

# CFD Simulations for the Methanation of CO<sub>2</sub> in Packed Bed Reactor Using Dual Function Materials

Eleana Harkou<sup>1</sup>, Anastasios I. Tsiotsias<sup>2</sup>, Nikolaos D. Charisiou<sup>2</sup>, Maria A. Goula<sup>2</sup>, George Manos<sup>3</sup> and Achilleas Constantinou<sup>1\*</sup>

*1 Department of Chemical Engineering, Cyprus University of Technology, 57 Corner of Athinon and Anexartisias, Limassol 3036, Cyprus; 2 Laboratory of Alternative Fuels and Environmental Catalysis (LAFEC), Department of Chemical Engineering, University of Western Macedonia, GR-50100, Greece; 3 Department of Chemical Engineering, University College London, WC1E 7JE, London, United Kingdom*

*\*Corresponding author: a.konstantinou@cut.ac.cy*

## Highlights

- CFD model was designed for CO<sub>2</sub> methanation using monometallic Ni<sub>20</sub> DFM and bimetallic Ru<sub>0.2</sub>Ni<sub>20</sub> DFM.
- Good agreement was obtained between experimental and simulated results.
- CH<sub>4</sub> concentration reached maximum for the monometallic DFM at 350 °C and for the bimetallic DFM at 300 °C.
- The bimetallic DFM showed the best performance achieving CH<sub>4</sub> concentration above 0.5 mol/m<sup>3</sup>.

## 1. Introduction

Greenhouse gas emissions are massive concern for scientists to minimize the effect of global warming. The development of carbon capture and utilization (CCU) technologies attempt to reduce the release of CO<sub>2</sub> emissions in the atmosphere [1]. CO<sub>2</sub> conversion to an energy carrier, CH<sub>4</sub>, is creating a power-to-gas platform and a circular economy [2]. Dual function materials (DFM) can couple the processes of capture and conversion of CO<sub>2</sub> into a two-step process [3]. In this work, we aim to develop a CFD model to validate experimental results according to the hydrogenation phase where CO<sub>2</sub> is already adsorbed on the surface of the catalyst and H<sub>2</sub> is injected and optimize the conversion of CO<sub>2</sub> with further studies.

## 2. Methods

CFD simulations were used to determine the transport phenomena of heterogeneous flows within the reactor. The reactor's height and length are 0.9 cm and 30 cm, respectively. 2D configurations were designed assuming that the gradients of concentrations and temperatures take place only in the axial directions. Further assumptions upon which the model was founded include: (a) application of unsteady-state and isothermal conditions, (b) the pressure drop along the length of the reactor is very small and it can be considered negligible, (c) ideal gas law is applicable for the gases, (d) there is a constant axial fluid velocity in the reactor with uniform physical properties and transport coefficients, and (e) the reaction zone in the reactor is packed with catalytic material in powdered form. The mass balance equation given below incorporates the diffusion and convection for the species in the packed bed:

$$\frac{\partial c_i}{\partial t} + \nabla \cdot J_i S_b + u \cdot \nabla c_i = R \quad (1)$$

where,  $J_i$  is the molar flux vector,  $u$  is the velocity, and  $S_b$  is the active specific surface area of the powder exposed to the reacting fluids in the packed bed. The mass balance across a spherical shell at  $r_{dim}$  and a predefined 1D extra dimension ( $r = r_{dim}/r_{pe}$ ) is given by:

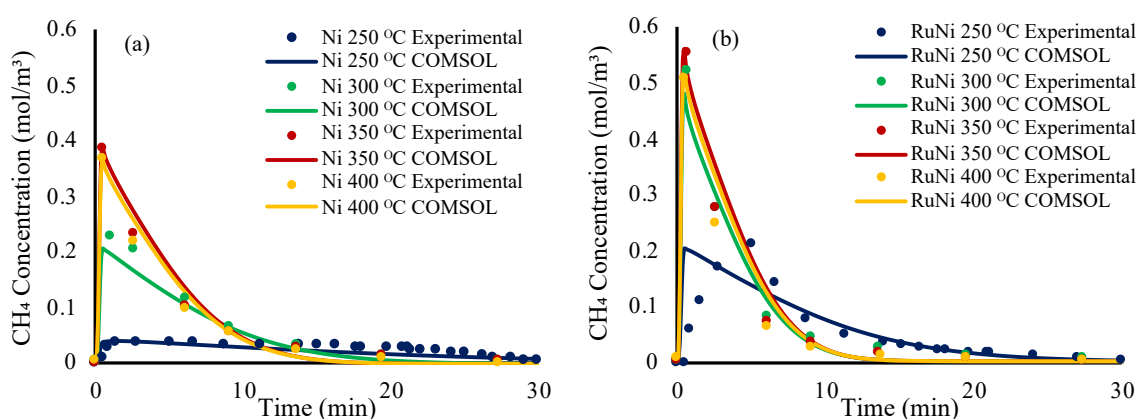
$$4\pi N \left\{ r^2 r_{pe}^2 \varepsilon_{pe} \frac{\partial c_{pe,i}}{\partial t} + \nabla \cdot (-r^2 D_{i,eff} \nabla c_{pe,i}) = r^2 r_{pe}^2 R_{pe} \right\} \quad (2)$$

where  $N$  is the number of pellets per unit volume of the bed,  $D_{i,eff}$  is the effective diffusion coefficient of the reacting fluid within the pores of the catalyst, and  $R_{pe}$  is the reaction rate per unit volume of pellet. The software that was used for this work was the COMSOL Multiphysics in version 5.6 to couple all the boundary conditions, mass balances and conservation equations. The solution was checked for

higher degrees of freedom and no difference in the results was obtained and the CFD results are mesh independent.

### 3. Results and discussion

The reactor was operated at pressure of 1 atm and temperature from 250 to 400 °C. Figure 1 shows the temperature effect on the concentration of the generated CH<sub>4</sub> for the (a) monometallic Ni<sub>20</sub> DFM (20% Ni) and (b) bimetallic Ru<sub>0.2</sub>Ni<sub>20</sub> DFM (0.2% Ru and 20% Ni). It was obtained that the concentration of CH<sub>4</sub> is increased with the temperature and according to the Arrhenius expression ( $k=A.exp(-E_a/RT)$ ) when the temperature of the reaction is increased the rate constant and herein the rate of the reaction is increased. Moreover, it was observed that the greatest difference for the generation of CH<sub>4</sub> is between 250 and 300 °C and the increase of temperature lead to sharper peaks. The concentration reached maximum for the monometallic DFM at 350 °C and for the bimetallic DFM at 300 °C and the further increase of temperature does not provide any additional increase in the methanation kinetics. The designed model was found in a good agreement with the experimental results showing the robustness of the CFD model.



**Figure 1.** Effect of temperature on the concentration of CH<sub>4</sub> for the (a) monometallic Ni<sub>20</sub> DFM and (b) bimetallic Ru<sub>0.2</sub>Ni<sub>20</sub> DFM.

### 4. Conclusions

In this study experimental results were used in order to design a robust CFD model and to validate them. A monometallic and a bimetallic DFM were used with the latest achieving greatest concentrations of CH<sub>4</sub> above 0.5 mol/m<sup>3</sup>. In the case of the monometallic DFM the concentration reached maximum at 350 °C while for the bimetallic DFM at 300 °C. It was obtained a good validation between the experimental and simulated results and the kinetic model will be used for further studies to optimize the performance of the reaction.

### References

- [1] W. Gao *et al.*, "Industrial carbon dioxide capture and utilization: state of the art and future challenges," *Chemical Society Reviews*, vol. 49, no. 23, pp. 8584–8686, 2020.
- [2] C. H. Tan, S. Nomanbhay, A. H. Shamsuddin, Y.-K. Park, H. Hernández-Cocoletzi, and P. L. Show, "Current Developments in Catalytic Methanation of Carbon Dioxide—A Review," *Frontiers in Energy Research*, vol. 9, p. 795423, 2022.
- [3] A. Bermejo-Lopez, B. Pereda-Ayo, J. A. González-Marcos, and J. R. Gonzalez-Velasco, "Modeling the CO<sub>2</sub> capture and in situ conversion to CH<sub>4</sub> on dual function Ru-Na<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst," *Journal of CO<sub>2</sub> Utilization*, vol. 42, p. 101351, 2020.

### Keywords

CO<sub>2</sub> methanation, Dual Function Materials (DFMs), Computational Fluid Dynamics (CFD).