

Dynamic 1D heterogeneous models for the simulation of CO₂ hydrogenation to CH₄ in a fixed bed reactor

Elena Gómez-Bravo, José Antonio González-Marcos,
Juan Ramón González-Velasco, Beñat Pereda-Ayo *

*Department of Chemical Engineering, Faculty of Science and Technology, Universidad del País Vasco
UPV/EHU, Barrio Sarriena s/n, 48940, Leioa, Bizkaia, Spain*

**Corresponding author: benat.pereda@ehu.eus*

Highlights

- Dynamic 1D-reactor models are built in *Matlab2022R* to simulate CO₂ hydrogenation to CH₄.
- Mass and energy transport is evaluated in pseudo-homogeneous and heterogeneous models.
- CO₂ conversion and temperature profiles are used to analyze the transient behavior of the reactor in the event of any operational change.

1. Introduction

The CO₂ hydrogenation with renewable hydrogen ($\text{CO}_2 + 4\text{H}_2 \rightleftharpoons \text{CH}_4 + 2\text{H}_2\text{O}$) allows the chemical storage of energy using CH₄ as an energy vector. The high exothermicity of the reaction can be an advantage to speed up the reaction kinetics, but an excessive temperature increase can lead to thermodynamic limitations or catalyst damage [1]. Thus, reactor design assisted by modeling can be crucial for the construction of large-scale methanation reactors with efficient heat management [2]. In this work, steady-state pseudo-homogeneous and heterogeneous 1D models have been used to estimate mass and heat transfer coefficients and validate the constructed models with experimental data. With that information, the objective of the present work is to analyze the transient behavior of the reactor in the event of any operational change. For that goal, dynamic 1D heterogeneous models will be built and solved by own programs developed in *Matlab2022R*. CO₂ conversion and temperature profiles will be used to analyze reactor performance and obtain insights for future reactor designs.

2. Methods

CO₂ hydrogenation reaction was carried out in a quartz reactor (D=9 mm; L=25 mm) loaded with 1 g of catalyst and placed inside a tubular furnace at 320 °C. The feed CO₂ gas flowrate was 100 mL/min (H₂/CO₂=4). Temperature was measured by 6 thermocouples equidistantly placed along the reactor axial coordinate, meanwhile the gas composition was measured by gas chromatography. First, steady-state models were constructed and solved. The stiffness of the ordinary differential equation (ODE) system for the pseudo-homogeneous plug-flow model was faced with the *ode15s* solver in *Matlab2022R*. The inclusion of axial mass and energy transport to the model led to a boundary value problem ODE system, which was solved by the *bvp4c* function. The heterogeneous model, accounting for the gas phase and solid catalyst phase, required simultaneous resolution of mass and energy balances on each phase. The model was solved by a main *bvp4c* function for the fluid phase and a secondary *bvp4c* subroutine for the solid phase. In the dynamic heterogeneous model with mass and energy transport in the axial direction, the gas phase and the solid phase share “time” as common independent variable. A unique partial differential equation (PDE) system was developed for the gas and the solid phase, which was reduced to an ODE system by discretization of the independent variables, i.e. the reactor length and particle radius. To meet reactor and catalyst boundary conditions, the ODE system was transformed into a system of differential algebraic equations (DAEs) using a singular mass matrix, which was solved by *ode15s* function.

3. Results and discussion

Figure 1 shows the CO₂ conversion and temperature profiles in the reactor length for the developed steady-state models, considering a global heat transfer coefficient of 75 W/(m²·K). The pseudo-homogenous plug-flow model (blue line) was unable to describe the temperature profile. The incorporation of mass and energy transport in the axial direction (green line), significantly improved the accuracy of the model to describe the temperature profile. The heterogeneous model (red line) obtained the best fitting with the following external ($k_g=0.89$ m/s and $h_f=1406$ W/m²/K) and internal ($D_{CO_2,p}=3 \cdot 10^{-6}$ m²/s and $\lambda_p=5$ W/m/K) mass and heat transport coefficients. Radial CO₂ concentration gradients were evident inside a catalyst particle situated at the reactor entrance. Although the catalyst particle was practically isothermal, a notable temperature gradient was observed between the particle surface and the bulk gas phase.

The mass and heat transport coefficients estimated with the steady-state models were used in the dynamic heterogeneous model. Figure 2 shows the CO₂ conversion and temperature profiles in the reactor length during the start-up of the methanation reaction. The reactor is initially filled with an inert gas at 320 °C ($t=0$ s), and then, the reacting gas mixture is fed to the reactor. For short times ($t<30$ s) a gradual increase of the CO₂ conversion is observed along the reactor in a kinetically controlled regime. Even at such operational conditions, with a somewhat flat temperature profile, the heat transport along the reactor axial coordinate is evidenced by the temperature at the reactor entrance (345 °C), which exceeds that of the feed (320 °C). For higher contact times ($t>60$ s), a hot spot develops in the temperature profile. Reaction kinetics is enhanced at the reaction entrance due to the heat transport along the reactor. The fast conversion of CO₂ at the reactor entrance releases a high amount of energy that cannot be dissipated by the reactor. Therefore, energy is accumulated, and temperature increases until it reaches a maximum. As temperature increases, the reaction progressively approaches equilibrium and reaction rate slows down. This fact favors heat removal and temperature is progressively reduced with the reactor length. As time advances, the hot spot progressively moves to the reactor entrance and increases its magnitude. Approaching steady-state, after 140 s, the hot spot is observed at $L=3.5$ mm with a temperature of 554 °C. Further simulations have been carried out from steady-state at 320 °C and changing the furnace temperature down to 290 °C. This temperature decrease led to a gradual extinction of the reaction. The hot spot is progressively displaced towards the reactor outlet and reduces its magnitude. Despite analogous profiles to the start-up, in this case the time required to approach the steady-state was longer (6.8 minutes).

4. Conclusions

The study developed a mathematical model which can be useful to assist reactor design in scale-up processes. Also, dynamic simulations will play a critical role in the study of the optimal conditions and control of this type of reaction.

References

- [1] F. Kosaka, T. Yamaguchi, Y. Ando, T. Mochizuki, H. Takagi, K. Matsuoka, K. Kuramoto, *International J. Hydrogen Energy*. 46 (2020) 4116-4125
- [2] Fache, A., Marias, F. *Renew. Energ.* 151 (2020) 865-886

Keywords

CO₂ hydrogenation; Reactor modeling and simulation; Dynamic.

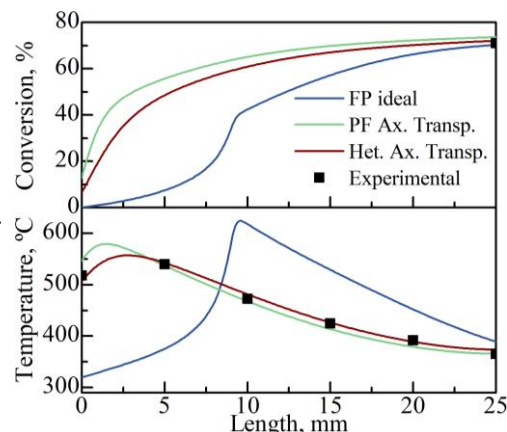


Figure 1. Conversion and temperature profiles at stationary state.

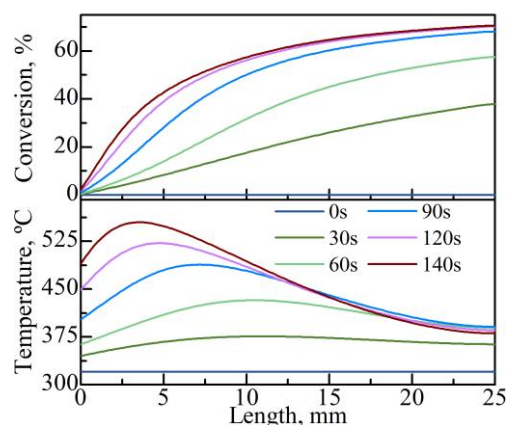


Figure 2. Conversion and temperature profiles during the start-up.