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

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Abstract

Several one-dimensional fixed-bed reactor models were simulated to evaluate their accuracy in CO_2 methanation. A parametric study identified mass and heat transfer coefficients that best fit experimental data. Including axial transport effects was essential to reproduce observed trends, and separating their contributions clarified their individual impact on reactor performance.

Introduction

The *Power-to-Methane* (PtM) process represents a relevant technology for both reducing greenhouse gas emissions and storing renewable energy in the form of synthetic natural gas (SNG). At the core of this process lies the *Sabatier* reaction (r.1), where CO_2 reacts with hydrogen to produce methane and water:

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \qquad (r.1)$$

To ensure environmental sustainability, the hydrogen must be sourced via water electrolysis powered by surplus renewable electricity, while the CO_2 feedstock may derive from flue gases, biogas, or direct air capture. The reaction is thermodynamically favored at low temperatures and high pressures (due to its exothermicity [$\Delta H_r^o = -165.1$ kJ mol^{-1}] and molar reduction); however, low-temperature operation limits kinetics, demanding efficient catalytic materials such as Ni or Ru supported on high-surface-area materials. To facilitate the methanation reaction at high CO_2 conversion and CH_4 selectivity, the active catalyst is packed into a fixed-bed reactor.

This study aims to validate and compare different 1D pseudo-homogeneous reactor models, ranging from ideal plug-flow to those incorporating axial dispersion, against experimental data obtained under non-isothermal conditions. The final objective is to identify a reliable simulation approach for predictive modeling under practical operating scenarios.

Experimental

The experiments were performed in a lab-scale isothermal fixed-bed reactor (12 cm length, 13 mm internal diameter), previously validated to operate under kinetic control (external and internal mass transfer limitations neglected). The catalytic bed consisted of 0.5 g of Ni_3-Fe-based catalyst mixed with 10 g of γ-Al_2O_3 as a thermal diluent. Prior to reaction, the catalyst was reduced in 50 vol% H_2 at 500 °C for 2 h. Kinetic data were collected over a temperature range of 250–400 °C, decreasing in 25 °C steps every 50 minutes. Each experiment was performed at different H_2:CO_2 molar ratios, from 2:1 to 6:1, with 10 vol% inert gas and a total flowrate of 250 mL/min (STP). Conversion, selectivity, yield, and reaction rate were determined and used to fit a *Langmuir–Hinshelwood* type rate expression (Eq.1) via nonlinear regression in *Excel*® and *MATLAB*® [1].

$$r_{CH_4} = \frac{kK_{CO_2}K_{H_2}p_{CO_2}p_{H_2}}{\left(1 + K_{CO_2}p_{CO_2} + K_{H_2}p_{H_2}\right)^2} \qquad (Eq.1)$$

Due to non-uniform heating along the reactor length caused by limitations in the oven's thermal control, temperature profiles were experimentally determined through a blank run (using only inert γ-Al_2O_3). These gradients were subsequently used to correct the thermal input in the simulation models.

Two reactor models in stationary state were implemented [2]: (i) a pseudo-homogeneous plug-flow model without axial dispersion (Eq.2-3), solved using MATLAB's *ode15s*, assuming that inlet temperature and CO_2 mole fraction are constant at the reactor entrance, and (ii) a model with axial dispersion of mass and energy (Eq.4-5), solved via *bvp4c* with *Danckwerts*-type boundary conditions.

$$u_s \frac{dC_A}{dz} = \rho_B r_A \qquad (Eq.2)$$

$$\rho_f u_s c_p \frac{dT}{dz} = (-\Delta H)\rho_B r_A - 4\frac{U_w}{\phi_t}(T - T_w) \qquad (Eq.3)$$

$$\varepsilon_B D_{eff,A} \frac{d^2 C_A}{dz^2} - u_s \frac{dC_A}{dz} - \rho_B r_A = 0 \qquad (Eq.4)$$

$$\lambda_{eff}\frac{d\,c_A}{dz^2} - \rho_f u_s c_p \frac{dT}{dz} + (-\Delta H)\rho_B r_A - 4\frac{U_w}{\emptyset_t}(T - T_w) = 0 \qquad (Eq.5)$$

Conclusions

All simulations presented were performed at a reference wall temperature of 300 °C. However, comparable trends were observed at other experimental temperatures. The influence of axial mass dispersion and thermal conductivity was evaluated independently in order to isolate their individual effects.

The analysis of different heat transfer coefficients, U_w (**Figure 1**), revealed that higher values promote better thermal regulation by reducing temperature peaks and smoothing the axial temperature profile, aligning with experimental trend. On the other hand, excessive heat removal suppresses reaction rates, slightly limiting overall conversion. In contrast, low U_w values lead to strong local heating, which increases conversion at the expense of stability. Based on these results, the axial dispersion analysis was performed using U_w = 100 W·(m^2·K)$^{-1}$, as it provided the best agreement with experimental data.

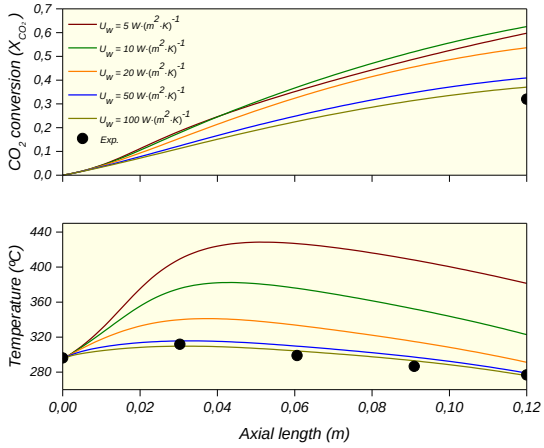

Figure 1: *Effect of overall heat transfer coefficient, U_w*

The impact of the axial mass dispersion coefficient, D_{eff} (**Figure 2**), is mainly observed in the conversion profile rather than in the temperature distribution. Higher values of D_{eff} promote back-mixing of species, which increases conversion near the reactor inlet and smooths the overall conversion profile. In contrast, lower dispersion values lead to profiles that closely resemble the ideal plug-flow case. The temperature profile remains unaffected, confirming that axial mass dispersion primarily influences reactor's conversion.

Finally, the effective thermal conductivity, λ_{eff} (**Figure 3**), was found to be a key parameter in capturing the observed temperature drop along the reactor length. Unlike the case of mass dispersion (**Figure 2**), here the conversion profile remains essentially unaffected. Lower values of λ_{eff} provided the closest match to the experimental temperature profiles, highlighting its role in controlling the location and intensity of the hot spot.

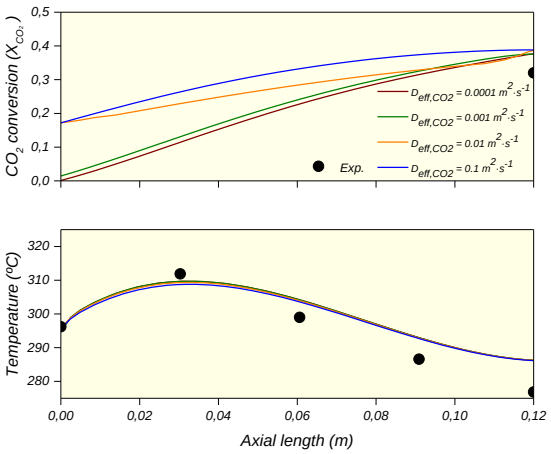

Figure 2: *Effect of axial mass dispersion coefficient, D_{eff,CO_2}*

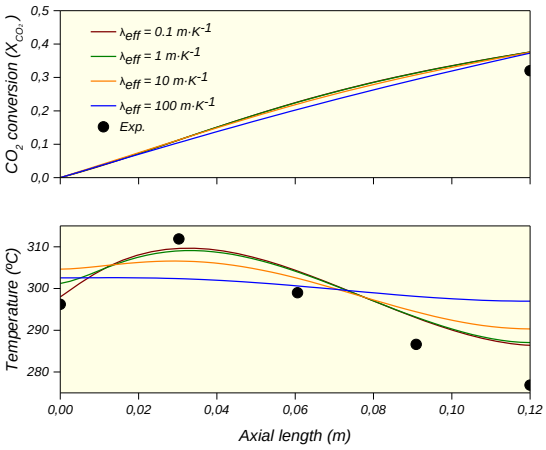

Figure 3: *Effect of effective thermal conductivity, λ_{eff}*

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