A modeling study on the effect of membrane properties in a packed bed membrane reactor for ammonia synthesis

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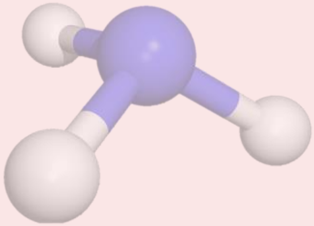
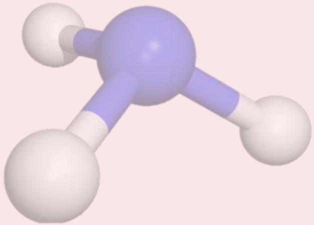
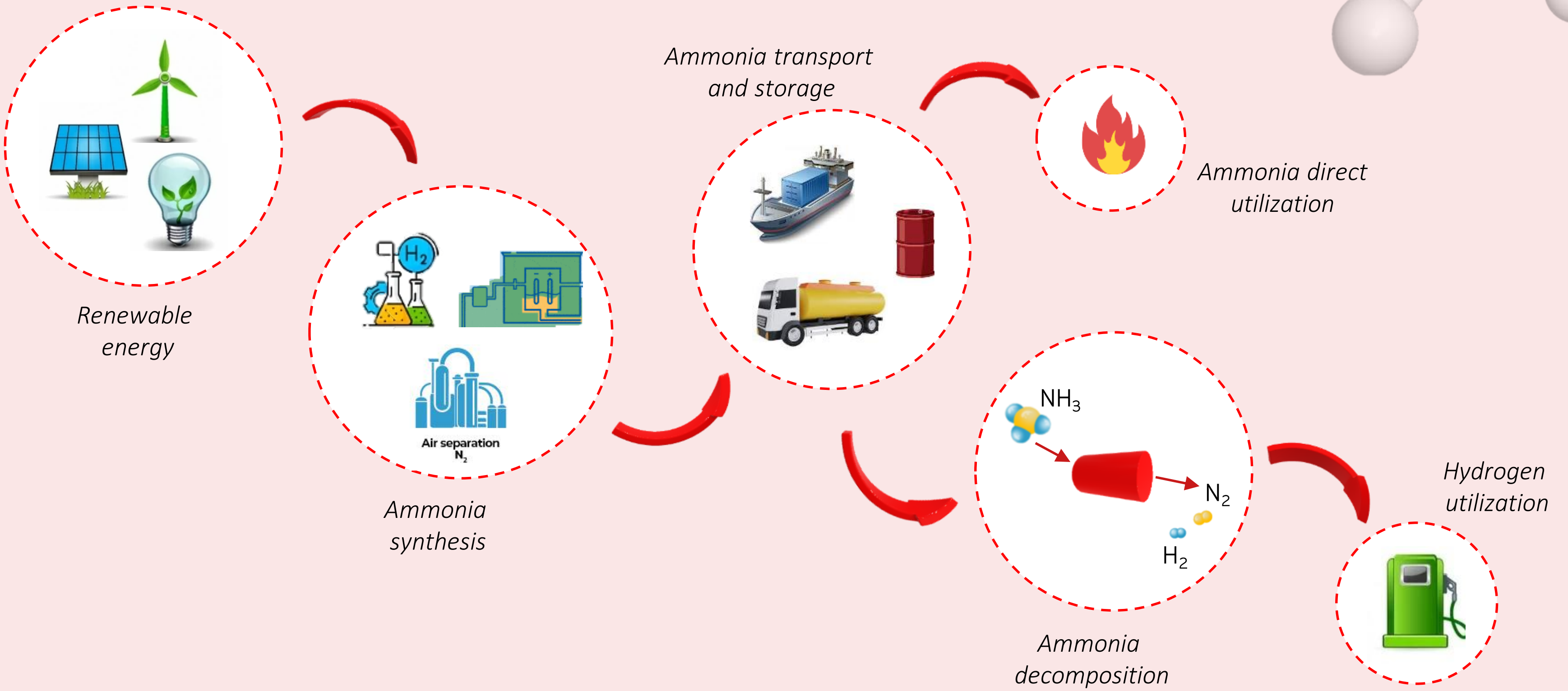
Outlook



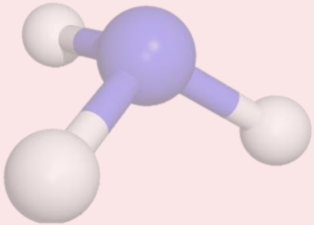
- Introduction
- Objective of the project
- Modeling approach
- Simulation results
- Conclusions

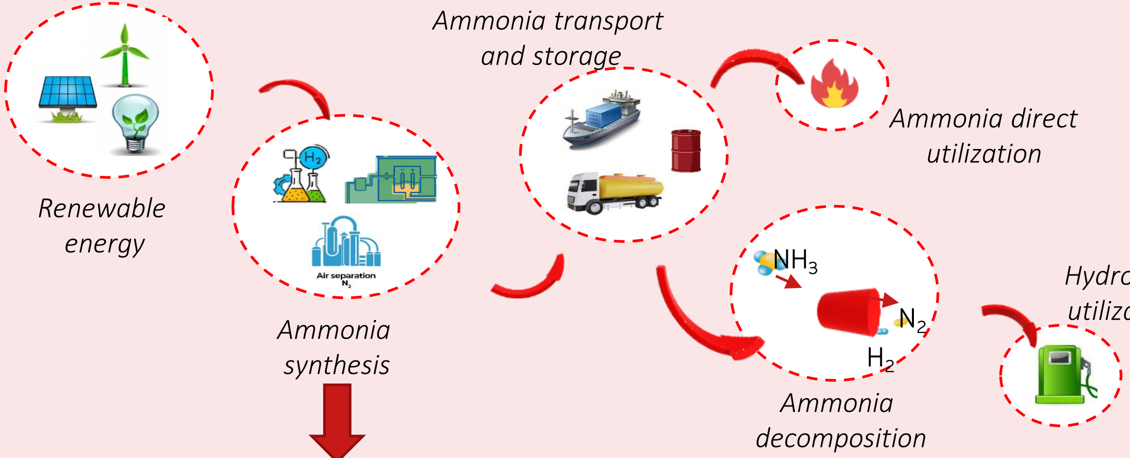
Introduction

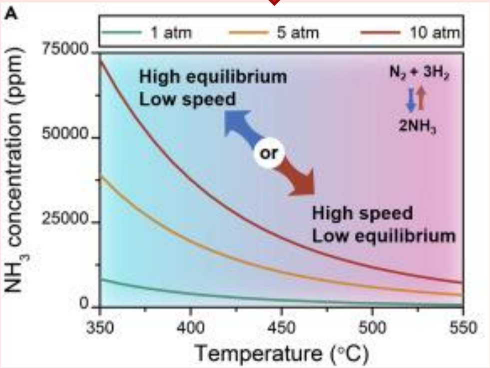




Introduction



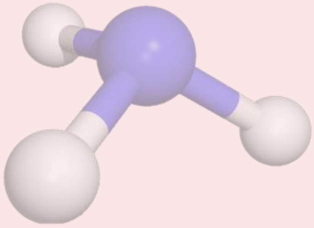


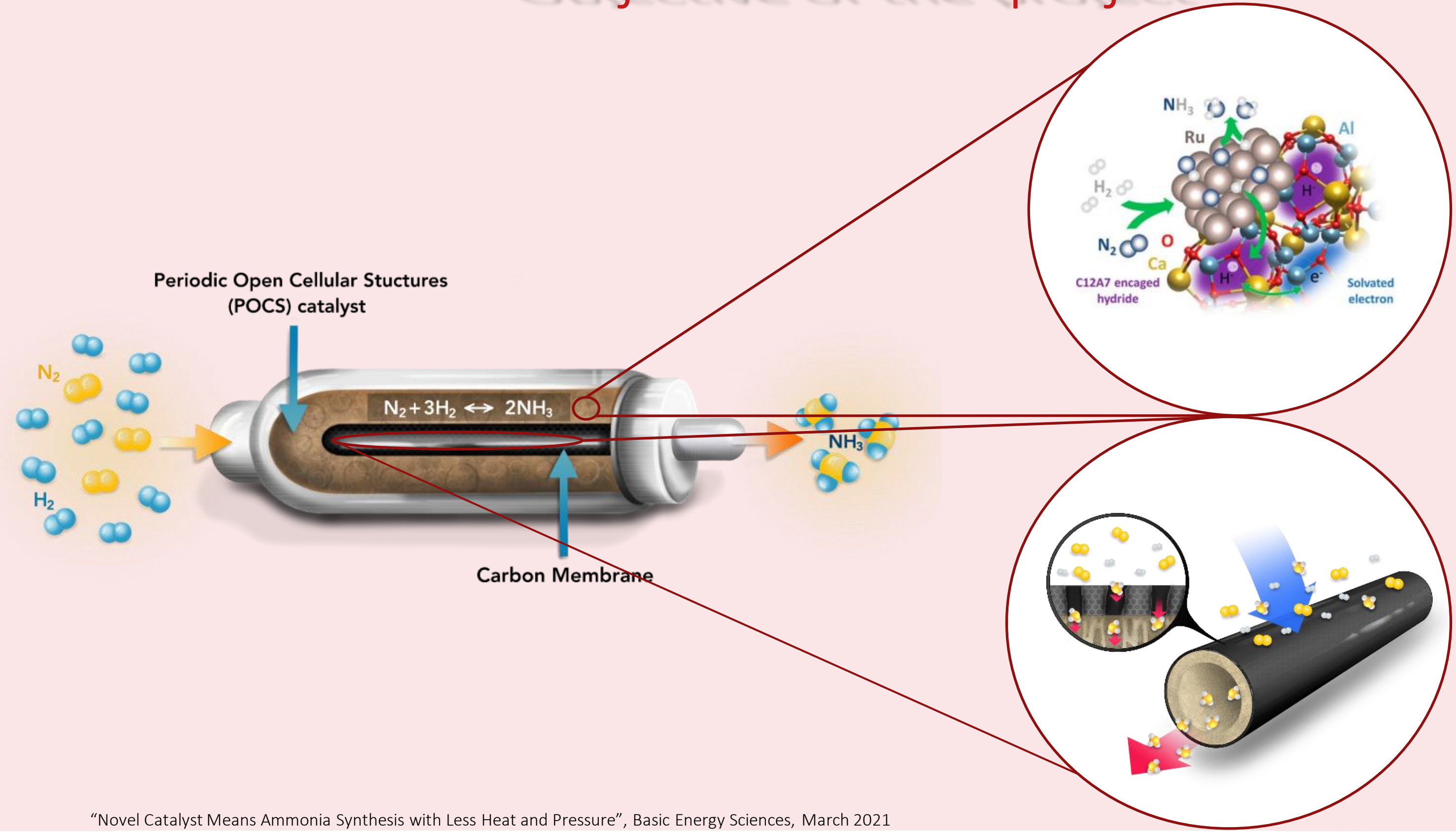


REACTOR REQUIREMENTS

- *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





"Novel Catalyst Means Ammonia Synthesis with Less Heat and Pressure", Basic Energy Sciences, March 2021

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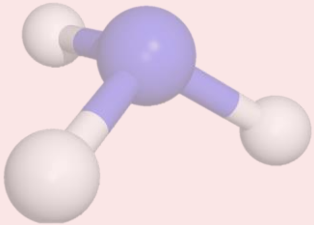
Modeling approach



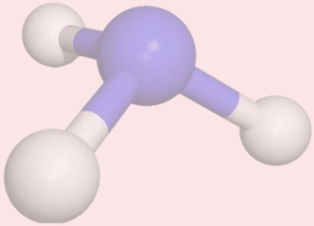
How CMR performances can be studied and predicted?

Development of a mathematical model

Assumptions:

- 1-D Ideal plug flow;
- Steady state;
- Solid-gas phase are modeled as a single phase;
- The membrane material is considered inert;

Modeling approach



How CMR performances can be studied and predicted?

Development of a mathematical model

Modeling steps:

- Validation of the *packed bed reactor model* with a kinetic model from literature
- Validation of the *membrane reactor model* with a membrane experimentally tested
- Optimization of *membrane properties* establishing minimum requirements for permeance and selectivity that would enable this application
- Study of operating condition on the *reactor performances*

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Validation of the PBR reactor

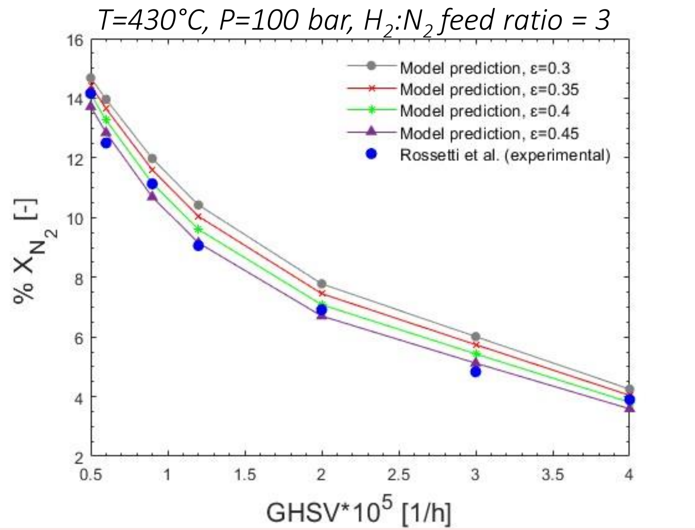
- *Rossetti et al.** kinetic model

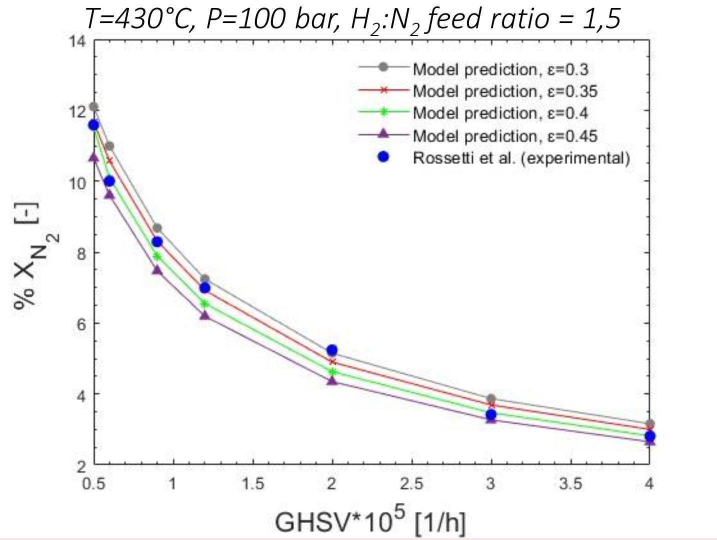
$$r_{N_2} = k_f \frac{\left((a_{N_2})^{0.5} \left[\frac{(a_{H_2})^{0.375}}{(a_{NH_3})^{0.25}} \right] - \frac{1}{K_a} \left[\frac{(a_{NH_3})^{0.75}}{(a_{H_2})^{1.125}} \right] \right)}{1 + K_{H_2} (a_{H_2})^{0.3} + K_{NH_3} (a_{NH_3})^{0.2}}$$

- T = 370-460 °C
- P= 50-100 bar
- H_2:N_2 feed ratio = 1.5-3
- GHSV= 0.5 - 5 * 10^5 1/h

16 kinetic tests have been validated, in function of the bed porosity

ε = 0.4 *as best trade-off*





*"Kinetic Study of Ammonia Synthesis on a Promoted Ru/C Catalyst", Ilenia Rossetti et al., Ind. Eng. Chem. Res. 2006

Validation of the membrane reactor

- **Mass balance in reaction and permeation side**

$$\frac{dF_i^R}{dL} = \frac{\vartheta_i * (r_i) * \rho_b * A}{\rho_C} - J_i * (\pi * D_m^O) * N_m$$

$$\frac{dF_i^P}{dL} = J_i * (\pi * D_m^O) * N_m$$

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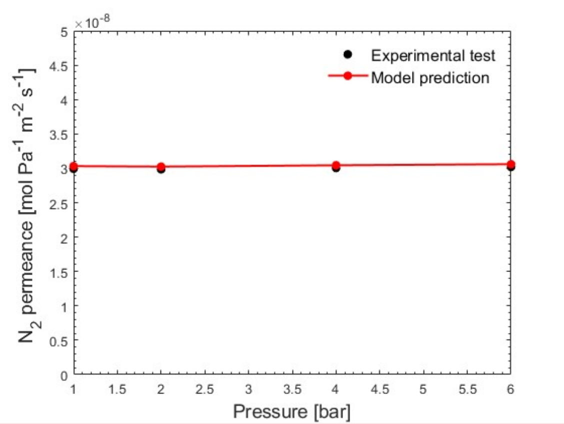
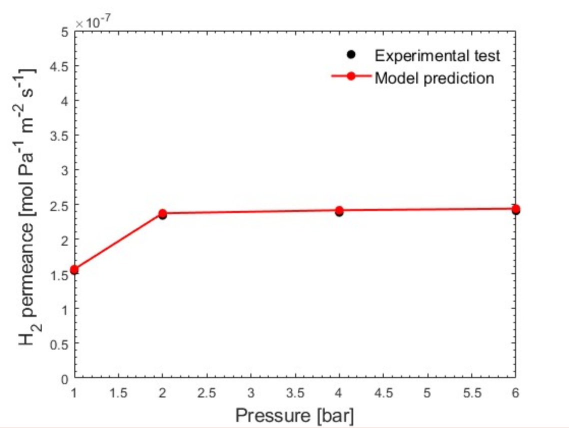
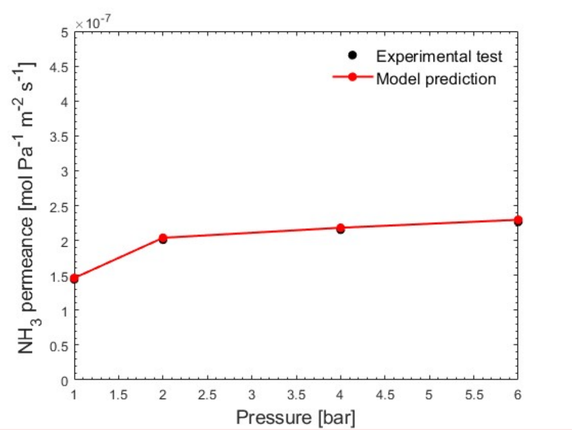
- Experimental results from permeation tests on CMSM
  - Single gas permeation test
  - T = 300 °C
  - P= 1-6 bar







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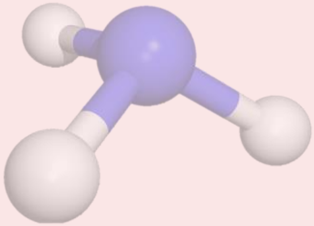
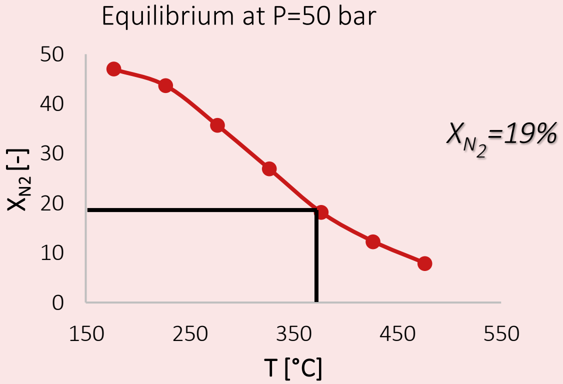
Optimization of membrane properties



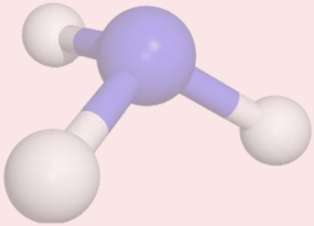
Reactor parameters used in the model

Parameter	Units	Value
Temperature	*°C*	370
Pressure	*bar*	50
H_2/N_2 feed ratio (ret. & perm.)	*mol/mol*	1.5
Reactor length	*m*	1
Reactor diameter	*m*	0.033
GHSV	*1/h*	1287
Catalyst bed density	*kg/m^3*	590
Bed porosity	*m^3_v/m^3_r*	0.4
SW	-	1

Equilibrium study with a R-Gibbs reactor



Optimization of membrane properties: ideal parametric study

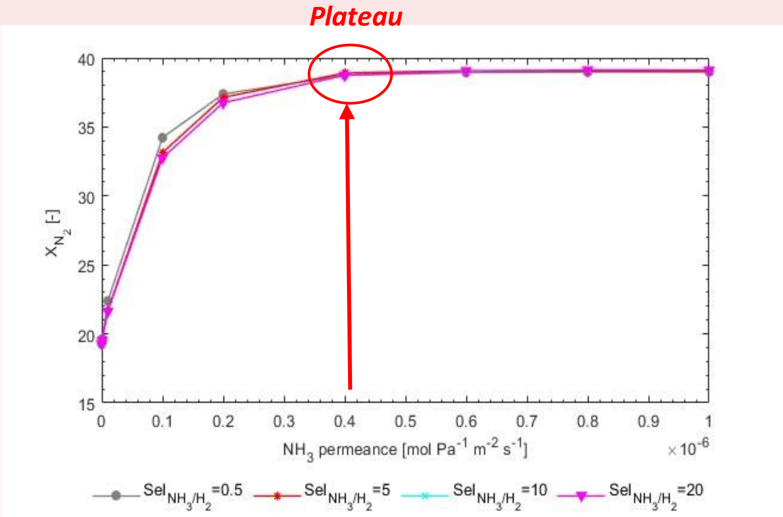


- *Ideal* membrane study →

$$P_{NH_3} = \frac{J_{NH_3}}{(p^R_{NH_3} - p^P_{NH_3})} = [0 - 10^{-6}]$$

$$S_{\frac{NH_3}{H_2}} = \frac{P_{NH_3}}{P_{H_2}} = [0 \; - 20]$$

$$S_{\frac{NH_3}{N_2}} = \frac{P_{NH_3}}{P_{N_2}} = \infty$$

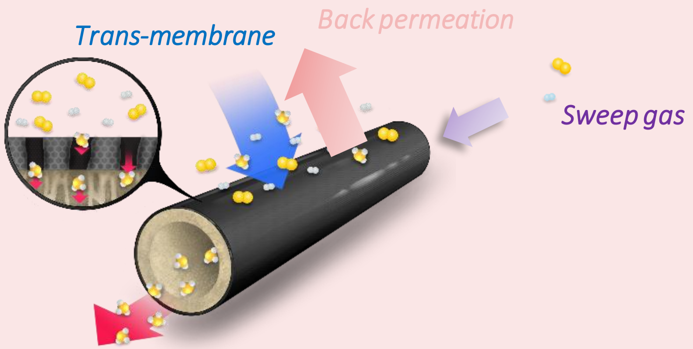


Equation:

$$X_{N2} = \frac{F^{ret}_{N2^0} - F^{ret}_{N2} - F_{N2,tm}}{F^{ret}_{N2^0} - F_{N2,bp}}$$

$F_{N2,tm}$=nitrogen loss passing from retentate to permeate (trans-membrane)

$F_{N2,bp}$=nitrogen loss in the sweep gas, moving to the retentate (back permeation)



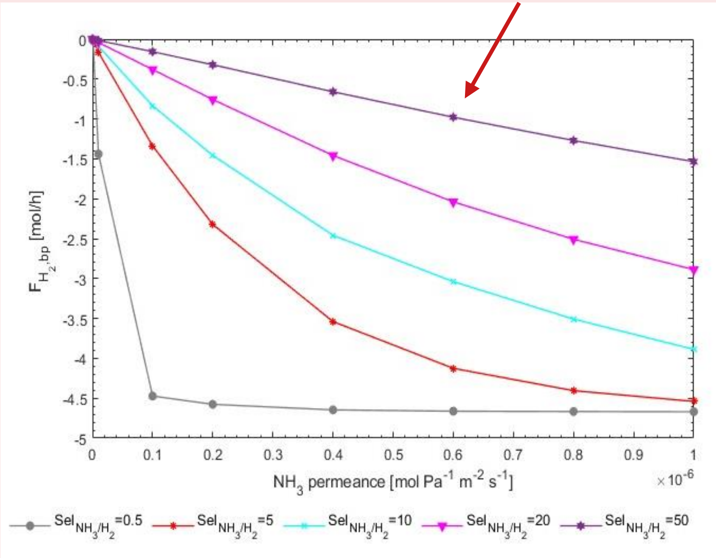
Optimization of membrane properties: ideal parametric study

- *Ideal* membrane study →

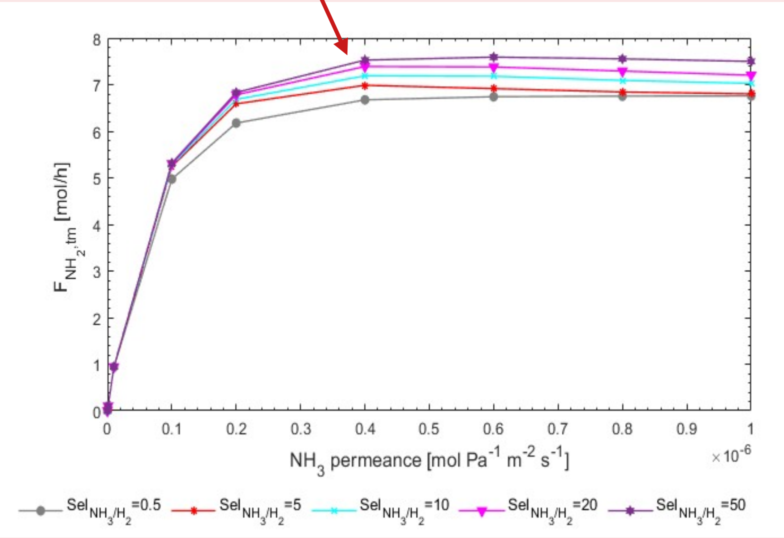
$$\mathbf{P_{NH_3}} = \frac{\mathbf{J_{NH_3}}}{(\mathbf{p^R_{NH_3}} - \mathbf{p^P_{NH_3}})} = [0 - 10^{-6}]$$

$$\mathbf{S_{\frac{NH_3}{H_2}}} = \frac{\mathbf{P_{NH_3}}}{\mathbf{P_{H_2}}} = [0 - 50]$$

$$S_{\frac{NH_3}{N_2}} = \frac{P_{NH_3}}{P_{N_2}} = \infty$$

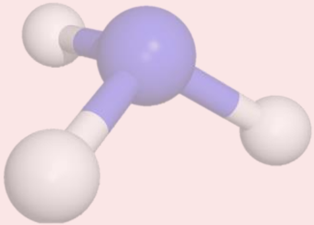


<u>*Back permeation of H_2.*</u>
Loss of Hydrogen from the sweep gas to the reaction side, affecting catalyst activity



<u>*Transmembrane flow of NH_3*</u> from the retentate stream

Optimization of membrane properties: real parametric study

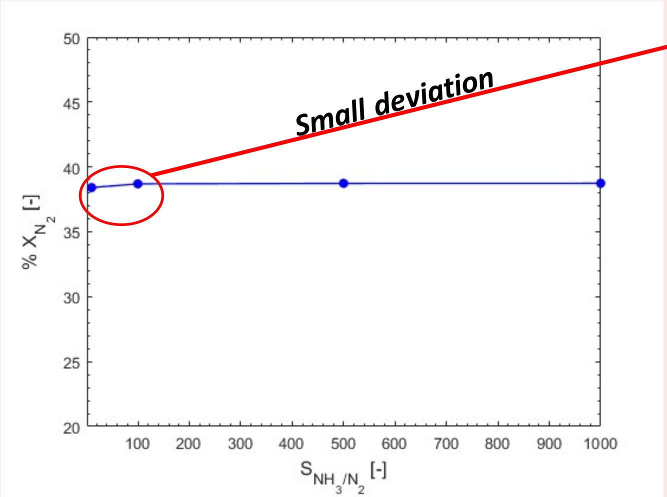


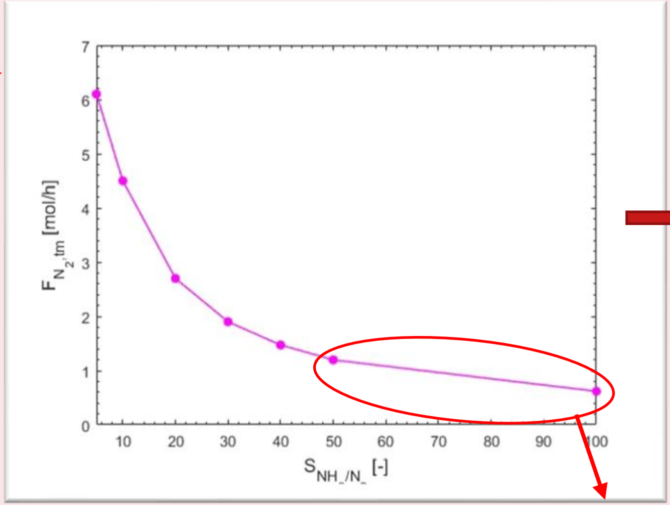
- *Real* membrane study →

$$P_{NH_3} = \frac{J_{NH_3}}{(p^R_{NH_3} - p^P_{NH_3})} = 0.4*10^{-6}$$

$$S_{\frac{NH_3}{H_2}} = \frac{P_{NH_3}}{P_{H_2}} = 50$$

$$\boldsymbol{S_{\frac{NH_3}{N_2}} = \frac{P_{NH_3}}{P_{N_2}} = [0 - 1000]}$$





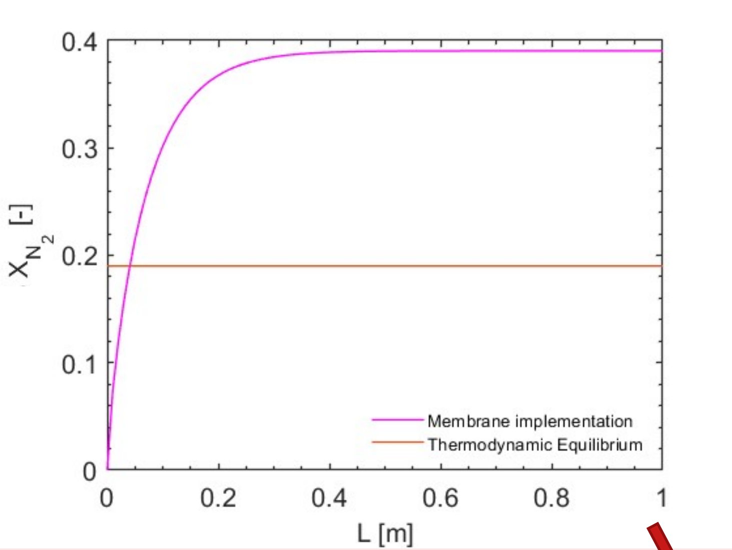
→ N_2 loss in the reaction zone

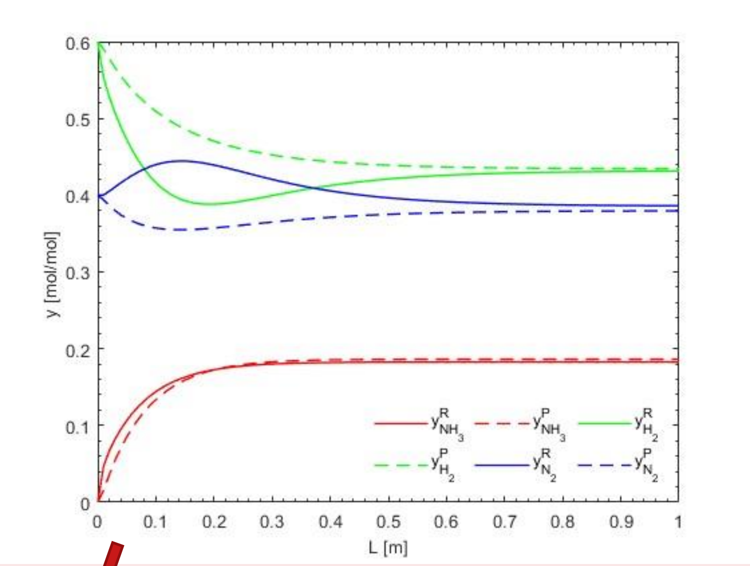
Best trade-off between reactant loss and selectivity

Optimal membrane properties in isothermal conditions

Best membrane properties in the isothermal reactor:

$$P_{NH_3} = 0.4*10^{-6} \text{ mol Pa}^{-1} \text{ m}^{-2} \text{ s}^{-1}$$
$$S_{\frac{NH_3}{H_2}} = 50$$
$$S_{\frac{NH_3}{N_2}} = 100$$



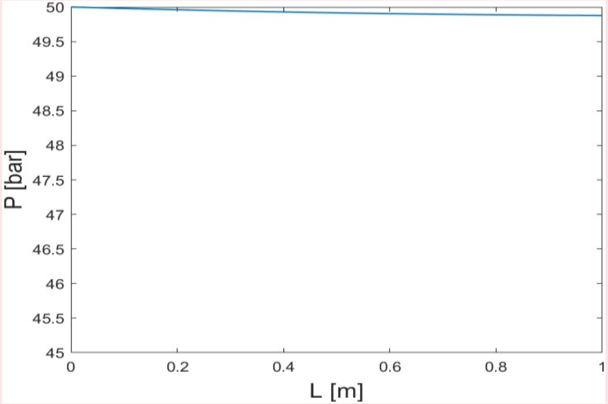


<u>Equilibrium reached between reaction and permeation zone</u>

Study of pressure drops

- *Momentum balance in the reaction side*

$$\frac{dP}{dL} = -\left(\frac{150 * \mu_{mix} * u * (1-\varepsilon)^2}{\varepsilon^3 * d_p^2} + \frac{1.75 * (1-\varepsilon) * \rho_{mix} * u^2}{\varepsilon^3 * d_p}\right) * 10^{-5} [=] \frac{bar}{m}$$



Pressure drops around 0.2 bar prevents:

- back-permeation of the sweep gas
- big compression costs after the recirculation of the reactants

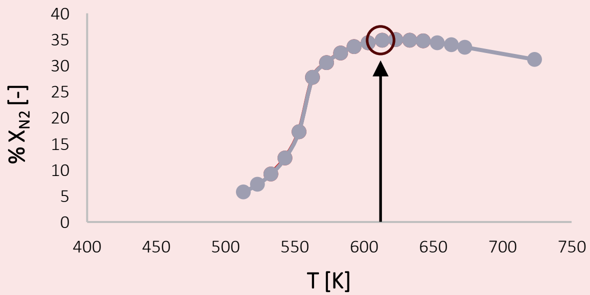
Heat exchange study between reaction and permeation zone

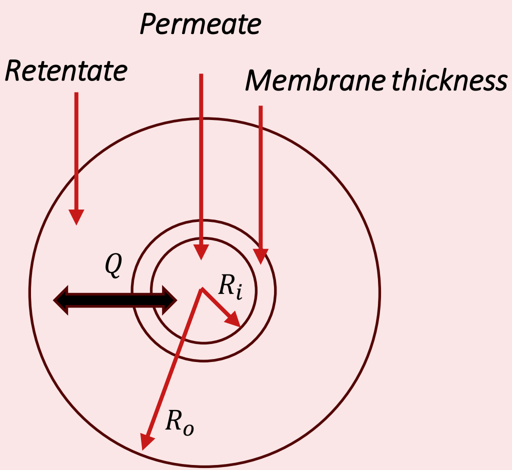
- *Energy balance in reaction and permeation side*

$$\frac{dT_R}{dL} = \frac{(-r_{N2}) * \Delta H * \rho_b * A}{\sum_i F_i^R * cp_i^R * \rho_c} - \frac{U * 2 * \pi * R_i * (TR - TP)}{\sum_i F_i^R * cp_i^R}$$

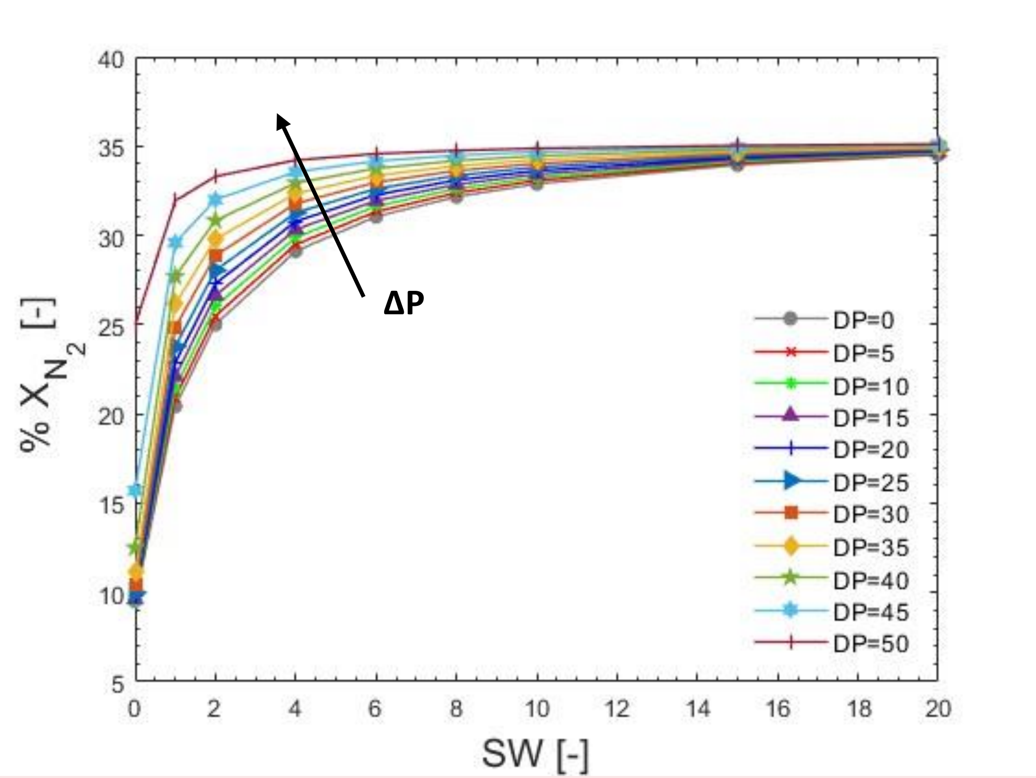
$$\frac{dT_P}{dL} = \frac{U * 2 * \pi * R_i * (TR - TP)}{\sum_i F_i^P * cp_i^P}$$

Permeation temperature: initial condition study





Study of the operational conditions: effect of SW and ΔP



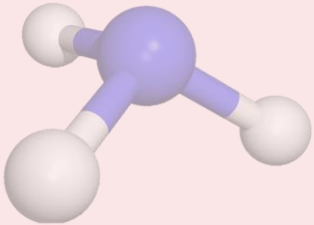
- ✓ *SW=[1-20]*
- ✓ *ΔP=[0-50]*
- ✓ *H_2:N_2 permeate side=1.5*
- ✓ *T_{IN}^{R}=370°C*
- ✓ *T_{IN}^{P}=370°C*

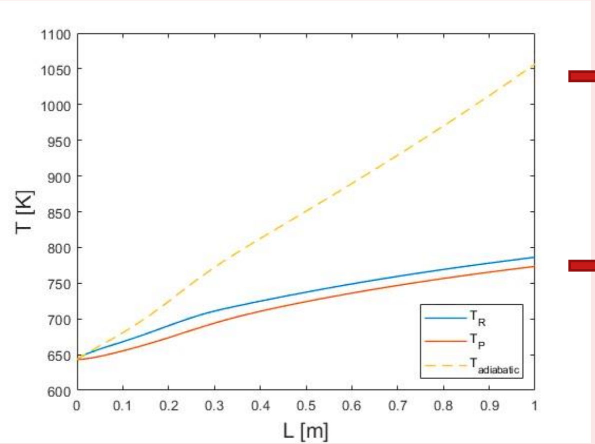
The conversion increases with SW and ΔP up to an asymptotic value of 34%

Final choice for the study

ΔP=50 & SW=4

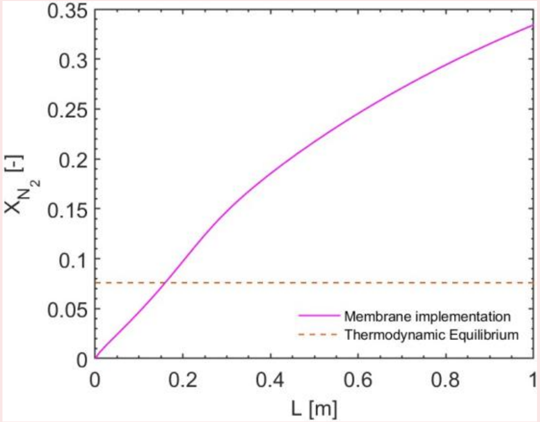
Membrane reactor performance: Temperature profile





Adiabatic case with membrane, without heat exchange

Adiabatic case with membrane, with heat exchange with sweep gas



Adiabatic case without membrane

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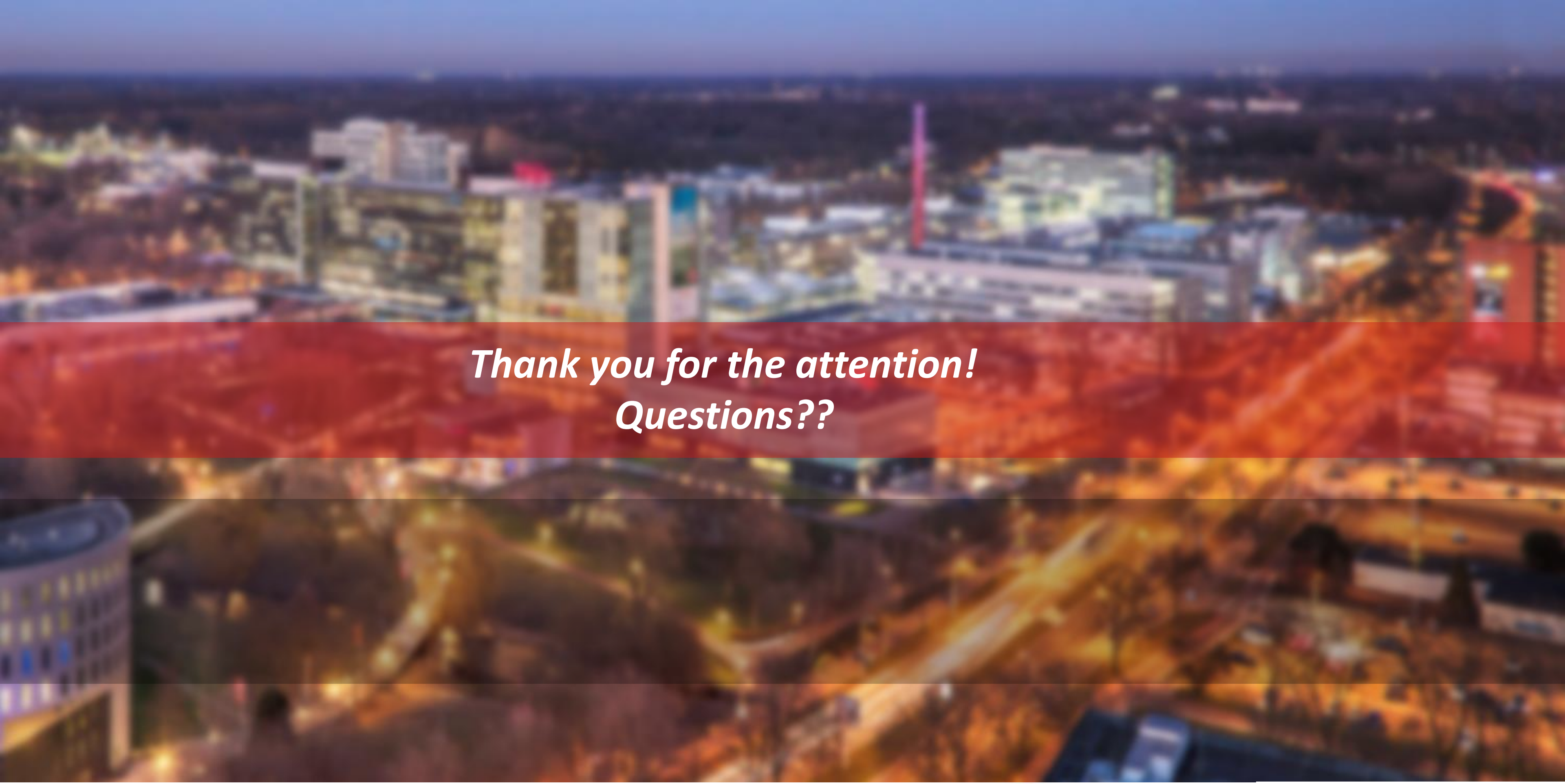
Conclusions

- A 1-D membrane reactor model was used to study the ***optimal membrane properties***, which showed :
  - $P_{NH_3} = 0.4*10^{-6}$ mol Pa^{-1} m^{-2} s^{-1}
  - $S_{\frac{NH_3}{H_2}} = 50$
  - $S_{\frac{NH_3}{N_2}} = 100$

- The ***operational conditions*** study, i.e. SW and ΔP, showed to play a key-role on the process performance

- Taking in account the ***heat integration***, using sweep gas, we prove that this technology is able to overcome the thermodynamic equilibrium



Thank you for the attention!

Questions??

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