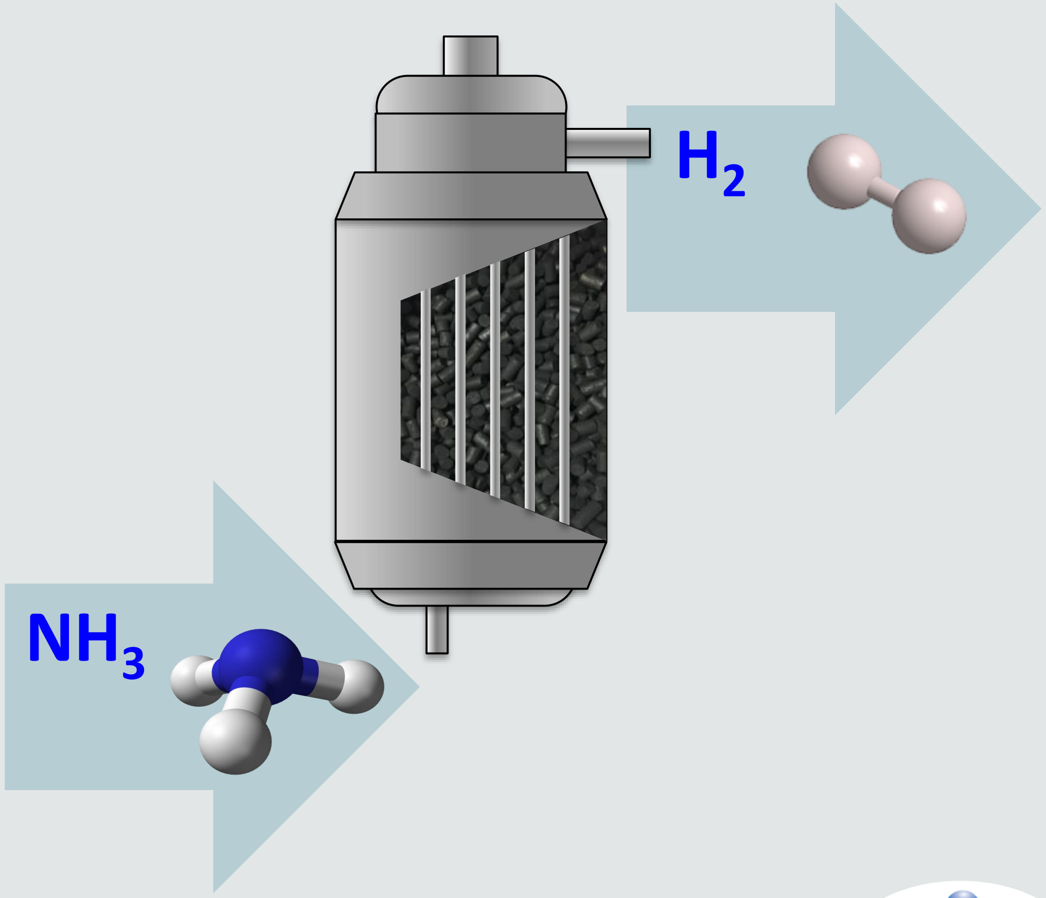


H_2 production via NH_3 decomposition in membrane reactors: experimental, process design and techno-economics

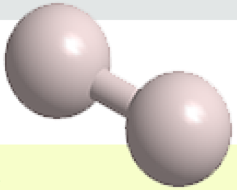
Valentina Cechetto
Luca Di Felice
F. Gallucci

EINDHOVEN UNIVERSITY OF TECHNOLOGY



Background

HYDROGEN



Ideal energy carrier

- ☐ Its combustion produces only water as by-product
- ☐ High efficiencies for energy conversion are achieved when it is employed as feedstock for power production.

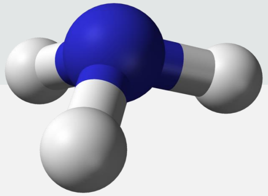
Challenging storage and distribution

Its low volumetric energy density and the difficulties associated with gas handling have so far prevented H_2 - based technologies to achieve popularity for commercial applications in the power production field.

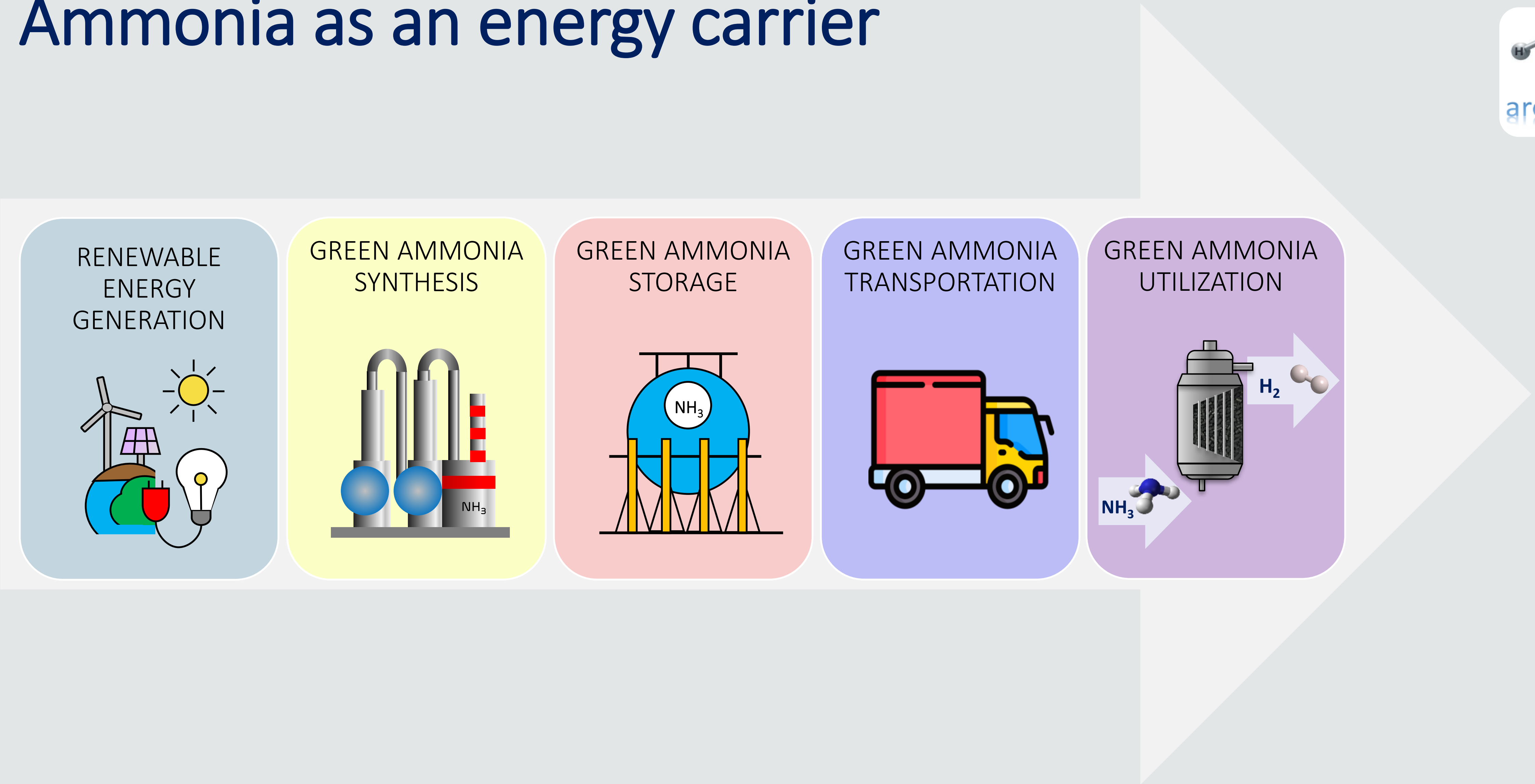
Hydrogen storage in **liquid carrier compounds**

- ☐ Easy to be transported over long distances
- ☐ Easy to be stored for long time
- ☐ In-situ decomposition to produce H_2 when required

AMMONIA



Ammonia as an energy carrier



RENEWABLE ENERGY GENERATION

GREEN AMMONIA SYNTHESIS

GREEN AMMONIA STORAGE

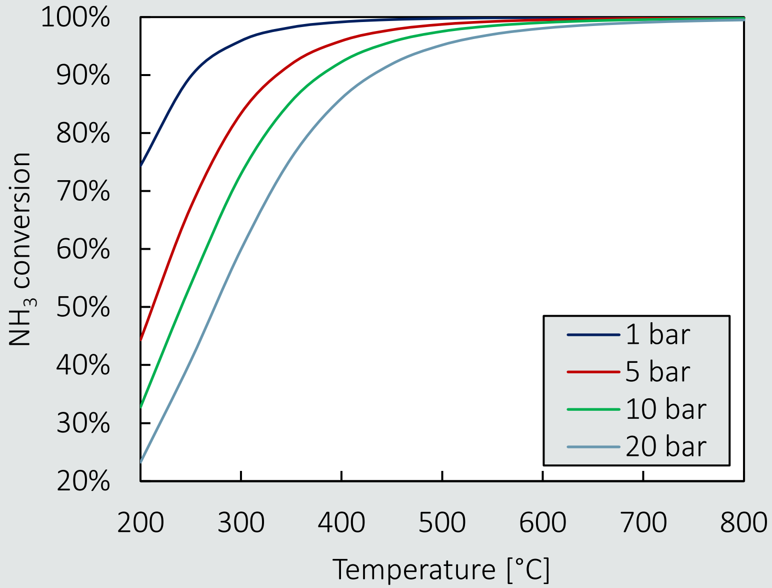
GREEN AMMONIA TRANSPORTATION

GREEN AMMONIA UTILIZATION

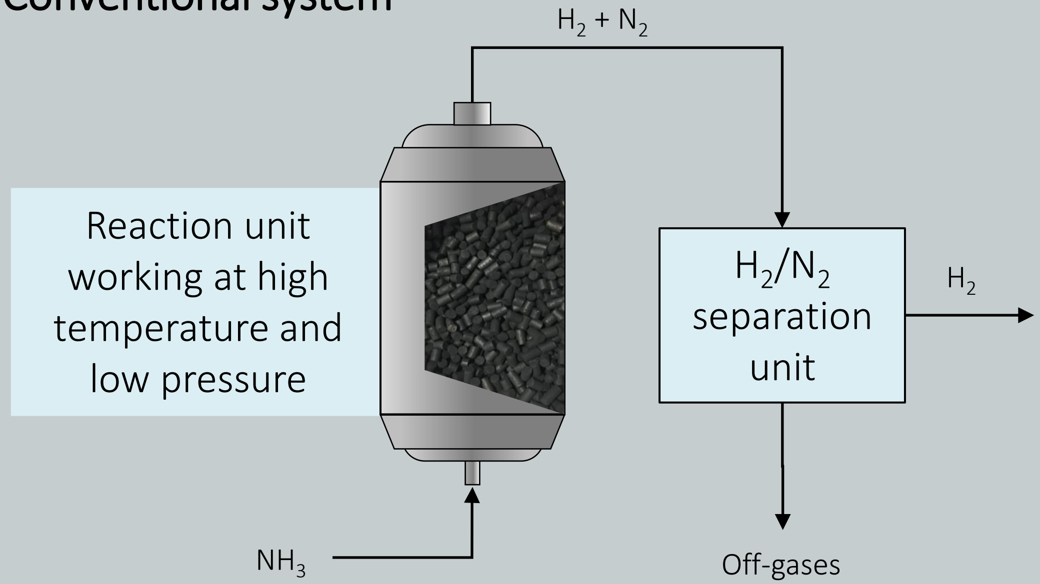
H_2 production from NH_3 decomposition

$$\boldsymbol{NH_3 \leftrightarrow 0.5\,N_2 + 1.5\,H_2}$$

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



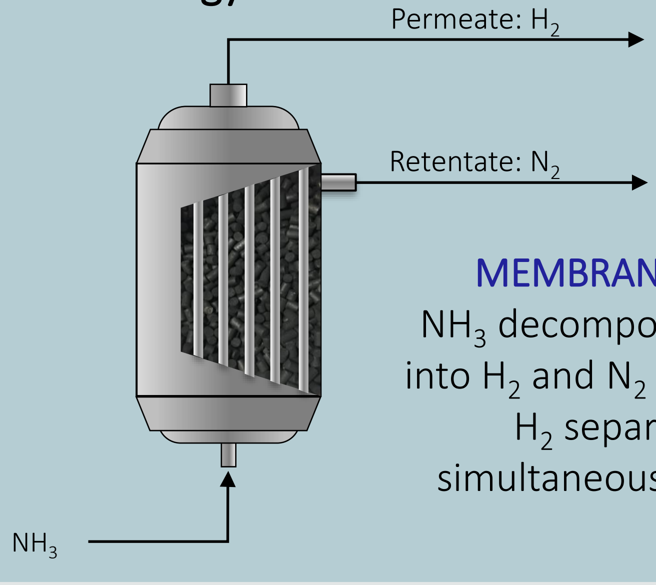
Conventional system



Reaction unit working at high temperature and low pressure

H_2/N_2 separation unit

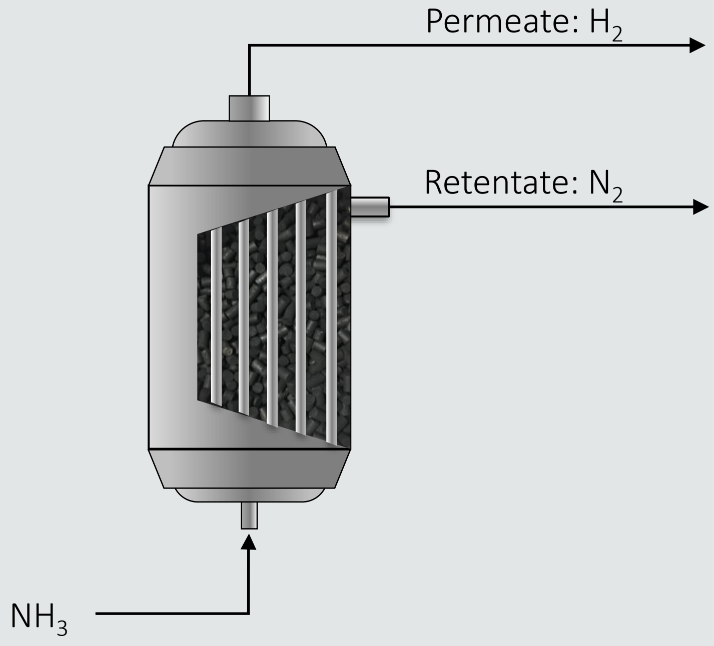
Novel technology



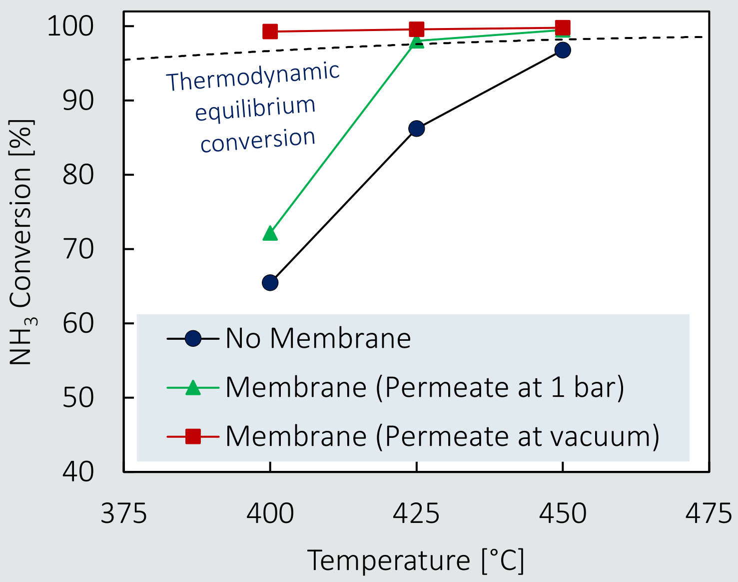
MEMBRANE REACTOR

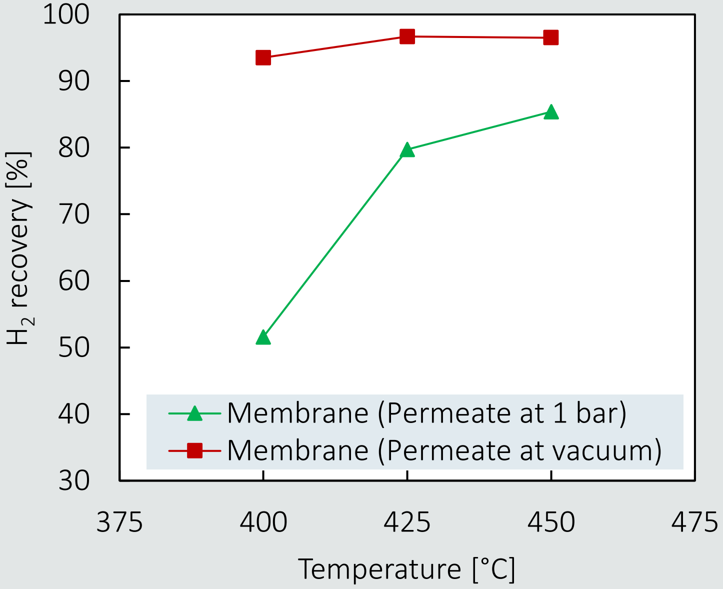
NH_3 decomposition reaction into H_2 and N_2 and high-purity H_2 separation are simultaneously performed

H_2 production from NH_3 decomposition 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



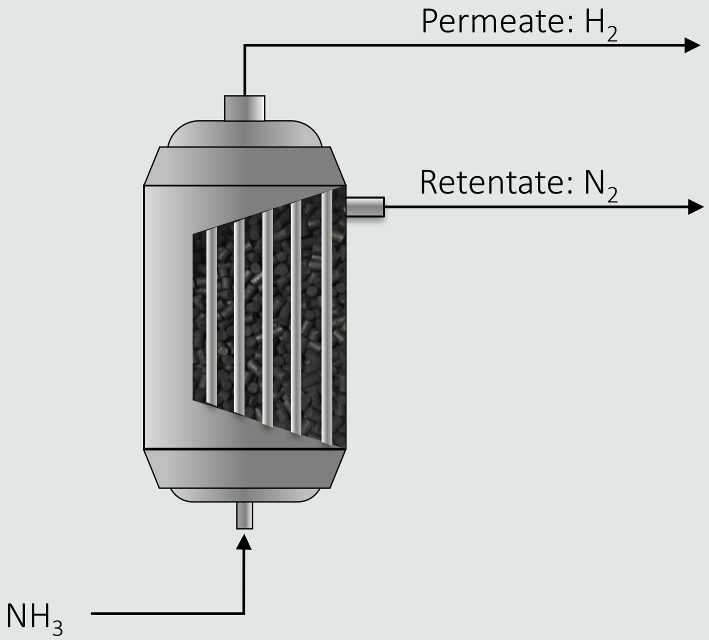


Compared to conventional systems, in a membrane reactor:

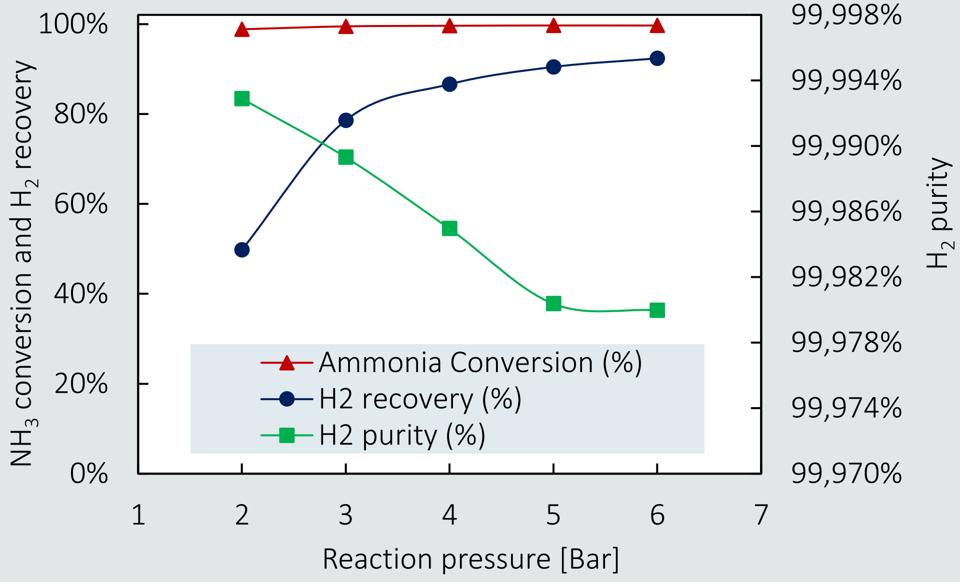
- ☐ Higher NH_3 conversion can be achieved at lower temperature (higher efficiencies)
- ☐ High-purity H_2 is recovered

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 decomposition 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



Compared to conventional systems, in a membrane reactor:

☐ Higher NH_3 conversion can be achieved at similar pressures (higher compactness)

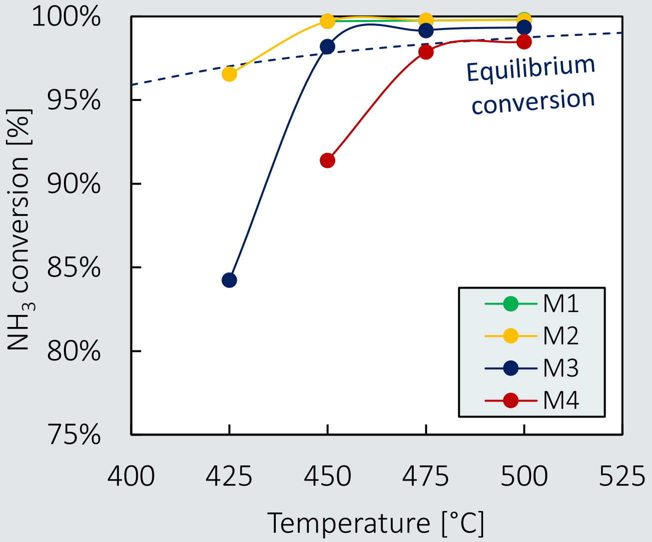
☐ Lower purities of H_2 recovered

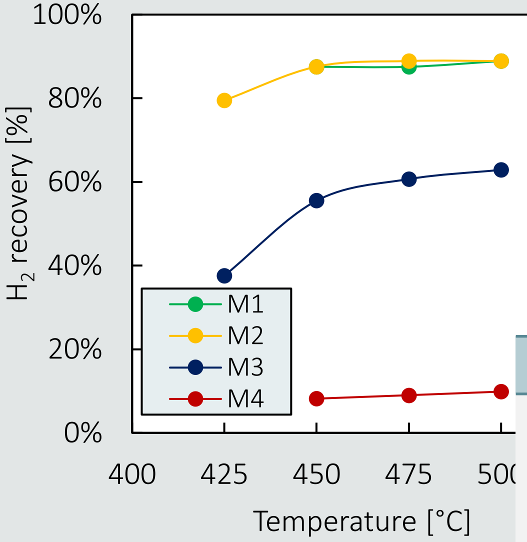
V. Cechetto, L. Di Felice, J. A. Medrano, C. Makhloufi, J. Zuniga, and F. Gallucci, “H_2 production via ammonia decomposition in a catalytic membrane reactor,” *Fuel Process. Technol.*, vol. 216, p. 106772, 2021, doi: https://doi.org/10.1016/j.fuproc.2021.106772.

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

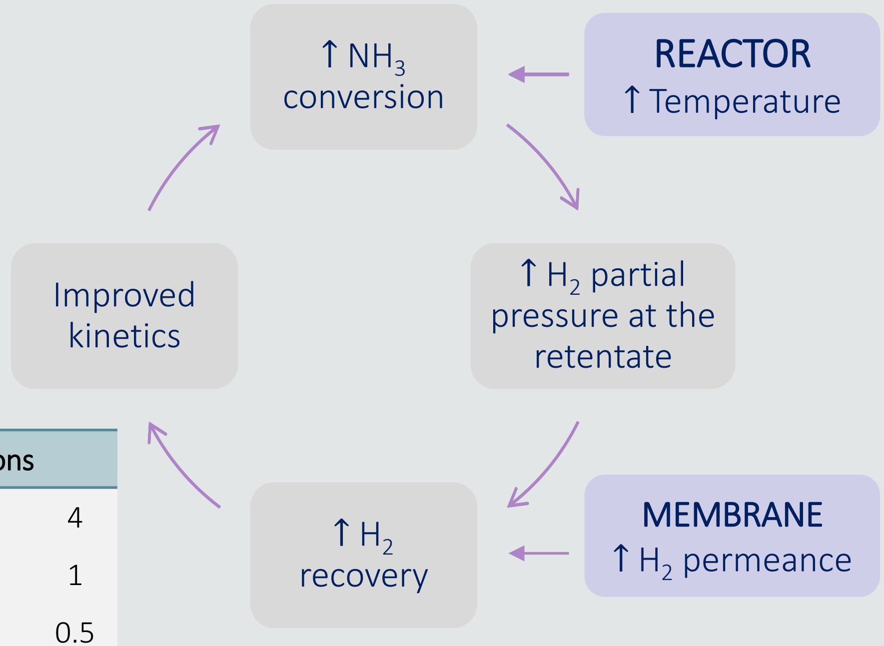
Membrane	Selective layer composition	Selective layer thickness [µm]	Membrane area [m^2]	Membrane configuration	Type of support	H_2 permeance [mol/s/m^2/Pa]	N_2 permeance [mol/s/m^2/Pa]	H_2/N_2 perm-selectivity [-]
M1	Pd-Ag	~ 4–5	$5.9 \cdot 10^{-3}$	Supported tubular DS	Ceramic	$1.64 \cdot 10^{-6}$	$3.47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

DS = Double -skinned





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



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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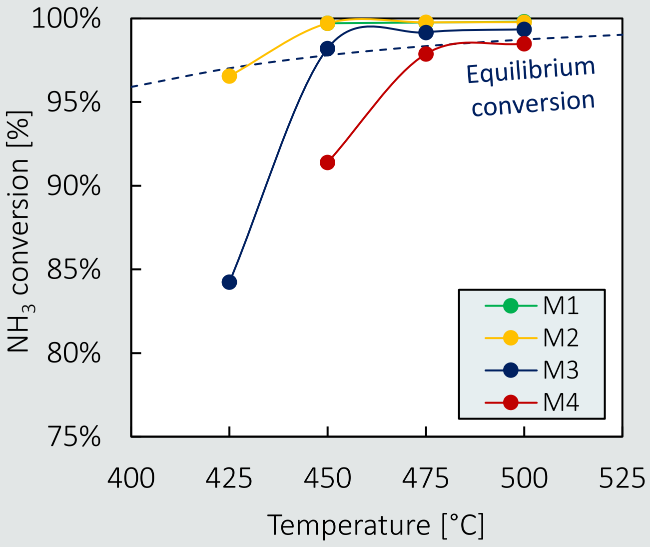

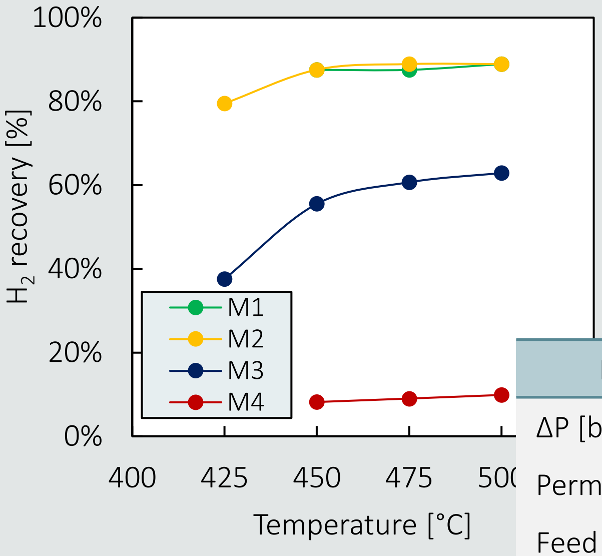

Experimental conditions	
ΔP [bar]	4
Permeate pressure [bar]	1
Feed flow rate [L_N/min]	0.5

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

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DS = Double -skinned

	NH_3 concentration in the permeate	
Temperature [°C]	M2	M4
450	11.8 ppm	4.0%
475	6.1 ppm	1.3%
500	1.6 ppm	0.6%

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

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

H_2 purification from residual NH_3

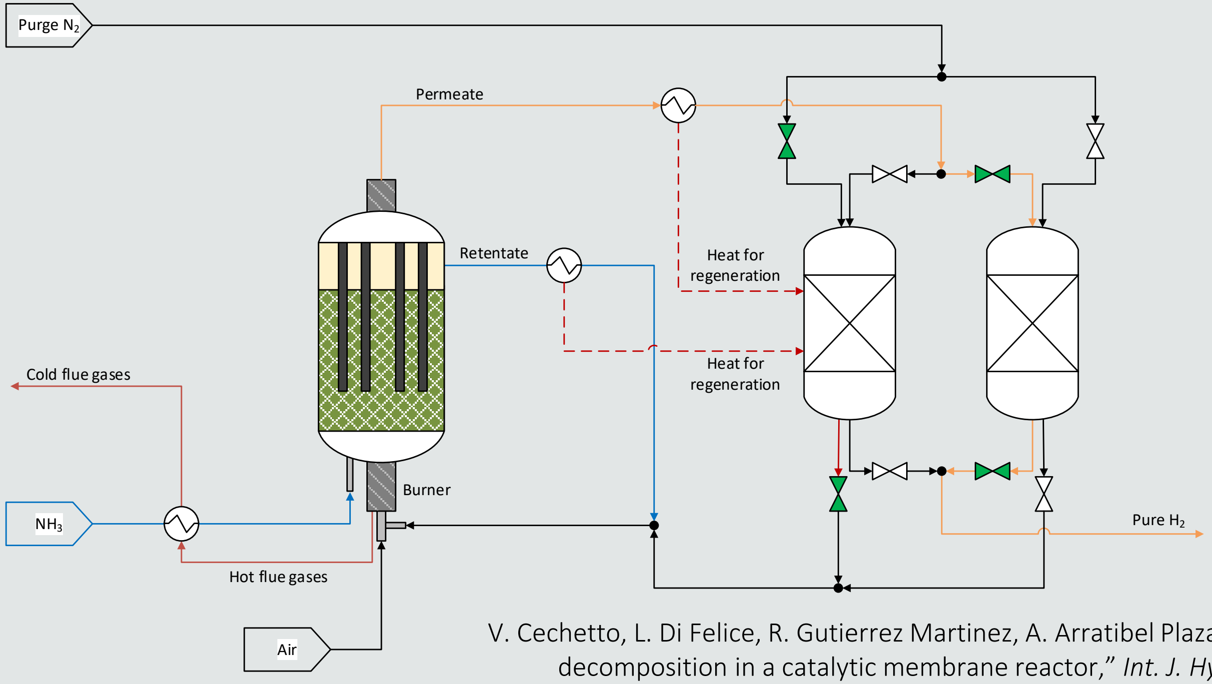
PEMFC specifications requires residual NH_3 concentration in the H_2 feed < 0.1 ppm.

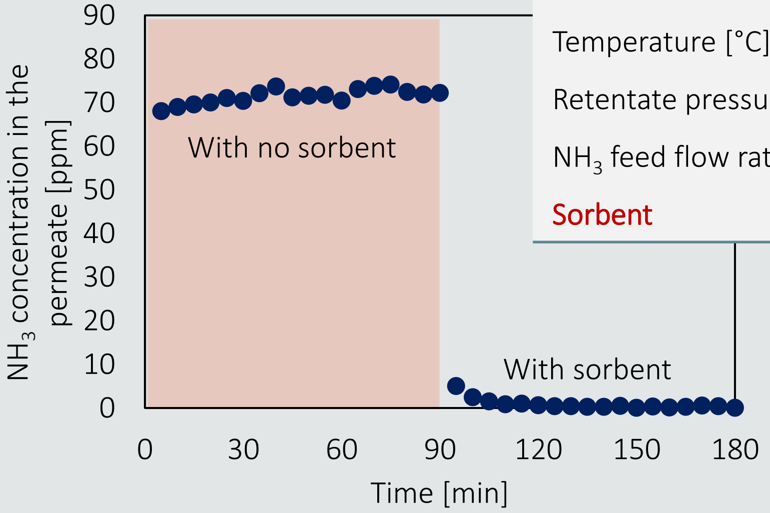
Strategy 1: Increase of the membrane selective layer thickness

Membrane	Thickness selective layer [µm]	H_2/N_2 perm-selectivity T=450°C and ΔP=1 bar	H_2 recovery [%]	NH_3 concentration in the permeate [ppm]
M4	~ 1	5210	93.2	47 (±2.1)
M2	~ 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 MR

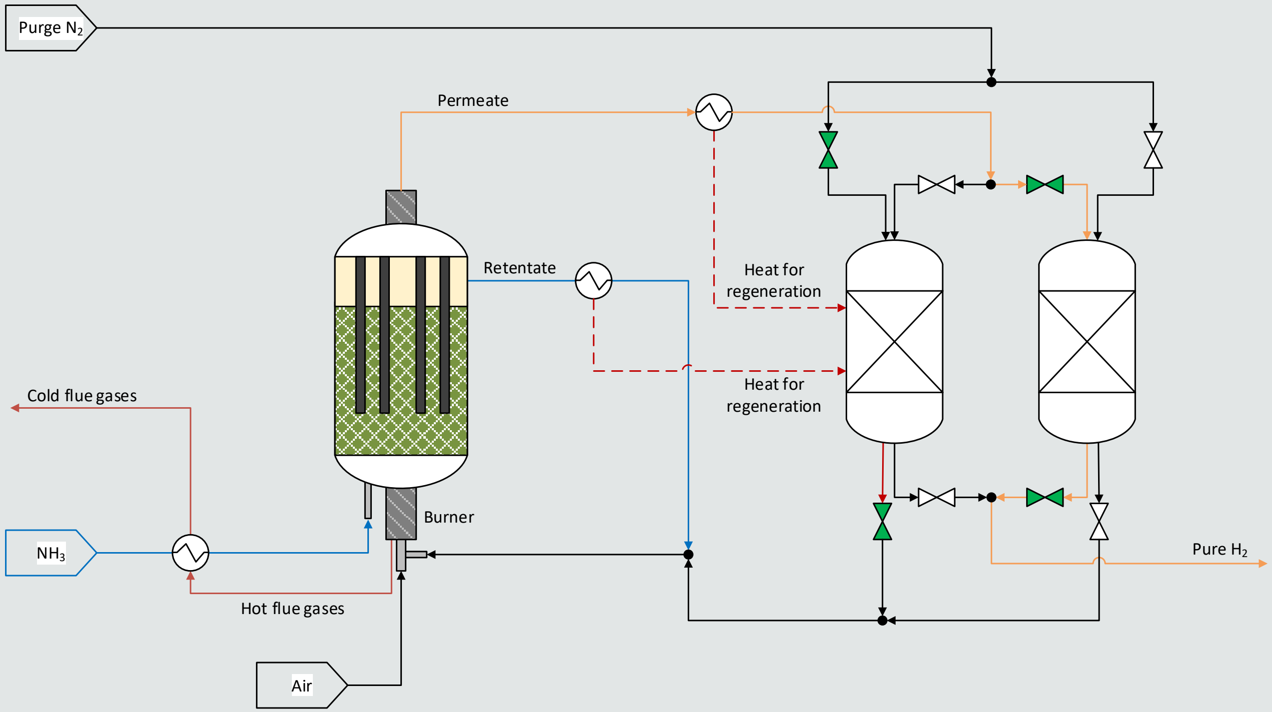




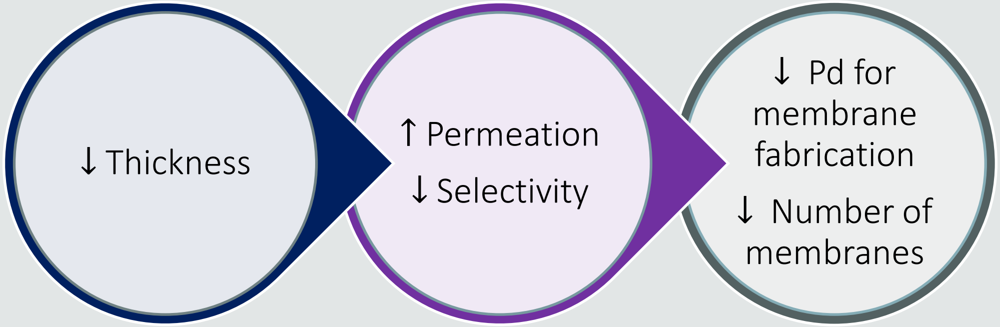
Experimental conditions	
Thickness selective layer [µm]	1
Permeate pressure [bar]	1
Temperature [°C]	450
Retentate pressure [bar]	3
NH_3 feed flow rate [L_N/min]	0.5
Sorbent	Zeolite 13X

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.

H_2 purification from residual NH_3



☐ Thinner membranes can be used with a consequent decrease of investment costs:



↓ Thickness

↑ Permeation
↓ Selectivity

↓ Pd for membrane fabrication
↓ Number of membranes

☐ The introduction of a hydrogen purification stage downstream the membrane reactor allows to operate the reactor at lower temperatures and to accept higher NH_3 concentration at the reactor outlet with benefits from an energetic point of view.

Techno-economics

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.

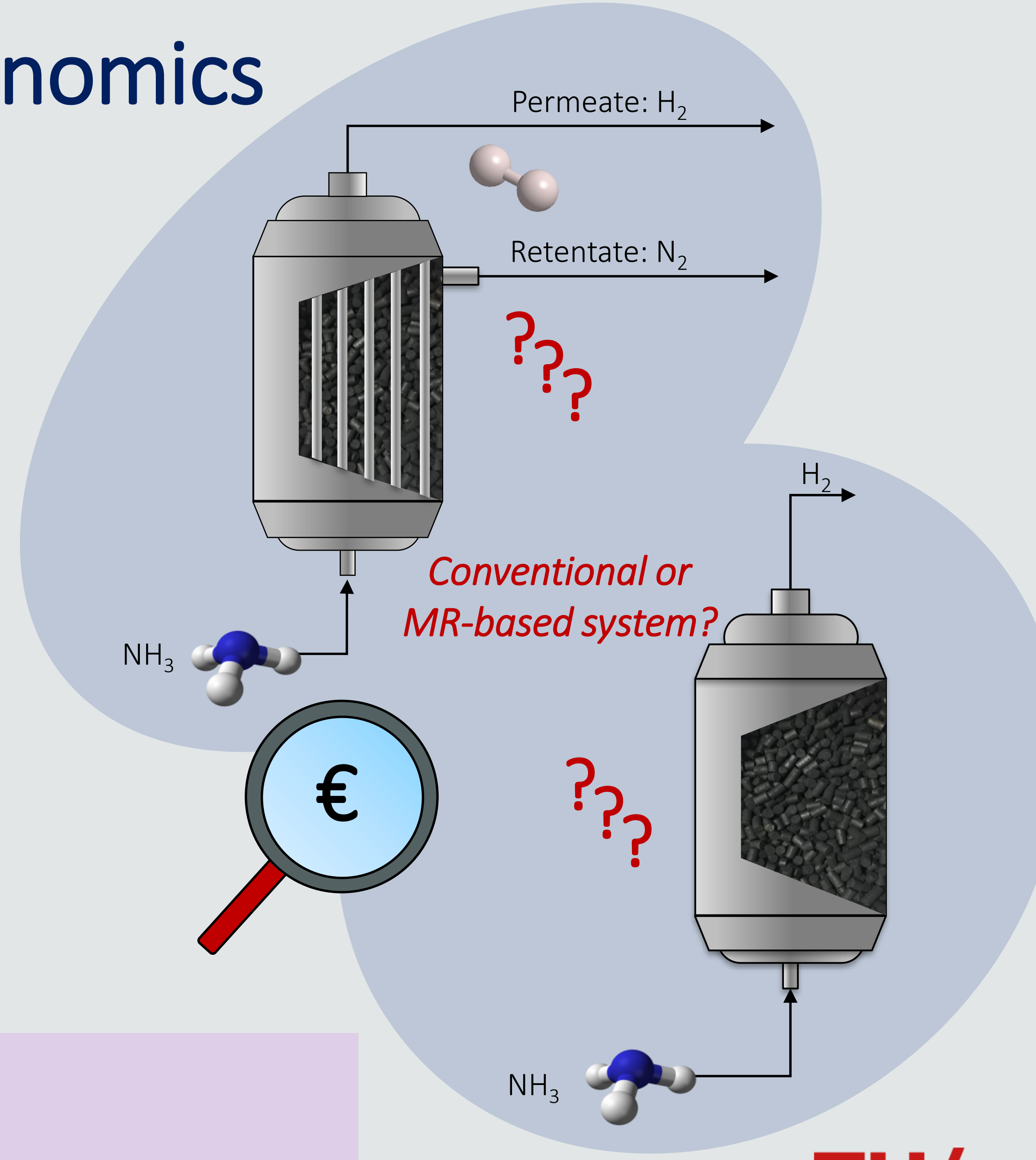
This work:

<u>Techno-economic assessment of a decentralized plant for hydrogen production from ammonia decomposition</u>

- H_2 for direct use in PEM fuel cells
- Stationary and vehicle applications

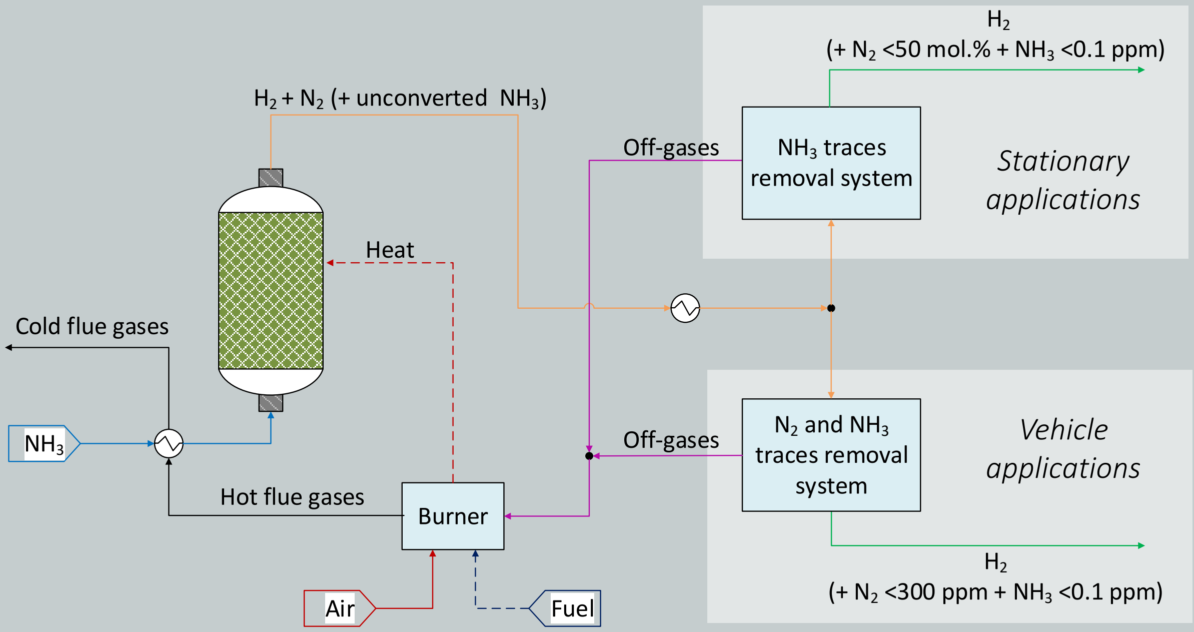
Target:

- 500 kg/day of H_2
- H_2 purity = 99.97%
- Max NH_3 concentration in H_2 stream = 0.1 ppm



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

Conventional system



H_2 + N_2 (+ unconverted NH_3)

Heat

Cold flue gases

NH_3

Hot flue gases

Burner

Air

Fuel

Off-gases

NH_3 traces removal system

H_2 (+ N_2 <50 mol.% + NH_3 <0.1 ppm)

Stationary applications

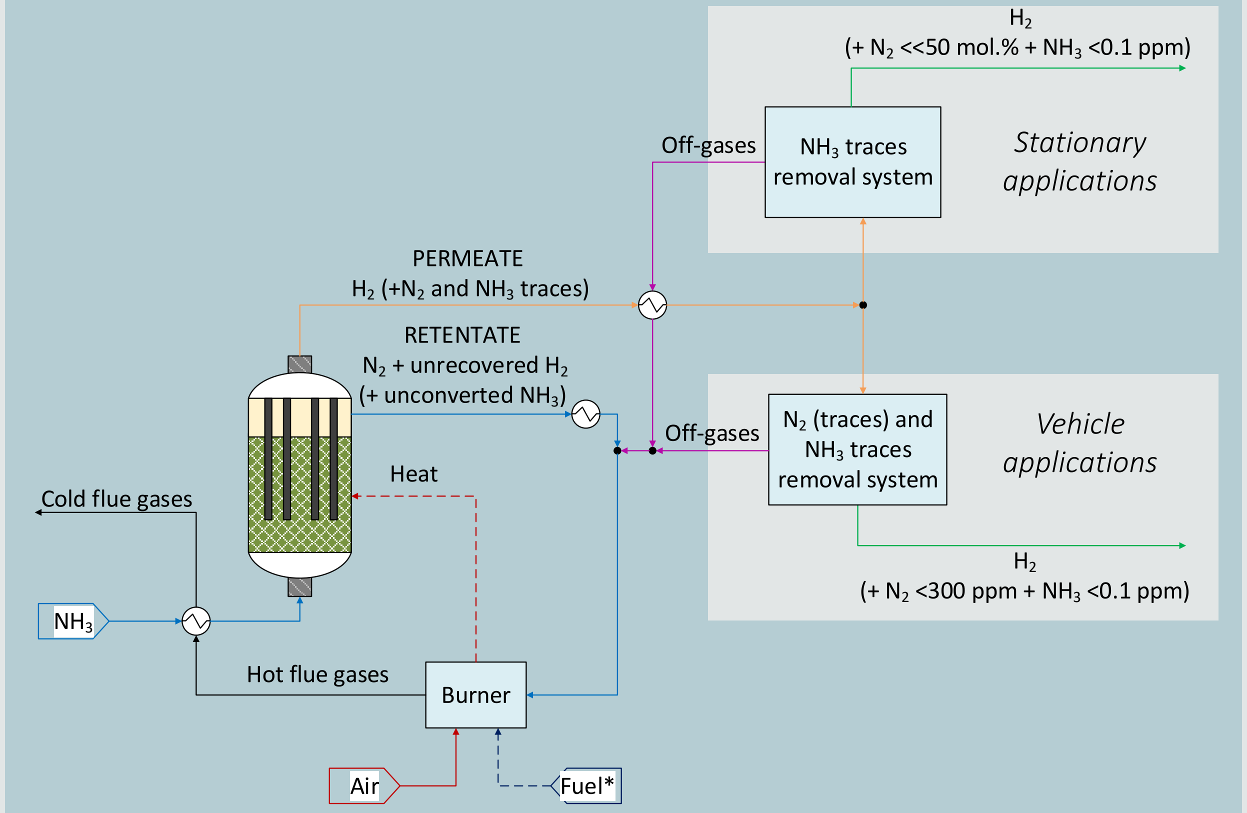
Off-gases

N_2 and NH_3 traces removal system

H_2 (+ N_2 <300 ppm + NH_3 <0.1 ppm)

Vehicle applications

Membrane reactor-based system



PERMEATE

H_2 (+N_2 and NH_3 traces)

RETENTATE

N_2 + unrecovered H_2 (+ unconverted NH_3)

Heat

Cold flue gases

NH_3

Hot flue gases

Burner

Air

Fuel*

Off-gases

NH_3 traces removal system

H_2 (+ N_2 <<50 mol.% + NH_3 <0.1 ppm)

Stationary applications

Off-gases

N_2 (traces) and NH_3 traces removal system

H_2 (+ N_2 <300 ppm + NH_3 <0.1 ppm)

Vehicle applications

Design choices:

Catalyst: Ru/Al_2O_3

NH_3 removal unit: TSA (2 beds configuration)

N_2 removal unit: PSA (4 beds configuration)

Economic evaluation

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

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	55982 €/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 [3]
Catalyst lifetime	5
Lifetime Zeolite 13X	5
Membrane lifetime	5
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

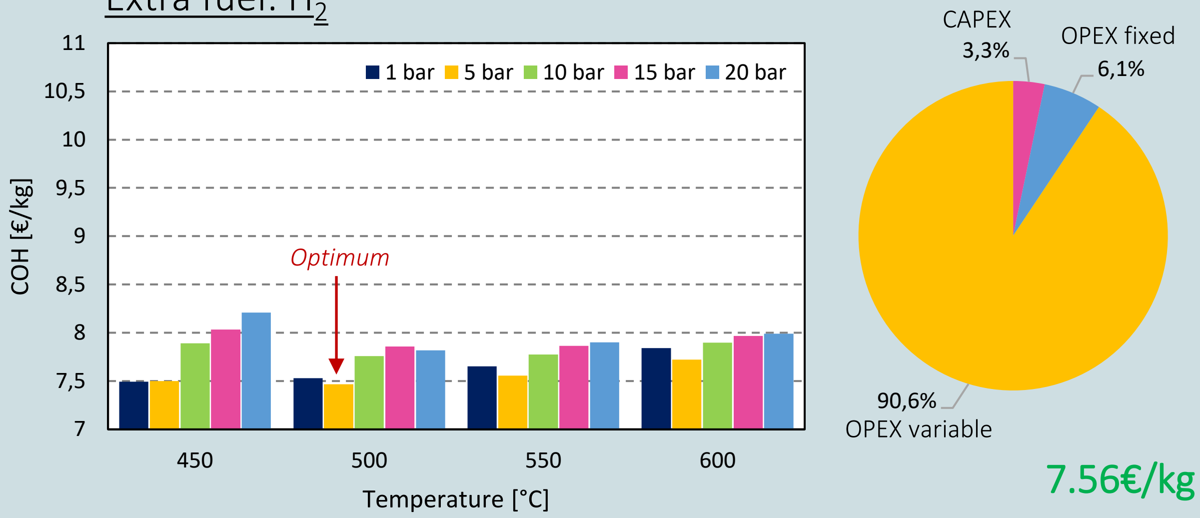
[3] S. Richard, A. Ramirez Santos, and F. Gallucci, "PEM genset using membrane reactors technologies An economic comparison among different e-fuels", International Journal of Hydrogen Energy

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

Cost of H_2 production: is extra fuel H_2 or NH_3?

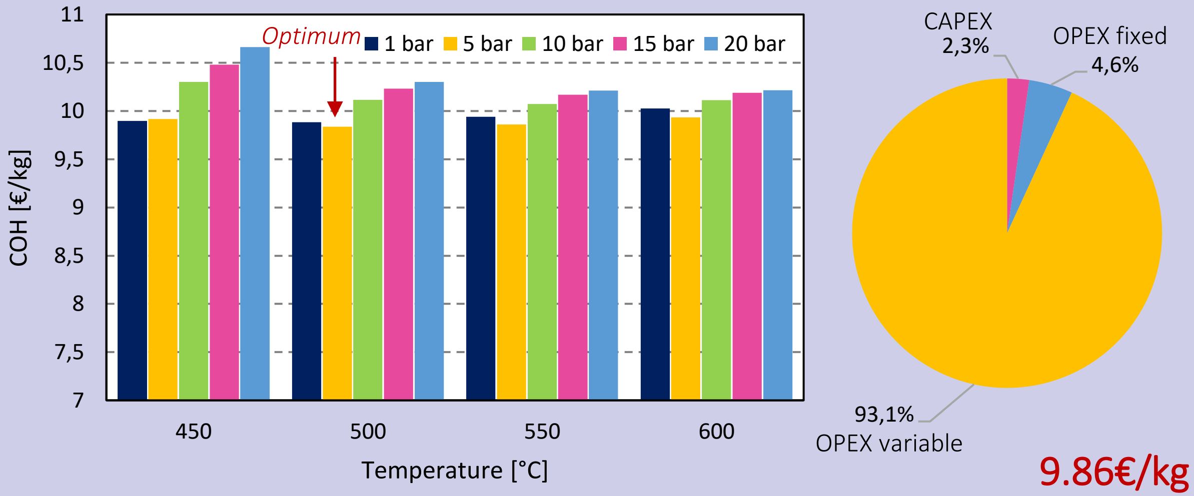
VEHICLE APPLICATIONS

Extra fuel: H_2



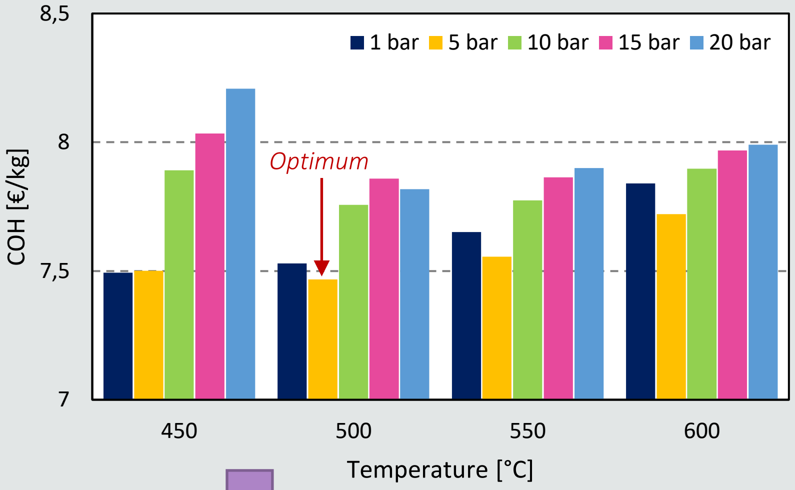
7.56€/kg

Extra fuel: NH_3



9.86€/kg

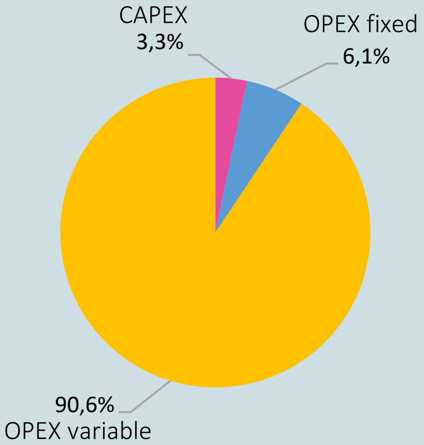
Vehicle applications: COH in a conventional system

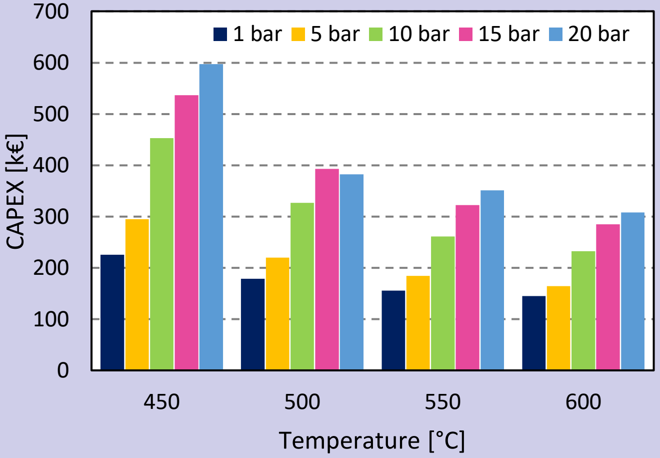


Economic optimum

T = 500 °C
P = 5 bar

SHARE COSTS	[€/kg]
CAPEX	0.25
OPEX FIXED	0.46
OPEX VARIABLE	6.85
COH	7.56





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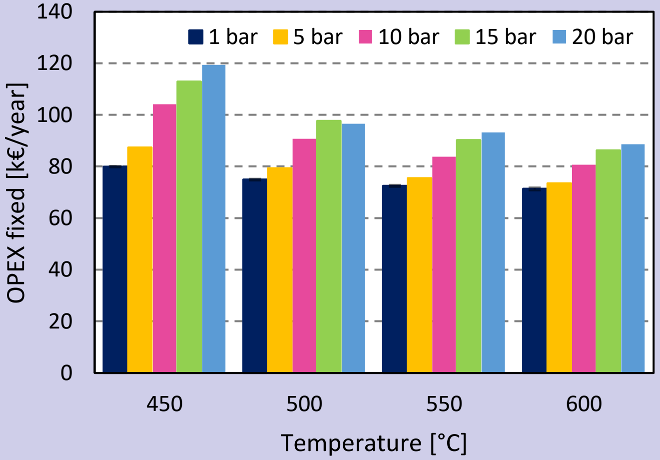

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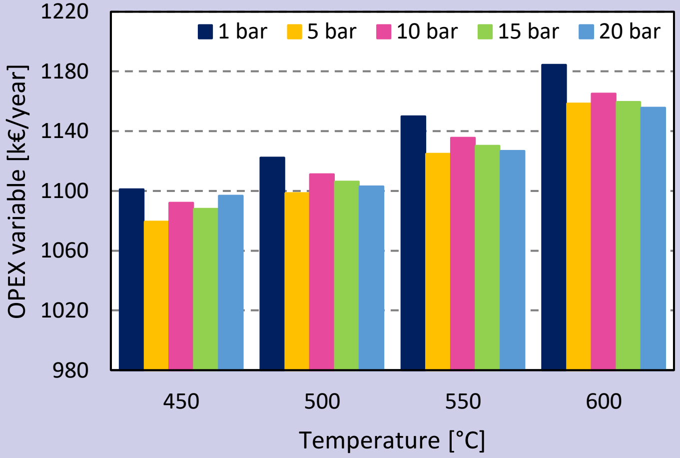


Vehicle applications: COH in a MR-based system

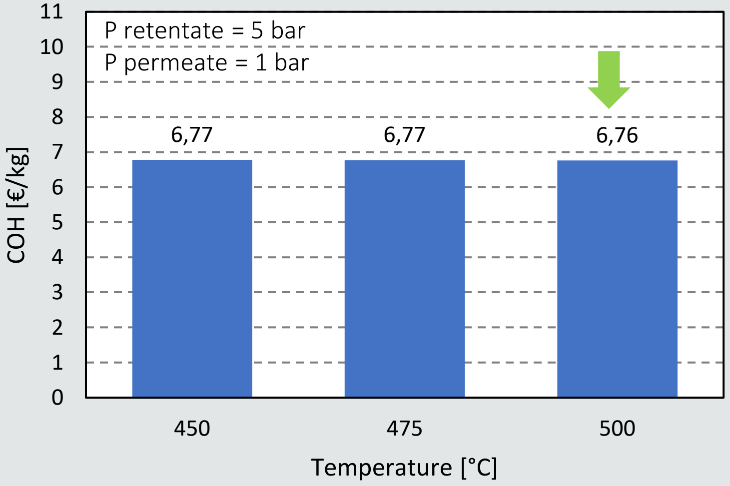
Experimental results

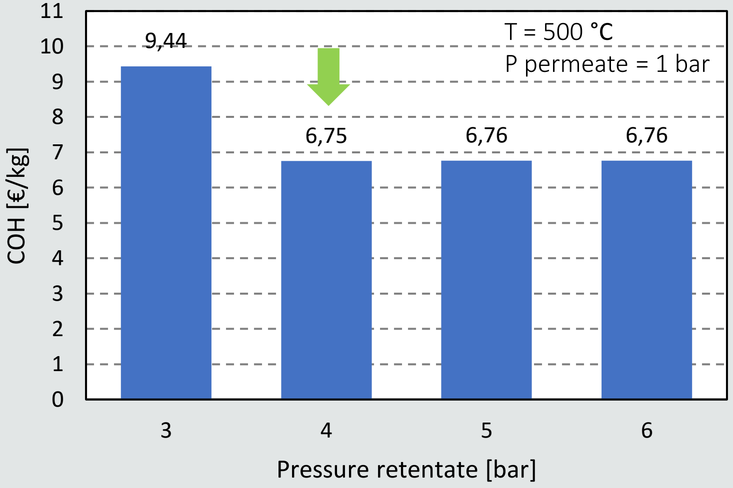
Experimental operating conditions	
Membrane	DS Pd-Ag
Membrane thickness [µm]	4-5
Membrane length [m]	0.135
Mass catalyst [g]	250
D reactor [m]	0.045
L reactor [m]	0.297

NH_3 in [L_N/min]	T [° C]	P retentate [bar]	P permeate [bar]	NH_3 conversion [%]	H_2 recovery [%]	H_2 purity [%]	NH_3 concentration permeate [ppm]
0.5	500	3	1	99.6	75.4	99.997	2.5
		4		99.8	84.8	99.995	4.3
		5		99.8	88.9	99.994	7.9
		6		99.8	91.6	99.992	12.5
0.5	450	5	1	99.7	87.5	99.994	46.6
	475			99.8	87.5	99.993	16.9
	500			99.8	88.9	99.991	8.1

> 99.97%

> 0.1 ppm

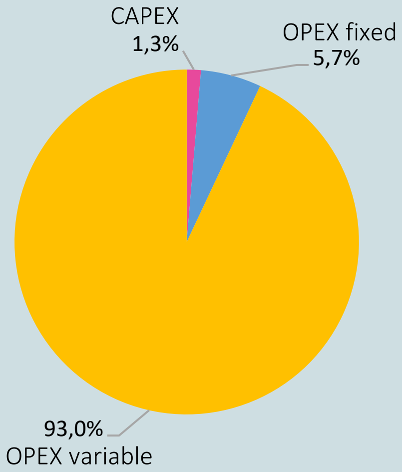




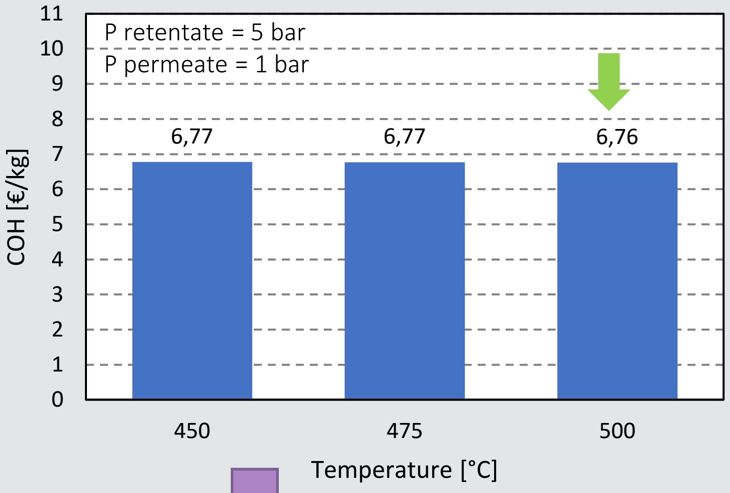
Economic optimum

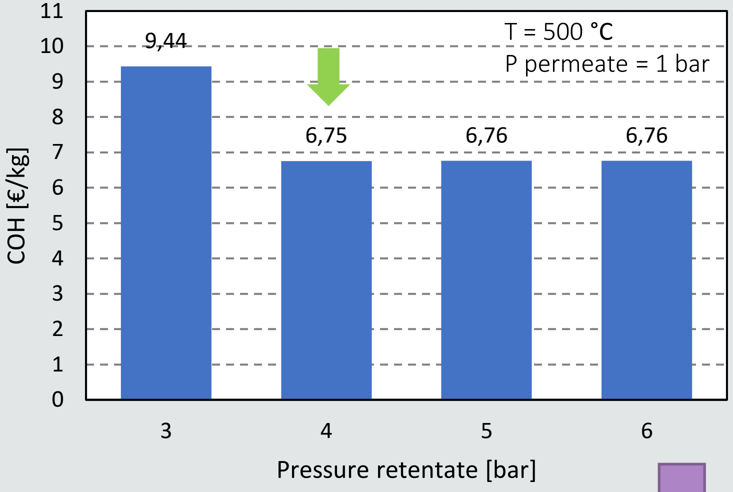
T = 500 °C
P = 4 bar

SHARE COSTS	[€/kg]
CAPEX	0.09
OPEX FIXED	0.38
OPEX VARIABLE	6.28
COH	6.75



Vehicle applications: COH in a MR-based system

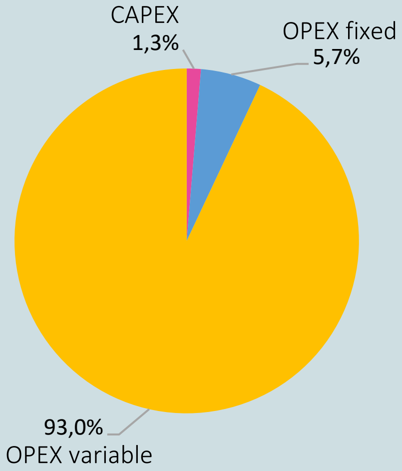


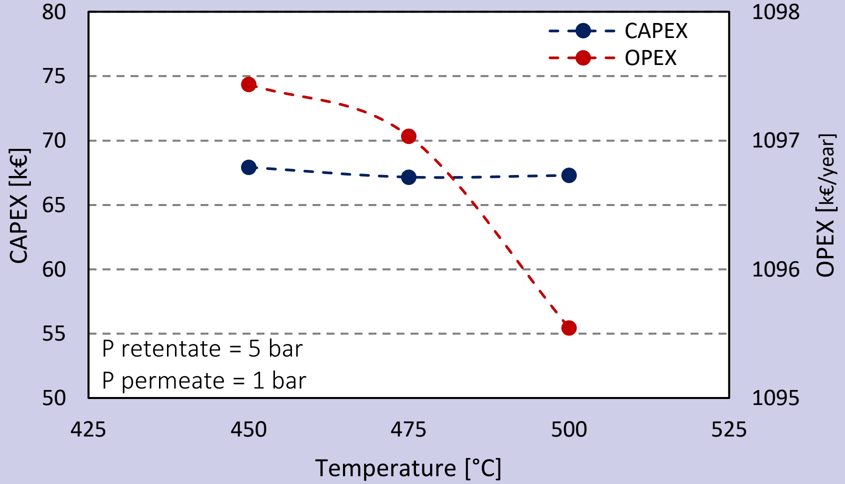


Economic optimum

T = 500 °C
P = 4 bar

SHARE COSTS	[€/kg]
CAPEX	0.09
OPEX FIXED	0.38
OPEX VARIABLE	6.28
COH	**6.75**

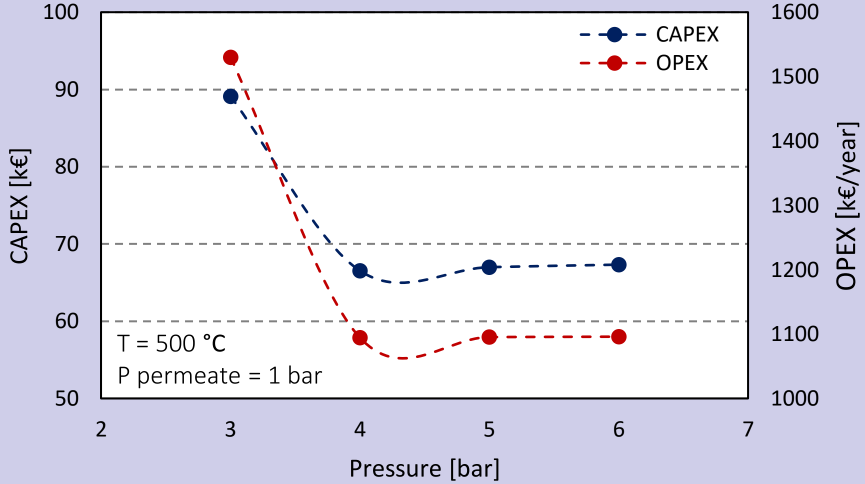




T ↑

H_2 recovery ↑

NH_3 feed ↓



P retentate ↓

H_2 recovery ↓

NH_3 feed ↑

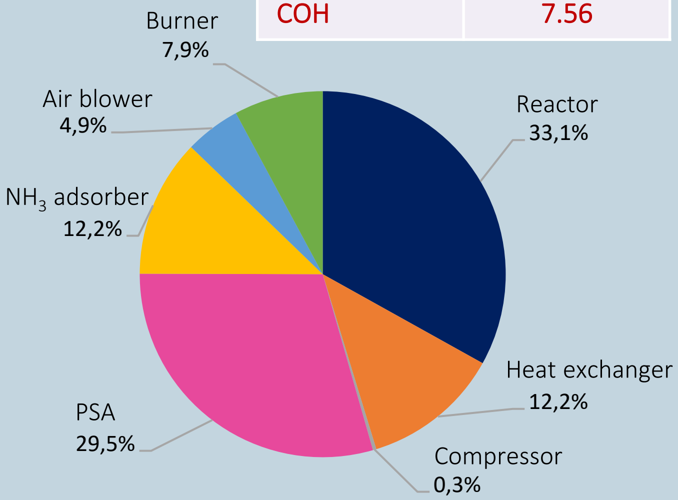
Vehicle applications: conventional vs MR-based system

CONVENTIONAL SYSTEM

SHARE COSTS	[€/kg]
CAPEX	0.25 (3.3%)
OPEX FIXED	0.46 (6.1%)
OPEX VARIABLE	6.85 (90.6%)
COH	7.56

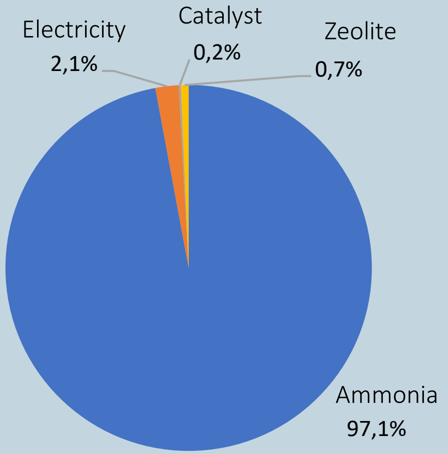
CAPEX

CAPEX	Cost [k€]
Reactor	72.77
Heat Exchangers	26.07
Compressors	0.66
PSA	64.82
NH_3 Adsorber	26.79
Air Blower	10.80
NH_3 pump	0.00
Burner	17.31
TOTAL	**329.18**



OPEX

OPEX variable	Cost [k€/year]
Ammonia	1066.5
Electricity	22.6
Catalyst	2.0
Zeolite	7.5
TOTAL	**1559.3**

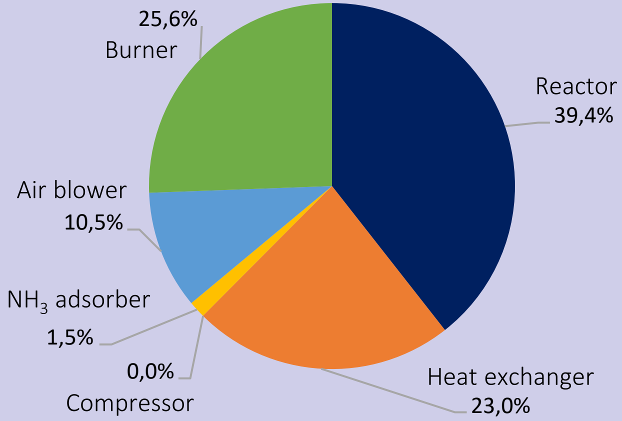


MR-BASED SYSTEM

SHARE COSTS	[€/kg]
CAPEX	0.09 (1.3%)
OPEX FIXED	0.38 (5.7%)
OPEX VARIABLE	6.28 (93.0%)
COH	6.75

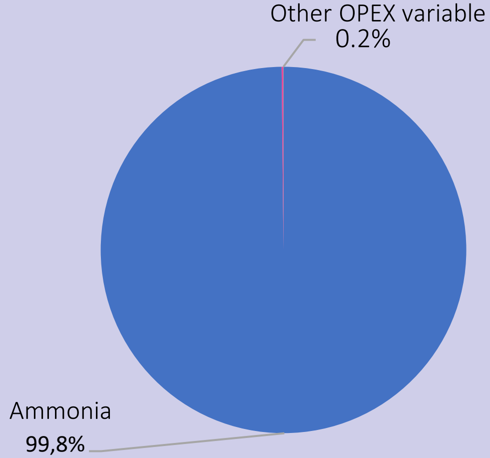
CAPEX

CAPEX	Cost [k€]
Reactor	26.22
Heat Exchangers	15.75
Compressors	0.00
PSA	0.00
NH_3 Adsorber	1.00
Air Blower	6.96
NH_3 pump	0.00
Burner	17.02
TOTAL	**66.53**

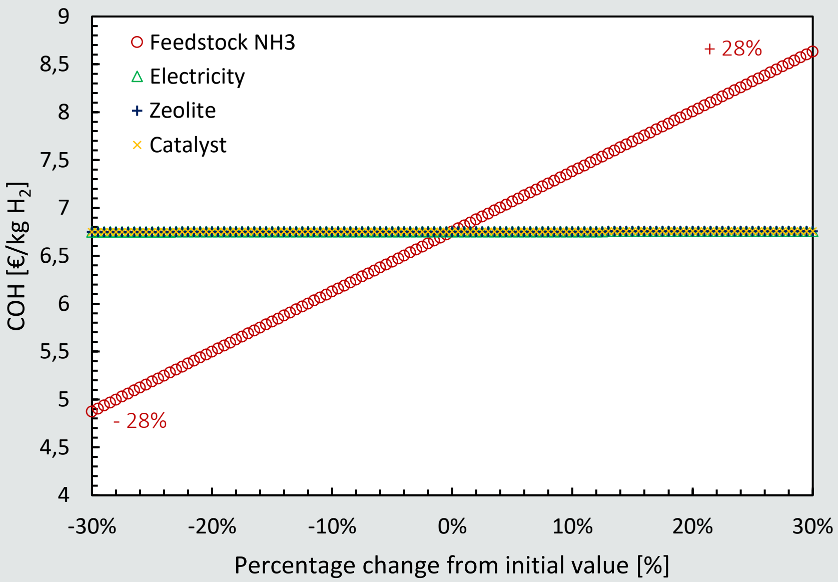


OPEX

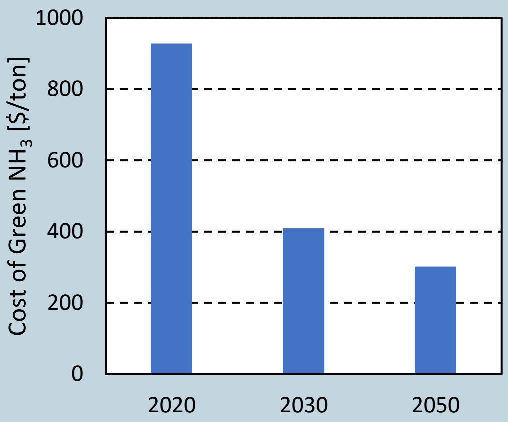
OPEX variable	Cost [k€/year]
Ammonia	1029.5
Electricity	1.5
Catalyst	0.1
Zeolite	0.0
Membrane	0.1
TOTAL	**1031.2**



Sensitivity Analysis and Forecasting

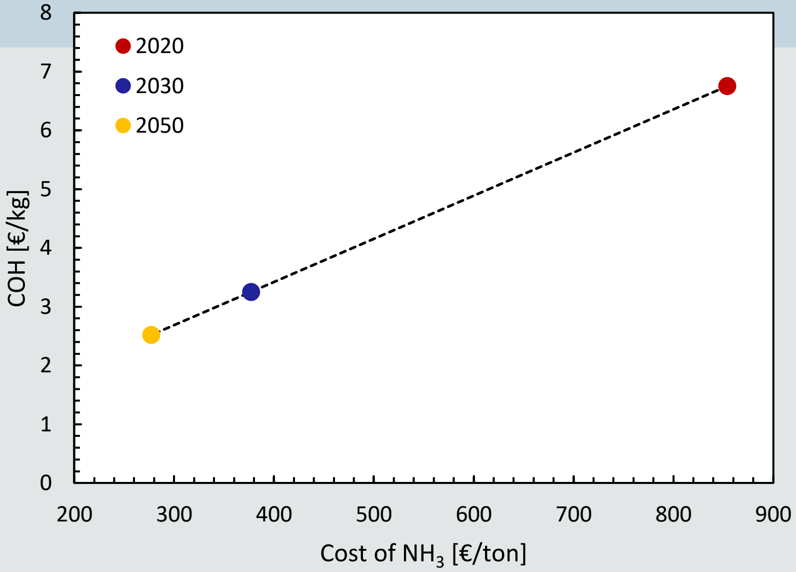


Cost of Green NH_3



Year	Cost of NH_3 [€/ton]	COH [€/kg]
2020	853.92	6.75
2030	377.07	3.25
2050	277.30	2.52

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



Conclusions

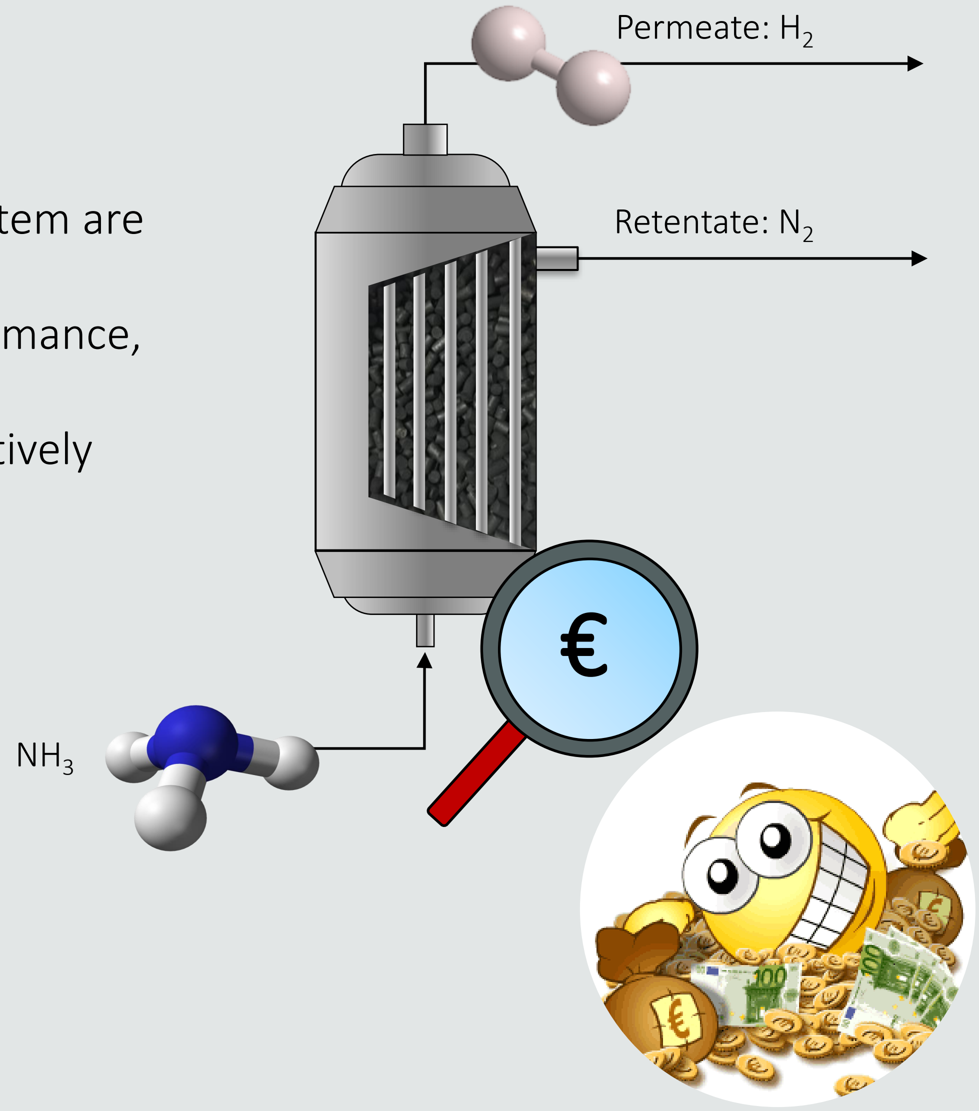
In a membrane reactor for H_2 production from NH_3:

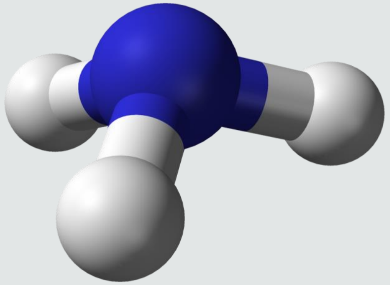
☐ Higher efficiency and compactness compared to a conventional system are achieved

☐ 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 the reactor.

☐ From an economic point of view, the technology installed in a decentralized plant for H_2 production is competitive compared to the conventional technology due to the reduced installation costs as well as operating costs for utilities consumption.





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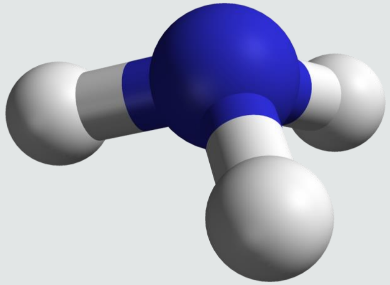


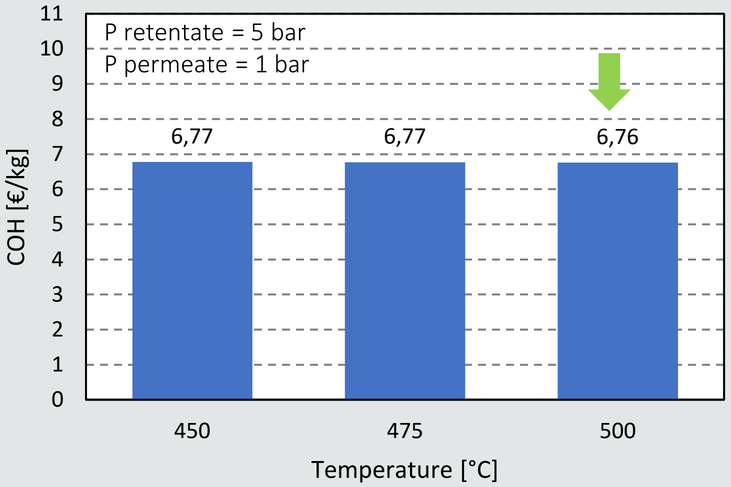
TU/e EINDHOVEN UNIVERSITY OF TECHNOLOGY

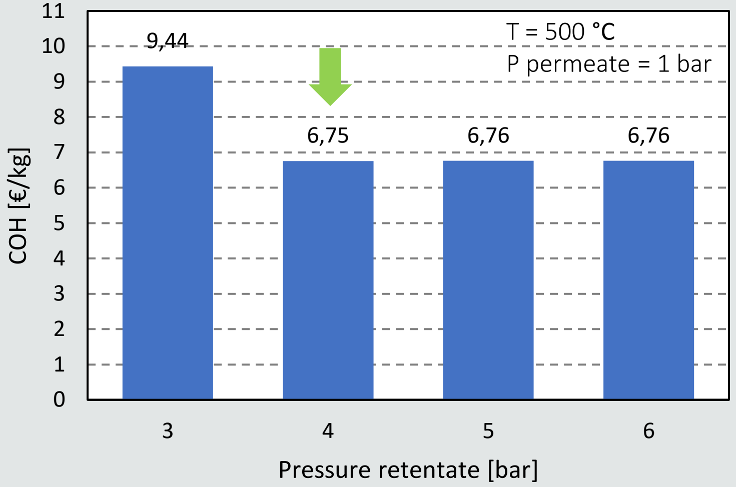
Inorganic Membranes & Membrane Reactors

areNH$_3$a
Advanced materials and Reactors for Energy storage tHrough Ammonia

This project receives support from the European Union's Horizon 2020 research and innovation under grant agreement No. 862482

Vehicle applications: COH in a MR-based system





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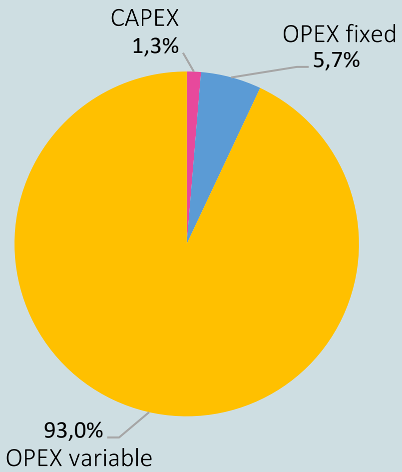
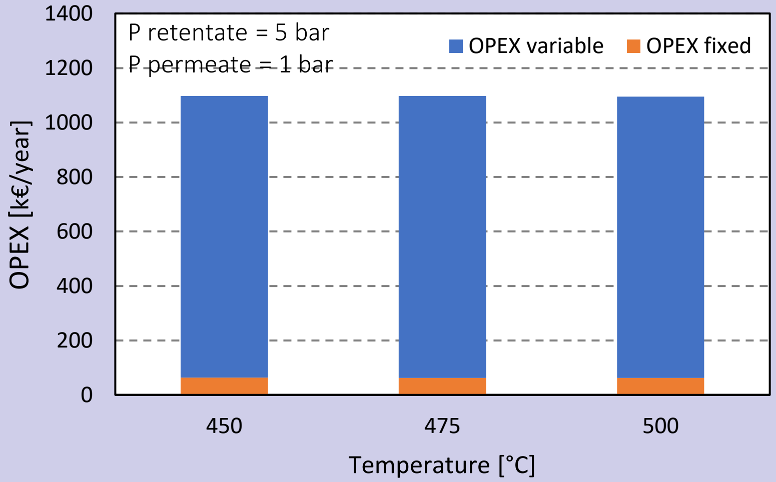
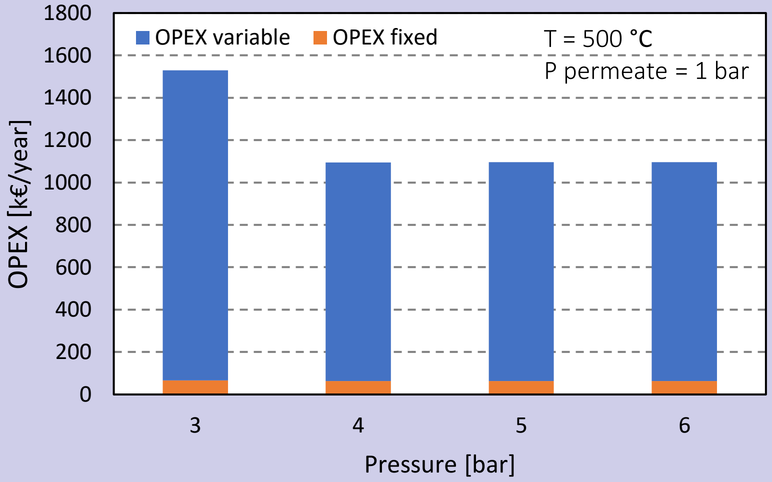




T ↑

H$_2$ recovery ↑

NH$_3$ feed ↓



P retentate ↓

H$_2$ recovery ↓

NH$_3$ feed ↑