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

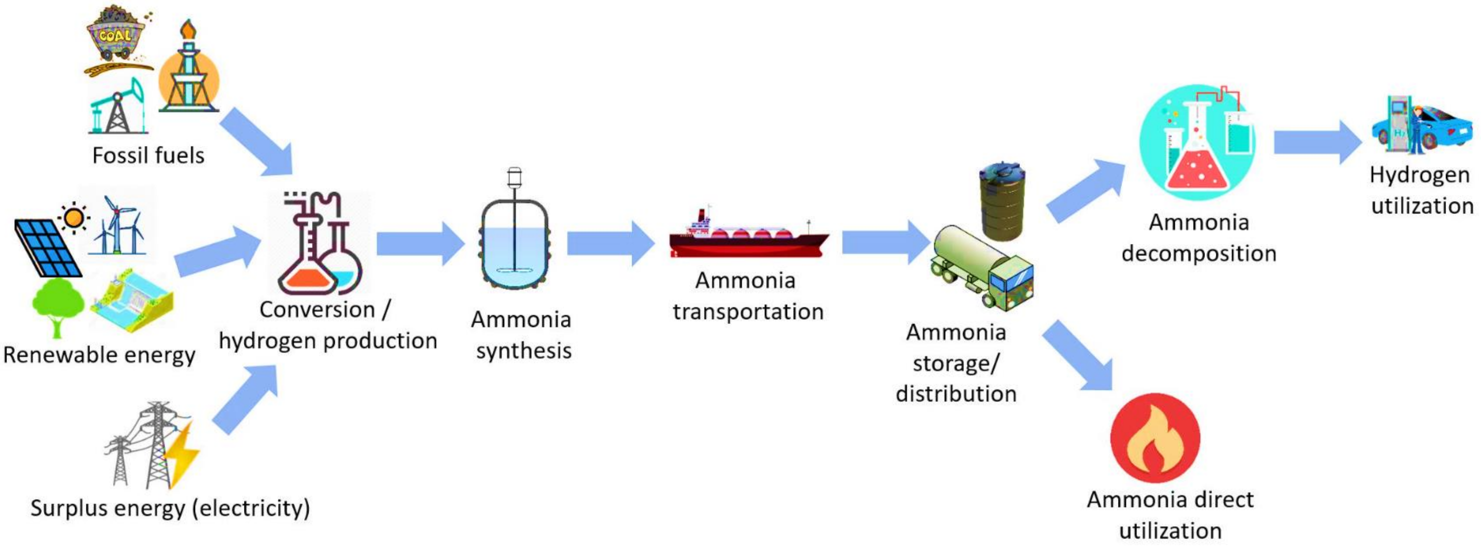
  - Validation of the kinetic model
  - Validation of the membrane
  - Optimization of the membrane properties

- ✓ Conclusions

Introduction

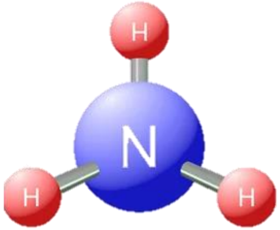
Amongst energy storage solution, ***Hydrogen*** produced from electrolysis offers great promises as flexible ***energy carriers***

Additional H_2 utility scale storage facilities are required and amongst all the possibilities, ***liquid carriers*** like ***Ammonia*** are perfect candidates



"Ammonia as Effective Hydrogen Storage: A Review on Production, Storage and Utilization", Muhammad Aziz et al., Energies 2020

Introduction



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

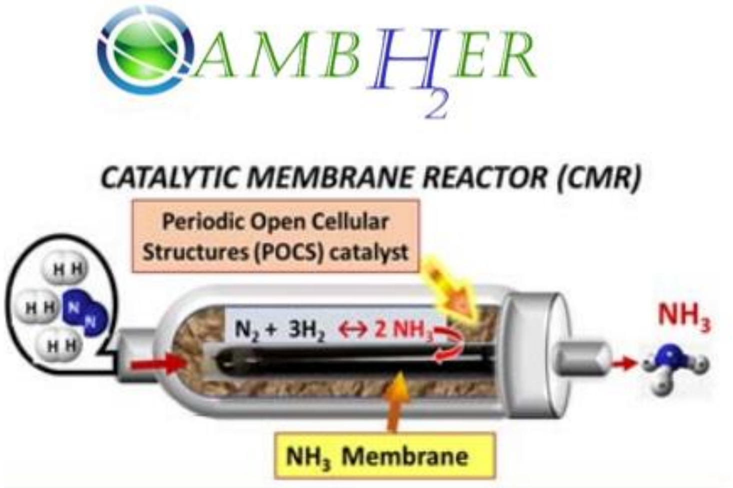
$$\frac{1}{2}N_2 + \frac{3}{2}H_2 \leftrightarrow NH_3$$

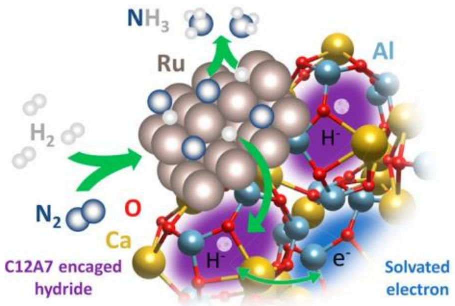
- ΔH_{298K} =-45.7kJ/mol
- T=400-500 °C P=100-200 bar
- Fe-based or Ru-based catalyst
- Rate limiting step: activation of the stable N≡N bond

REACTOR REQUIREMENTS →

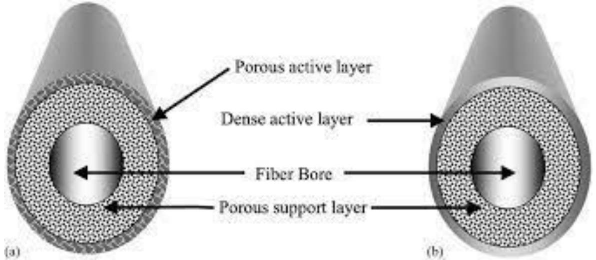
- High inlet temperature to achieve high reaction rate
- Low outlet temperature to achieve a high equilibrium conversion
- High pressure to shift the equilibrium towards the products

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

Modeling approach

Reactor model based on the integration of a Ru/C catalyst with an inorganic membrane that is selective to NH_3

Assumptions:

- Ideal plug flow;
- Steady state;
- Isothermal reactor;
- No pressure drops;
- Solid-gas phase are modeled as a single phase;
- The membrane material is considered inert;

Modeling steps:

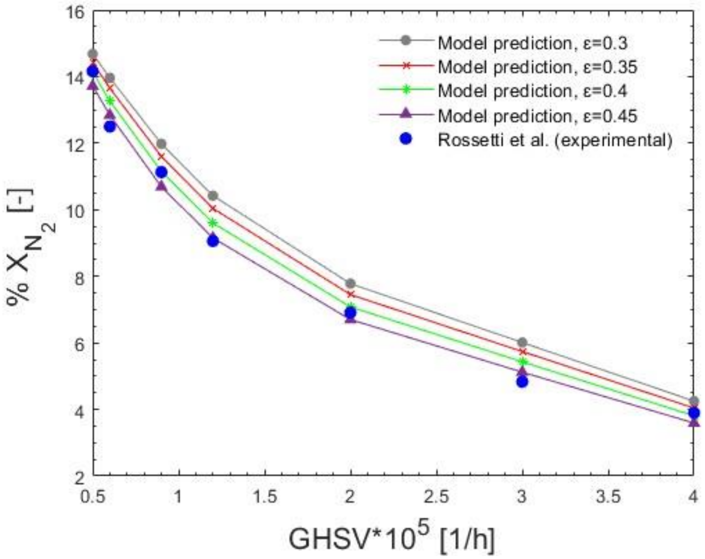
- Validation of the model with a kinetic model from literature
- Validation of the model with a membrane experimentally tested
- Optimization of membrane properties

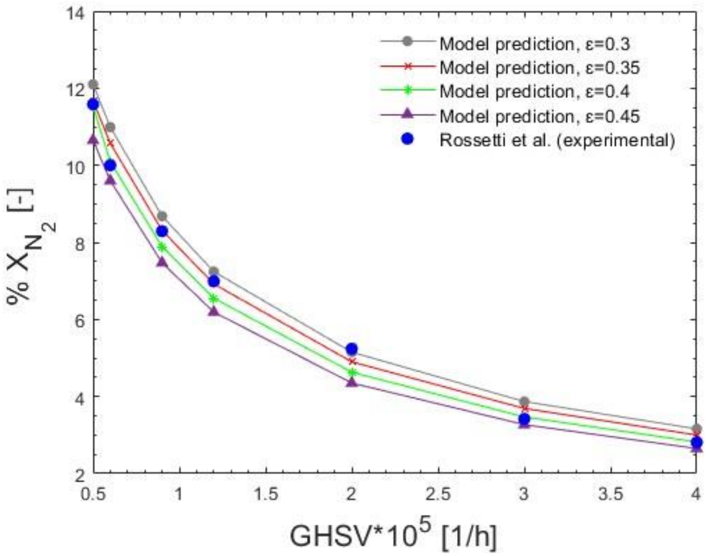
Validation of the kinetic model

- *Rossetti et al.** kinetic model
  - 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

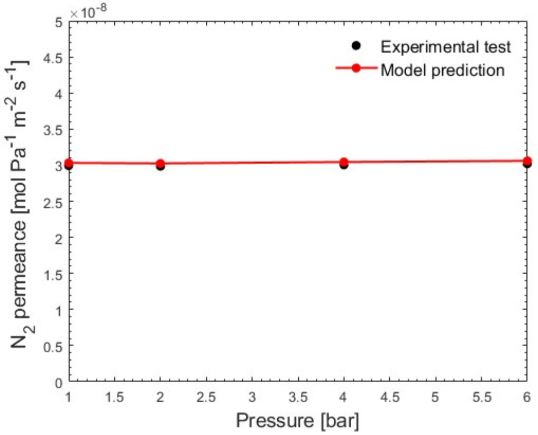


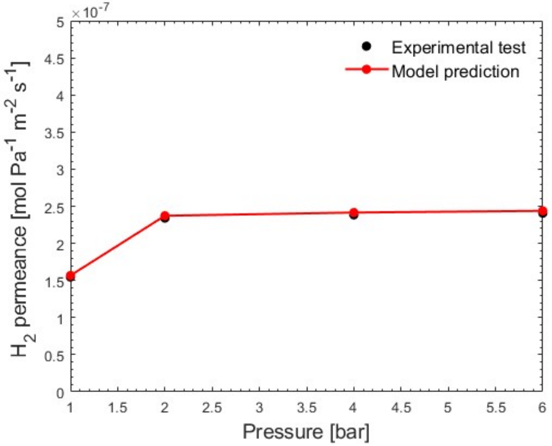


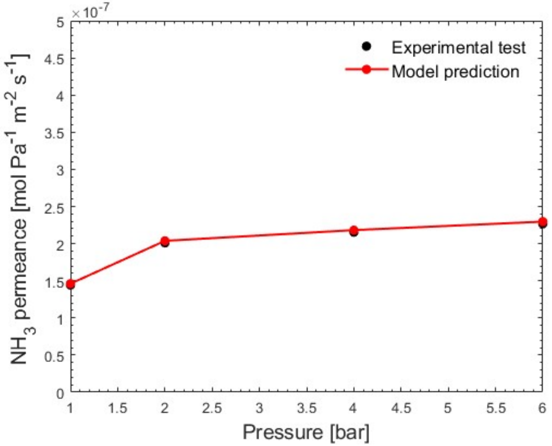
*"Kinetic Study of Ammonia Synthesis on a Promoted Ru/C Catalyst", Ilenia Rossetti et al., Ind. Eng. Chem. Res. 2006

Validation of the membrane

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





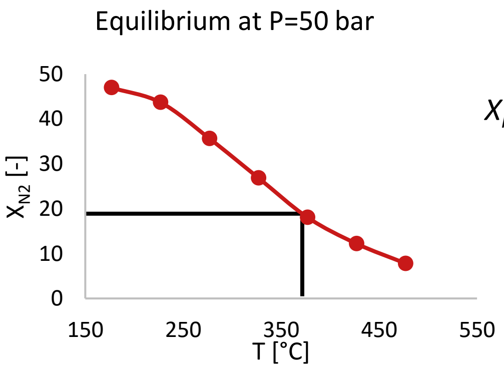


Optimization of membrane properties

Reactor parameters used in the model

Parameter	Units	Value
Temperature	°C	370
Pressure	bar	50
H_2/N_2 feed ratio	mol/mol	1.5
Reactor length	m	1
Reactor diameter	m	0.033
GHSV	1/h	1000
Catalyst bed density	Kg/m^3	590
Bed porosity	m^3_v/m^3_r	0.4

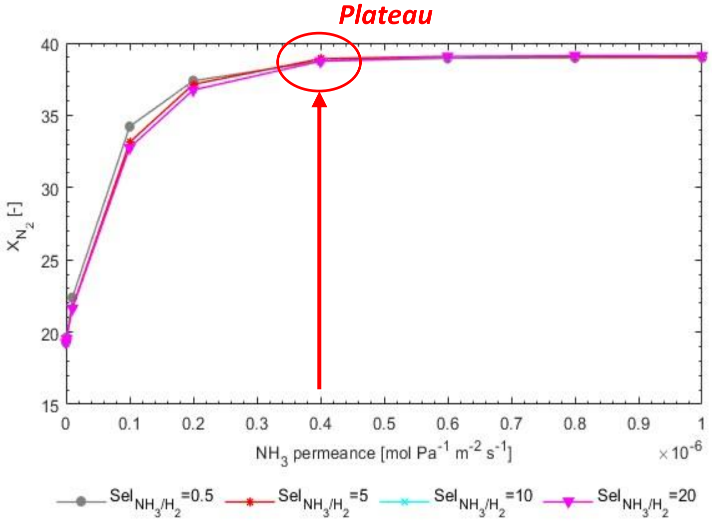
Equilibrium study with a R-Gibbs reactor



X_{N_2}=19%

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:

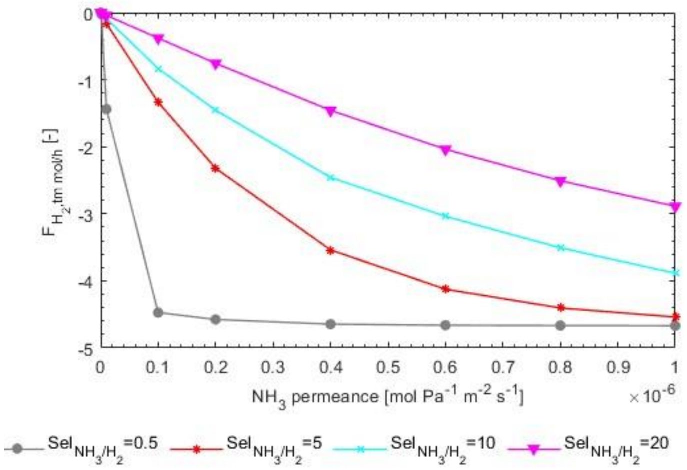
$$X_{N2} = \frac{F_{N2^0}^{ret} - F_{N2}^{ret} - F_{N2}^{passing\ the\ membrane}}{F_{N2^0}^{ret} - F_{N2}^{back\ perm}}$$

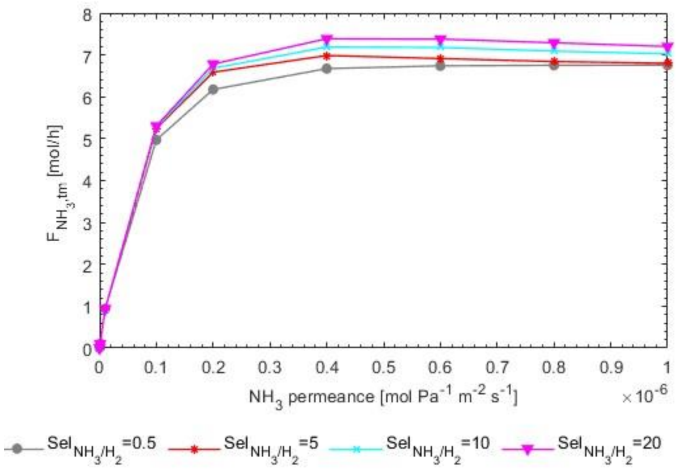
$F_{N2}^{passing\ the\ membrane}$*=nitrogen loss passing from retentate to permeate*

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

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}=∞



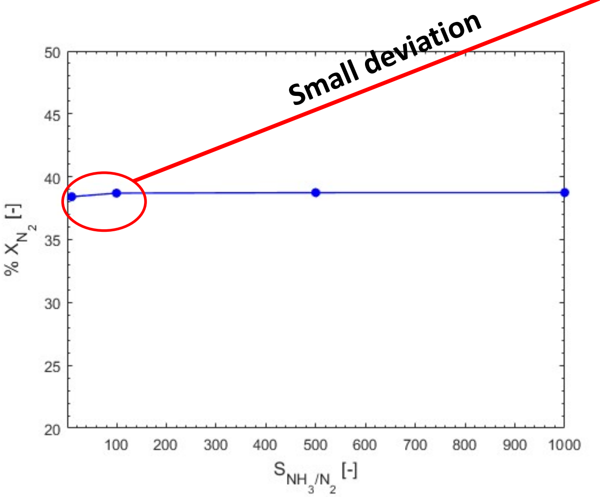


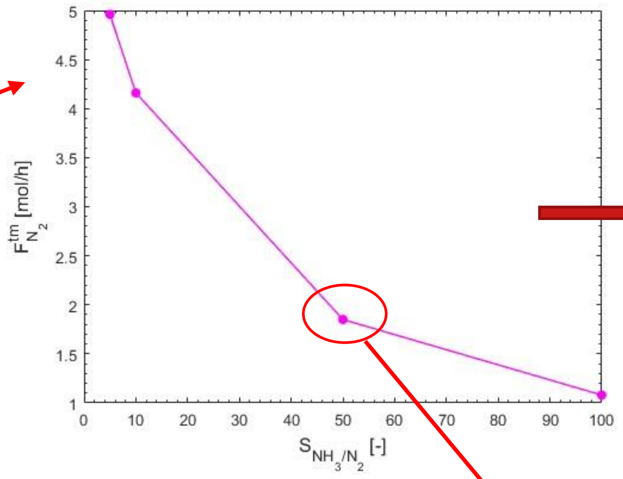
Back permeation of H_2, loss of Hydrogen in the sweep gas

Separation of NH_3 from the retentate stream

Optimization of membrane properties

- Real membrane study → P_{NH_3} =[4*10^{-7}]
  S_{NH_3/H_2}=[20]
  S_{NH_3/N_2}=[0 – 100]



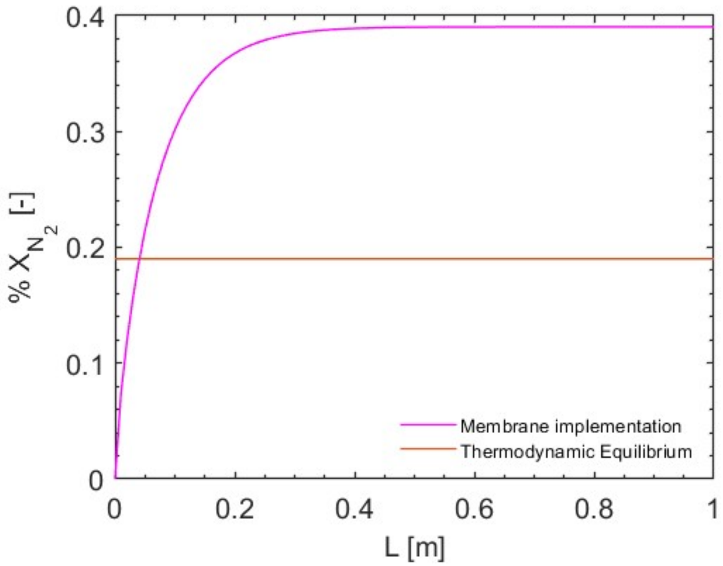


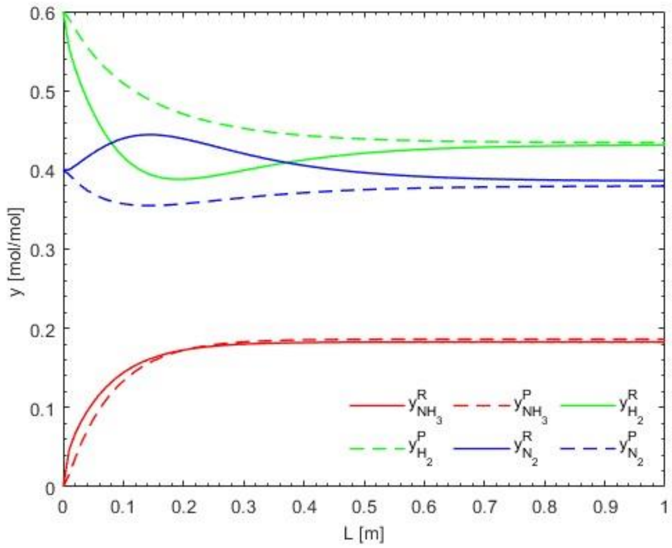
Nitrogen loss in the reaction zone

Best trade-off between reactant loss and selectivity

Optimization of membrane properties

Best membrane properties:
*P_{NH_3} =[4*10^{-7}]*
S_{NH_3/H_2}=[20]
S_{NH_3/N_2}=[50]





Equilibrium reached between reaction and permeation zone

Conclusions

- A 1-D reactor model was developed for ammonia production
- The model has been validated with experimental data from literature
- The membrane reactor has been validated with data derived through experimentally tests
- The membrane reactor has been studied in relation to membrane properties:
  - *Ammonia permeance*: this plays a key role for both conversion and separation, and the membrane must have a minimum of $4*10^{-7}$
  - *Ammonia Selectivity*: the ammonia selectivity over H_2 and N_2 does not affects as much the conversion as the molar flow passing through the membrane of both the reactants. In case of NH_3/H_2 the selectivity has to be >20 , while in case of NH_3/N_2 the selectivity has to be >50

Thank you for the attention!
Questions??

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