Inorganic Membranes
& Membrane Reactors

AMBH2ER

TU/e EINDHOVEN UNIVERSITY OF TECHNOLOGY

Membrane Reactors for Chemical Production

Fausto Gallucci, Inorganic Membranes and Membrane Reactors

Chemical Engineering and Chemistry, Sustainable Process Engineering

Outlook

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

Our Lab(s)


NORTH SEA
NETHERLANDS
Amsterdam
Schiphol
Eindhoven
BELGIUM
GERMANY

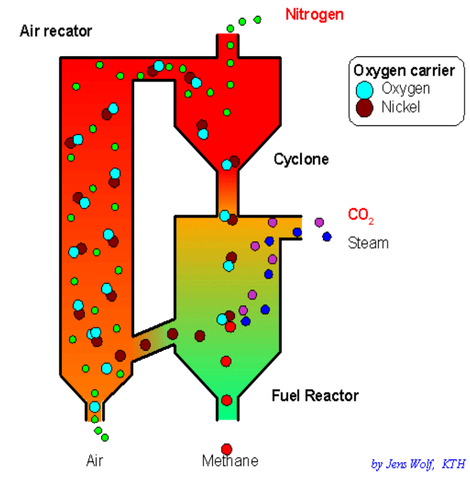

San Sebastian
Basque
La Rioja
Navarra
PORTUGAL
SPAIN

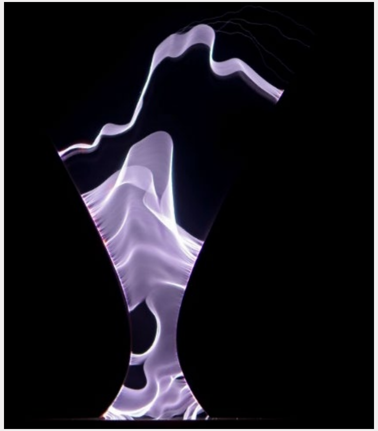
Research themes - SIR

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

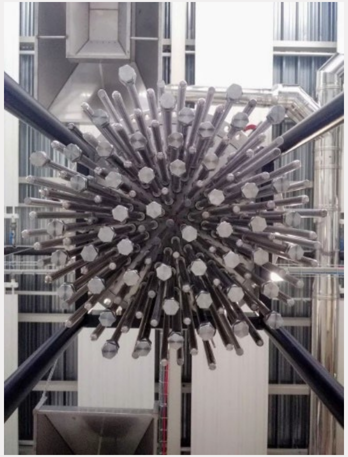
Research themes - SIR

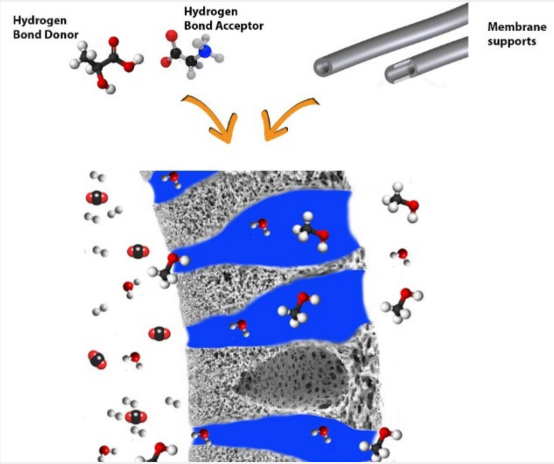
Integration reaction + separation

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





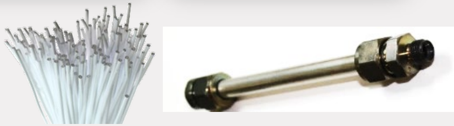
MEMBRANE TECHNOLOGY

MEMBRANE MATERIALS

- Polymer
- Mixed-matrix
- Carbon molecular sieve
- Palladium

Hollow fiber membranes

Tubular membranes

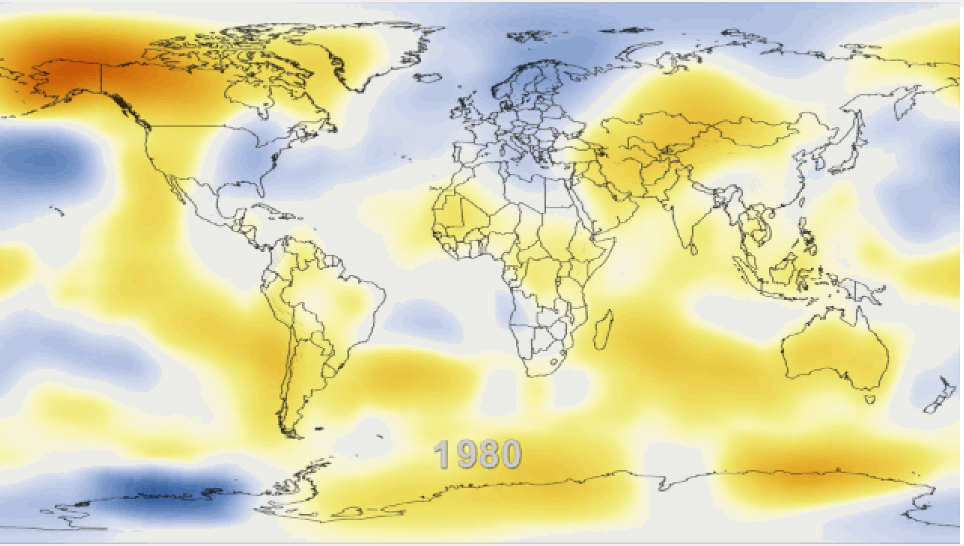


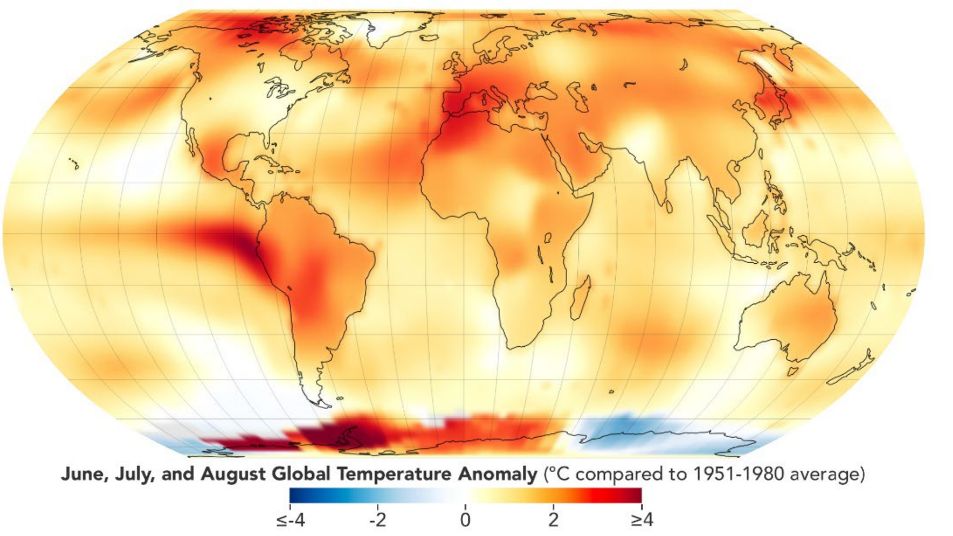
SCALABLE MEMBRANE CONFIGURATIONS

- CO_2 capture
- H_2 purification
- CH_4 purification
- Olefin / paraffin separation
- Water separation

APPLICATIONS

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

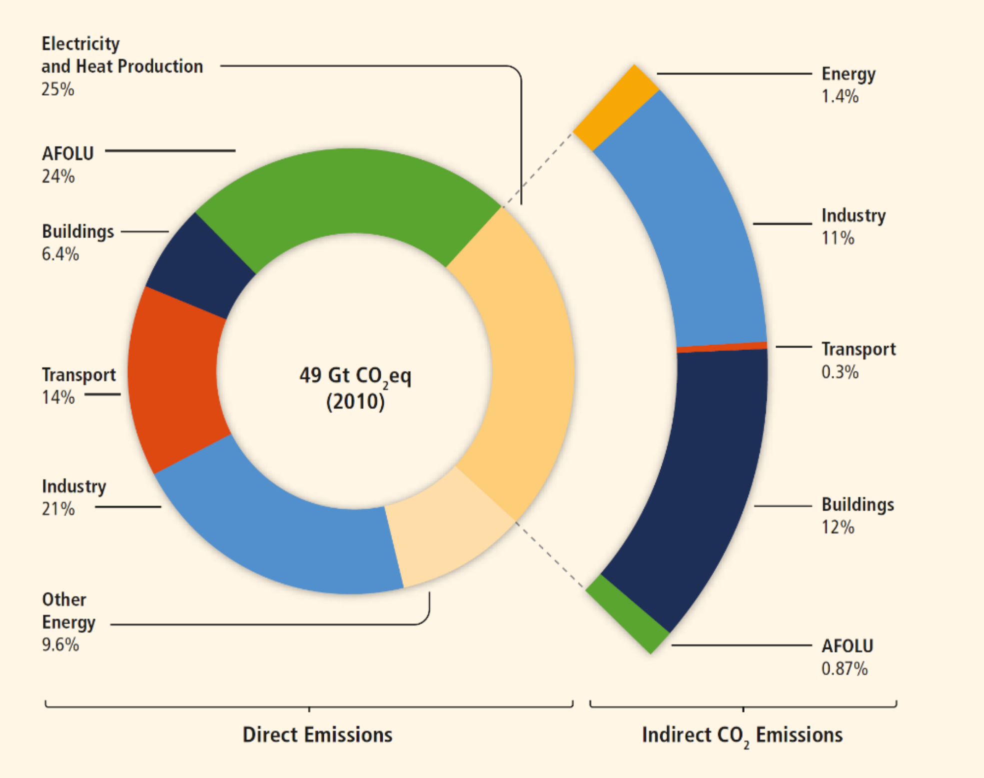
Solutions

1) Reduce the number of people;

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

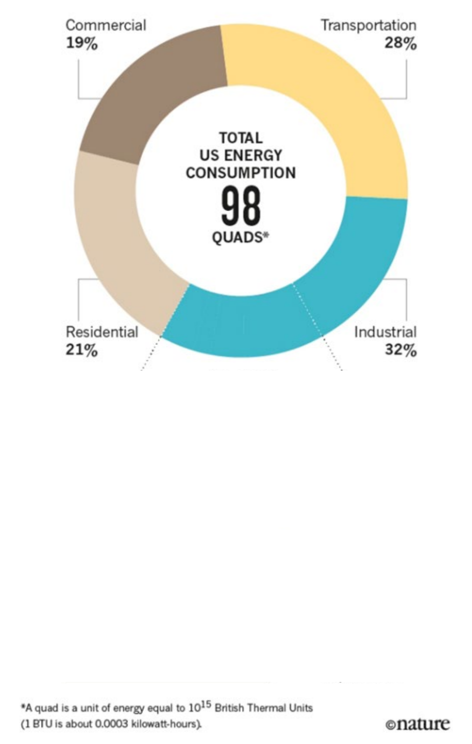
3) Capture the CO_2 (at the production point but also from the atmosphere)

Who is responsible



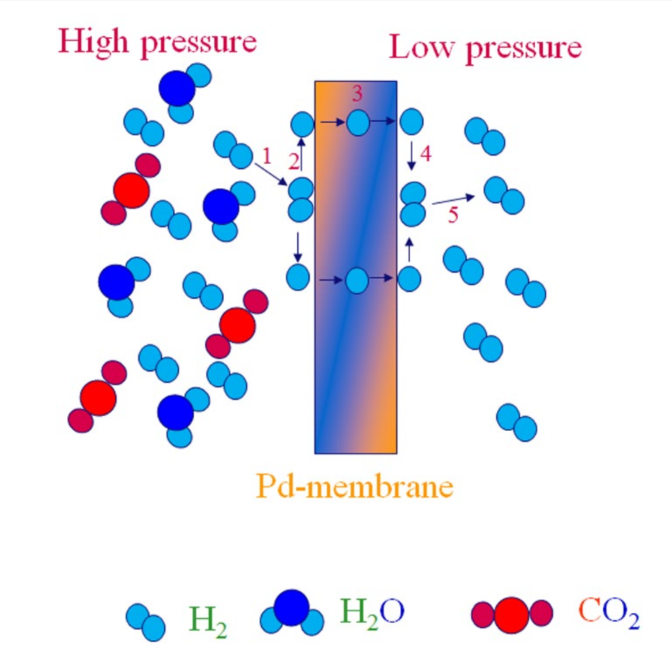
IPCC report

A possible solution

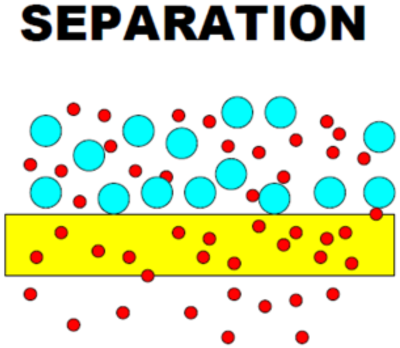


*A quad is a unit of energy equal to 10^{15} British Thermal Units (1 BTU is about 0.0003 kilowatt-hours).

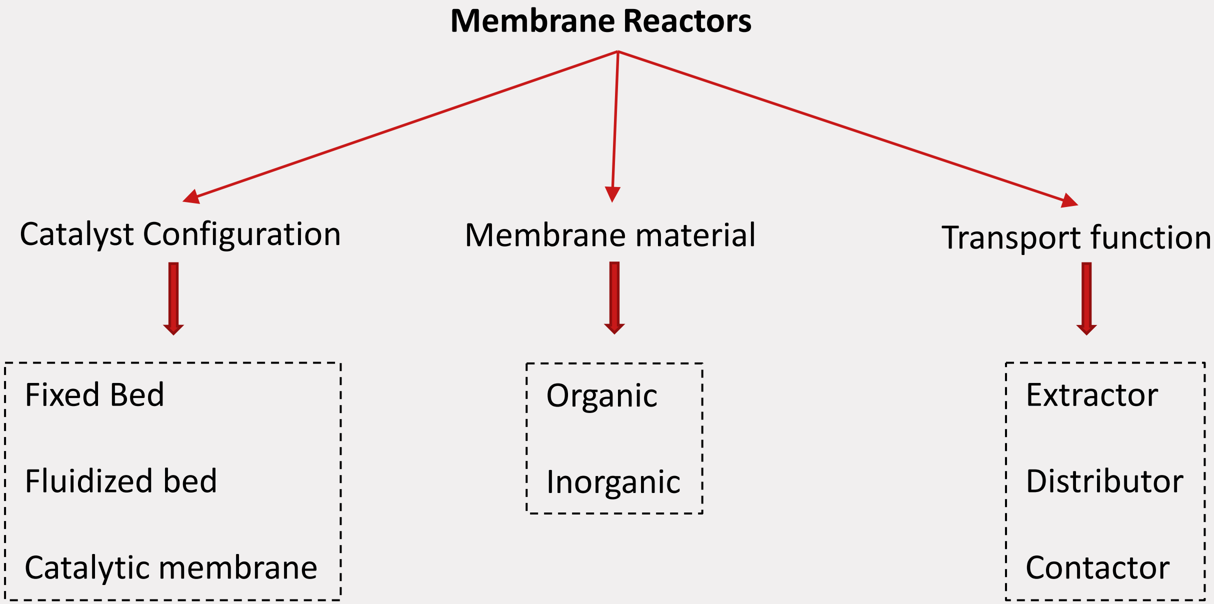
©nature



Membrane functions



Classification



Membrane Reactors

Catalyst Configuration

- Fixed Bed
- Fluidized bed
- Catalytic membrane

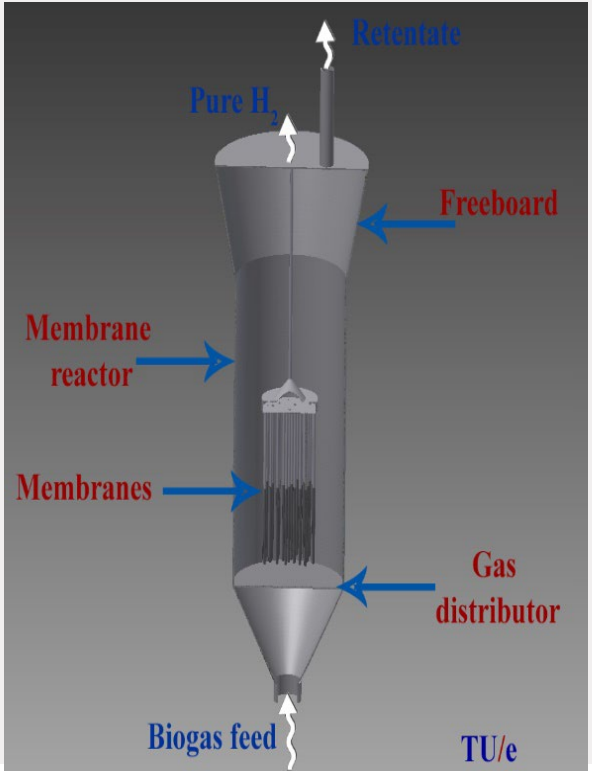
Membrane material

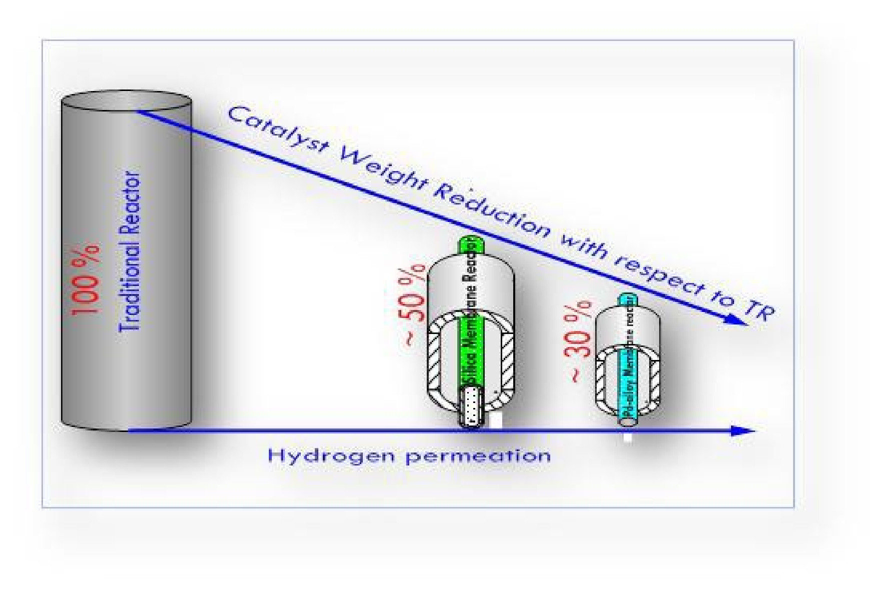
- Organic
- Inorganic

Transport function

- Extractor
- Distributor
- Contactor

A membrane reactor

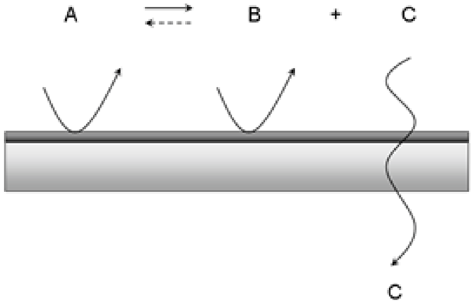


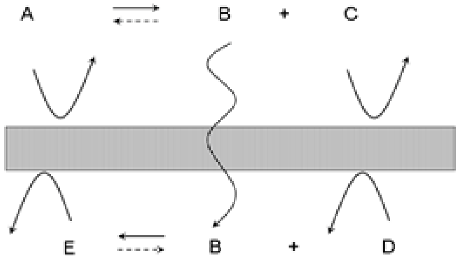


Brunetti A.; Caravella C.; Barbieri G.; Drioli E.; "Simulation study of water gas shift in a membrane reactor", *J. Membr. Sci.*, 2007, 306(1-2), 329-340

Why a membrane reactor?

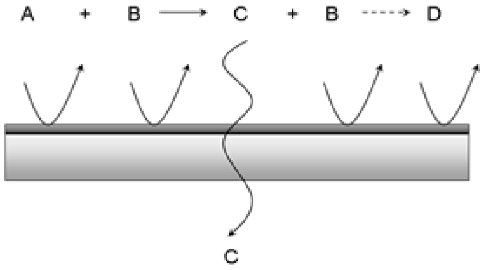
conversion enhancement by selective permeation of a reactant product of an equilibrium limited reaction

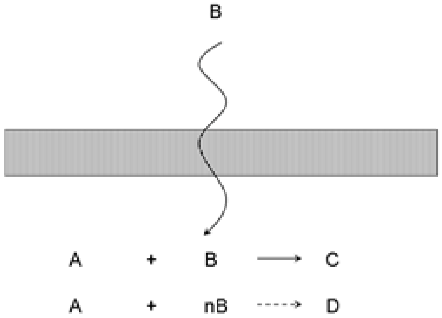




conversion enhancement by coupling of reactions

selectivity enhancement by selective permeation of an intermediate product

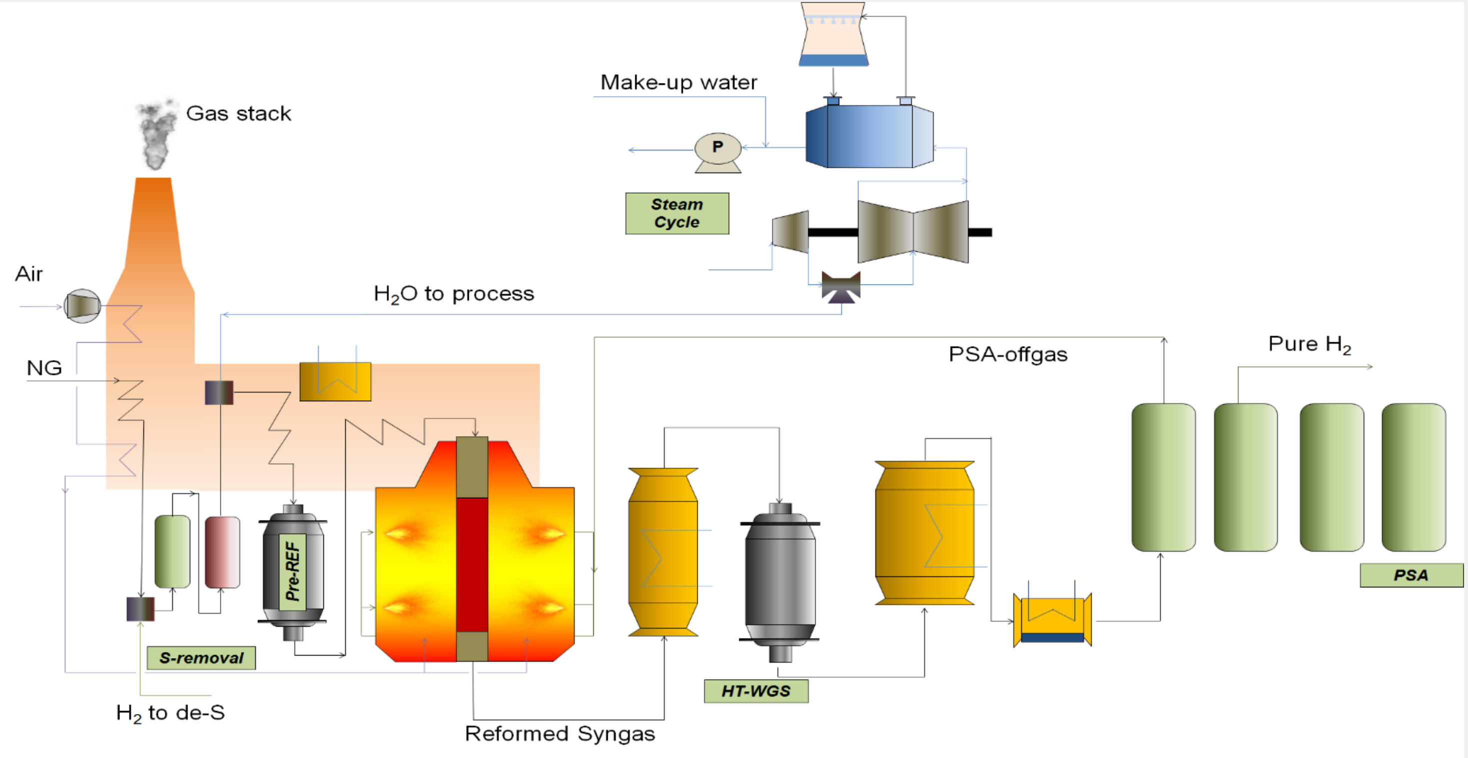




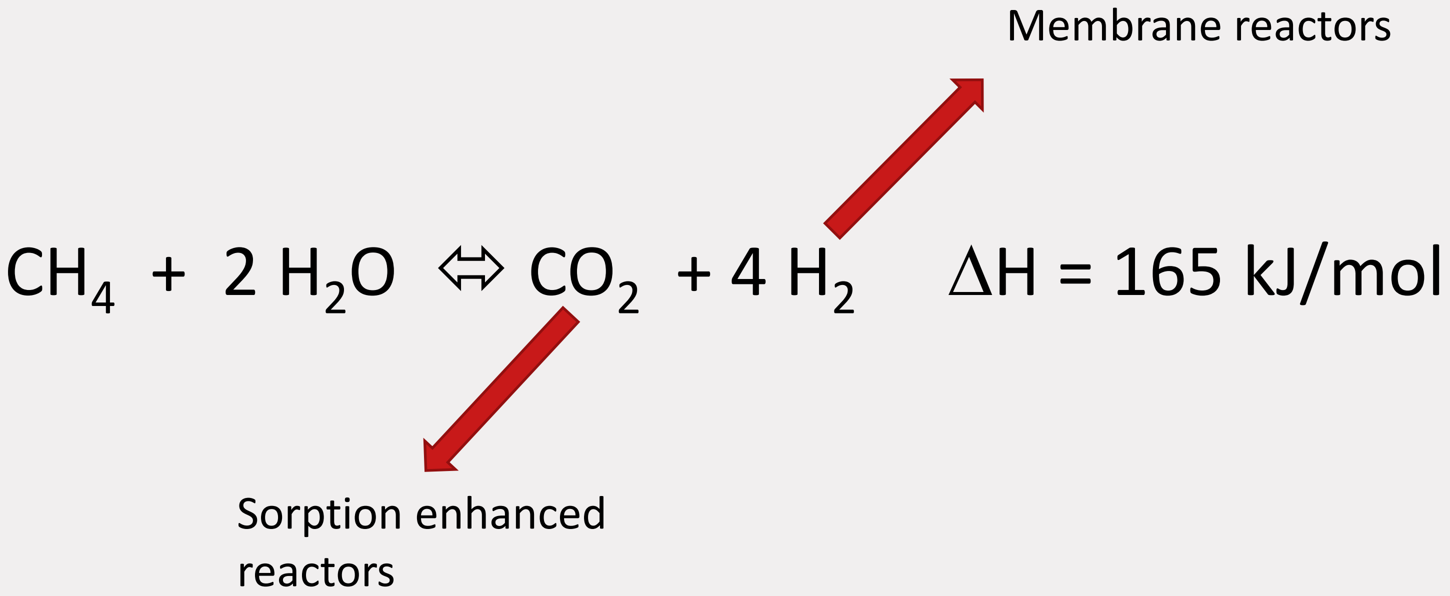
selectivity enhancement by dosing a reactant through the membrane

Examples: Hydrogen

Hydrogen production



Hydrogen production - chemistry

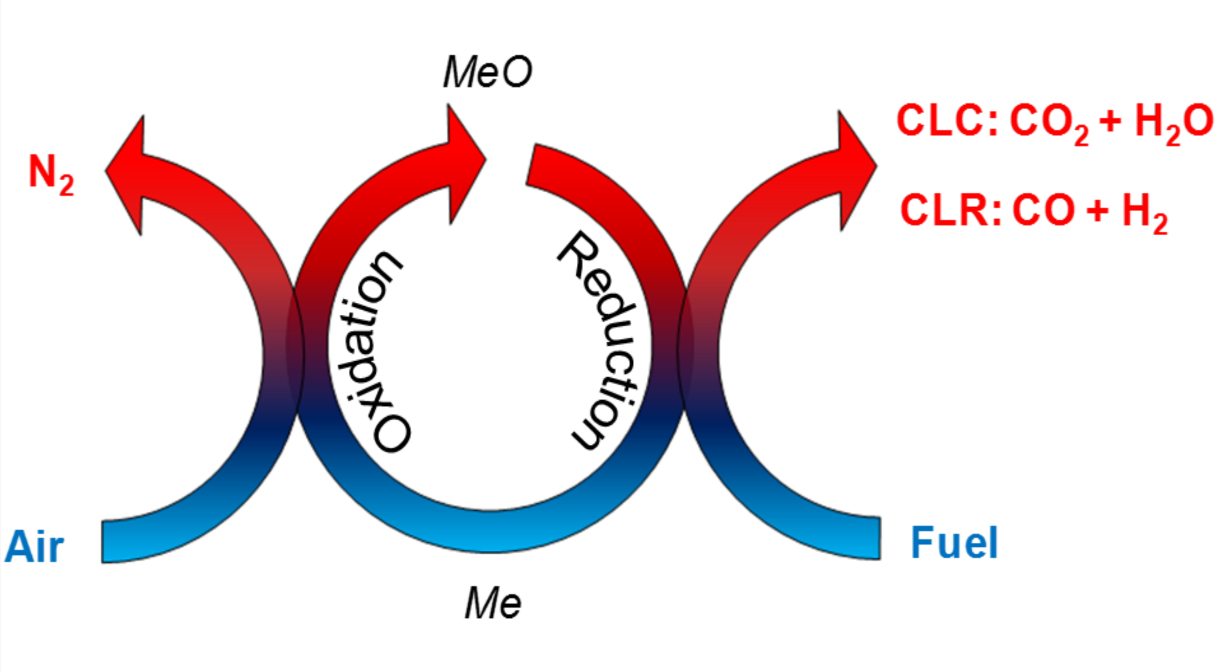


Membrane reactors

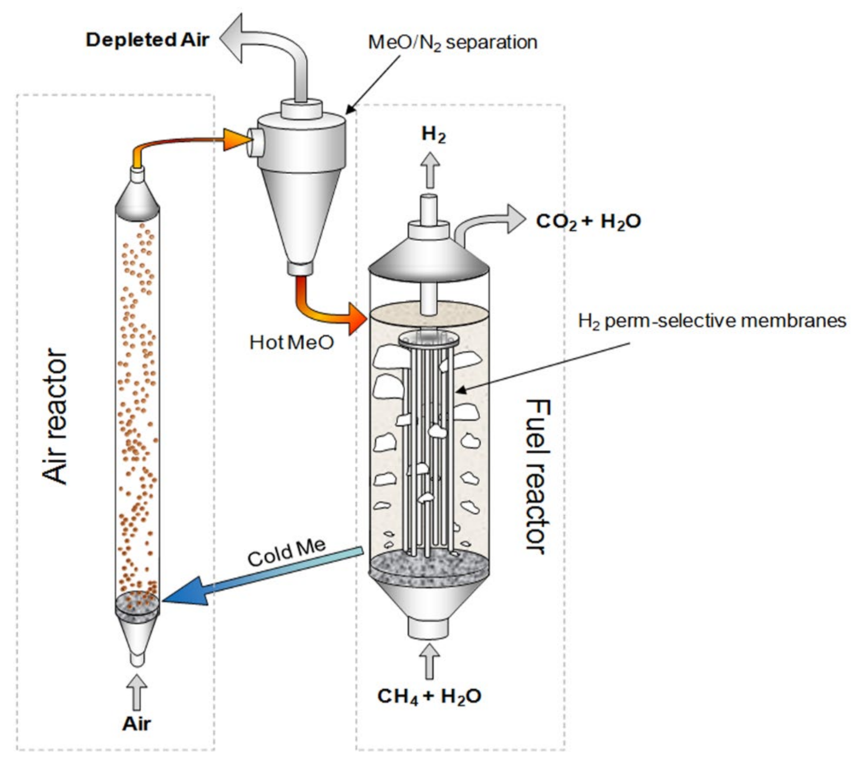
$$CH_4 + 2\,H_2O \Leftrightarrow CO_2 + 4\,H_2 \qquad \Delta H = 165\ \text{kJ/mol}$$

Sorption enhanced reactors

Interesting technologies to improve reforming with CO_2 capture



Integrate Membranes and CLC



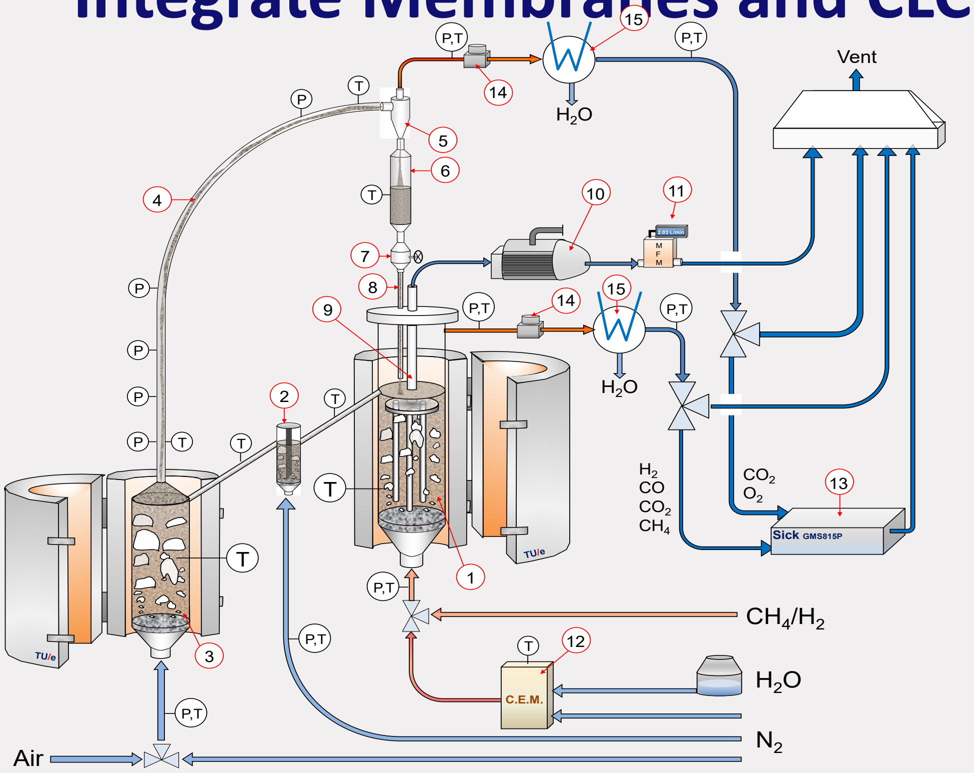
Netherlands Organisation for Scientific Research

VIDI - 12365

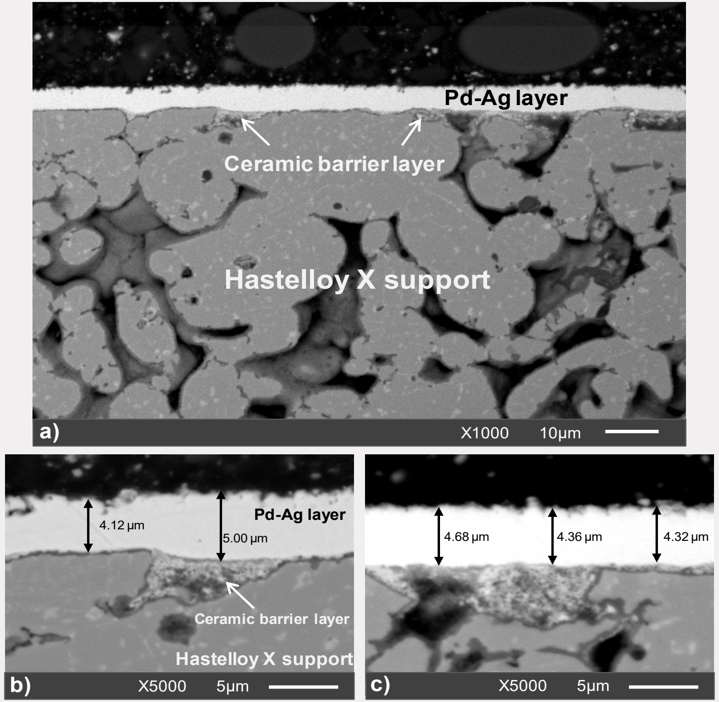
2012 – TRL1

2017 – TRL4/5

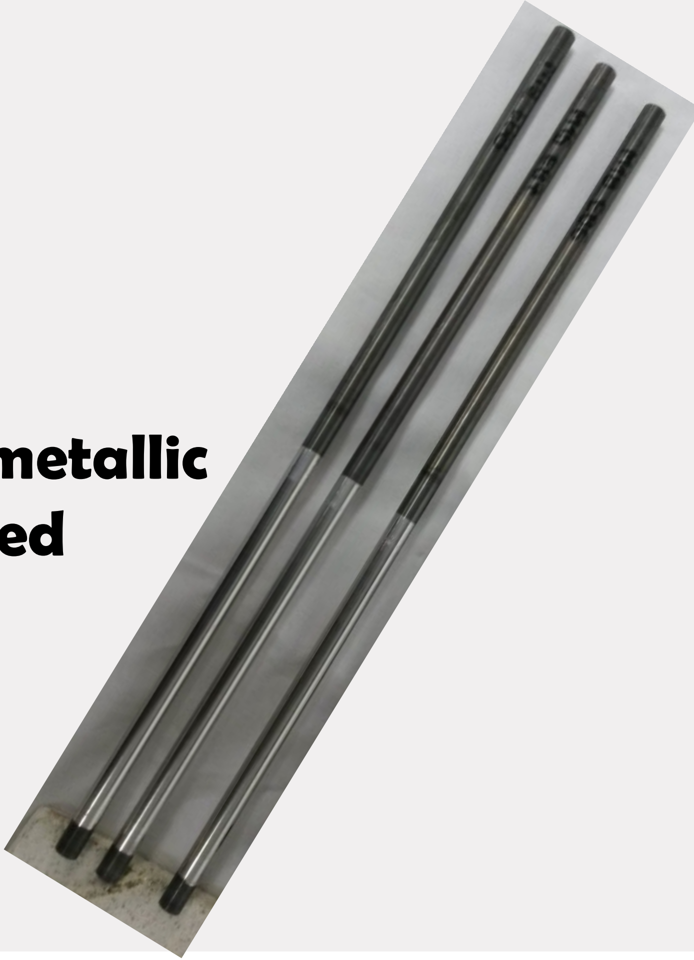
Integrate Membranes and CLC



Integrate Membranes and CLC

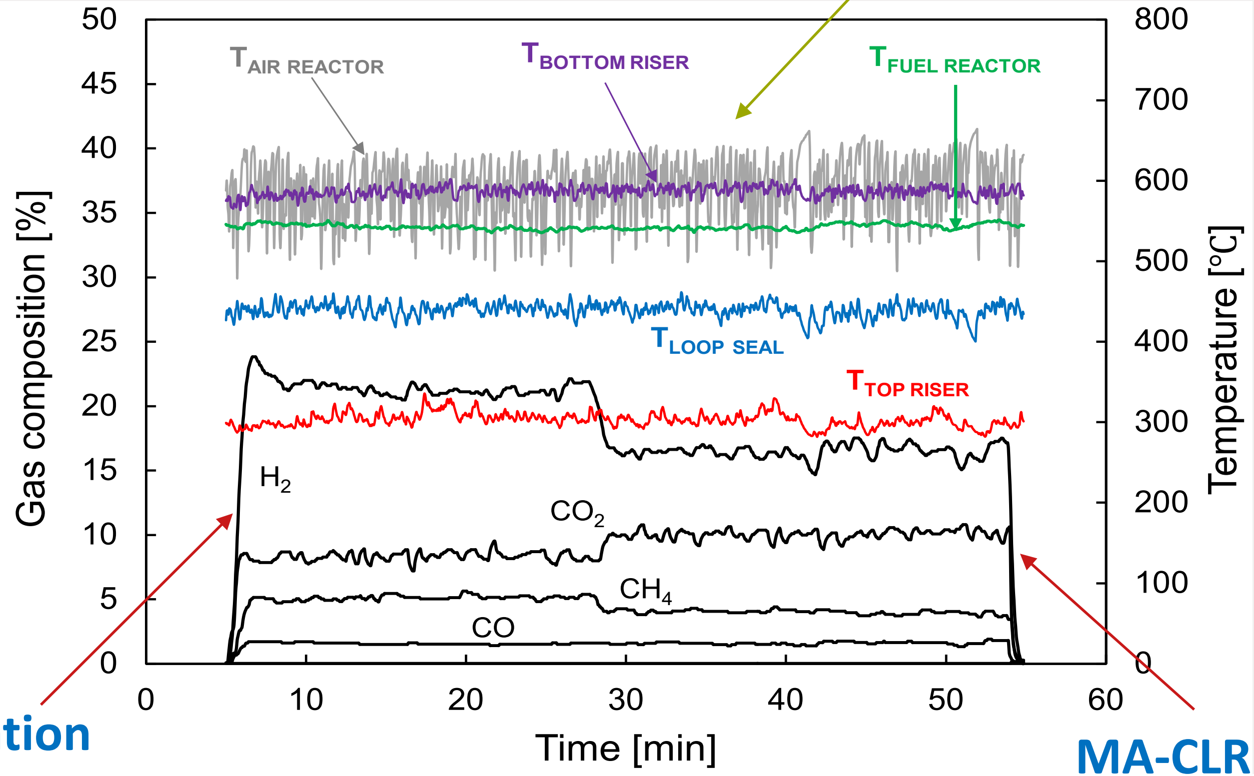


Pd-Ag metallic supported



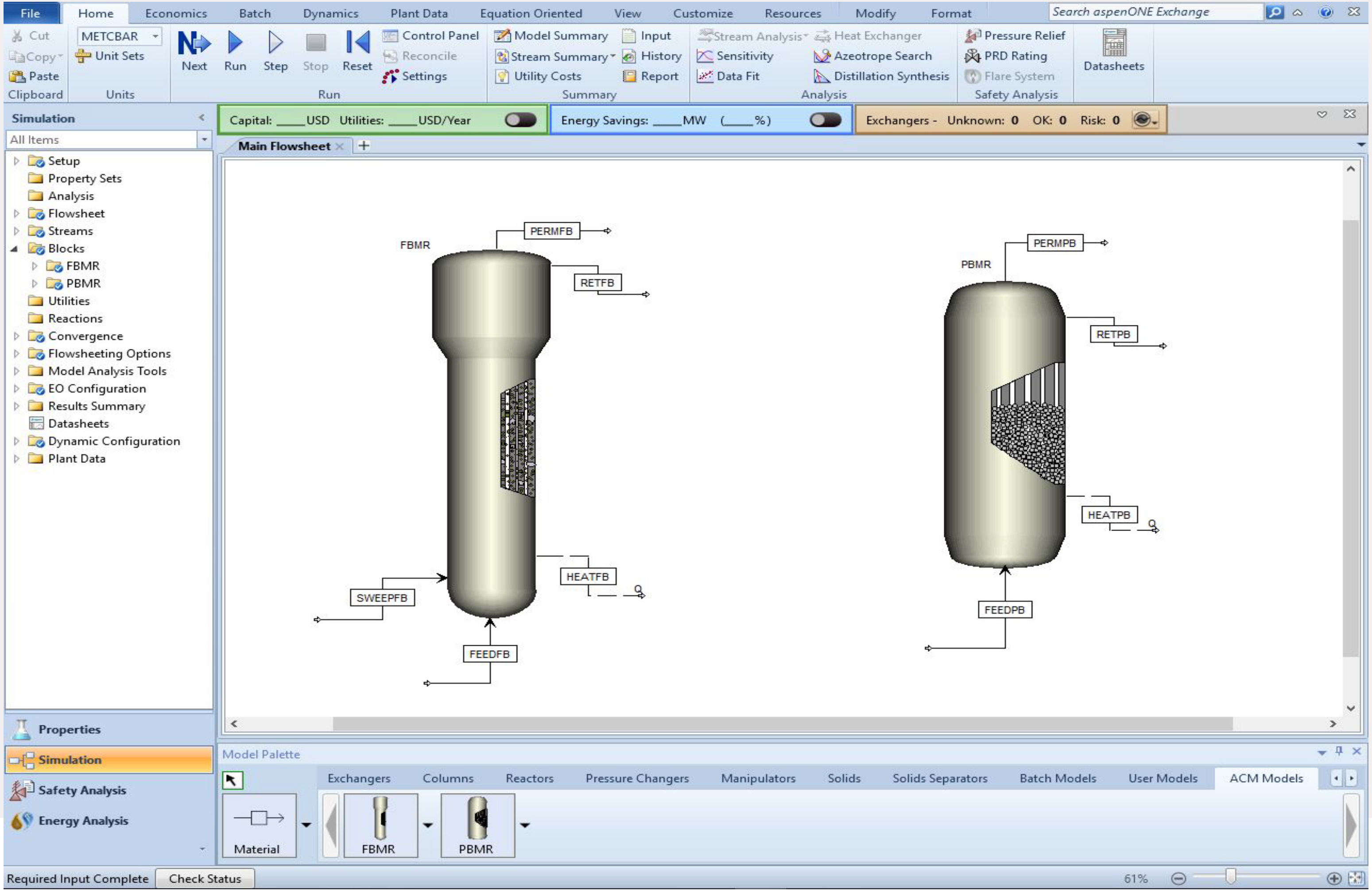
Integrate Membranes and CLC

Oscillations in temperature indicate solids movement



CLR configuration

MA-CLR configuration


File
Home
Economics
Batch
Dynamics
Plant Data
Equation Oriented
View
Customize
Resources
Modify
Format
Search aspenONE Exchange
Cut
Copy
Paste
Clipboard
METCBAR
Unit Sets
Units
Next
Run
Step
Stop
Reset
Control Panel
Reconcile
Settings
Run
Model Summary
Stream Summary
Utility Costs
Input
History
Report
Summary
Stream Analysis
Sensitivity
Data Fit
Heat Exchanger
Azeotrope Search
Distillation Synthesis
Analysis
Pressure Relief
PRD Rating
Flare System
Safety Analysis
Datasheets
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
Properties
Simulation
Safety Analysis
Energy Analysis
Capital: ____USD Utilities: ____USD/Year
Energy Savings: ____MW (____%)
Exchangers - Unknown: 0 OK: 0 Risk: 0
Main Flowsheet
FBMR
PERMFB
RETFB
HEATFB
SWEEPFB
FEEDFB
PBMR
PERMPB
RETPB
HEATPB
FEEDPB
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
61%

MODELTA

MODELLING SOLUTIONS FOR MEMBRANE TECHNOLOGY

an official spin-off

TU/e EINDHOVEN UNIVERSITY OF TECHNOLOGY

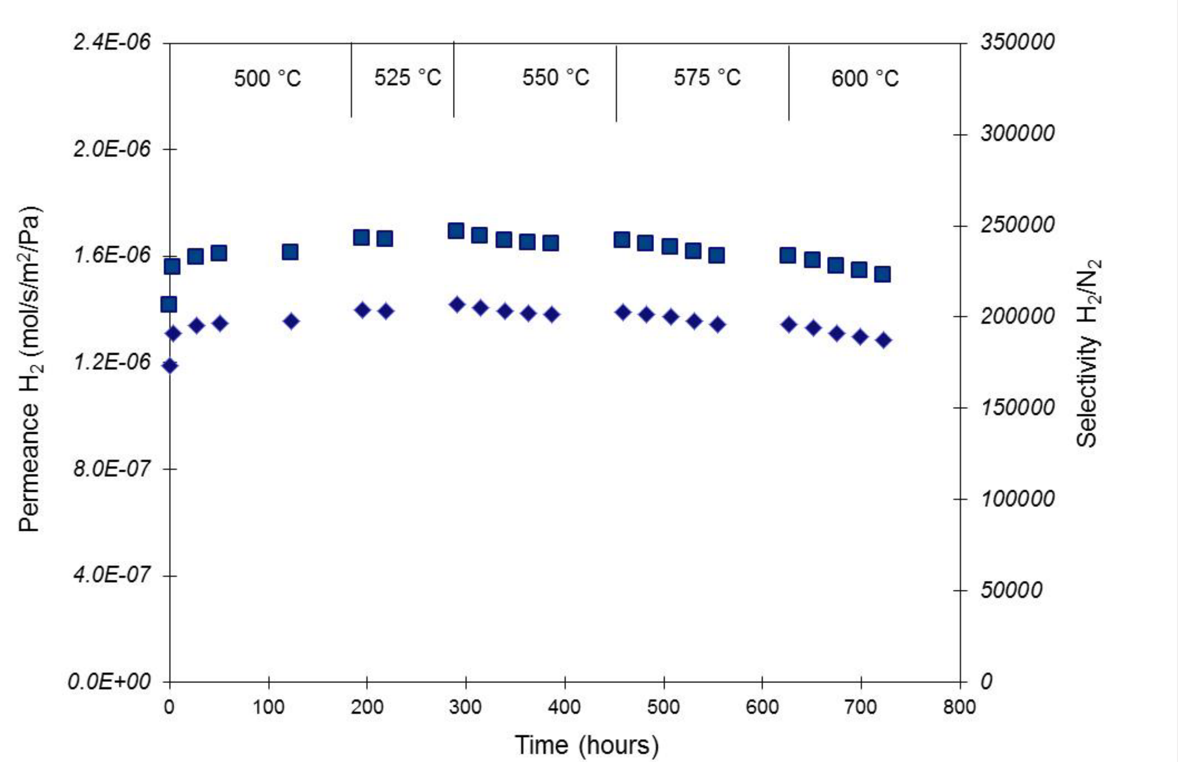
MACBETH
Membranes And Catalysts Beyond Economic and Technological Hurdles

spin off®
POLITECNICO DI MILANO

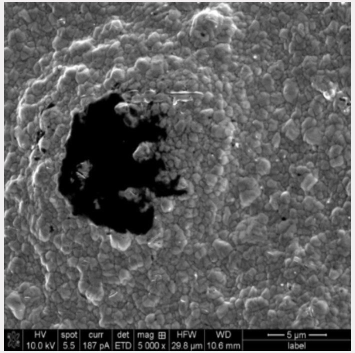
Is MA-CLR really interesting?

	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

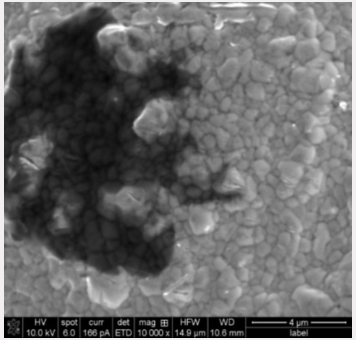
Challenges



Permeance H_2 (mol/s/m^2/Pa)
2.4E-06
2.0E-06
1.6E-06
1.2E-06
8.0E-07
4.0E-07
0.0E+00
500 °C
525 °C
550 °C
575 °C
600 °C
350000
300000
250000
200000
150000
100000
50000
0
Selectivity H_2/N_2
0
100
200
300
400
500
600
700
800
Time (hours)

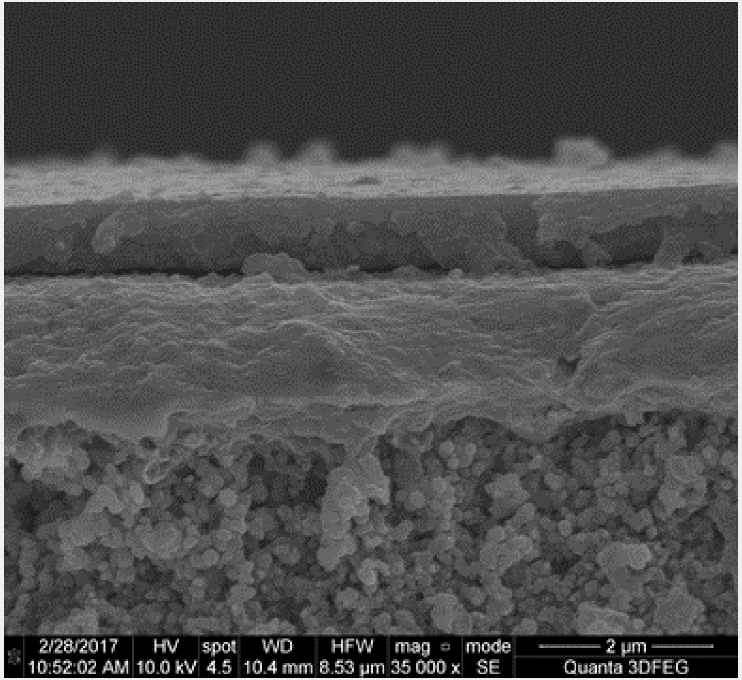


HV 10.0 kV
spot 5.5
curr 187 pA
det ETD
mag 5 000 x
HFW 29.8 µm
WD 10.6 mm
5 µm
label



HV 10.0 kV
spot 6.0
curr 166 pA
det ETD
mag 10 000 x
HFW 14.9 µm
WD 10.6 mm
4 µm
label

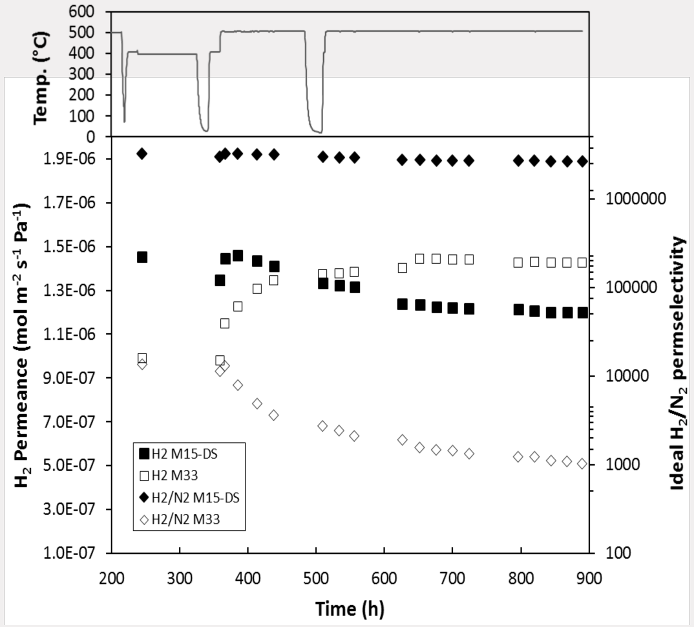
Challenges = Research questions



Protective layer

Selective layer

Asymmetric support

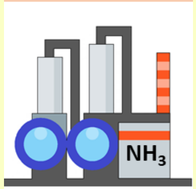


Ammonia as an energy carrier

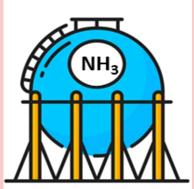
areNH$_3$a
Advanced materials and Reactors for Energy storage tHrough Ammonia

RENEWABLE ENERGY GENERATION

GREEN AMMONIA SYNTHESIS



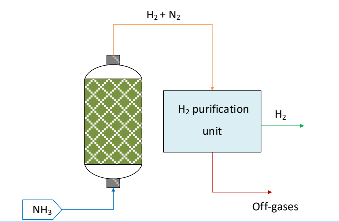
GREEN AMMONIA STORAGE



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



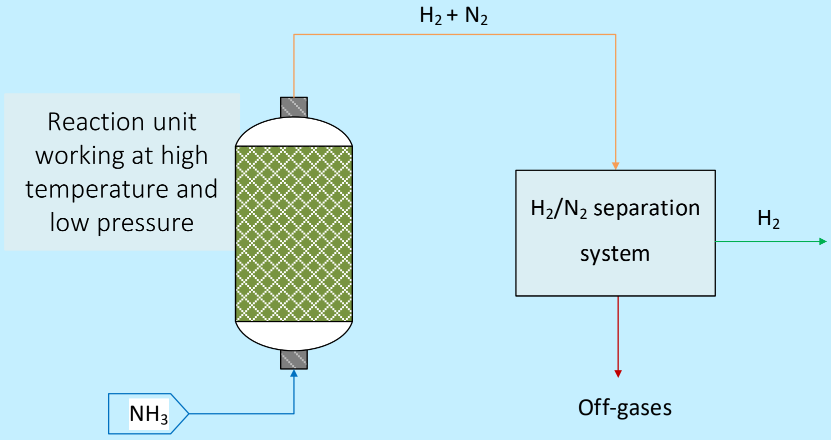
H_2 production from NH_3 decomposition

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

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

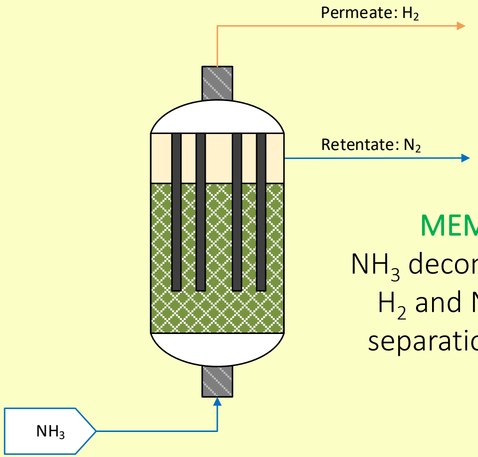
NH_3 decomposition is favored at
low pressure and high temperature

Conventional system



Reaction unit working at high temperature and low pressure

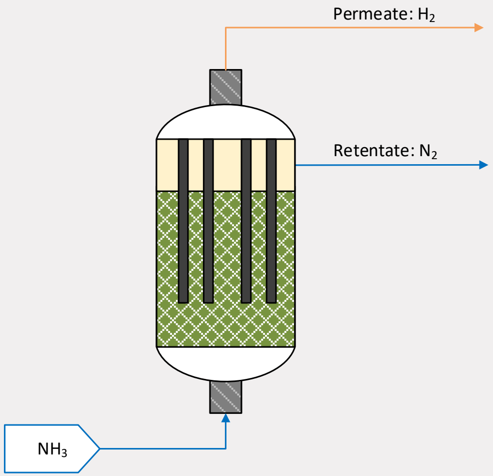
Novel technology



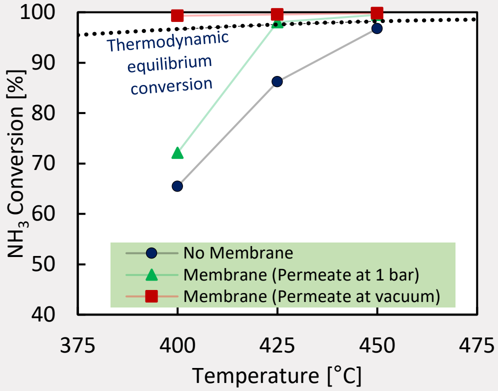
MEMBRANE REACTOR

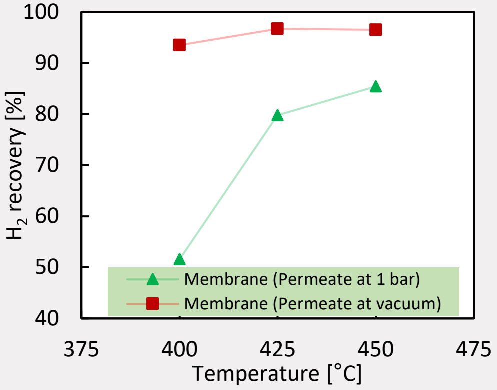
NH_3 decomposition reaction into H_2 and N_2 and high-purity H_2 separation are simultaneously performed

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



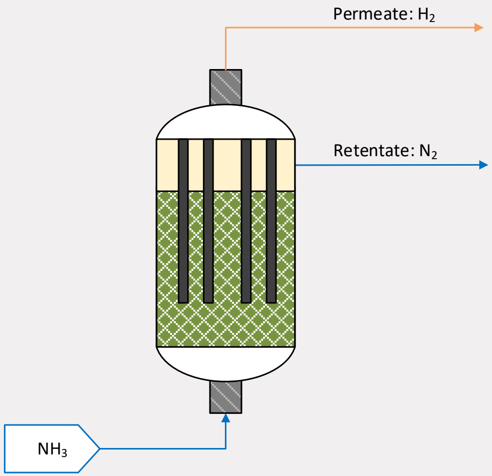


Compared to conventional systems, in a membrane reactor:

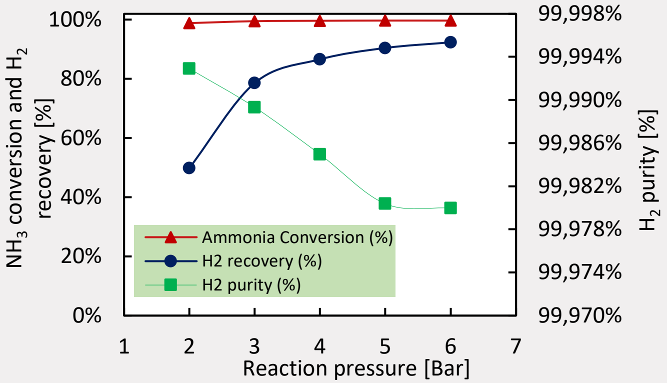
- ☐ Higher NH_3 conversion can be achieved at lower temperature (higher efficiencies)
- ☐ High-purity H_2 is recovered
- ☐ the footprint of the technology is reduced

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

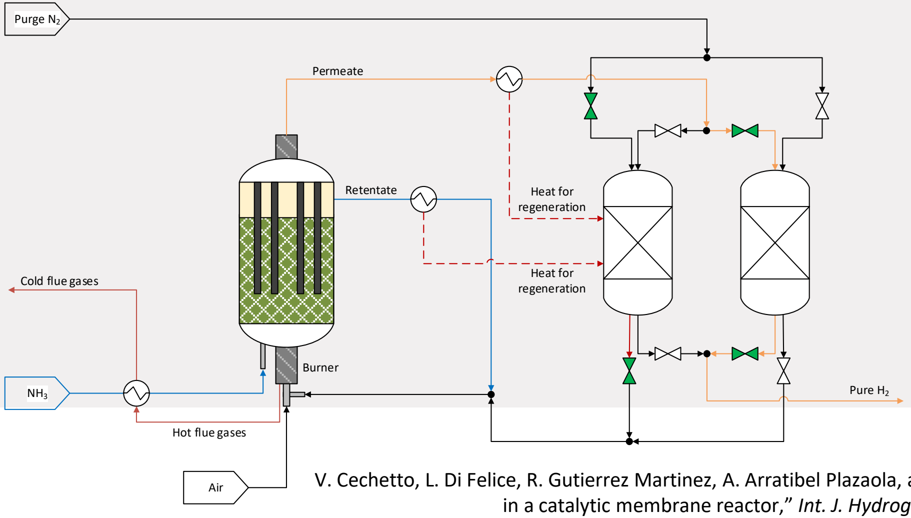
Strategy 1: Increase of the membran lective layer thickness

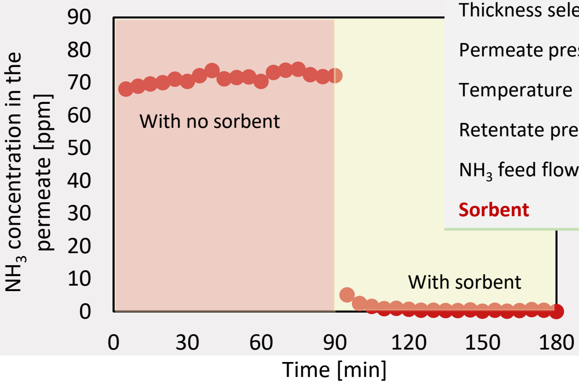
PEMFC specifications requires residual NH_3 concentration in the H_2 feed < 0.1 ppm.

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

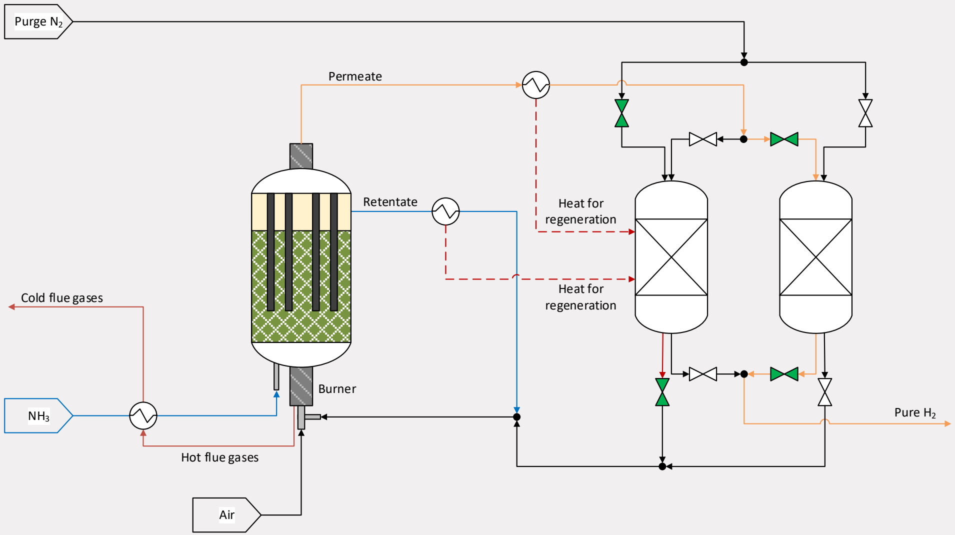




Experimental conditions	
Thickness selective layer [µm]	1
Permeate pressure [bar]	1
Temperature [°C]	450
Retentate pressure [bar]	3
NH_3 feed flow rate [L_N/min]	0.5
Sorbent	**Zeolite 13X**

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.

Hydrogen purification from ammonia



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

↓ Thickness

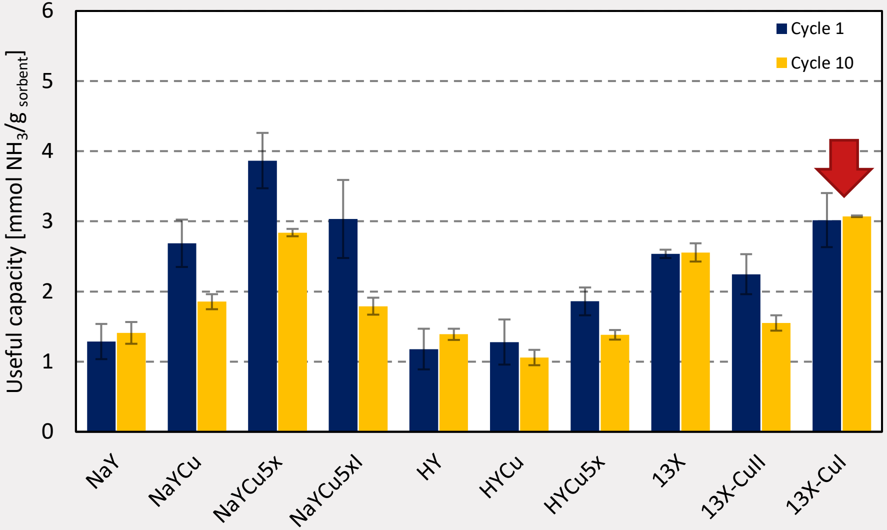
↑ Permeation
↓ Selectivity

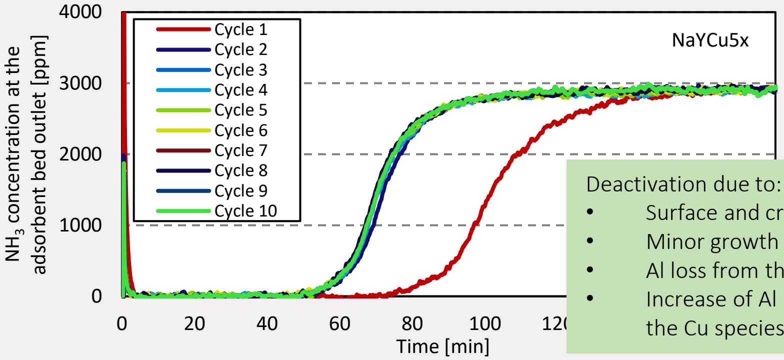
↓ Pd for membrane fabrication
↓ Number of membranes

☐ 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.

Adsorbent materials for hydrogen cleanup

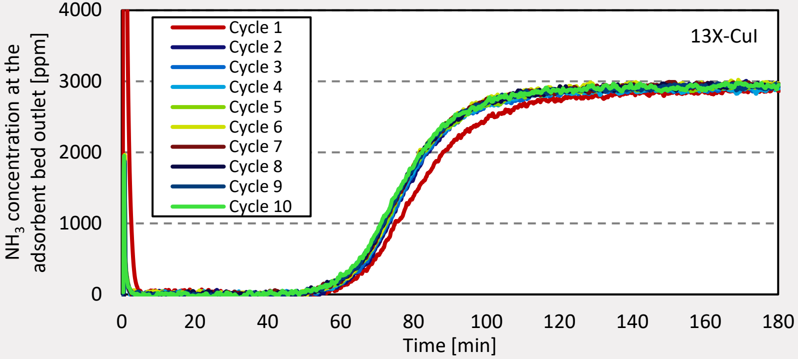
Experimental conditions	
Conditions for saturation:	NH_3/He mixture containing 3000 ppm of NH_3
Conditions for regeneration:	623 K in He





Deactivation due to:

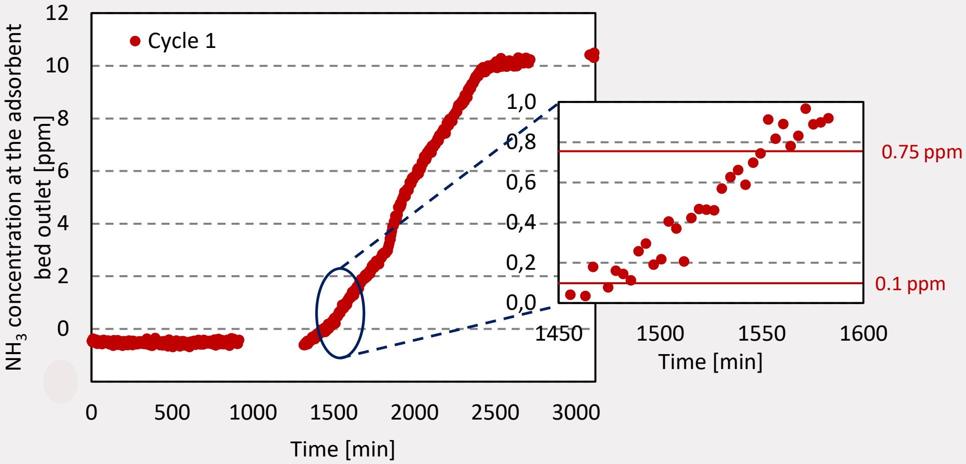
- Surface and crystallinity loss
- Minor growth of Cu particles
- Al loss from the framework
- Increase of Al in proximity of the Cu species

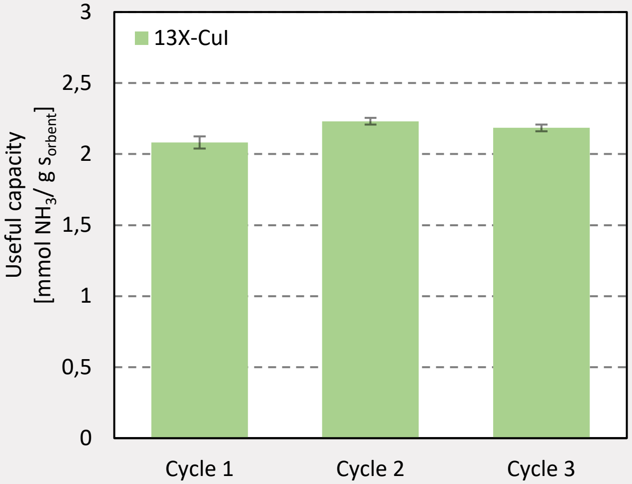


V. Cechetto, C. L. Struijk, L. Di Felice, A. W. N. de Leeuw den Bouter, and F. Gallucci, “Adsorbents development for hydrogen cleanup from ammonia decomposition in a catalytic membrane reactor,” *Chem. Eng. J.*, p. 140762, 2022, doi: https://doi.org/10.1016/j.cej.2022.140762.

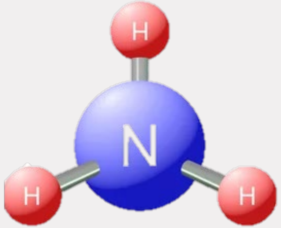
Adsorbent materials for hydrogen cleanup

Experimental conditions	
Sorbent:	13X-CuI
Conditions for saturation:	NH_3/H_2 mixture containing 10.0 ppm (cycle 1) and 86.5 ppm (cycle 2 and 3) of NH_3
Conditions for regeneration:	623 K in N_2





Introduction



NH_3 is a carbon-free and dispatchable energy carrier allowing to store large quantities of renewable electricity

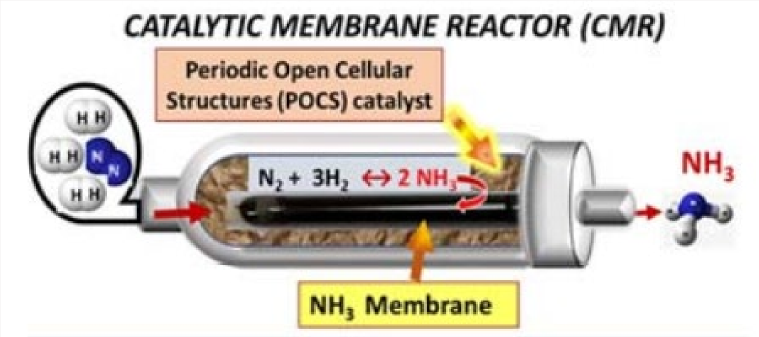
$$\frac{1}{2}N_2 + \frac{3}{2}H_2 \leftrightarrow NH_3$$

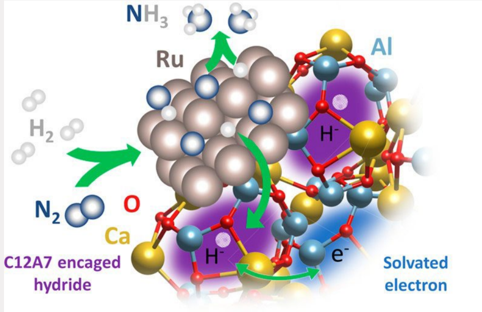
- ΔH_{298K} =-45.7kJ/mol
- T=400-500 °C P=100-200 bar
- Fe-based or Ru-based catalyst
- Rate limiting step: activation of the stable N≡N bond

REACTOR REQUIREMENTS →

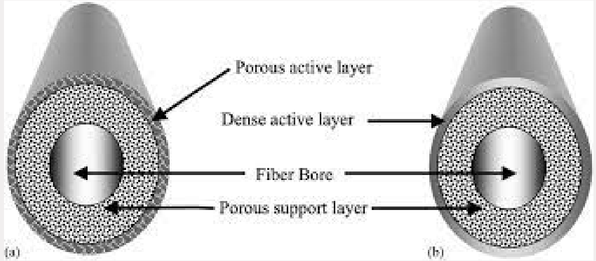
- High inlet temperature to achieve high reaction rate
- Low outlet temperature to achieve a high equilibrium conversion
- High pressure to shift the equilibrium towards the products

Objective of the project





POCS catalyst with a lower activation energy barrier, allowing to reduce the operational Temperature



Carbon molecular sieving membrane which separates NH_3, shifting the equilibrium, allowing to reduce the operational Pressure

Validation of the membrane

- ➢ Experimental results from permeation tests on CMSM
  - ➢ Single gas permeation test
  - ➢ T = 300 °C
  - ➢ P= 1-6 bar

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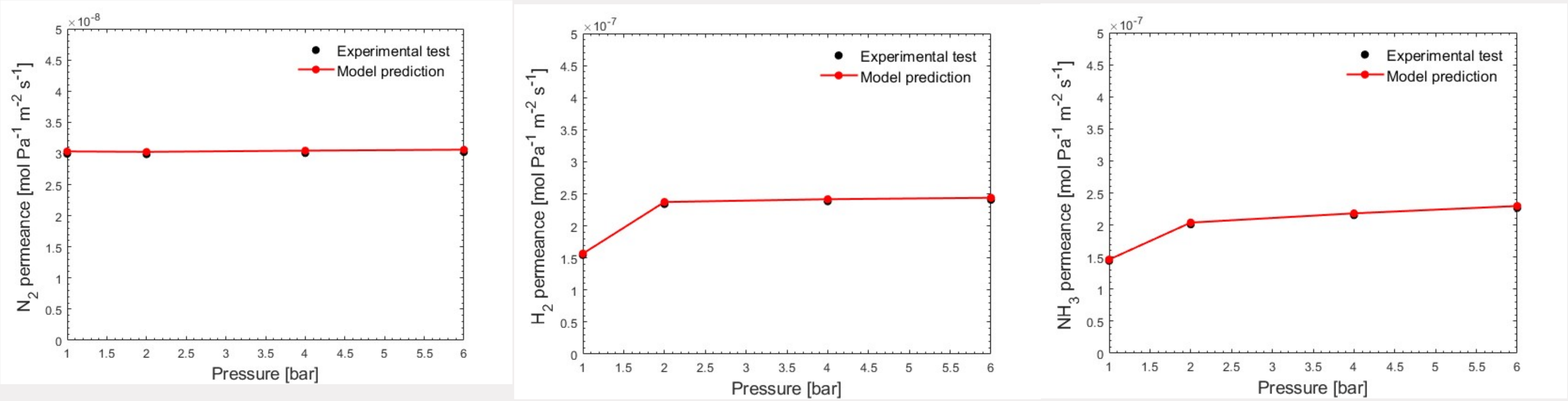


Optimization of membrane properties

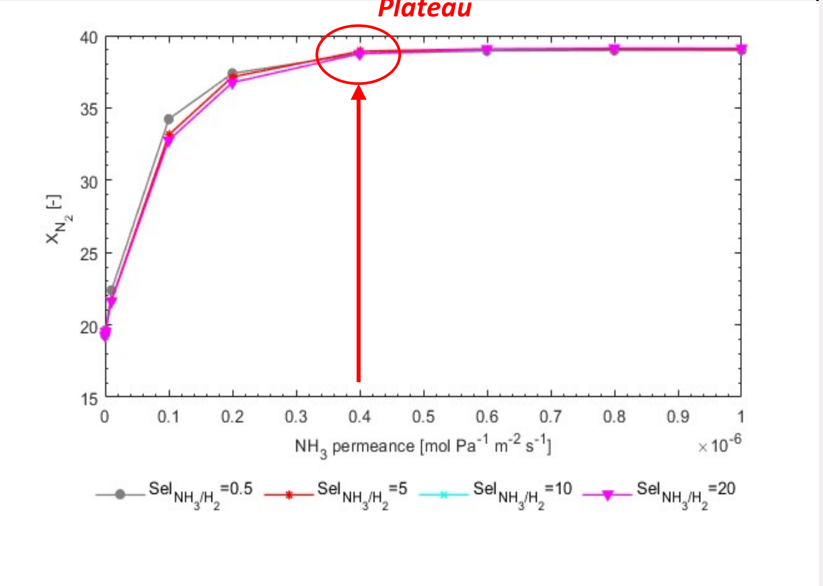
- Ideal membrane study →

P_{NH_3} =[0 - 10^{-6}]

S_{NH_3/H_2}=[0 - 20]

S_{NH_3/N_2}=∞

Plateau

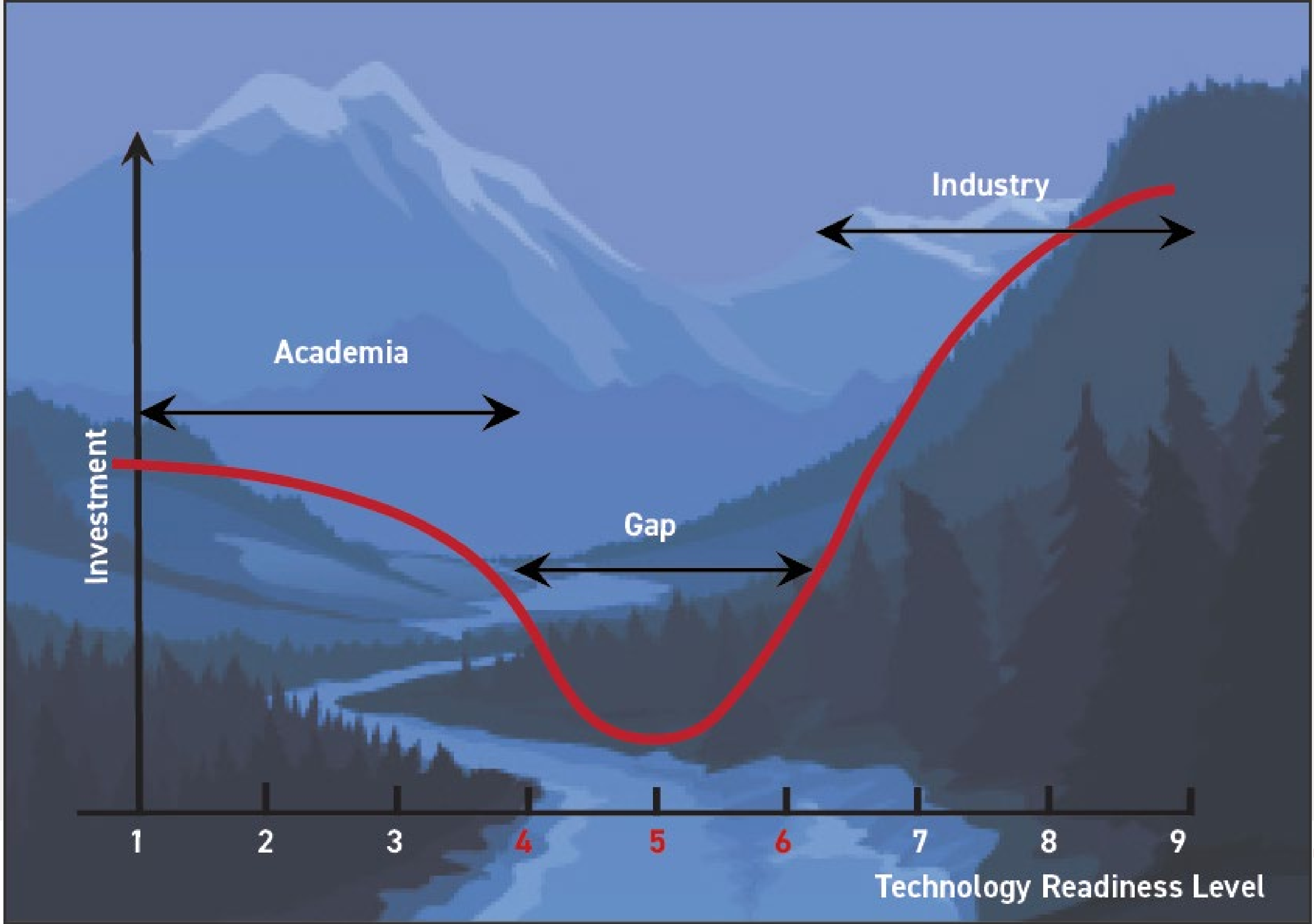


Equation:

$$X_{N2} = \frac{F_{N2^0}^{ret} - F_{N2}^{ret} - F_{N2}^{passing\ the\ membrane}}{F_{N2^0}^{ret} - F_{N2}^{back\ perm}}$$

$F_{N2}^{passing\ the\ membrane}$=*nitrogen loss passing from retentate to permeate*

$F_{N2}^{back\ perm}$=*nitrogen loss in the sweep gas, moving to the retentate*


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

Scale-up steps

SINGLE
MEMBRANE
TUBE
10CM LONG

2010

MULTI TUBE
MEMBRANE
15CM LONG

2012

MULTI TUBE
MEMBRANE
15CM LONG
Fluid bed
<10 ppm CO

2014

MEMBRANE
25CM LONG
Fluid bed
ethanol

2016

MEMBRANE
50CM LONG
Fluid bed
>65% recovery
Biogas reforming
>99.8% purity

Design and
construction
2m^3/h prototype

2018

Design and
construction
20m^3/h prototype

2019

11 EU projects
Several Spanish
and Dutch projects

Scale-up steps

H2 SITE
Membrane reactors for H2 generation

Running EU projects related to membranes and MRs

MEMBER

C2FUEL

Bio Co Mem

GiCO$_2$

Gasification Integrated with CO2 capture and conversion

BiZeolCat

INNOMEM

MACBETH

Membranes And Catalysts Beyond Economic and Technological Hurdles

MEASURED

BIKE

HIGFLY

areNH$_3$a

AMBH$_2$ER

AndreaH


TE KOOP
088 030 6325

EINDHOVEN
UNIVERSITY OF
TECHNOLOGY

Inorganic Membranes
& Membrane Reactors

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