Modeling and simulation of CO_2 methanation in a fixed-bed reactor: Evaluation of 1D pseudo-homogeneous approaches.

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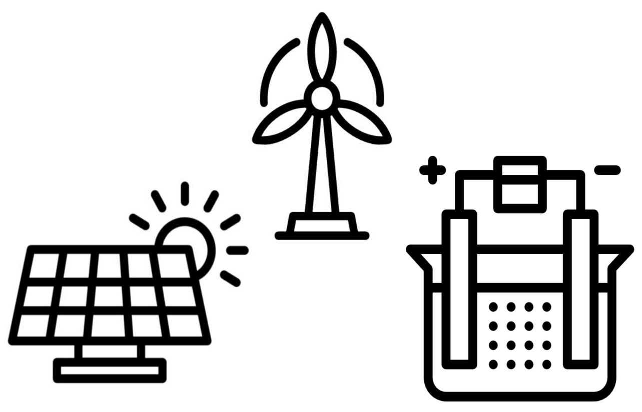
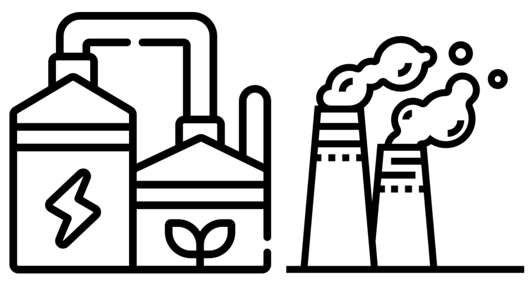
Introduction

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$



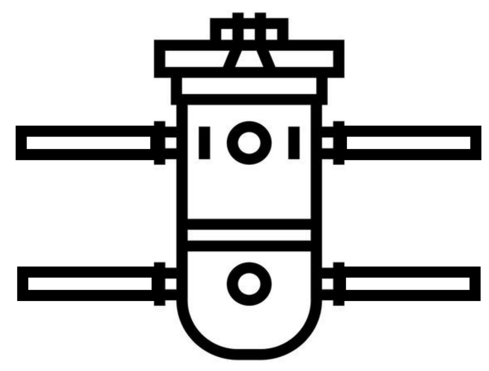
Renewable H_2 production

Hydrogen is produced via water electrolysis powered by surplus renewable electricity. This approach enables the storage of renewable energy in form of chemical vectors, such us hydrogen and subsequently biomethane.



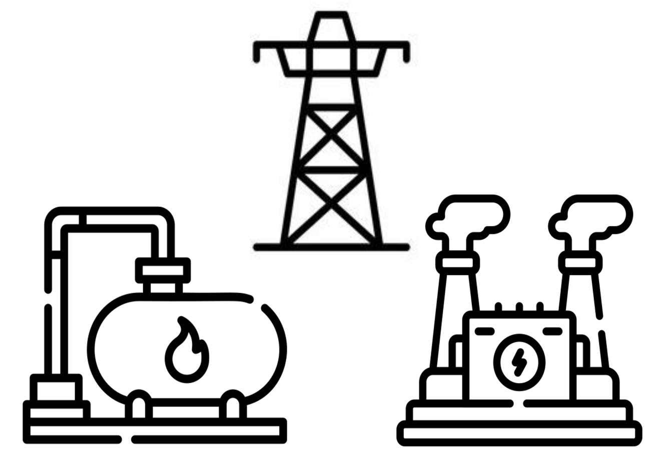
CO_2 mitigation

Flue gases or biogas can serve as CO_2 sources due to their high CO_2 content. Carbon capture technologies help to reduce pollution by limiting its release to the atmosphere.



Methanation

Hydrogen and carbon dioxide combine to produce methane and water, via *Sabatier* reaction. After water removal, Synthetic Natural Gas (SNG) can be produced, which is a higher-energy-density (per volume) product.



Storage and power generation

The resulting Synthetic Natural Gas (or Biomethane due the natural origin of CO_2) can be stored or injected into existing natural gas net infrastructure, enabling integration with current energy systems and supporting long-term energy supply.

Methodology

Experimental setup

- **Reactor: lab-scale, isothermal fixed-bed (12 cm length × 13 mm I.D.), validated under kinetic control (no transport limitations).**
- **Catalyst: 0.5 g Ni_3-Fe supported on γ-Al_2O_3, diluted with 10 g γ-Al_2O_3. Pretreatment consists in a reduction at 500 °C for 2 h in 50% H_2.**
- **Operating Conditions: temperature: 400–250 °C (-25 °C steps every 50 min). 250 mL/min (STP) and molar ratios (H_2:CO_2) from 2:1 to 6:1 with inert (10 vol%).**
- **Measured conversion, selectivity, yield, and reaction rate. Parameters used to fit a *Langmuir–Hinshelwood* expression using *Excel*® and *MATLAB*®.**

Temperature correction

Due to thermal gradients from oven limitations, a blank run with γ-Al_2O_3 was conducted. Resulting temperature profiles were used to correct model inputs.

Modeling approaches (1D, non-isothermal, without radial dispersion)

Ideal Pseudo-homogeneous plug-flow model (Eq. 1-2). Solved with *ode15s*.

Mass balance

$$u_S \frac{dC_A}{dz} = \rho_B r_A \quad (Eq. 1)$$

Energy balance

$$\rho_f u_S c_p \frac{dT}{dz} = (-\Delta H)\rho_B r_A - \frac{4U_w}{\emptyset_t}(T - T_w) \quad (Eq. 2)$$

Pseudo-homogeneous plug-flow model with axial dispersion (Eq. 3-4). Solved with *bvp4c* using Danckwerts-type boundary conditions.

Mass balance

$$\varepsilon_B D_{eff,A} \frac{d^2C_A}{dz^2} - u_S \frac{dC_A}{dz} = \rho_B r_A \quad (Eq. 3)$$

Energy balance

$$\lambda_{eff} \frac{d^2T}{dz^2} - \rho_f u_S c_p \frac{dT}{dz} = (-\Delta H)\rho_B r_A - \frac{4U_w}{\emptyset_t}(T - T_w) \quad (Eq. 3)$$

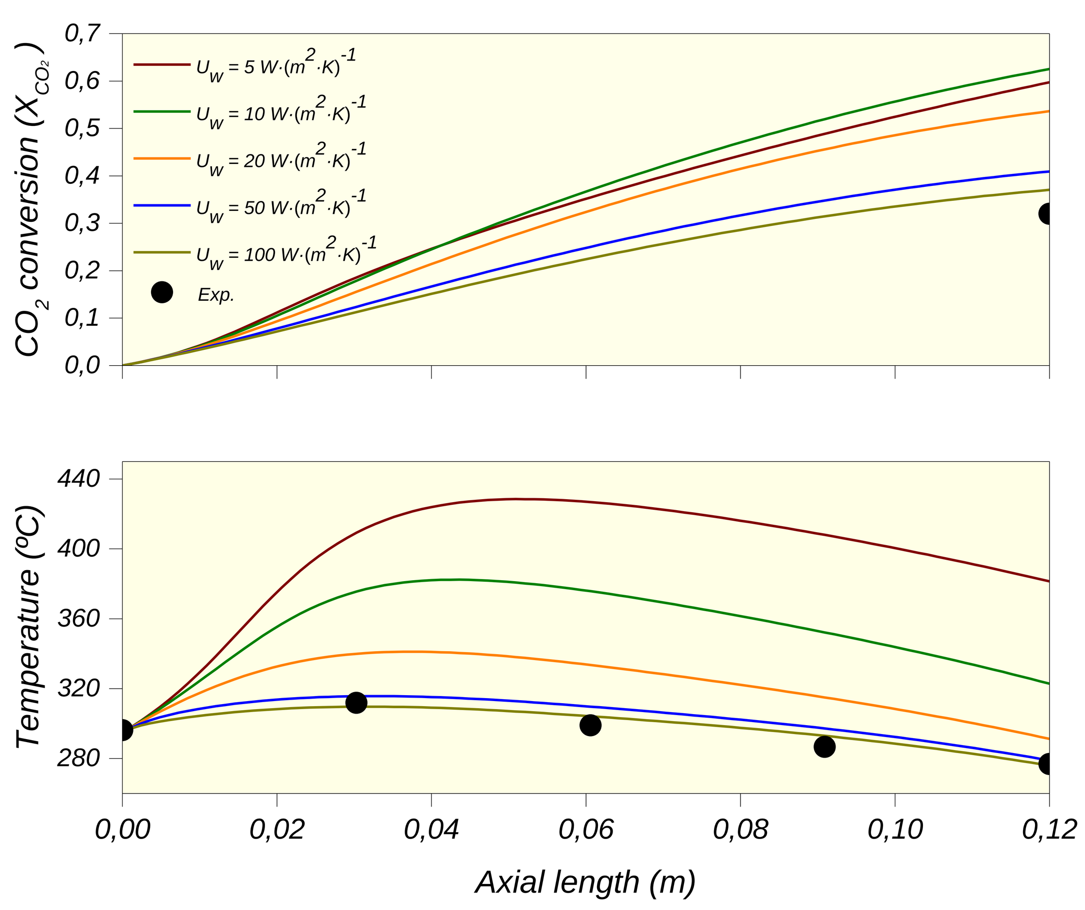


Figure 1: *Effect of overall heat transfer coefficient, U_w*

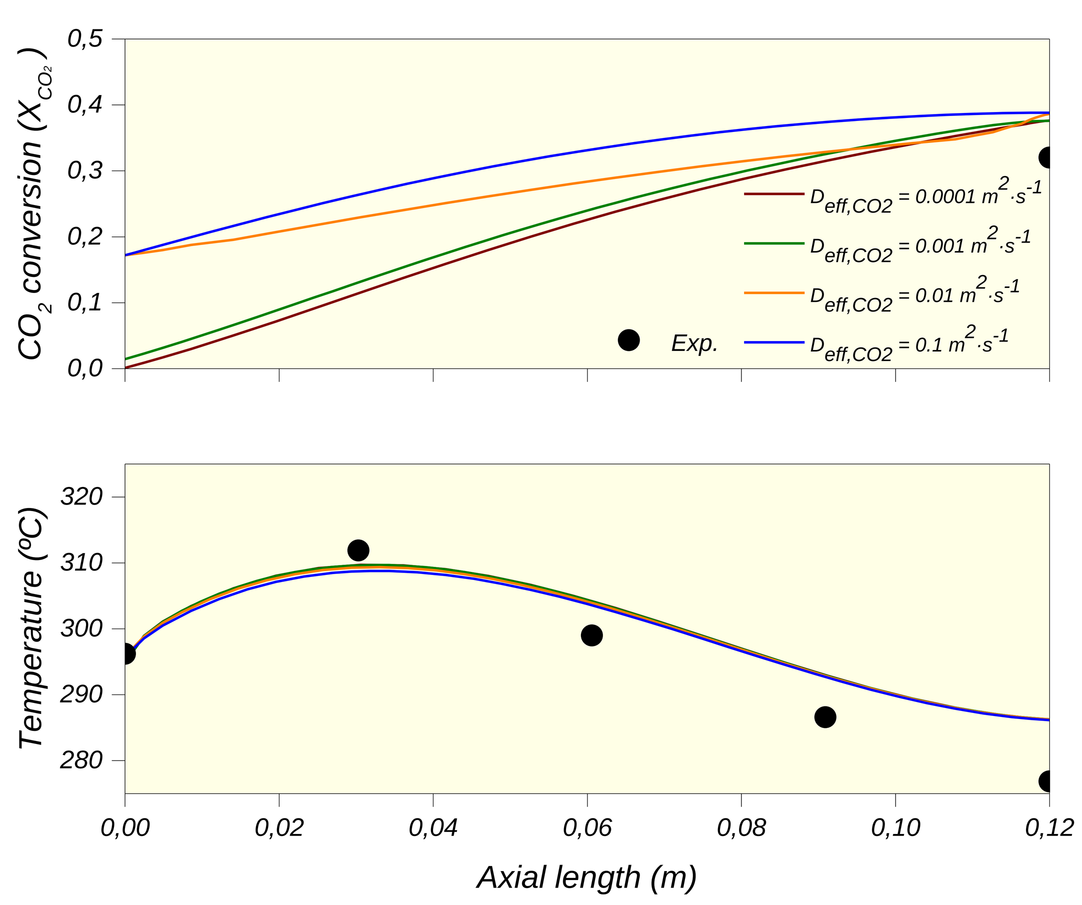


Figure 2: *Effect of axial mass dispersion coefficient, $D_{eff_{CO_2}}$*

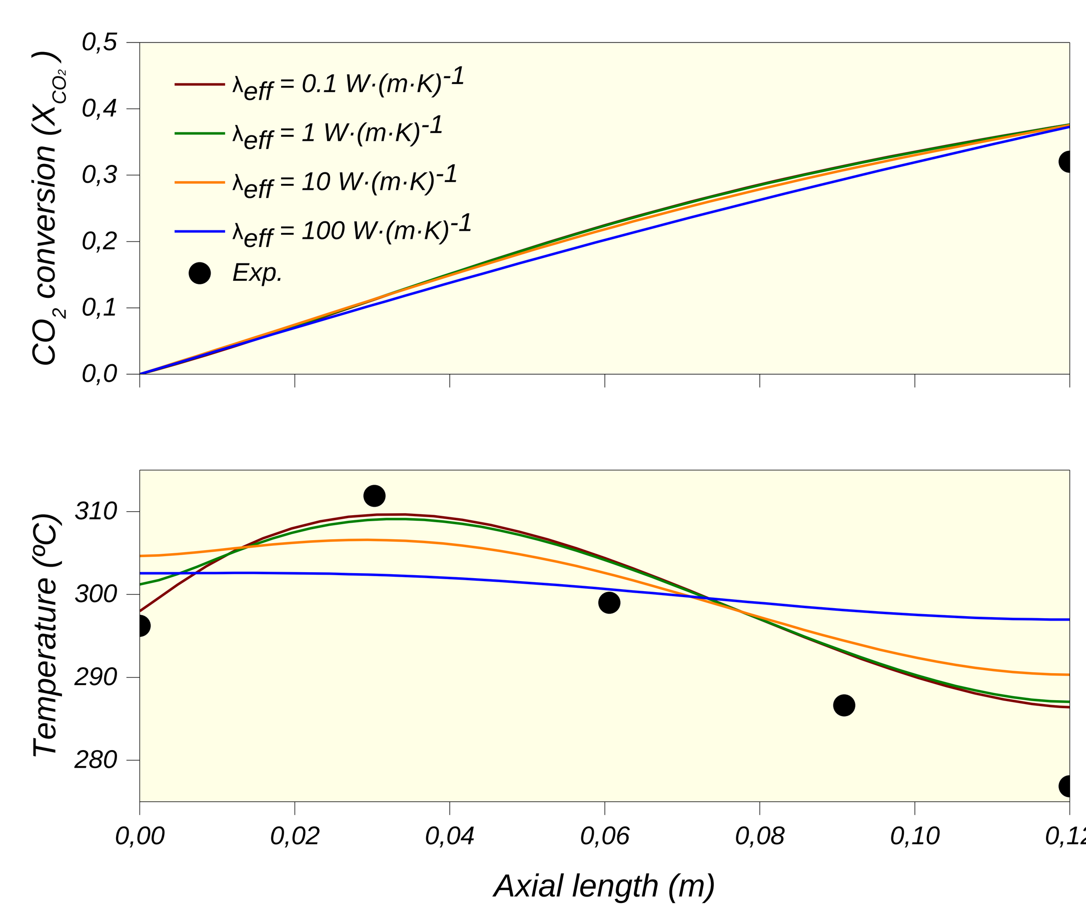


Figure 3: *Effect of effective thermal conductivity, λ_{eff}*

Results and Conclusions

Effect of Heat Transfer Coefficient (U_w). Higher U_w values ≈100 W/(m²•K):

- Improve thermal regulation.
- Reduce hot spots and smooth axial temperature profiles.
- Match experimental temperature trends.
- Slightly decrease conversion due to excessive heat removal.

Effect of Axial Mass Dispersion (D_{eff}). Influences conversion, but not temperature. Higher D_{eff}:

- Promotes back-mixing.
- Boosts conversion near inlet.
- Smooths overall conversion profile.

Effect of Effective Thermal Conductivity (λ_{eff}). Affects temperature profile, but not conversion. Lower λ_{eff} values:

- Provide best fit to experimental temperature drop.
- Control hot spot location and intensity.

Key Insights

- **Axial dispersion significantly alters conversion trends**
- **Thermal conductivity governs temperature shaping**
- **Proper parameter tuning (U_w, D_{eff}, λ_{eff}) is essential for accurate model calibration**

References

[1] SANZ-MONREAL, P., MERCADER, V.D., DURÁN, P., FRANCÉS, E., HERGUIDO, J., PEÑA, J.A. Modelado cinético para la metanación de CO_2 sobre un catalizador Ni_3Fe/Al_2O_3., Jornada de Jóvenes Investigadores del I3A 12 (2024), doi: 10.26754/jjii3a.202410693.

[2] FROMENT, G. F. Analysis and Design of Fixed Bed Catalytic Reactors, (1972), pp. 1-55. doi: 10.1021/ba-1972- 0109.ch001.

Acknowledgements

Research funded by MICIU (Spanish *Ministerio de Ciencia, Innovación y Universidades*), *Agencia Estatal de Investigación* (AEI) project **PID2022-136947OB-I00** and *European Union Next Generation* **PRTR-C17.I1 Task LA4.A1**. The consolidated research group CREG (T43-23R) has received financial support from *Gobierno de Aragón* (Spain) through the European Social Fund – FEDER.