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ADVANCED **PO**WER CONVERSION TECHNO**L**OGIES BASED ON **O**NBOARD AMMONIA CRACKING THROUGH NOVEL MEMBRANE REACTORS

TU/e EINDHOVEN UNIVERSITY OF TECHNOLOGY

APOLO

Packed Bed Membrane Reactor Modeling for Hydrogen Separation Using Supported Pd- Membranes in Ammonia Cracking Process

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ICCMR-17
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OUTLINE

- Hydrogen as green Fuel for Energy transition
- Hydrogen Storage and Transport limitations: Ammonia as potential Hydrogen carrier
- Ammonia cracking Process: problems and limitaions
- Advanced Kinetic modelling on custom made Ruthenium based catalyst
  - Experimental campaign and data collection
  - Kinetic modelling: Fitting and Validation
- Scale up
  - Packed Bed Reactor (PBR) scale up
  - Packed Bed Membrane Reactor (PBMR) scale up
- Conclusions & Outlook

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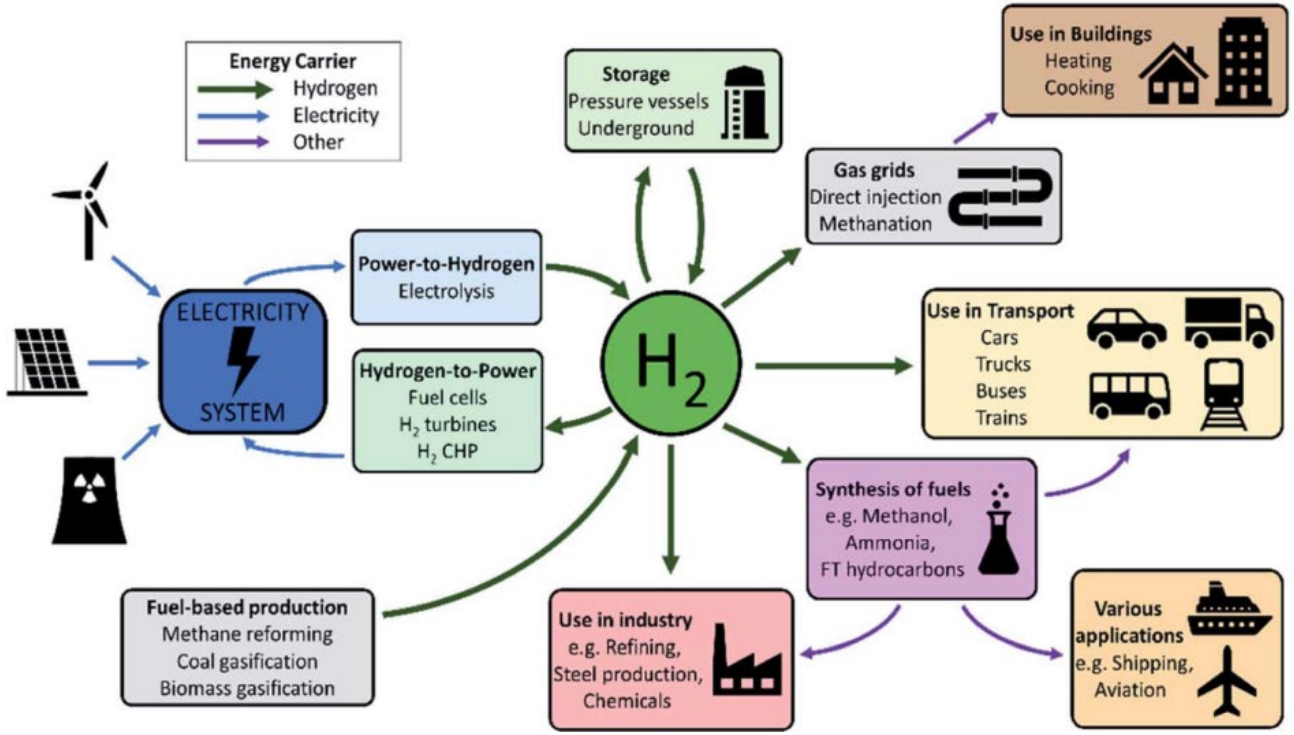
Hydrogen as Green Fuel



Storage problem of renwable energy:

- ✗ **Fluctuation in production**
- ✗ **Storage and capacity of batteries**
- ✗ **Long term storage**

✓ Hydrogen Production

Green production from renewable energetic sources

- Solar energy
- Nuclear energy
- Aeolian energy

Different methods of storage

- Pressured reservoirs (gasous)
- Criogenich reservoir(Liquid)
- Chemical Storage
- Physical Sorption
- Chemical Sorption

[1] **Qureshi et al.** – A State-of-The-Art Review on the Latest trends in Hydrogen production, storage, and transportation techniques – Fuel, 340. 127574, 1-18 (2023)
[2] **Trung et al.** –The current status of hydrogen energy: an overview – Royal Society of Chemistry,13, 28262-28287 (2023)

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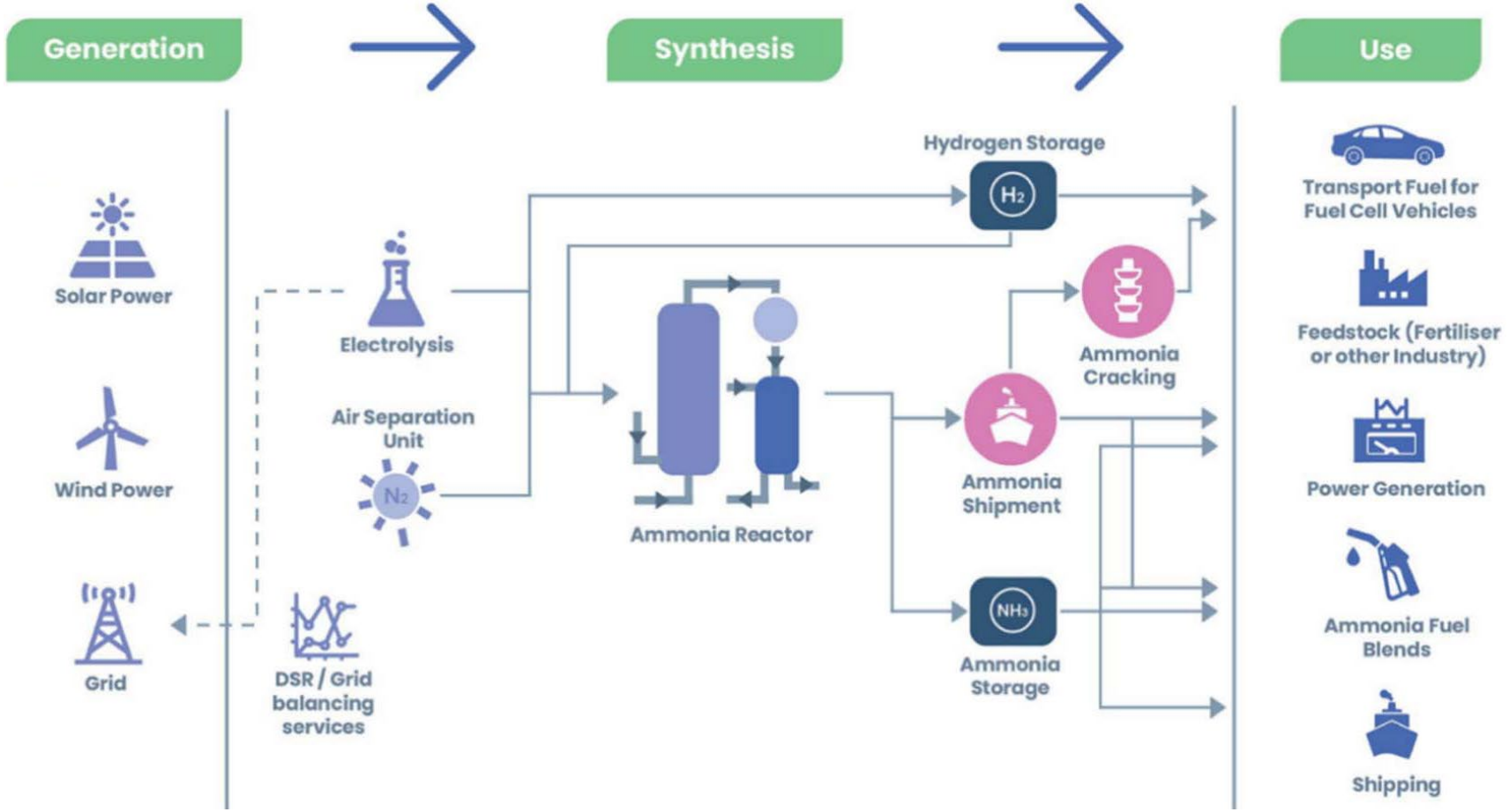
Ammonia as Hydrogen Storage



Generation:

- Renewable energy (solar, wind) → electrolysis → green H_2
- Air separation provides N_2 for ammonia synthesis

Synthesis:

- In situ ammonia synthesis
- Ammonia storage and shipment
- Usage

- Onboard hydrogen production via ammonia cracking
- Hydrogen usage: Fuel cells and pilot gas for ammonia combustion engines

[1] **Qureshi et al.** – A State-of-The-Art Review on the Latest trends in Hydrogen production, storage, and transportation techniques – Fuel, 340. 127574, 1-18 (2023)
[2] **Trung et al.** –The current status of hydrogen energy: an overview – Royal Society of Chemistry,13, 28262-28287 (2023)
[3] **Aziz et al.** – Ammonia as Hydrogen storage: A review on production, Storage and Utilization – Energies, 13. 3062, 1-25 (2020)

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Ammonia cracking conventional reactor technology

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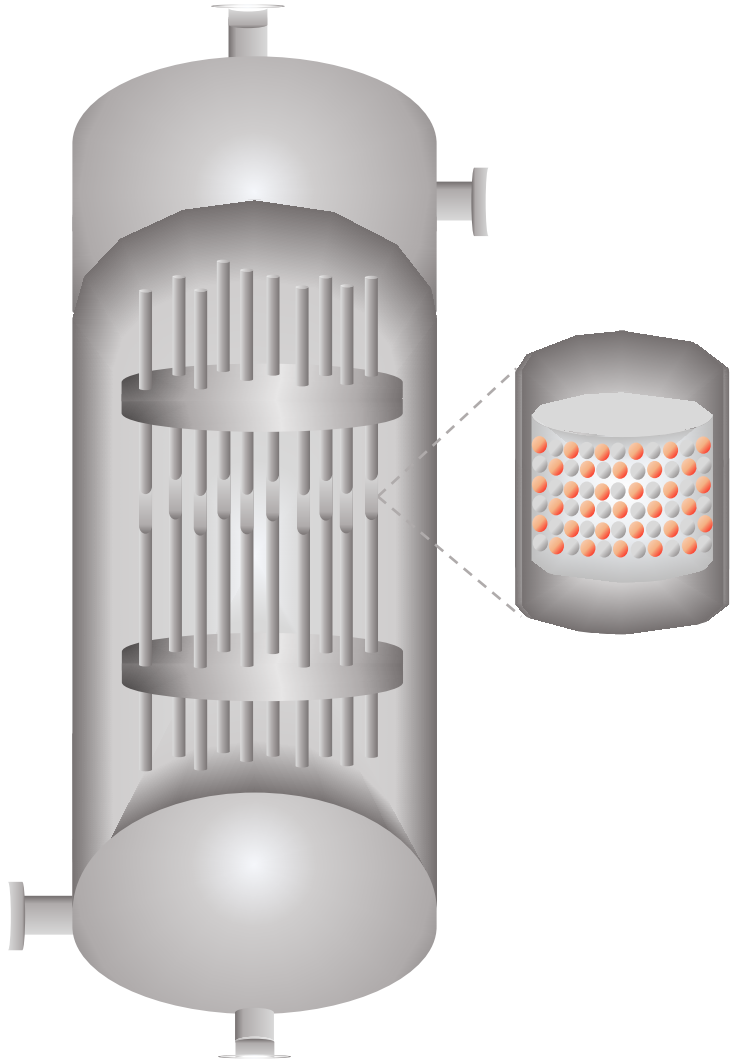
Packed Bed Reactor(PBR)

- ✓ well-established technology on industrial scale
- ✓ Operates near atmospheric pressure, which is thermodynamically favorable for ammonia cracking reaction
- ✓ Lower cost, robust, and easily scalable for large industrial systems

- X Requires downstream purification units to obtain pure H_2
- X Limited by thermodynamic equilibrium. Is impossible remove H_2 during reaction. Process intensification not possible!!



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Ammonia cracking New reactor technology

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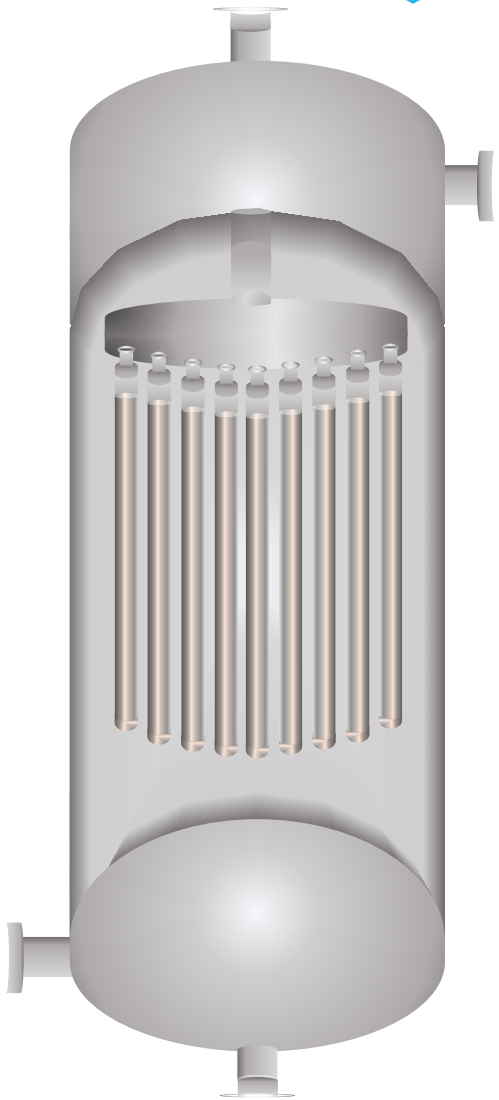
Packed Bed Membrane Reactor(PBMR)

- ✓ Integrates reaction and in situ H_2 separation via Pd based membranes
- ✓ In–Situ Hydrogen separation | Production: High-Purity H_2
- ✓ process intensification: Equilibrium is shifted due to Hydrogen removal from retentate side

- X Pressure gradient (ΔP) from retentate to permeate side is required to drive H_2 permeation
- X higher retentate pressure is thermodynamically unfavorable for ammonia cracking reaction



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Problems and limitations

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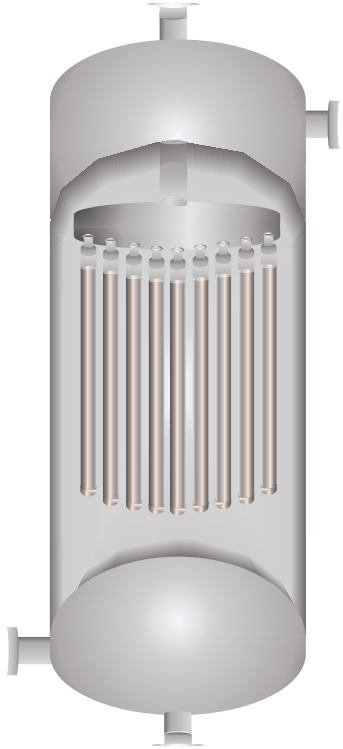
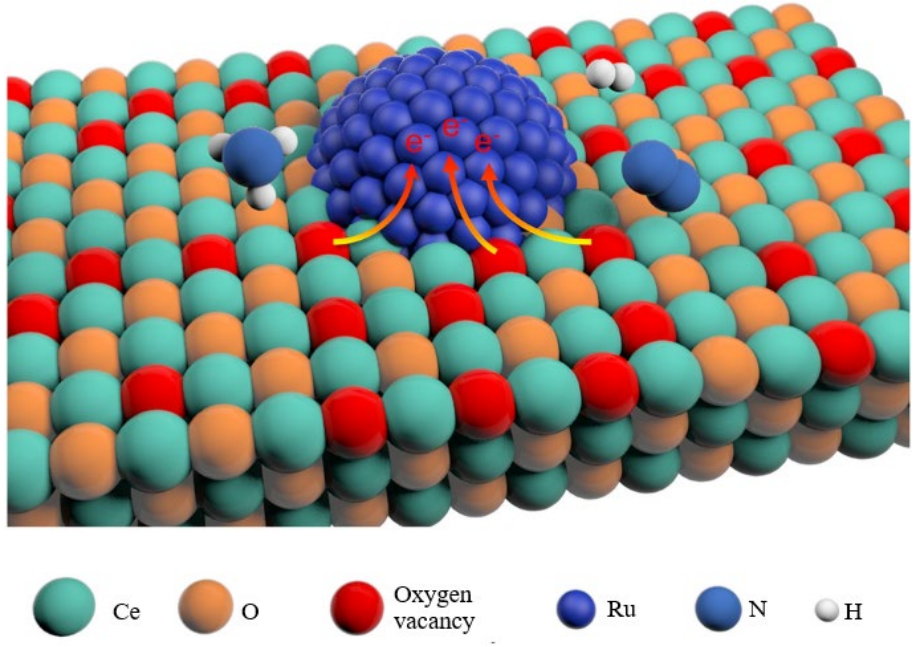
X Ammonia cracking: Energy demand process

✓ New (PBMR) reactor technology



✓ New generation Catalyst (Ru-based catalyst)



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Main Objective

The main objective of this work is to develop a Packed Bed Membrane Reactor model Using Custom made Ru based catalyst and a custom made Pd based membrane

The kinetic model development:

- Experimental Data on different reactor scale were collected → Kinetic Fitting and Validation
- Kinetic fitting and Kinetic model validation

Pd based membrane:

- Permeation Tests were carried out
- Permeation modelling was assessed

Packed Bed membrane reactor modelling:

- Experiments: Experimental Data on Packed Bed membrane reactor were obtained
- Modelling: Kinetic model and permeation model integration in a custom-made reactor unit

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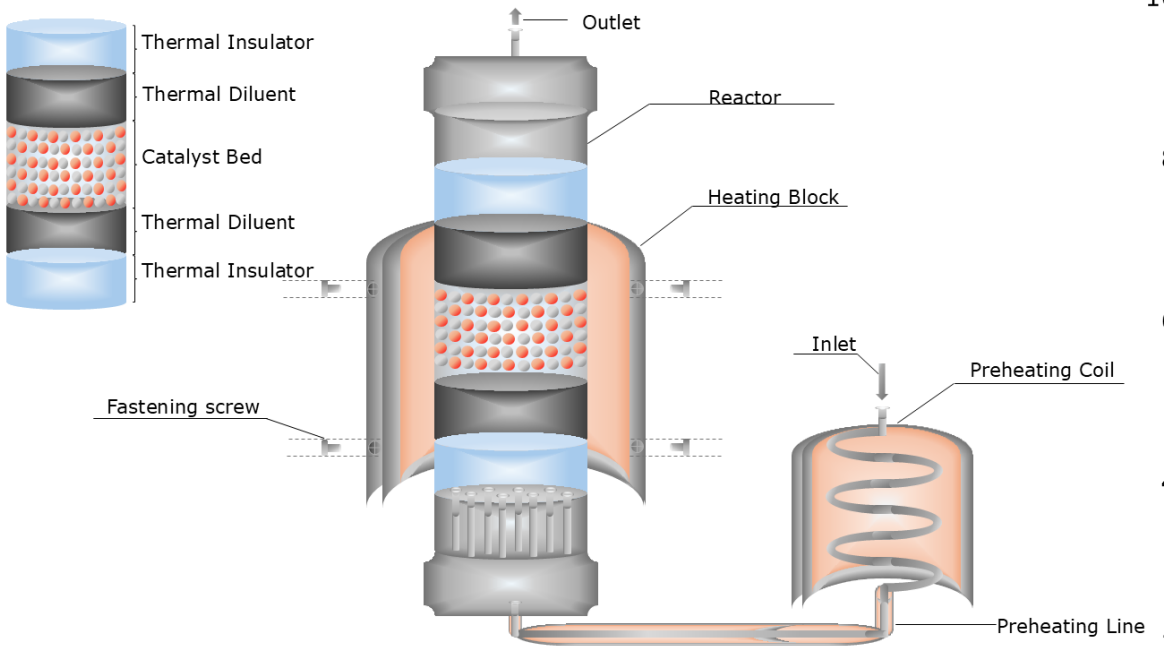
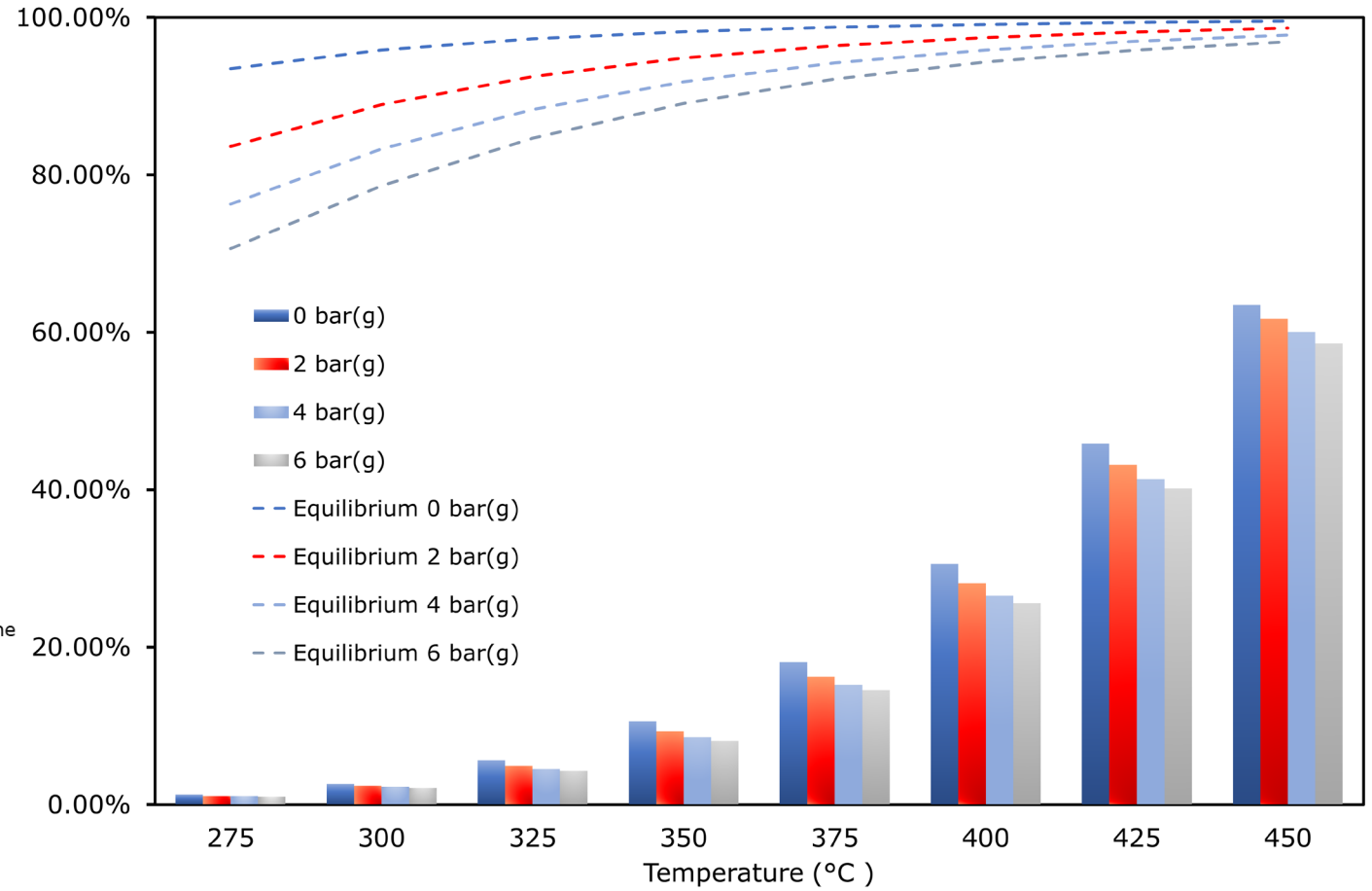
Kinetic Test - Data collection





Kinetic Tests		
Catalyst bed Properties		
Mass Sample	0.1	*g*
Particle size	150-250	*μm*
Catalyst/SiC	1:5	-
Working Conditions		
Feed (NH_3)	100	*Nml* min^{-1}
GHSV	60000	*Nml* $g_{(cat)}^{-1}$ h^{-1}

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Kinetic Fitting Equations

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Mass Balance:

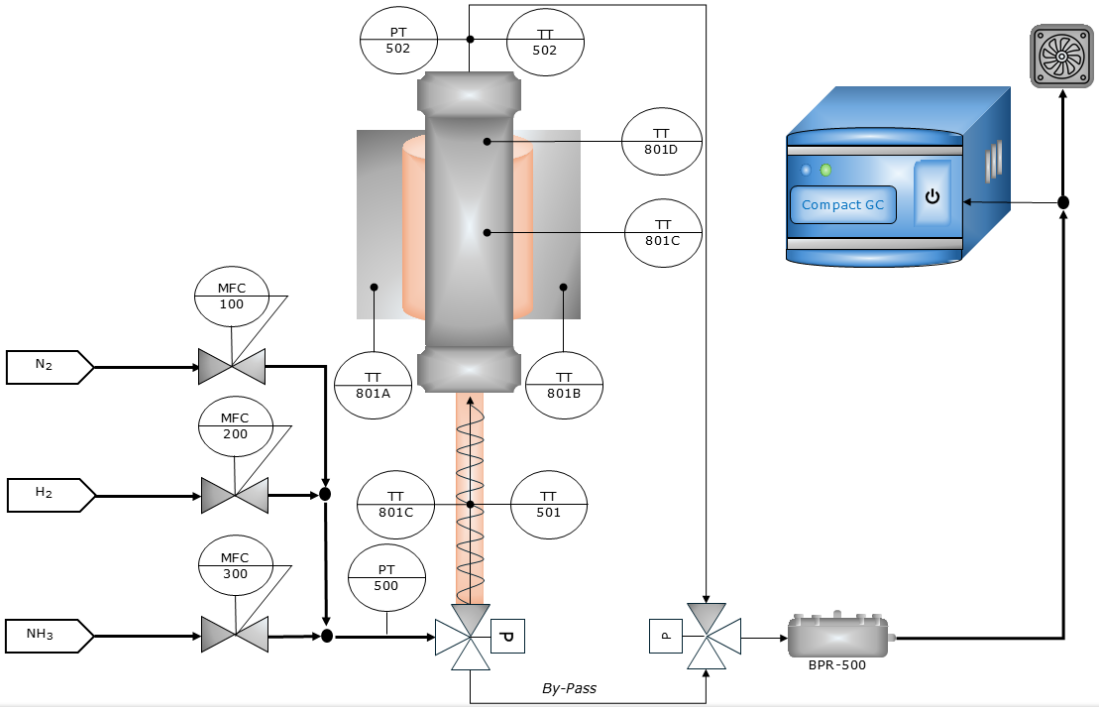
$$\frac{\partial c_{NH_3}}{\partial t} + \frac{\partial}{\partial z}\left(v \cdot c_{NH_3} + \frac{\mathrm{D}_{AB}\partial\left(c_{NH_3}\right)}{\partial z}\right) = r_{NH_3}$$

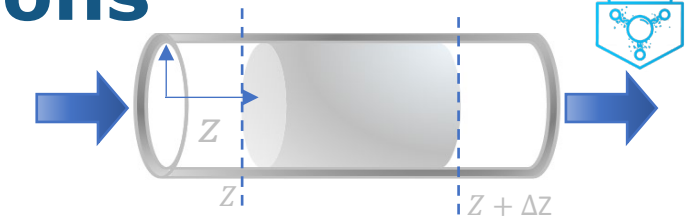
Energy Balance:

$$\left(\varepsilon \cdot \rho_f \cdot Cp_f + (1-\varepsilon) \cdot \rho_s \cdot Cp_s\right)\frac{\partial T}{\partial z} + v \cdot \varepsilon\rho_f \cdot Cp_f \frac{\partial T}{\partial z} - \frac{\partial}{\partial z}\left(\lambda_{a_z}\frac{\partial T}{\partial z}\right) = \dot{\mathrm{H}}_r$$

Considerations:

- ✓ Based on the experimental results the thermal management of the reactor was perfectly kept in Isothermal conditions.





Kinetic Tests		
Catalyst bed Properties		
Mass Sample	0.1	*g*
Particle size (PSD)	150-250	*μm*
Catalyst/SiC	1:5	-
Working Conditions		
Feed (NH_3)	100	*Nml* min^{-1}
GHSV	60000	*Nml* $g_{(cat)}^{-1}$ h^{-1}

Kinetic Law - Temkin Pyzhev	
Temkin Pyzhev	$r_{NH_3} = k\left[\left(\frac{P_{NH_3}^2}{P_{H_2}^3}\right)^{\beta} - \frac{P_{N_2}}{K_{eq}^2}\left(\frac{P_{H_2}^3}{P_{NH_3}^2}\right)^{1-\beta}\right]$
Kinetic law - Langmuir Hinshelwood Kinetic law	
Hp 1:Rate determining step - N Desorption Hp 2:Dominant species on the surface – (N)	$r_{NH_3} = k\left\{\frac{P_{NH_3}{}^2 - \frac{\left(P_{H_2}{}^3 \cdot P_{N_2}\right)}{K_P}}{\left(\sqrt{P_{H_2}{}^3} + \sqrt[6]{K_\sigma \cdot P_{H_2}{}^2}\right)^2}\right\}$
Hp 1:Rate determining step - N Desorption Hp 2:Dominant species on the surface – (H)	$r_{NH_3} = k\left\{\frac{K_P \cdot P_{NH_3}{}^2 - P_{H_2}{}^3 \cdot P_{N_2}}{\left(\sqrt[6]{P_{H_2}{}^3} + \sqrt[6]{K_\sigma \cdot P_{NH_3}{}^2}\right)^6}\right\}$
Hp 1:Rate determining step - H Desorption Hp 2:Dominant species on the surface – (H)	$r_{NH_3} = k\left\{\frac{\frac{K_P \cdot P_{NH_3}{}^2}{P_{N_2}} - P_{H_2}{}^3}{\left(1 + \sqrt[6]{K_\sigma \cdot \frac{P_{NH_3}{}^2}{P_{N_2}}}\right)^6}\right\}$

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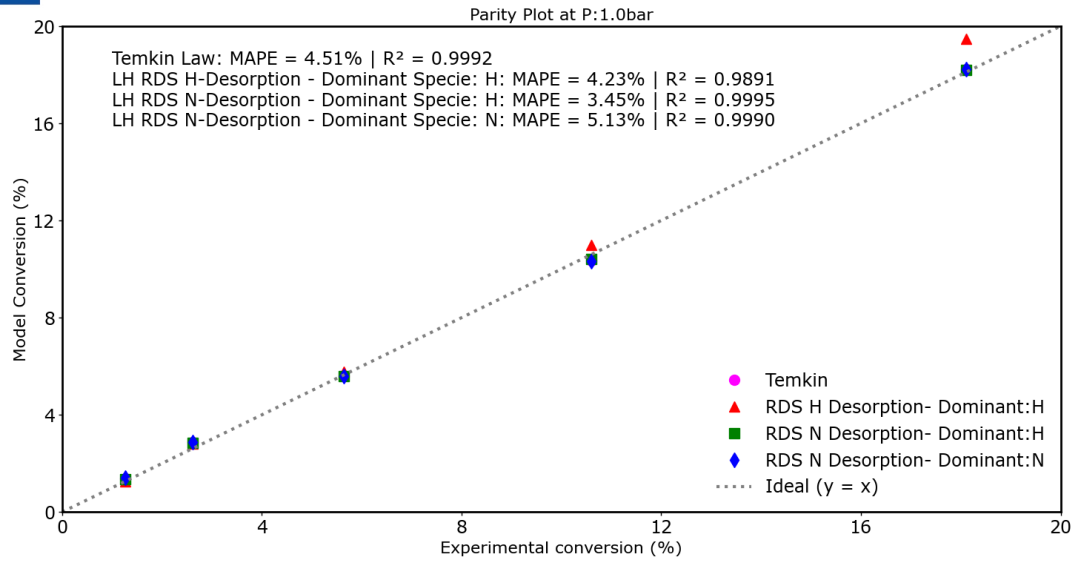
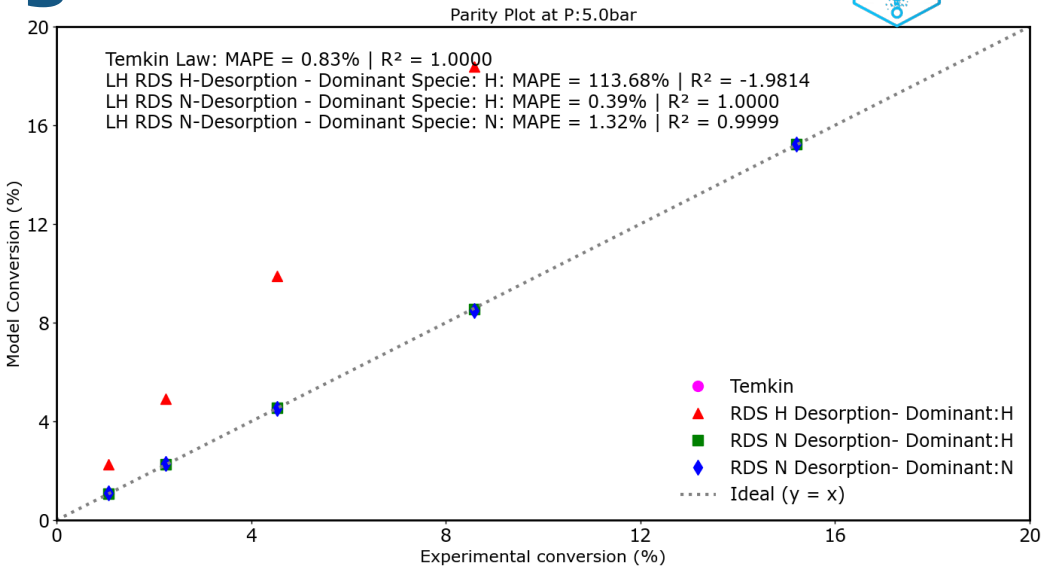
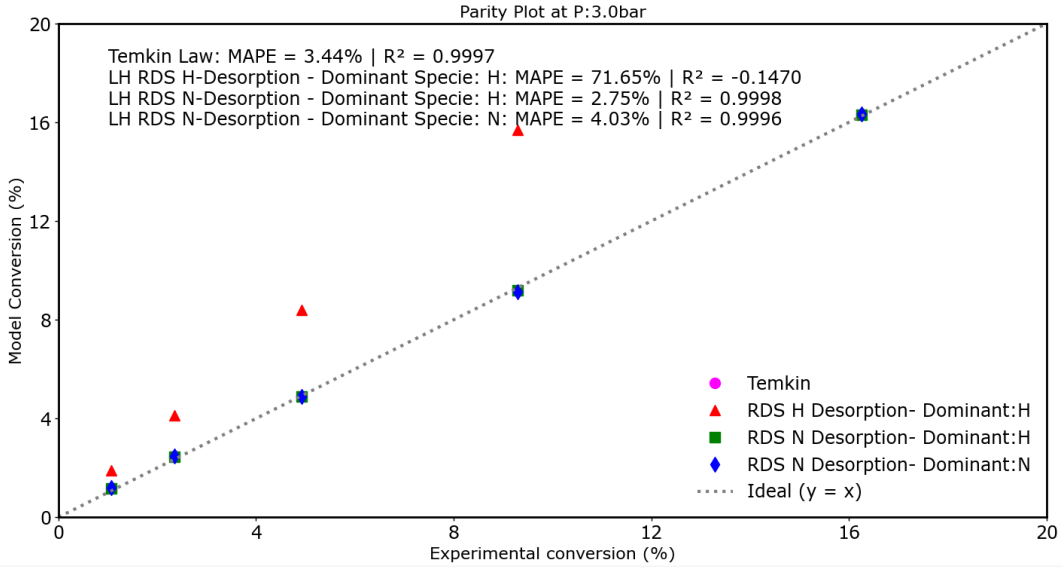
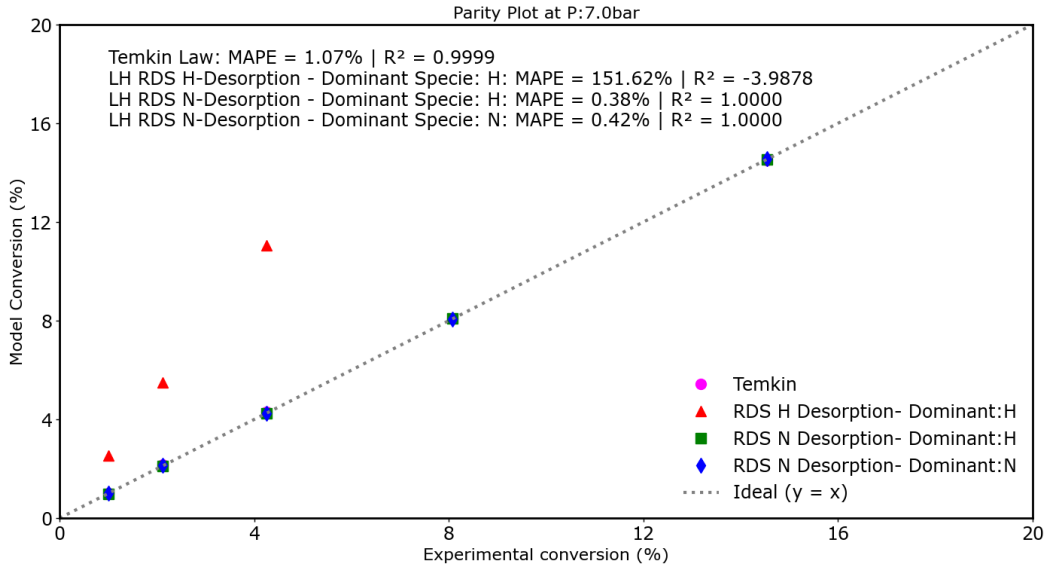
Kinetic model Fitting – Kinetic Tests









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Kinetic model validation: Equations and PBR configuration

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Mass Balance:

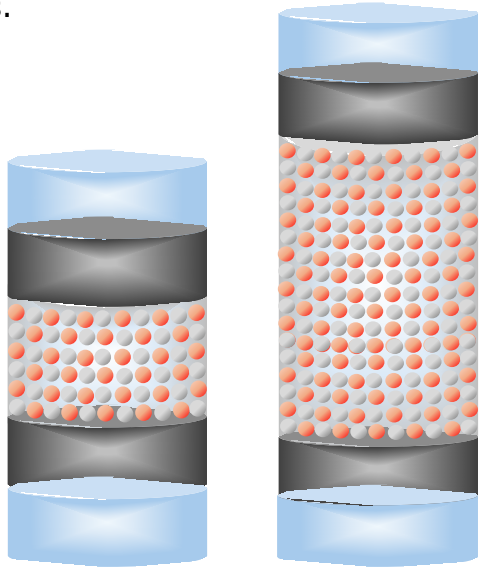
$$\frac{\partial c_{NH_3}}{\partial t} + \frac{\partial}{\partial z}\left(v \cdot c_{NH_3} + \frac{\mathfrak{D}_{AB}\partial\left(c_{NH_3}\right)}{\partial z}\right) = r_{NH_3}$$

Energy Balance:

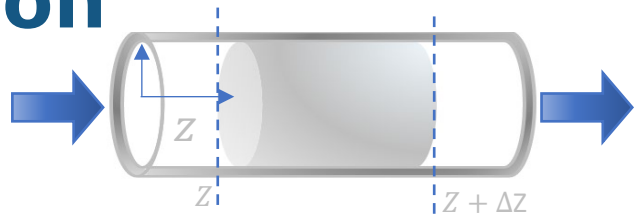
$$\left(\varepsilon \cdot \rho_f \cdot Cp_f + (1-\varepsilon) \cdot \rho_s \cdot Cp_s\right)\frac{\partial T}{\partial z} + v \cdot \varepsilon\rho_f \cdot Cp_f \frac{\partial T}{\partial z} - \frac{\partial}{\partial z}\left(\lambda_{a_z}\frac{\partial T}{\partial z}\right) = \dot{\mathrm{H}}_r$$

Considerations:

- ✓ Not possible keep Isothermal conditions (Axial temperature gradients)
- ✓ Using 1 g of catalyst the reactor length was 10 times bigger than the one used for kinetic tests.



Kinetic Bed *Activity Bed*



Catalyst bed Properties			
Parameter	Activity Test	Kinetic Test	*Unit*
Mass Sample	1	0.1	*g*
Particle size (PSD)	150-250	150-250	*μm*
Catalyst/SiC	1:5	1:5	-
Working Conditions			
Feed (NH_3)	100	100	*Nml min^{-1}*
GHSV	6000	60000	*Nml g$_{(cat)}^{-1}$ h^{-1}*

Kinetic Law - Temkin Pyzhev	
Temkin Pyzhev	$r_{NH_3} = k\left[\left(\frac{P_{NH_3}^2}{P_{H_2}^3}\right)^{\beta} - \frac{P_{N_2}}{K_{eq}^2}\left(\frac{P_{H_2}^3}{P_{NH_3}^2}\right)^{1-\beta}\right]$
Kinetic law - Langmuir Hinshelwood Kinetic law	
Hp 1:Rate determining step - N Desorption Hp 2:Dominant species on the surface – (N)	$r_{NH_3} = k\left\{\frac{{P_{NH_3}}^2 - \frac{\left({P_{H_2}}^3 \cdot P_{N_2}\right)}{K_P}}{\left(\sqrt{{P_{H_2}}^3} + \sqrt[6]{K_\sigma \cdot {P_{H_2}}^2}\right)^2}\right\}$
Hp 1:Rate determining step - N Desorption Hp 2:Dominant species on the surface – (H)	$r_{NH_3} = k\left\{\frac{K_P \cdot {P_{NH_3}}^2 - {P_{H_2}}^3 \cdot P_{N_2}}{\left(\sqrt[6]{{P_{H_2}}^3} + \sqrt[6]{K_\sigma \cdot {P_{NH_3}}^2}\right)^6}\right\}$

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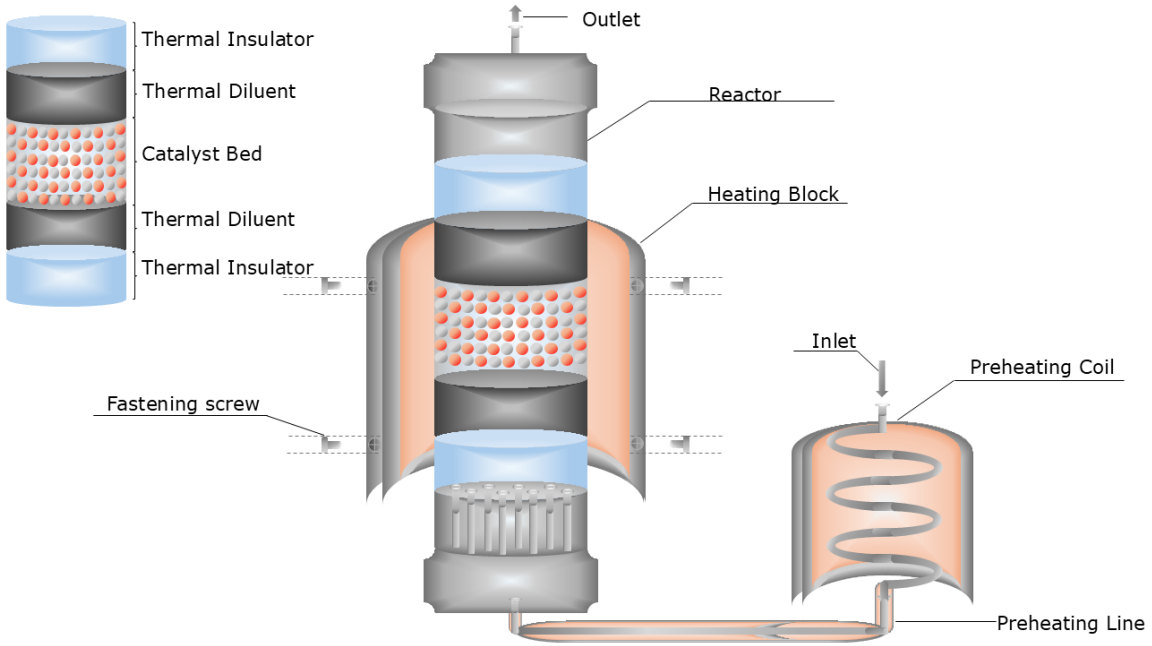
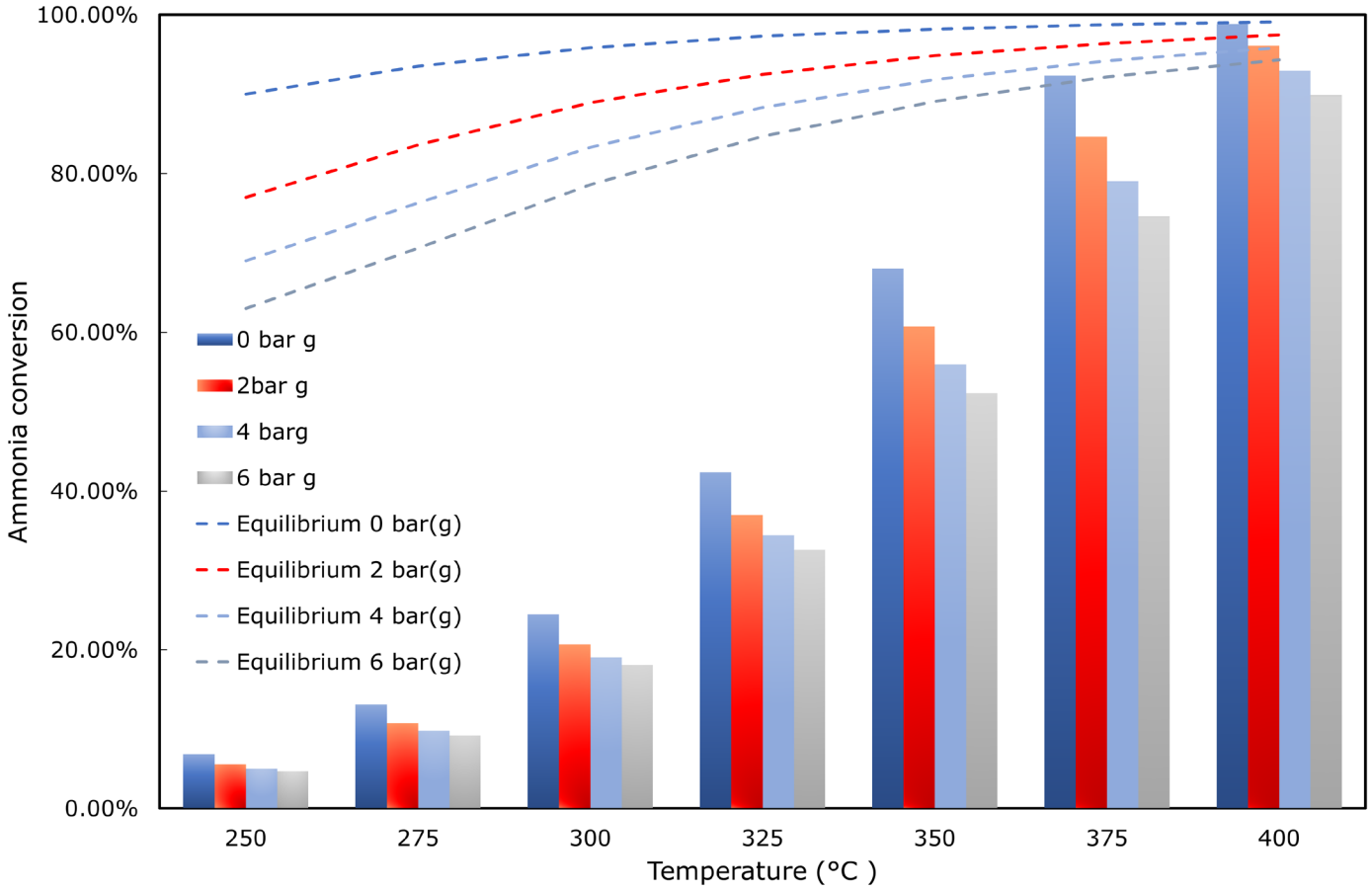
Kinetic model validation – Activity Tests



Activity Tests		
Catalyst bed Properties		
Mass Sample	1	*g*
Particles size	150-250	*μm*
Catalyst/SiC	1:5	-
Working Conditions		
Feed (NH_3)	100	*Nml* min^{-1}
GHSV	6000	*Nml* $g_{(cat)}^{-1}$ h^{-1}



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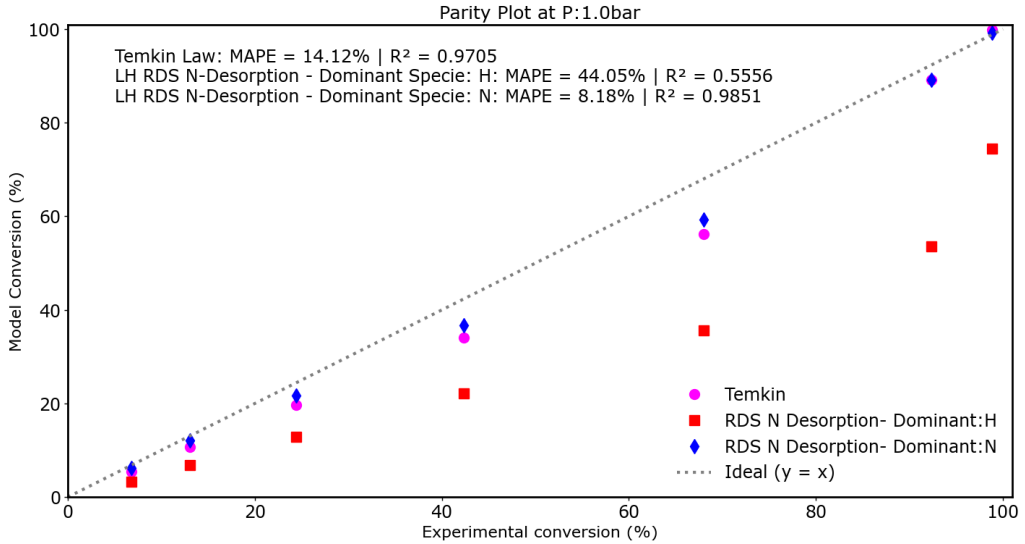
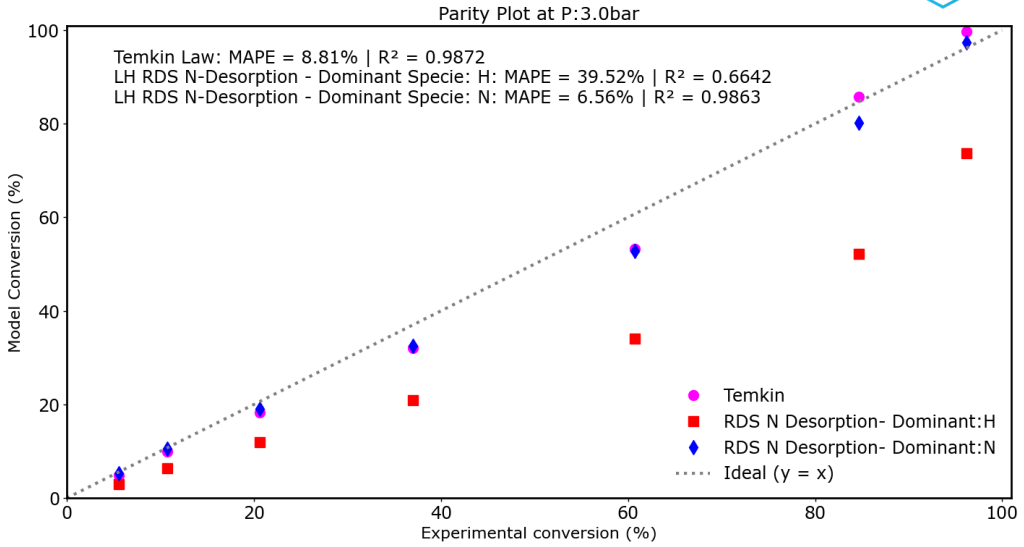
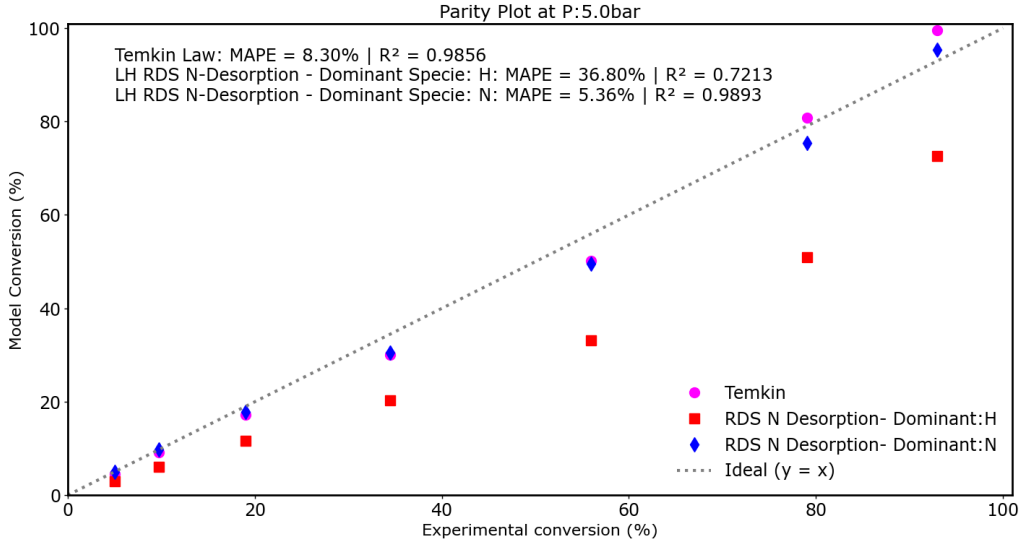
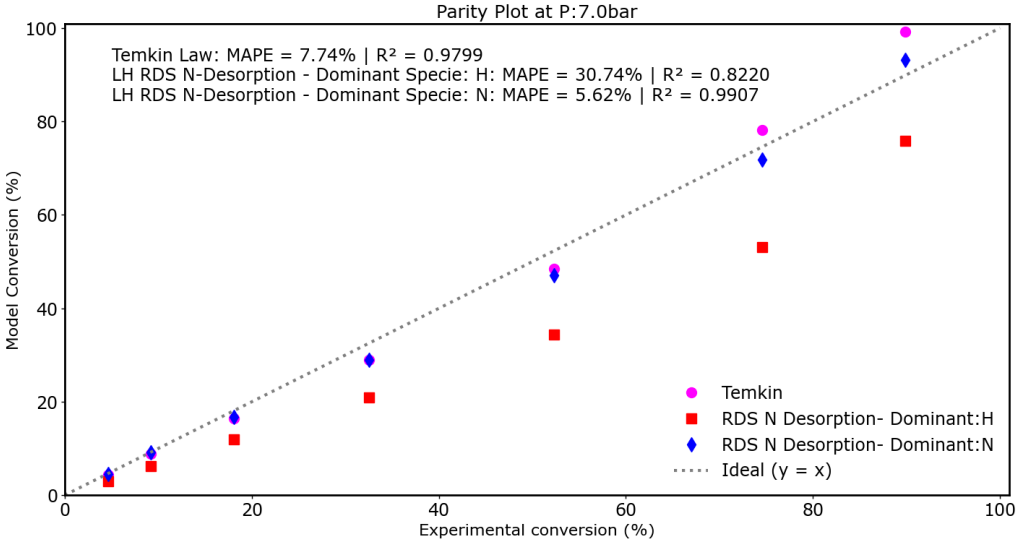
Kinetic model validation – Activity Tests









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Reactor Scale up

Objective of Reactor scale up :

- ✓ Evaluate how accurately the 1D-reactor model with the implemented kinetics could predict the experimental data obtained in a different and larger reactor block
- ✓ Enable the integration of the Pd based membrane inside the reactor unit

Experimental:

- ❖ After validating the kinetic model, an experimental campaign was carried out in a scaled-up PBR and PBMR
- ❖ The reactor was loaded with a catalyst mass 100 times larger than that used in the kinetic tests, and 10 times larger than that used during the validation section.
- ❖ Experimental Data were collected at 4 bar in a temperature range 350 – 425 °C

Scale up PBR Modelling:

- ❖ The experimental data obtained from the scaled-up reactor configuration were used to further assess model reliability.
- ❖ The validated kinetics were implemented in a 1D Plug Flow Reactor (PBR) model to reproduce the experimental results from the scaled PBR

PBMR Modelling:

- ❖ Permeation validation
- ❖ Permeation model integration in PBMR model

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Scaled-up Packed Bed Reactor (PBR)

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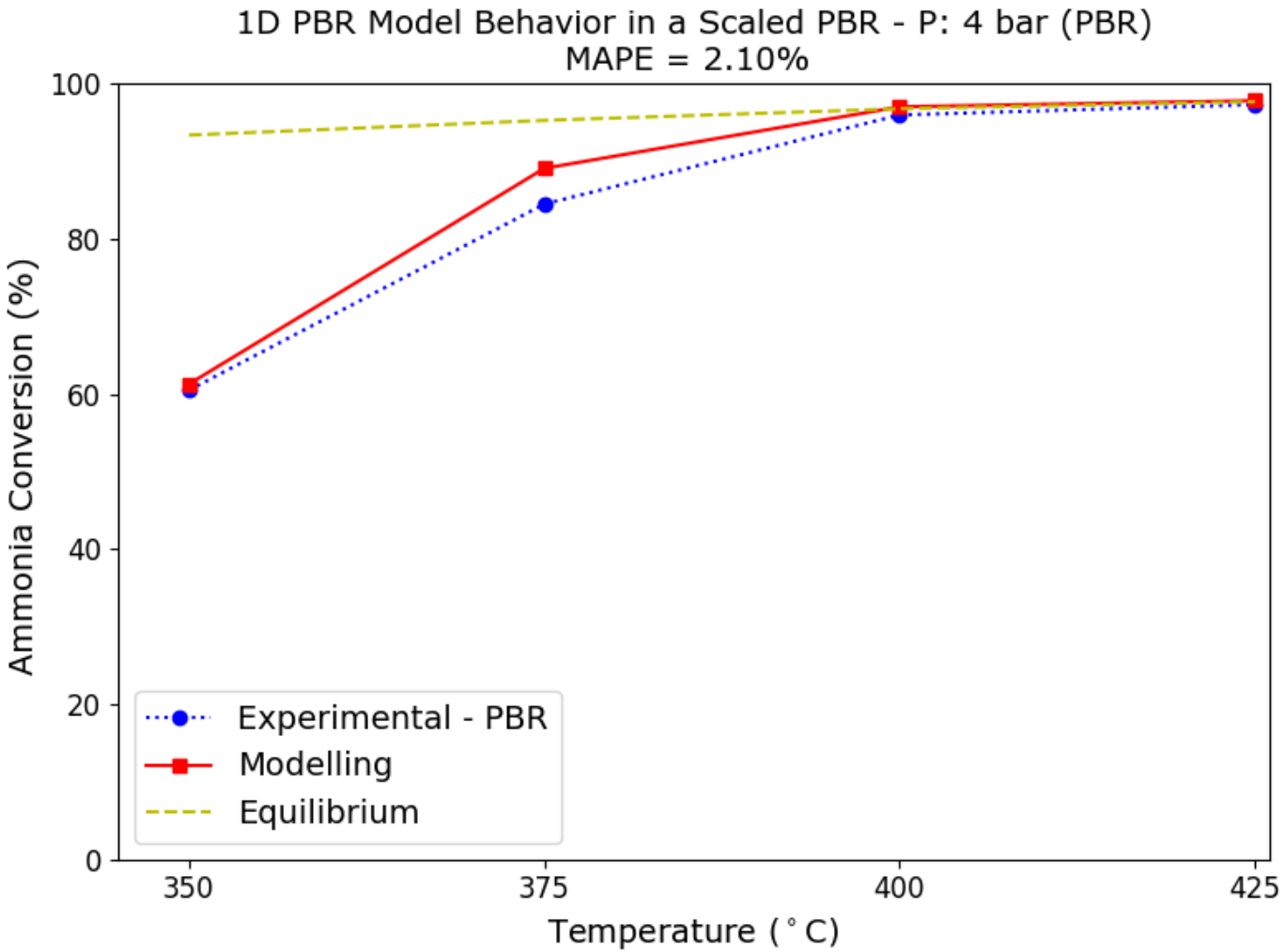

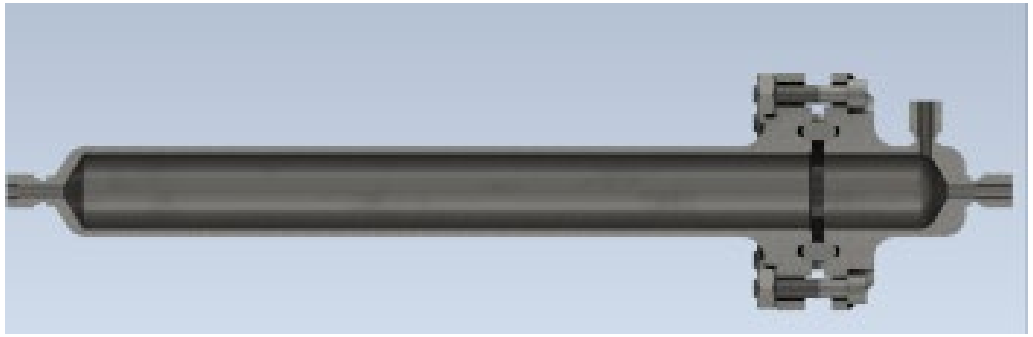

Catalyst bed Properties		
Mass Catalyst	10	g
Particles size	500-1000	µm
Catalyst/SiC	1:17	-
Working Conditions		
Pressure	4	bar
Temperature range	350-425	°C
GHSV	6000	Nml $g_{(cat)}^{-1}$ h^{-1}
$T_{(Skin)}$	$T_{(bed)}$+10	°C

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Permeation modelling

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Balance Equations

Mass Balance:

$$\frac{\partial c_{NH_3}}{\partial t} + \frac{\partial}{\partial z}\left(\nu \cdot c_{NH_3} + \frac{\mathfrak{D}_{AB}\partial\left(c_{NH_3}\right)}{\partial z}\right) = r_{NH_3} \rightarrow \frac{\partial\left(\nu \cdot c_{NH_3}\right)}{\partial z} = k\left\{\frac{{P_{NH_3}}^2 - \frac{\left({P_{H_2}}^3 \cdot P_{N_2}\right)}{K_P}}{\left(\sqrt{{P_{H_2}}^3} + \sqrt[6]{K_\sigma \cdot {P_{H_2}}^2}\right)^2}\right\}$$

Energy Balance:

$$\left(\varepsilon \cdot \rho_f \cdot Cp_f + (1-\varepsilon) \cdot \rho_s \cdot Cp_s\right)\frac{\partial T}{\partial z} + v \cdot \varepsilon\rho_f \cdot Cp_f \frac{\partial T}{\partial z} - \frac{\partial}{\partial z}\left(\lambda_{a_z}\frac{\partial T}{\partial z}\right) = \dot{\mathrm{H}}_r$$

$$\rightarrow v \cdot \varepsilon\rho_f \cdot Cp_f \frac{\partial T}{\partial z} = \dot{\mathrm{H}}_r$$

Richardson Law:

$$J_{H_2} = \Pi_{(T)} \cdot \left({P_{H_2}}_{(Retentate)}^{\ n} - {P_{H_2}}_{(Permeate)}^{\ n}\right)$$

$$\rightarrow \Pi_{(T)} = \Pi_{(0)} \cdot e^{\left(\frac{E_a}{RT}\right)}$$

Feed flow rate		
F_0	0.074358	mmol·s^{-1}
Reactor Internal Diameter (Di)		
D_i	1.4	cm
$D_{(mem)}$	0.7	cm
Particle Size Distribution (PSD)		
PSD	150-250	µm
Catalyst Density		
$\rho_{(cat)}$	7.3697	g ·cm^{-3}
Void Fraction		
ε	0.5763	$V_{(Void)} \cdot V_{(cat)}^{-1}$

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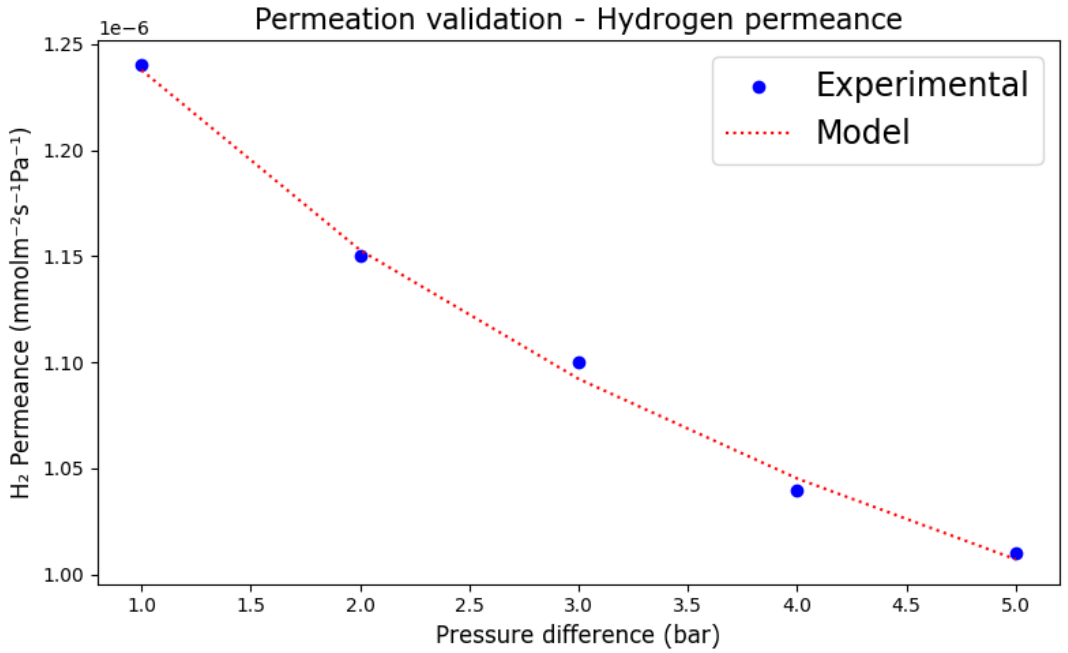
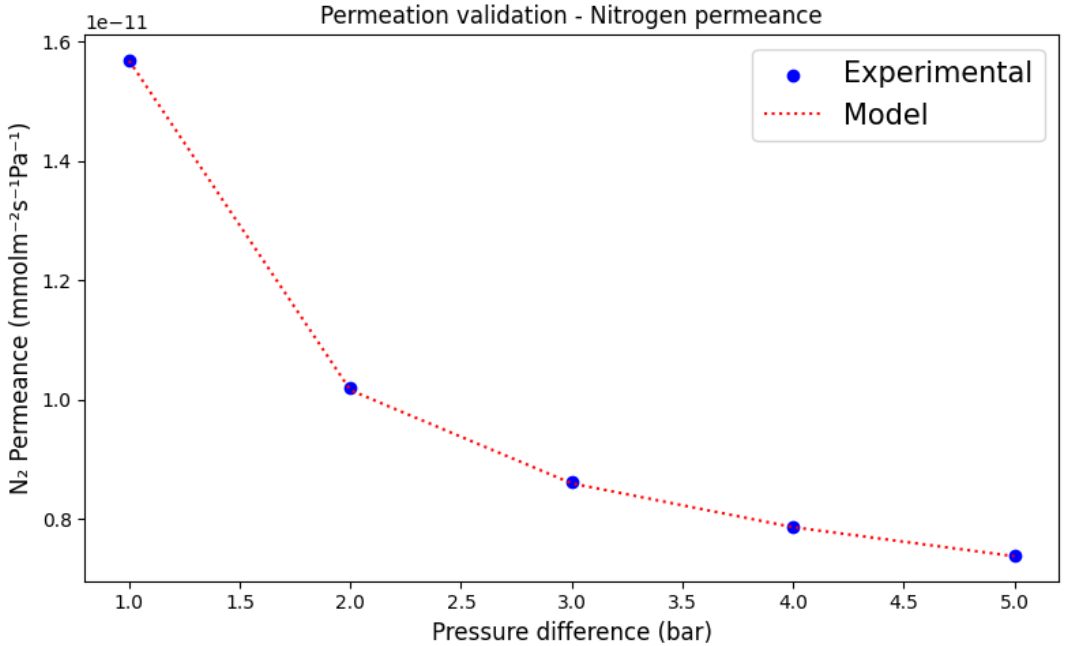
Permeation Validation

Permeance Validation using Existing Pd-Based Membrane Permeation Data Set





The permeance of ammonia (P_{NH3}) can be calculated using the equation below obtained from the work of B.Lundin [2]

$$P_{NH3} = P_{N2}.\sqrt{\frac{M_{N2}}{M_{NH3}}}$$

- M_{N2} – molecular weight of nitrogen (g mol^{-1})
- M_{NH3} – molecular weight of Ammonia (g mol^{-1})
- P_{N2} – permeance of Nitrogen (mol s^{-1} m^{-2} Pa^{-1})

[2]. Sean-Thomas B. Lundin, "Modelling of an ammonia decomposition membrane reactor including purity with complex geometry and non-isothermal behavior", Journal of Membrane Science 693 (2024) 122345

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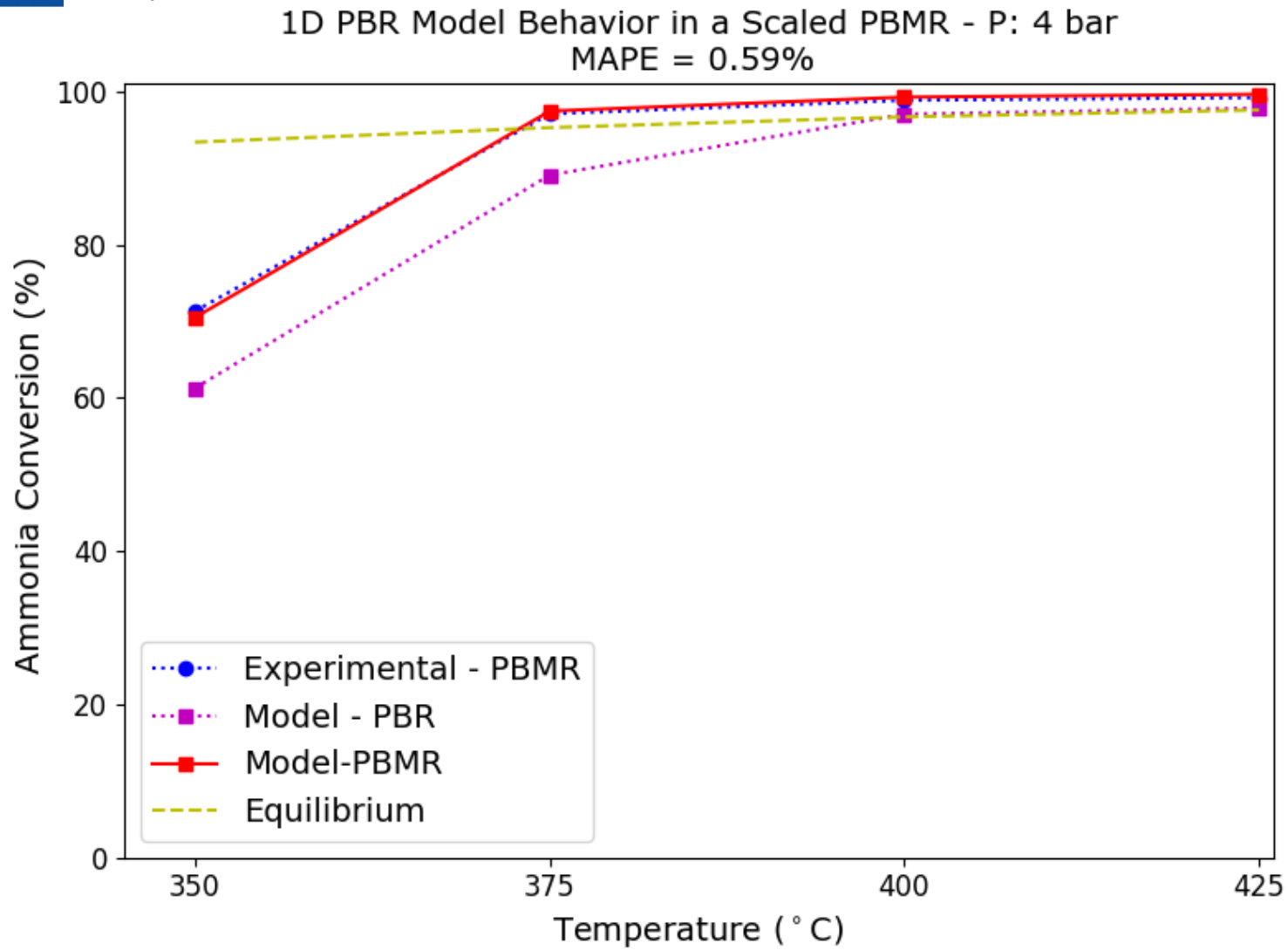
Packed Bed Membrane Reactor



Catalyst bed Properties		
Mass Catalyst	10	g
Particles size	500-1000	µm
Catalyst/SiC	1:17	/
Working Conditions		
Pressure	4	bar
Temperature range	350-425	°C
GHSV	6000	Nml $g_{(cat)}^{-1}$ h^{-1}
$T_{(Skin)}$	$T_{(Skin)[PBR]}$+20	°C
Membrane		
Selective Layer		
Pd-Ag		
synthesis method	electroless plating	
Al_2O_3Support		
Pore Size Distribution	100	nm
Protective layer		
Al_2O_3-YSZ		
Synthesis Method	dip-coating	
Geometry		
D_i	10	mm
D_e	14	mm

[1] A.Gaetano, "Low-temperature ammonia decomposition in a packed bed membrane reactor", PhD Thesis

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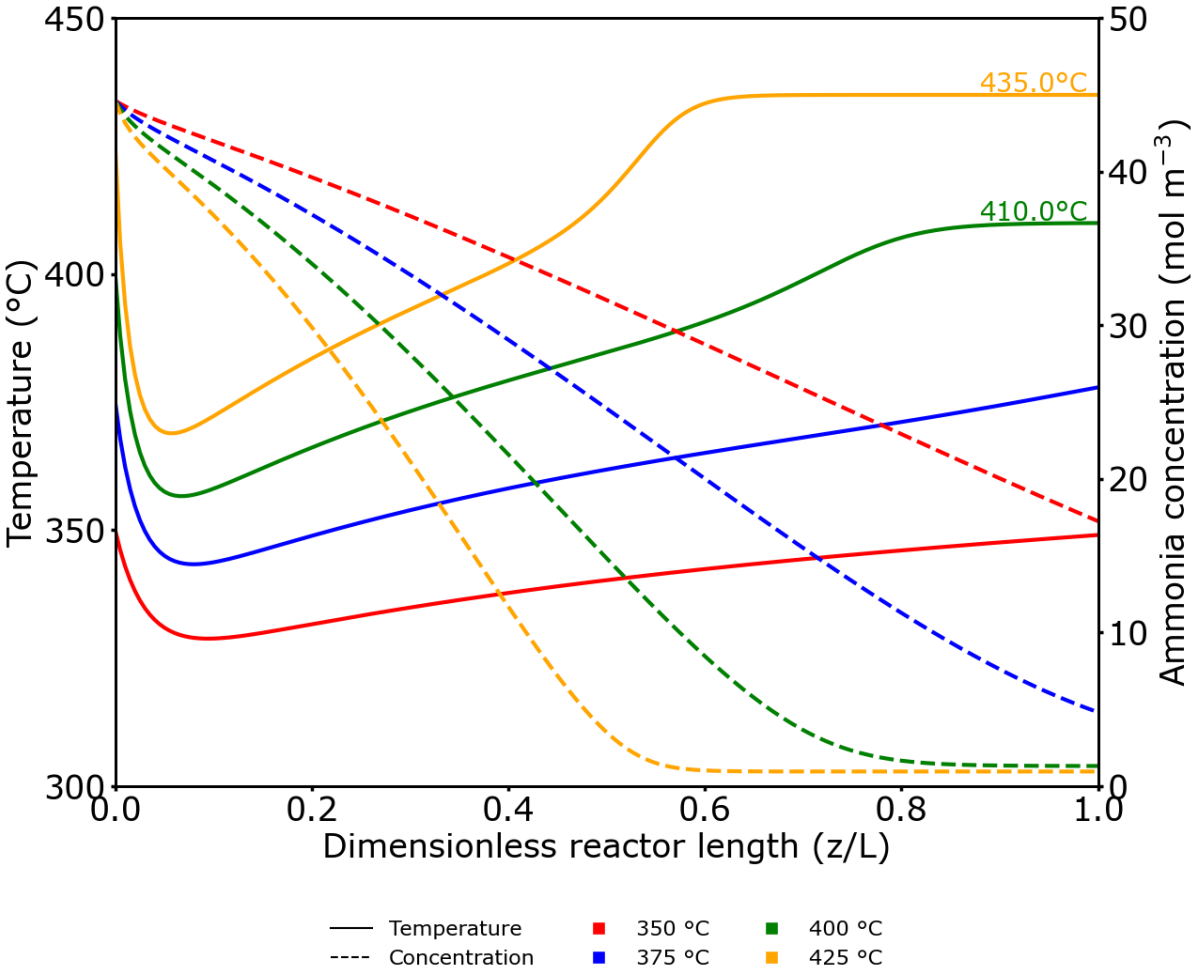
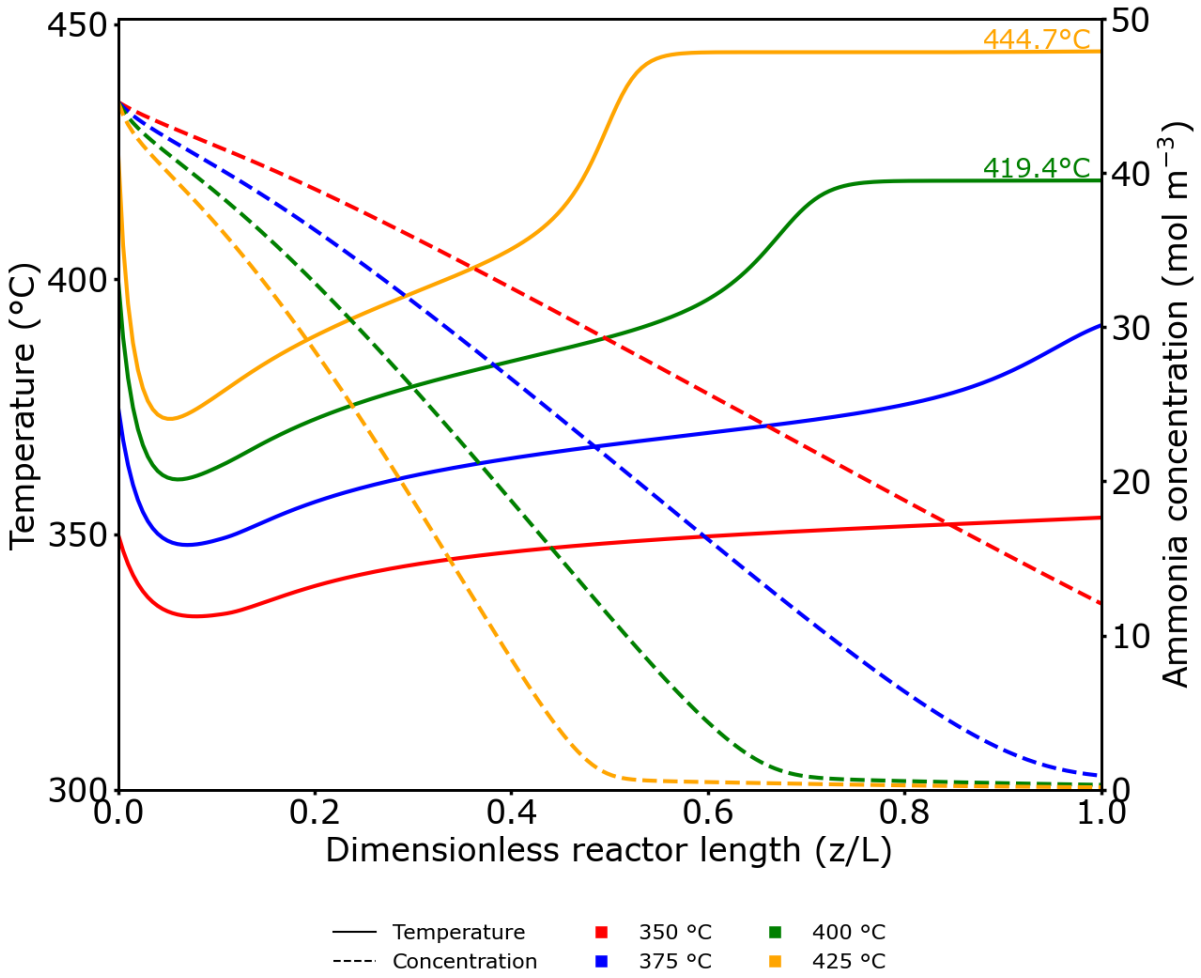
PBR and PBMR Temperature Profile comparison





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PBR and PBMR concentration profile comparison

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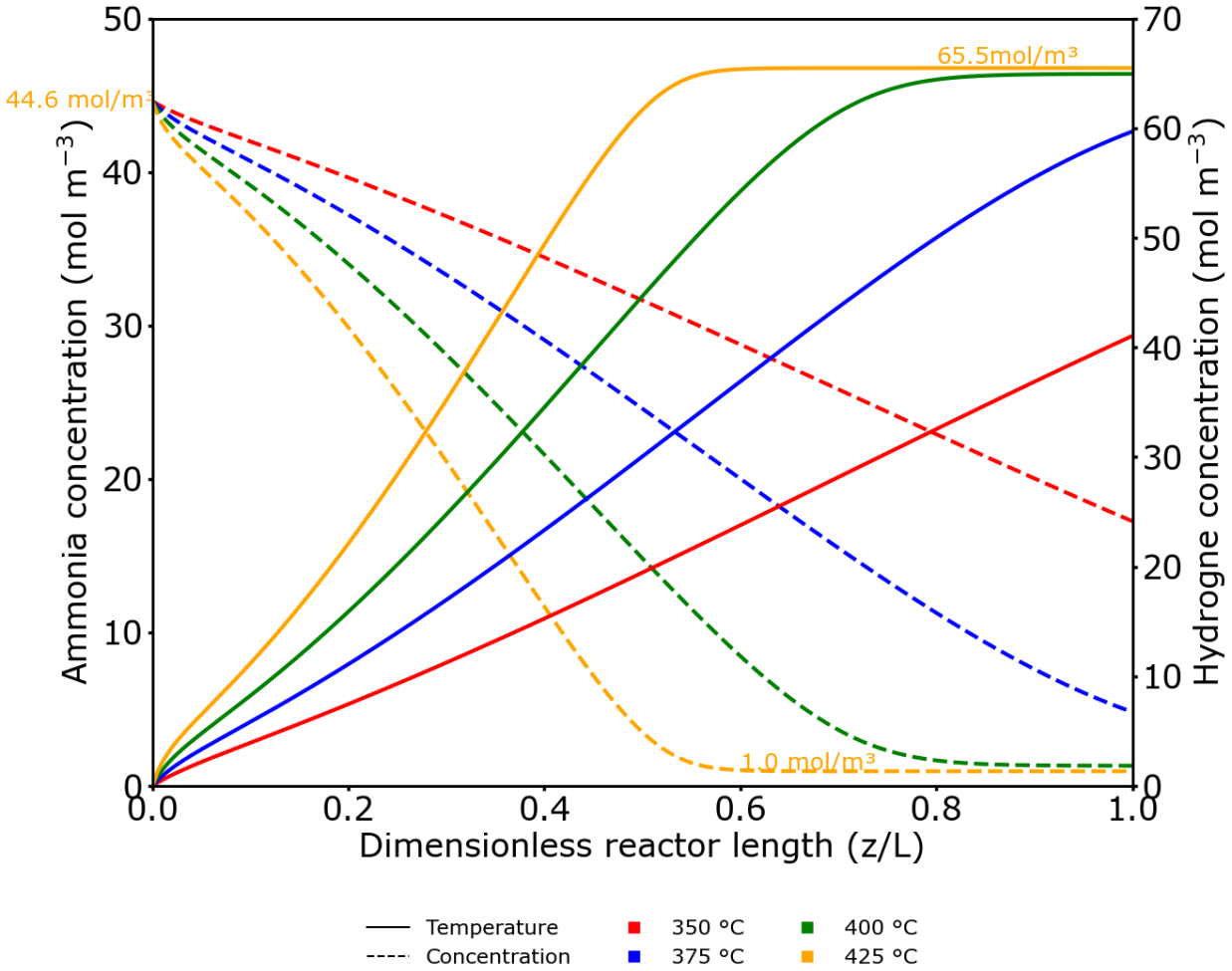

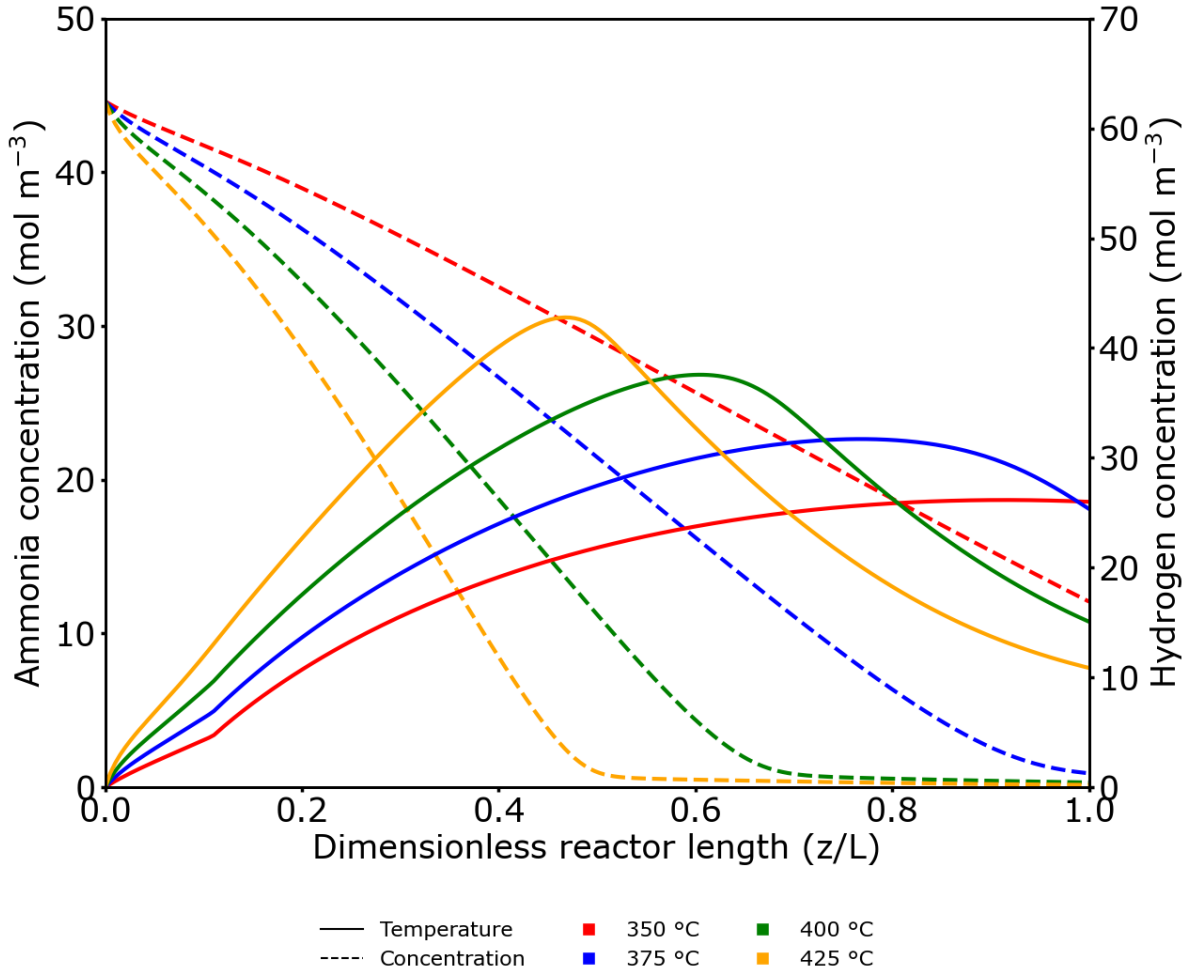

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Conclusions & Outlook

Conclusions:

Experiments

- ✓ A custom-made reactor unit was design for the catalytic tests
- ✓ Experimental campaign on custom made Ruthenium catalyst was assessed
- ✓ Experimental campaign on custom made Pd- based membrane was assessed

Modelling

- ✓ Kinetic fitting based on experimental results was made and a custom-made kinetic law (Langmuir –Hinshelwood) was obtained
- ✓ Kinetic model validation using an independent set of data was successfully carried out
- ✓ Permeation model development and validation using indipendent set of data was successfully carried out
- ✓ PBR scaled up 1D model development successfully assessed
- ✓ PBMR scaled up 1D model development successfully assessed

Outlook:

- ❖ Custom made multi layer permeation model development on Pd base membrane

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ADVANCED **PO**WER CONVERSION TECHNO**L**OGIES
BASED ON **O**NBOARD AMMONIA CRACKING
THROUGH NOVEL MEMBRANE REACTORS

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ICCMR-17
Nanjing, 27-10-2025

THANK YOU FOR YOUR ATTENTION!

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