
# Intensified reactors for ammonia energy

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Professor Inorganic Membranes and Membrane Reactors

# Outlook

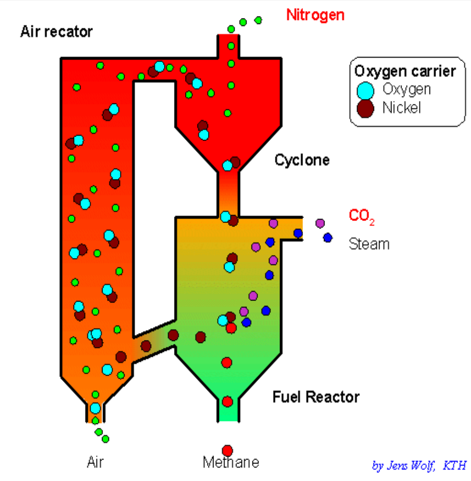
- Who we are
- Why integrated reactors
- Hydrogen
- PDH
- Next steps

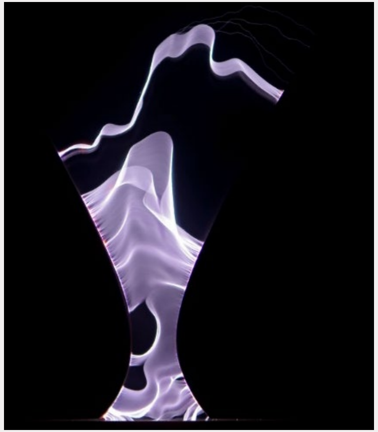
# Research themes - SIR

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

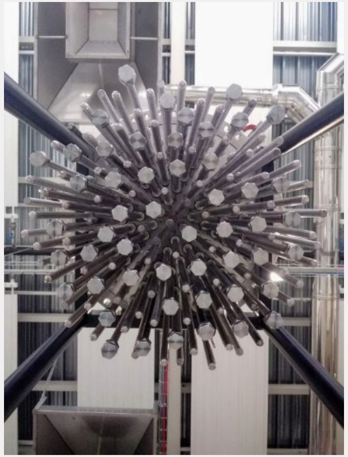
# Research themes - SIR

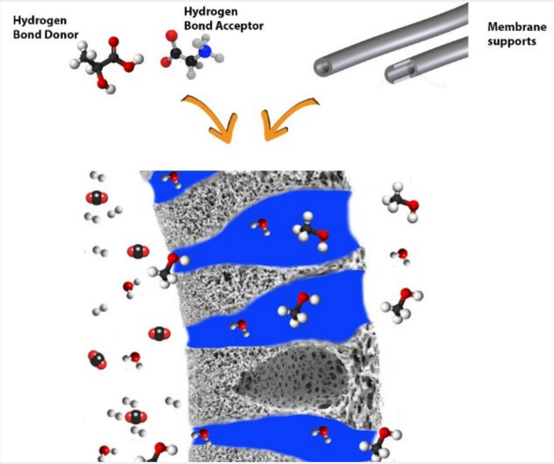
## Integration reaction + separation

*Packed bed and fluidized bed membrane reactors*

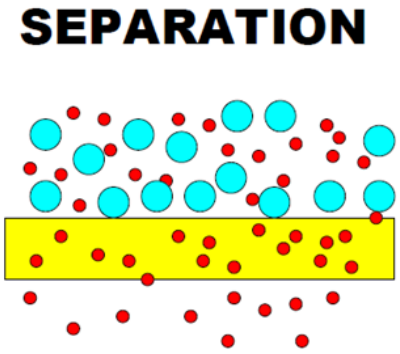
($H_2$, syngas, oxidative dehydrogenations, partial oxidations)

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





# Membrane functions

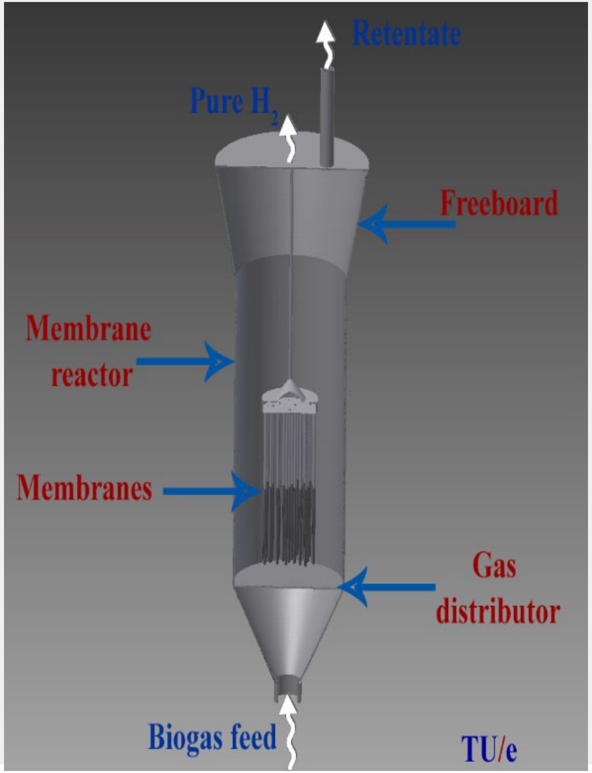


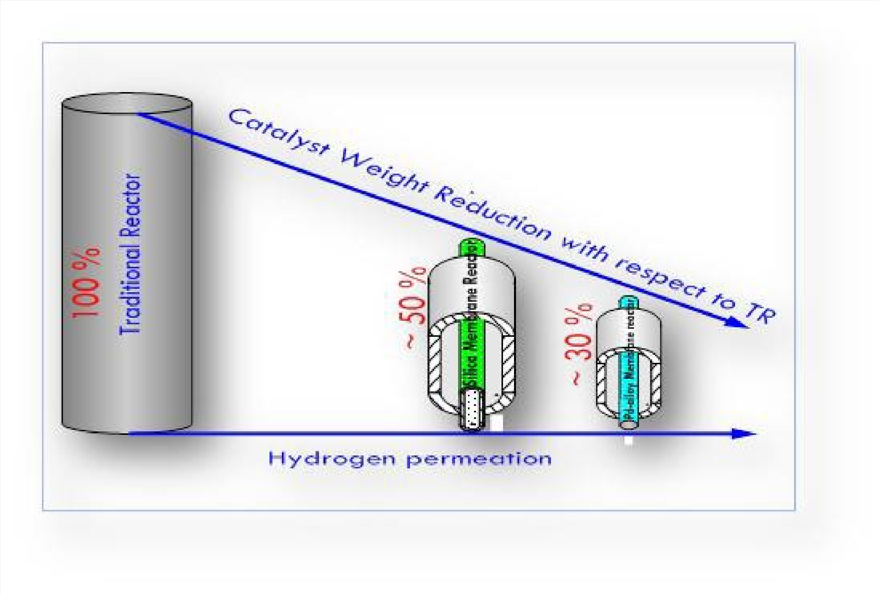
# Classification

**Membrane Reactors**

- Catalyst Configuration
  - Fixed Bed
  - Fluidized bed
  - Catalytic membrane
- Membrane material
  - Organic
  - Inorganic
- Transport function
  - Extractor
  - Distributor
  - Contactor

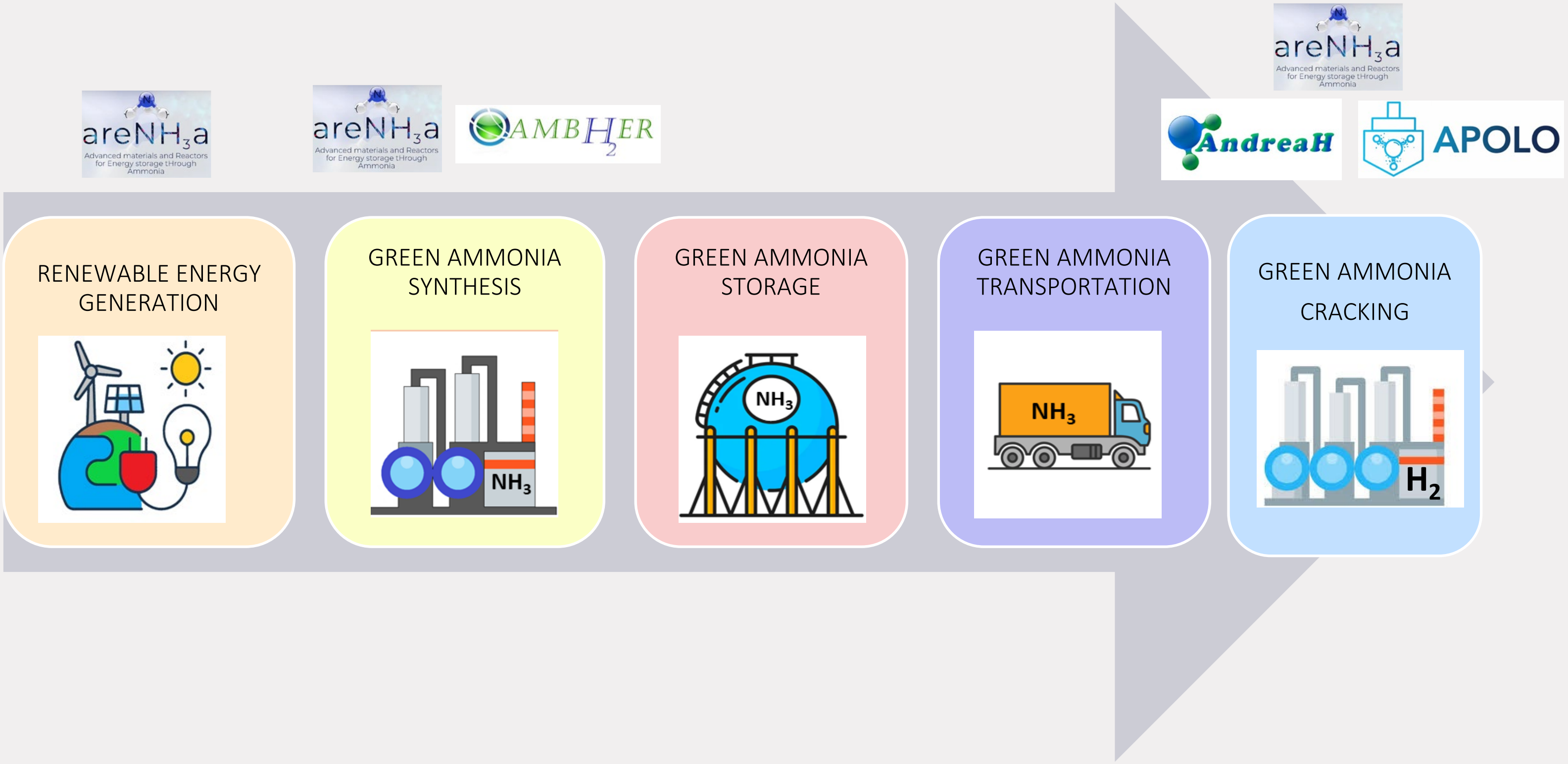
# A membrane reactor




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

# Ammonia as an energy carrier



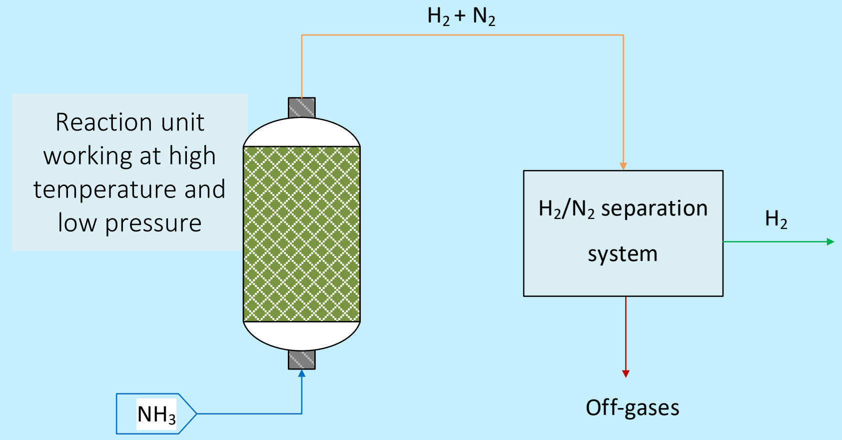
# $H_2$ production from $NH_3$ decomposition

$$NH_3 \leftrightarrow 0.5\ N_2 + 1.5\ H_2$$

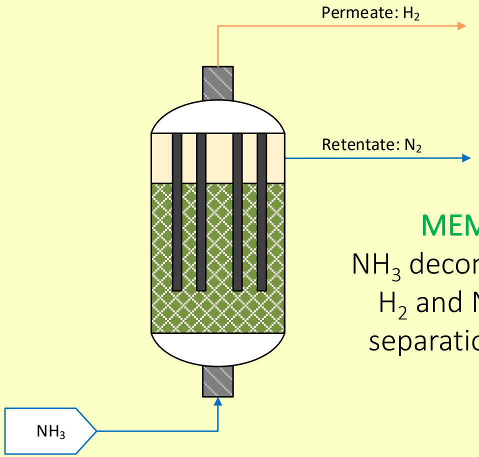
$$\Delta H_f^o = 45.9\ ^{kJ}/_{mol}$$

$NH_3$ decomposition is favored at low pressure and high temperature

## Conventional system



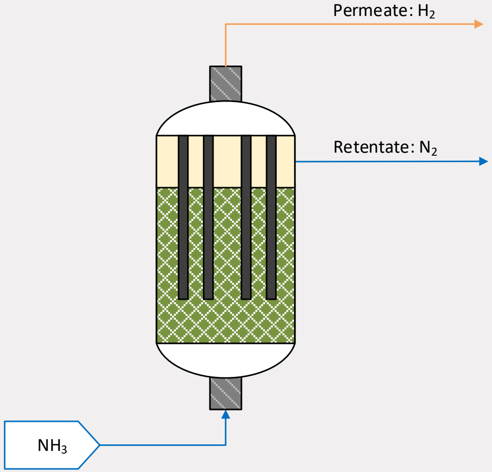

## Novel technology

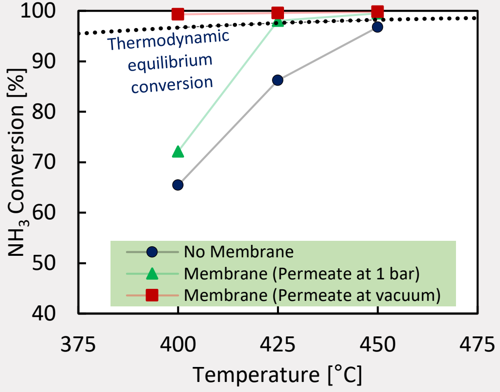


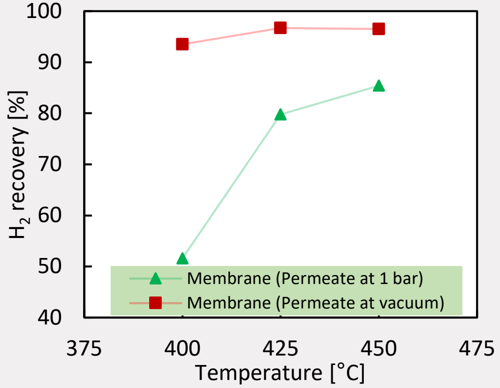

**MEMBRANE REACTOR**

$NH_3$ 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 |

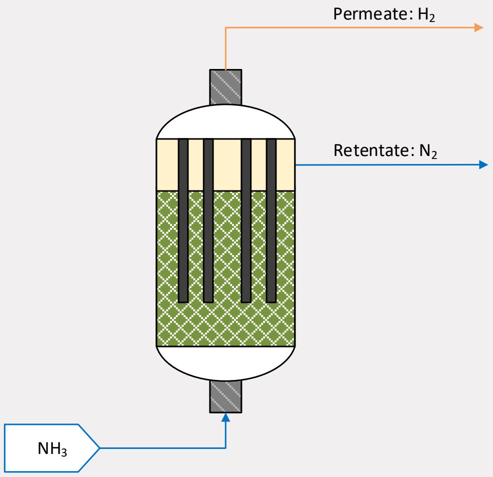
Compared to conventional systems, in a membrane reactor:

- ❑ 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

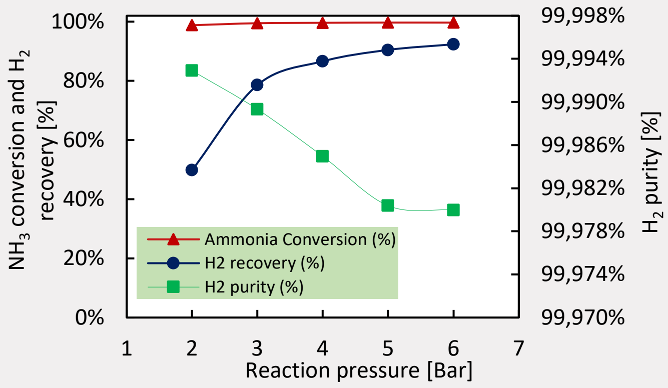


V. Cechetto, L. Di Felice, J. A. Medrano, C. Makhloufi, J. Zuniga, and F. Gallucci, "$H_2$ production via ammonia decomposition in a catalytic membrane reactor," *Fuel Process. Technol.*, vol. 216, p. 106772, 2021, doi: https://doi.org/10.1016/j.fuproc.2021.106772.

# $H_2$ 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

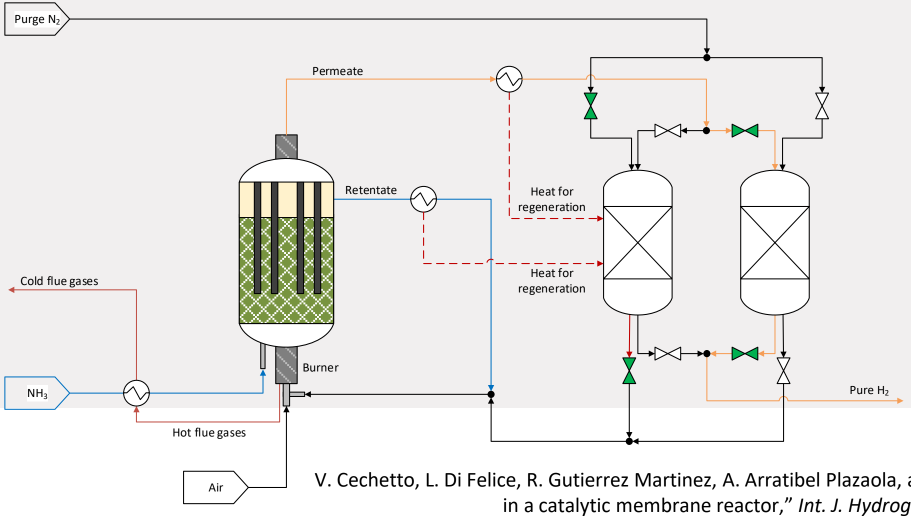
## Strategy 1: Increase of the membrane selective layer thickness

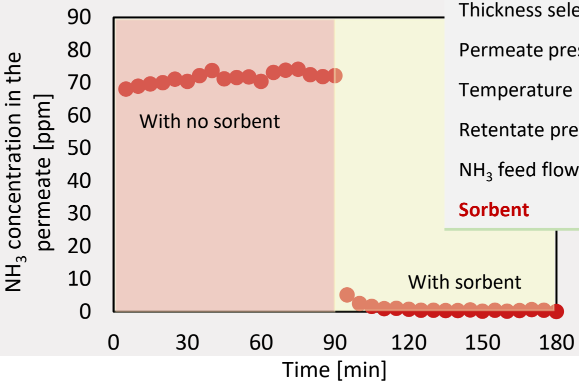
PEMFC specifications requires residual $NH_3$ concentration in the $H_2$ feed < 0.1 ppm.

| 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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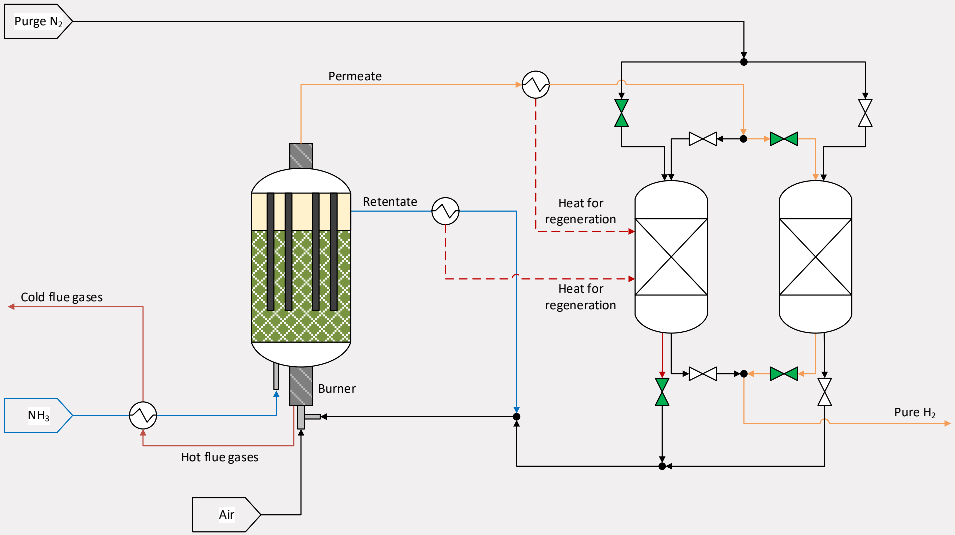
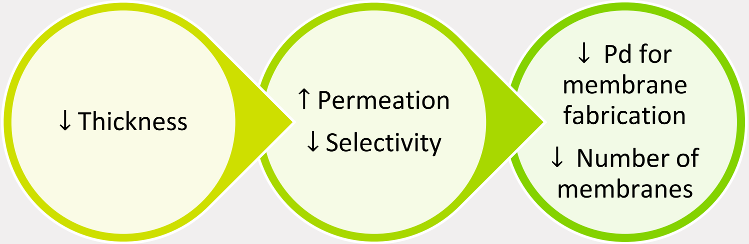
# Hydrogen purification from ammonia



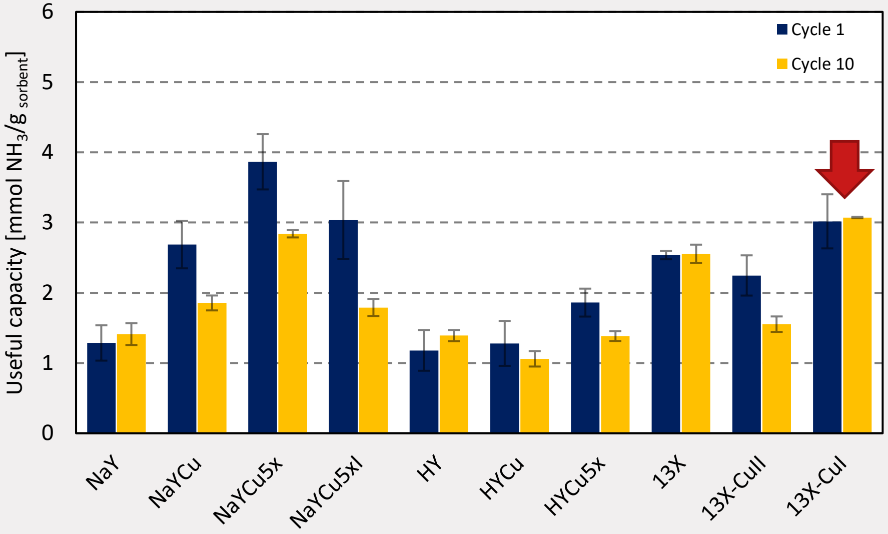

- Thinner membranes can be used with a consequent decrease of investment costs:

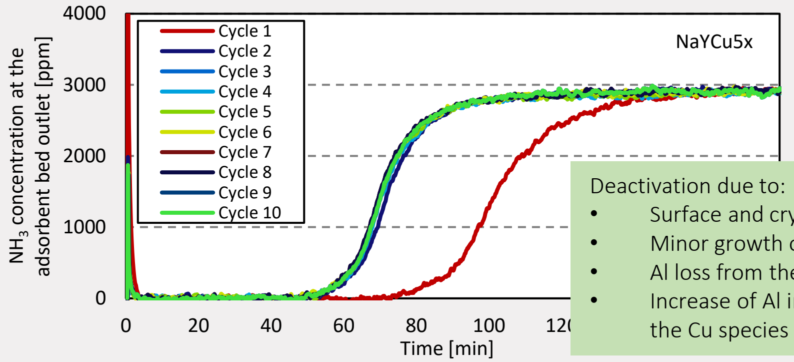



- The introduction of a hydrogen purification stage downstream the membrane reactor allows to operate the reactor at lower temperatures and to accept higher $NH_3$ concentration at the reactor outlet with benefits from an energetic point of view.

# Adsorbent materials for hydrogen cleanup

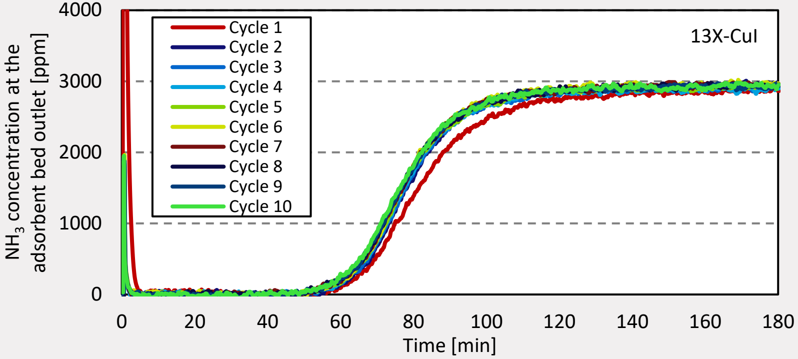
| Experimental conditions | |
|---|---|
| Conditions for saturation: | $NH_3$/He mixture containing 3000 ppm of $NH_3$ |
| Conditions for regeneration: | 623 K in He |




Deactivation due to:

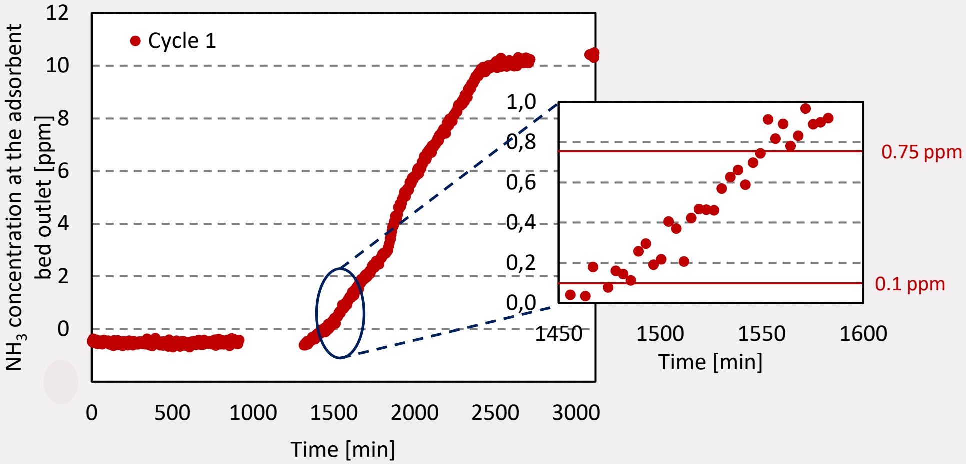
- Surface and crystallinity loss
- Minor growth of Cu particles
- Al loss from the framework
- Increase of Al in proximity of the Cu species

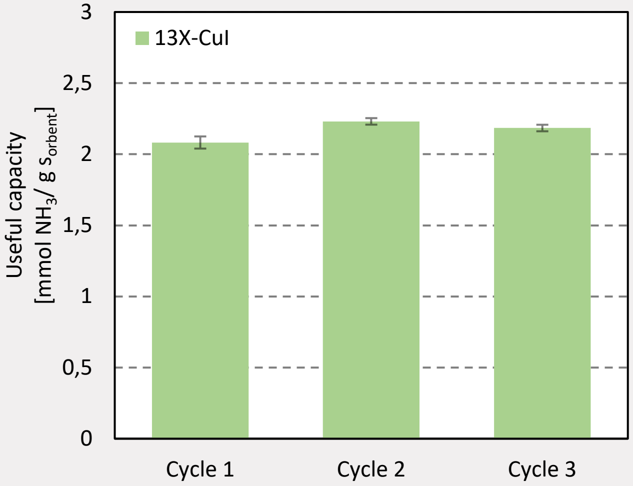



V. Cechetto, C. L. Struijk, L. Di Felice, A. W. N. de Leeuw den Bouter, and F. Gallucci, “Adsorbents development for hydrogen cleanup from ammonia decomposition in a catalytic membrane reactor,” *Chem. Eng. J.*, p. 140762, 2022, doi: https://doi.org/10.1016/j.cej.2022.140762.

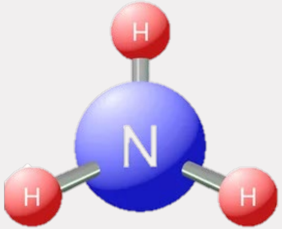
# Adsorbent materials for hydrogen cleanup

| 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*

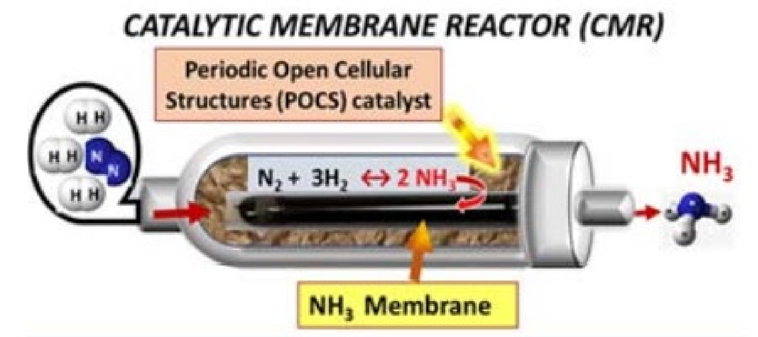
$$\frac{1}{2}N_2 + \frac{3}{2}H_2 \leftrightarrow NH_3$$

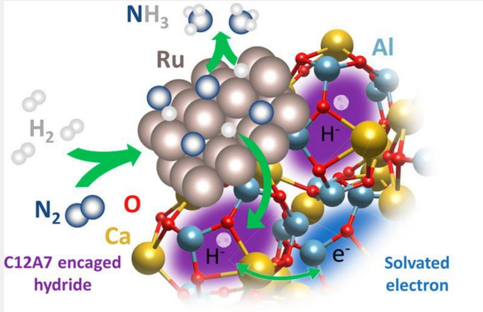
- $\Delta H_{298K}$ =-45.7kJ/mol
- T=400-500 °C  P=100-200 bar
- Fe-based or Ru-based catalyst
- Rate limiting step: activation of the stable N≡N bond

REACTOR REQUIREMENTS →

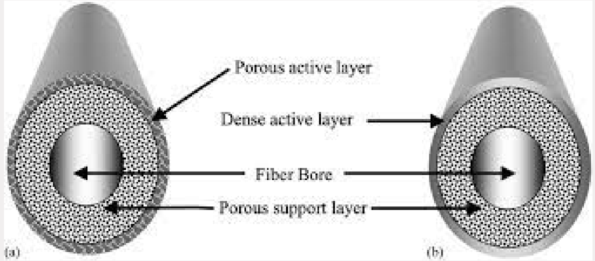
- High inlet temperature to achieve high reaction rate
- Low outlet temperature to achieve a high equilibrium conversion
- High pressure to shift the equilibrium  towards the products

# 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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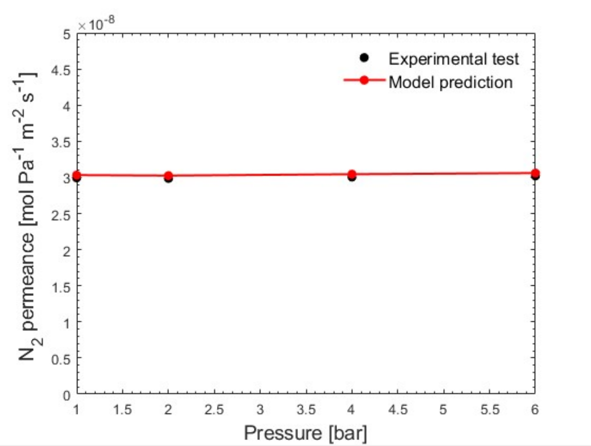
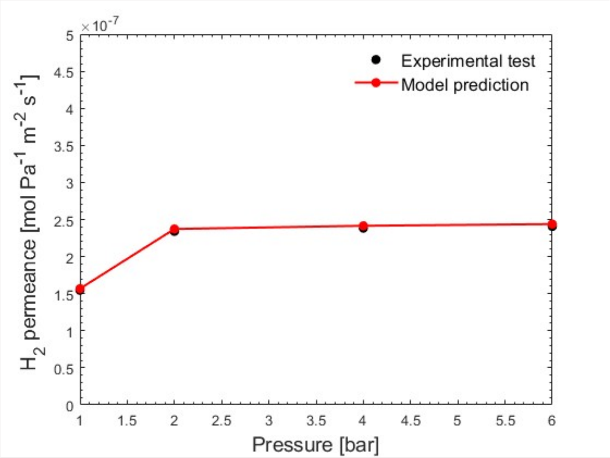
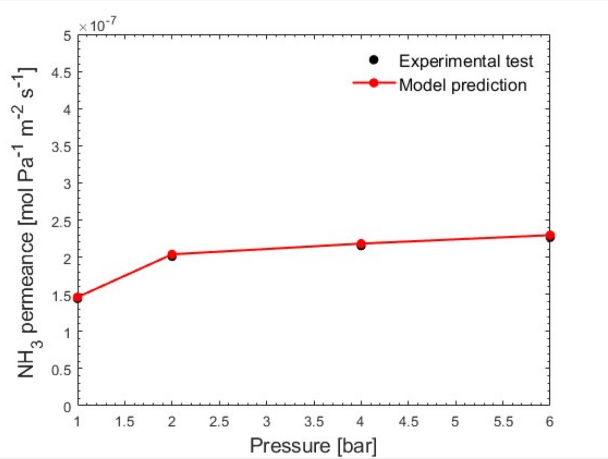
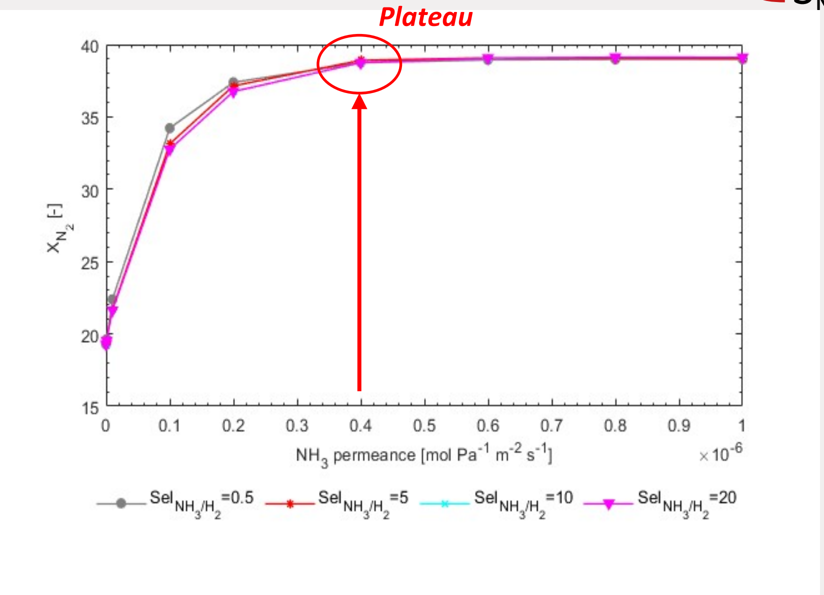


# Optimization of membrane properties

- Ideal membrane study →
  - $P_{NH_3}$ =[0 - $10^{-6}$]
  - $S_{NH_3/H_2}$=[0 - 20]
  - $S_{NH_3/N_2}$=∞




***Equation:***

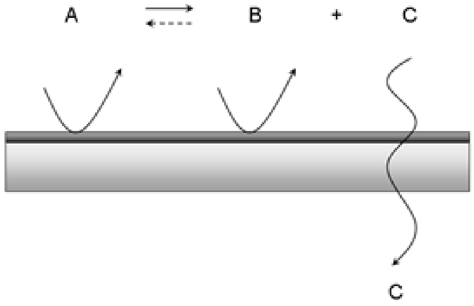
$$X_{N2} = \frac{F_{N2^0}^{ret} - F_{N2}^{ret} - F_{N2}^{passing\ the\ membrane}}{F_{N2^0}^{ret} - F_{N2}^{back\ perm}}$$

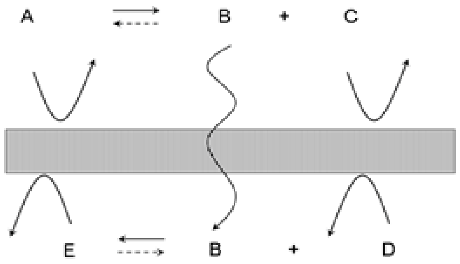
$F_{N2}^{passing\ the\ membrane}$=*nitrogen loss passing from retentate to permeate*

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

# Why a membrane reactor?

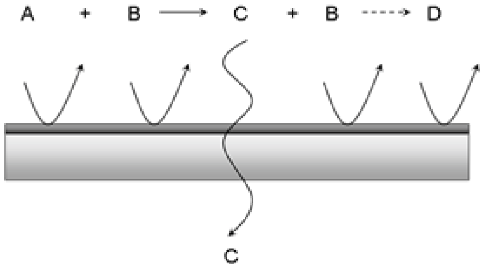
conversion enhancement by selective permeation of a reactant product of an equilibrium limited reaction

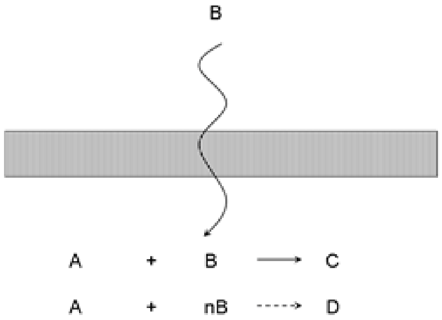


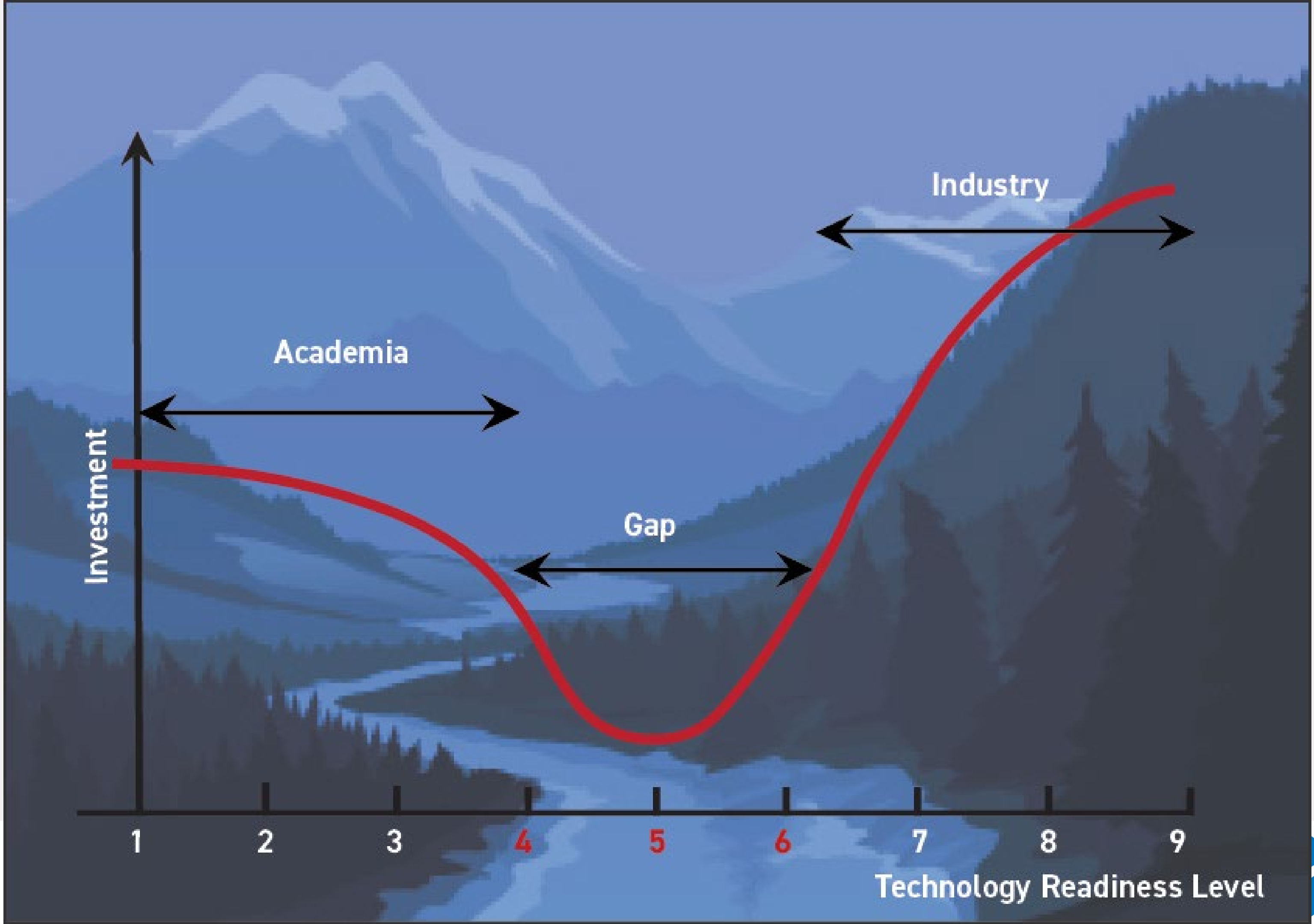

conversion enhancement by coupling of reactions

selectivity enhancement by selective permeation of an intermediate product




selectivity enhancement by dosing a reactant through the membrane


Industry
Academia
Gap
Investment
1
2
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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 $2 m^3/h$ prototype**

2018

**Design and construction $20 m^3/h$ prototype**

2019

**11 EU projects**
**Several Spanish and Dutch projects**



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# Scale-up steps


201

2016

2014

2012

2010

H2 SITE
Membrane reactors for H2 generation



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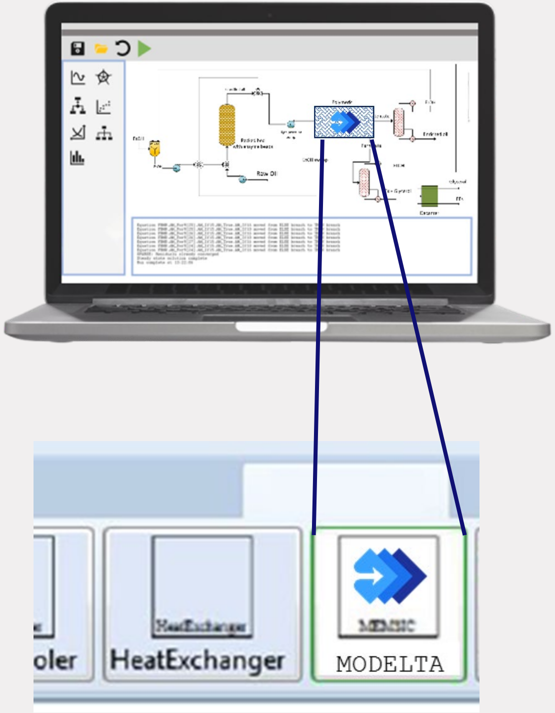
# Modelta cloud-based unit operation

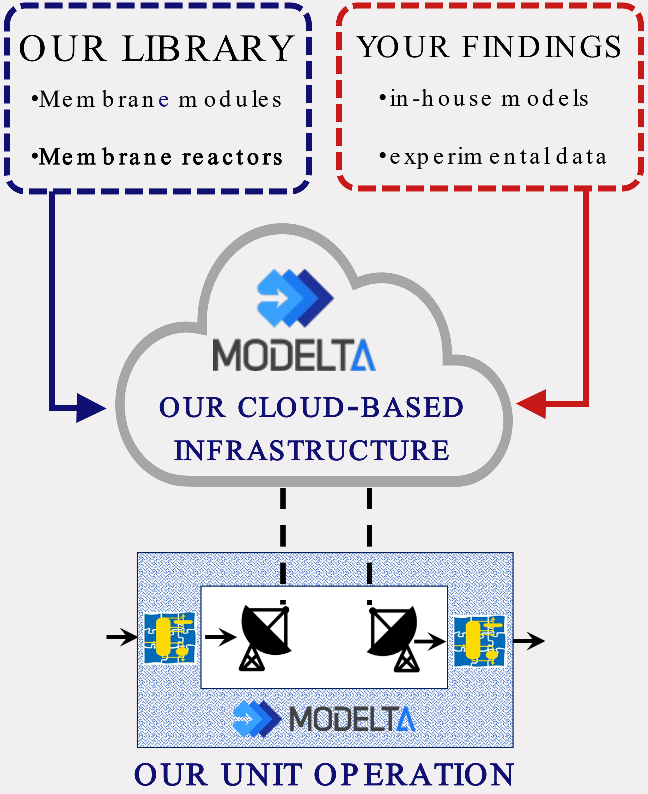



Just one block
in the flowsheet

a whole library of
models
available

that *we can swiftly*
*customize* via cloud

and *combine*
*with your own*
*models*






MODELTA

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