

# CFD Analysis of a Packed Bed Reactor for Green Hydrogen Production by Biogas Reforming

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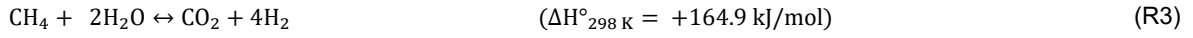
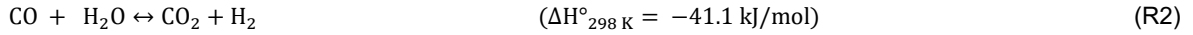
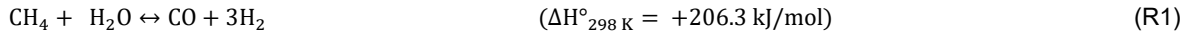
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This study involved the development of a mathematical model of a multi-tubular packed-bed reactor to produce hydrogen via catalytic steam reforming of biogas. The model was validated by comparing its results with experimental data from published literature, and good agreement was observed. COMSOL Multiphysics was used to build and simulate the 3D computational fluid dynamics model, considering mass and momentum transfer processes. Given that species transport and chemical reaction occur at dimensions of different orders of magnitude, a multiscale approach was taken in model development, enabling the characterization of gas composition at both micro- and macro scales, as well as pressure drop profiles along the reactor length. Sensitivity studies were carried out to evaluate the effects of various biogas compositions, with a particular focus on the carbon dioxide mole fraction, as well as gas velocities.

## 1. Introduction

Hydrogen has the potential to be a nearly emission-free energy source, making it an attractive option for power generation and fuel applications. Hydrogen can also be used in industrial processes, including ammonia, direct reduced iron, methanol production, and refinery processes. Despite an estimated hydrogen demand of 115 Mt by 2030, as of 2021, the production of low-emission H<sub>2</sub> was less than 1 Mt (IEA, 2022). Hydrogen gas can be produced by water electrolysis, gas reforming, coal, or biomass gasification. Steam methane reforming (SMR) is the most commonly used method for hydrogen production due to its highly economical performance and satisfactory results compared to other methods (dry-reforming, bi-reforming, tri-reforming, or oxy-CO<sub>2</sub> reforming). However, SMR relies heavily on depletable resources and produces high CO<sub>2</sub> emissions (Zhao et al., 2020). Using alternative energy sources, like wind and solar, may not be enough for a fully sustainable approach to hydrogen production. Thus, it may also be necessary to consider changing the raw material, natural gas, used in SMR. Biogas is a suitable substitute for natural gas in the SMR process due to its accessibility, affordability, and lower carbon footprint (Gustafsson and Anderberg, 2020). Produced through the gasification of biomass, biogas has a similar composition to natural gas, containing high quantities of methane (30 – 70 %), along with carbon dioxide (25 – 50 %), nitrogen (2 – 6 %), oxygen, hydrogen, light hydrocarbons and traces of hydrogen sulphide, ammonia, chlorines, and siloxanes (Nahar et al., 2017). Its composition depends on the biowastes from which it is produced (from the water treatment plants, animal manure, municipal, lignocellulosic, or organic industrial waste). Since it can be obtained from many different sources, biogas is a versatile energy source and within reach of any community (Pérez-Chávez and Mayer, 2019).

The SMR process requires a multi-tubular reactor with cylindrical tubes filled with nickel-alumina-packed bed catalysts, as shown in Figure 1. The tubes are surrounded by side-fired furnaces to ensure the necessary heat for the overall endothermic process expressed by the reactions R1-R3 (Ghouse and Adams, 2013). The pressure is selected between  $2 \cdot 10^5$  and  $5 \cdot 10^5$  Pa (Chisalita et al., 2022), and the temperature range in the reactor is between 700 and 1,150 K, with a constant gas flow and a specific ratio of biogas to steam of about 1:4 to avoid catalyst sintering (Nazir et al., 2019).



The present work aims to develop a computational fluid dynamics model, taking into account mass and momentum transfer processes, to simulate a packed bed reactor for hydrogen production via biogas steam reforming. The multiscale model was developed and solved using COSMOL Multiphysics. Sensitivity studies were conducted to investigate the effects of varying the gas velocity, pressure, and biogas composition inflow, specifically with respect to different  $\text{CO}_2$  concentrations in the biogas. The models were validated with experimental data available in the literature.

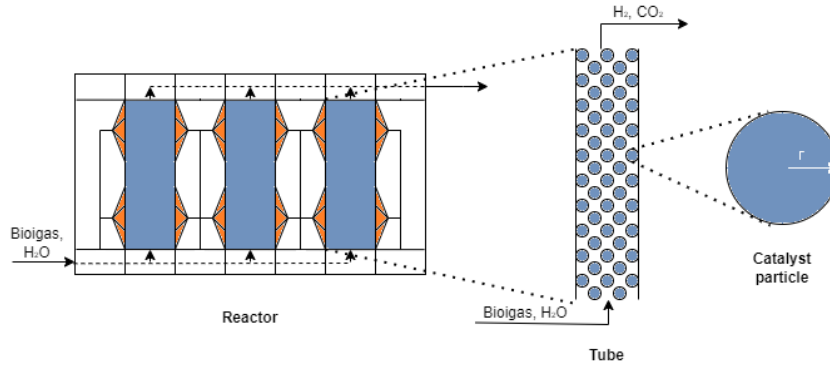


Figure 1: The multi-tubular reactor with catalyst and side-fired furnaces

## 2. Mathematical modelling

The 3D dynamic models were developed to simulate biogas steam reforming in space and time, considering a high concentration of carbon dioxide in the biogas at the reactor inlet. The model accounted for two scales: the microscale, represented by the pores of the catalyst granules, and the macroscale, which includes the void space between the catalyst particles (Table 1).

In order to develop the model, the following primary assumptions have been made:

- (i) over the entire length of the reactor, mass transfer through the catalyst layer occurs by convection and diffusion mechanisms;
- (ii) within the pores of the catalyst, mass transfer is achieved only by diffusion and only the radial direction is taken into account;
- (iii) reaction rates depend on mass transfer within the catalyst pores;
- (iv) the porous structure of the catalyst granules is homogeneous.

Table 1: Mathematical model balance equations

Macroscale	
Component mass balance	$\frac{\partial c_i}{\partial t} + \nabla \cdot (-D_i \cdot \nabla c_i) + u \cdot \nabla c_i = 0 \quad (1)$
Momentum balance	$\nabla \cdot \left[ \rho_g \cdot \left( -\frac{\kappa}{\mu_i} \cdot \nabla p_i \right) \right] = Q_m \quad (2)$
Microscale	
Component mass balance	$\epsilon_{pe} \frac{\partial c_{pe,i}}{\partial t} + \frac{1}{r^2 r_{pe}^2} \frac{\partial}{\partial r} \left( -r^2 D_{pe,i} \frac{c_{pe,i}}{\partial r} \right) = \epsilon_{pe} \cdot R_{pe,i} \quad (3)$

The kinetics model considered in this work, Eqs.(4-8), is based on a Langmuir-Hinshelwood approach and uses nickel catalyst on alumina support (Xu and Froment, 1989). The kinetic parameters are presented in Table 2, noting that  $K_3$  is the multiplication product of  $K_1$  and  $K_2$  (Zi et al., 2016).

$$R_1 = \frac{k_1}{p_{H_2}^{2.5} \cdot DEN^2} \cdot \left[ p_{CH_4} \cdot p_{H_2O} - \frac{p_{H_2}^3 \cdot p_{CO}}{K_1} \right] \quad (4)$$

$$R_2 = \frac{k_2}{p_{H_2} \cdot DEN^2} \cdot \left[ p_{CO} \cdot p_{H_2O} - \frac{p_{H_2} \cdot p_{CO_2}}{K_2} \right] \quad (5)$$

$$R_3 = \frac{k_3}{p_{H_2}^{3.5} \cdot DEN^2} \cdot \left[ p_{CH_4} \cdot p_{H_2O}^2 - \frac{p_{H_2}^4 \cdot p_{CO_2}}{K_3} \right] \quad (6)$$

$$DEN = 1 + K_{CO} \cdot p_{CO} + K_{H_2} \cdot p_{H_2} + K_{CH_4} \cdot p_{CH_4} + \frac{K_{H_2O} \cdot p_{H_2O}}{p_{H_2}} \quad (7)$$

$$k_i = K_i = K_j = a \cdot \exp\left(-\frac{b}{T_c} + c\right) \quad (8)$$

Table 2: Kinetic variables (Xu and Froment; 1989; Zi et al., 2016)

Variable	k <sub>1</sub>	k <sub>2</sub>	k <sub>3</sub>	K <sub>1</sub>	K <sub>2</sub>	K <sub>CH<sub>4</sub></sub>	K <sub>H<sub>2</sub>O</sub>	K <sub>H<sub>2</sub></sub>	K <sub>CO</sub>
a	9.49·10 <sup>16</sup>	4.39·10 <sup>4</sup>	2.29·10 <sup>16</sup>	10,266.76	1	6.65·10 <sup>-6</sup>	1.77·10 <sup>3</sup>	6.12·10 <sup>-11</sup>	8.23·10 <sup>-7</sup>
b	28,879	8,074.3	29,336	26,830	4,400	4,604.28	10,666.35	9,971.13	8,497.71
c	0	0	0	30.11	-4.063	0	0	0	0

The parameters used for the model simulation are presented in Table 3, together with the parameters used for the model validation (Soliman et al., 1988). It should be mentioned that the parameters presented by Soliman were obtained for a reactor in which the tube heating is achieved using a side-fired furnace, while there may be other arrangements of burners to ensure the thermal needs.

Table 3: Process parameters (Soliman et al., 1988)

Plant specifications	Parameter	Value
Feed conditions	F <sub>vol,total</sub> [m <sup>3</sup> /day]	88·10 <sup>5</sup>
	F [mol/h]	23,271
	T <sub>g</sub> [K]	723
	P <sub>g</sub> [Pa]	3.65·10 <sup>6</sup>
Input gas composition	x <sub>CH<sub>4</sub></sub>	0.1808
	x <sub>H<sub>2</sub>O</sub>	0.7981
	x <sub>CO</sub>	0.0049
	x <sub>H<sub>2</sub></sub>	0.0098
	x <sub>CO<sub>2</sub></sub>	0.0061
Properties of solid catalyst	D <sub>p</sub> [m]	0.017
	T <sub>c</sub> [K]	750
	ε <sub>pe</sub>	0.519
Reactor design parameters	D <sub>t</sub> [m]	0.107
	X <sub>t</sub> [m]	0.015
	L <sub>cat</sub> [m]	9.18
	N <sub>tube</sub>	247

### 3. Results and discussions

Model predictions for methane conversion and the percentage of the produced hydrogen in the dry basis were compared with literature data, and similarities were observed, as shown in Table 4 (Ghouse and Adams, 2013; Soliman et al., 1988). The simulation results are slightly different from values presented in the literature, because in this stage of developing model, the heat balance is not included, the temperature being constant both in micro and macroscale.

Table 4: Results validation (Ghouse and Adams, 2013; Soliman et al., 1988)

Variable	Model	Literature
CH <sub>4</sub> conversion %	50.15	69.00
H <sub>2</sub> %	66.88	70.60

Simulation results included profiles corresponding to the change of gas concentrations in the microscale. The variation of hydrogen concentration in the catalyst layer increases at different heights of the reactor as the biogas passes through, as can be seen in Figure 2. At the initial simulated time, Figure 2a, the concentration has a minimum value and as time progresses, it appears to have a uniform distribution throughout the catalyst pellet.

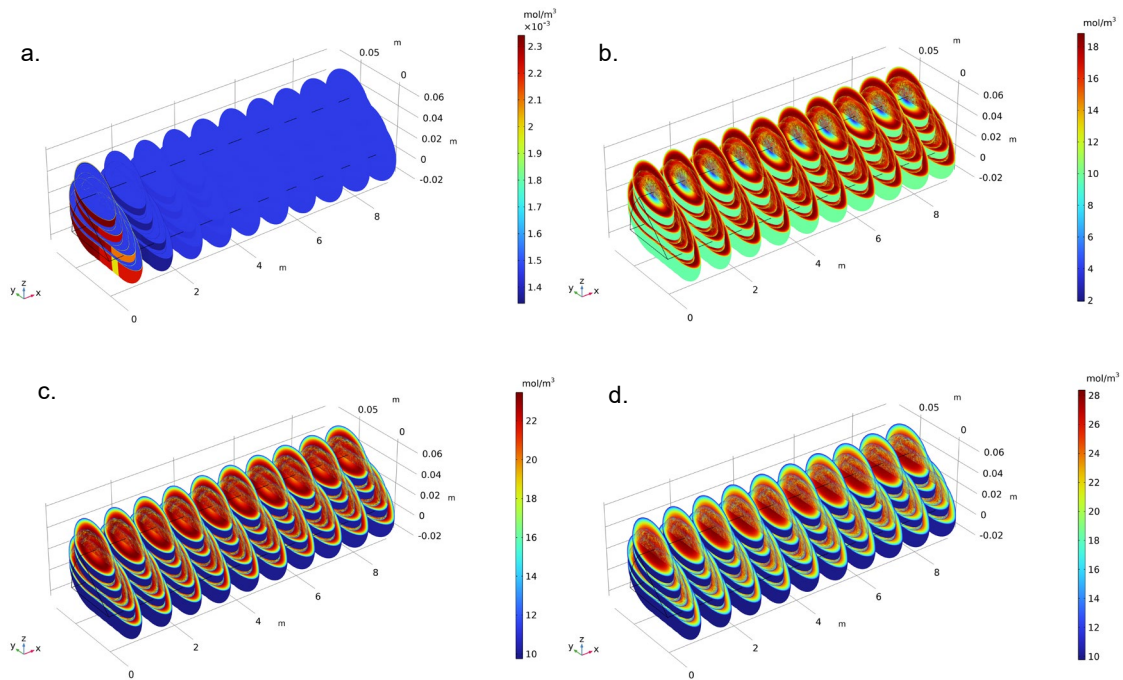


Figure 2: The hydrogen concentration in the catalyst particle at different times, a.  $t=0$  s, b.  $t=60$  s, c.  $t=120$  s, d.  $t=180$  s

According to Figure 3, the concentration of methane in the macroscale has a maximum value until the onset of the chemical reaction, at which point it begins to decrease to the value of  $54.42 \text{ mol/m}^3$ , representing its maximum conversion given the working conditions. As the methane conversion is not 100 %, the resulting methane gas can be recirculated after separation from the reactor exhaust to achieve a higher final amount of hydrogen or it can be used as a fuel to maintain a consistent temperature in the reactor.

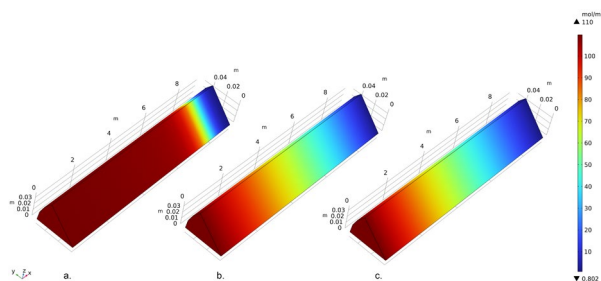


Figure 3: The methane concentration in the reactor at different times, a.  $t=5$  s, b.  $t=10$  s, c.  $t=180$  s

After conducting a sensitivity study to investigate the influence of different biogas compositions (specifically carbon dioxide concentrations), the profiles for H<sub>2</sub> concentration along the reactor length were obtained, as

shown in Figure 4. When the  $\text{CO}_2$  concentration increases from  $x_{\text{CH}_4}:x_{\text{CO}_2} = 1:0.034$  to  $x_{\text{CH}_4}:x_{\text{CO}_2} = 1:0.75$ , the  $\text{H}_2$  concentration slightly decreases with  $0.2 \text{ mol/m}^3$ , since the  $\text{CO}_2$  presence reduces the transformation degree of reactions R1 and R3. In Figures 4a and 4b, alongside each  $\text{H}_2$  concentration distribution in the reactor, is the  $\text{CO}_2$  concentration variation in the catalyst particle at  $t=180 \text{ s}$ .

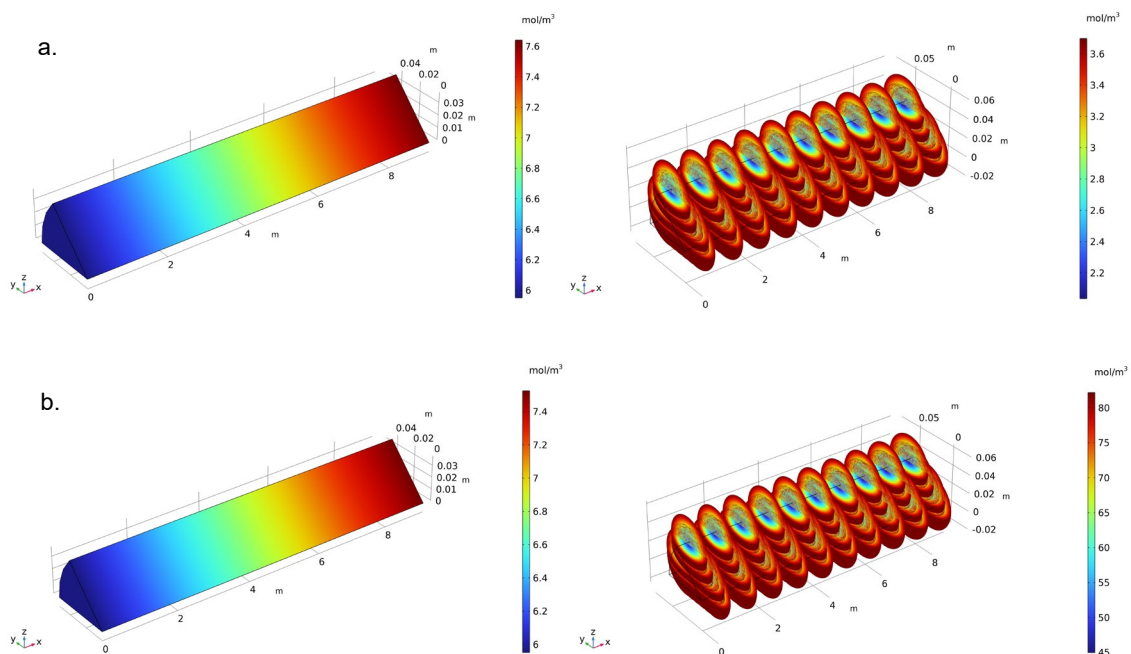


Figure 4: The hydrogen concentration in the macroscale at different carbon dioxide concentrations at the inlet, a.  $x_{\text{CH}_4}:x_{\text{CO}_2} = 1:0.034$ , b.  $x_{\text{CH}_4}:x_{\text{CO}_2} = 1:0.75$

Based on the sensitivity study evaluating the influence of fluid velocity on the outlet pressure, as shown in Figure 5, it was found that when the velocity decreases by 25 %, the system pressure drops significantly to almost 16 bar, but at the work fluid velocity of 1.23 m/s, the outlet pressure is about 26 bar. At the same time, by changing the value of the working pressure, the amount of hydrogen produced in the reactor also changes, indicating that at lower values of the flow velocity, the concentration of main product increased by  $0.4 \text{ mol/m}^3$ .

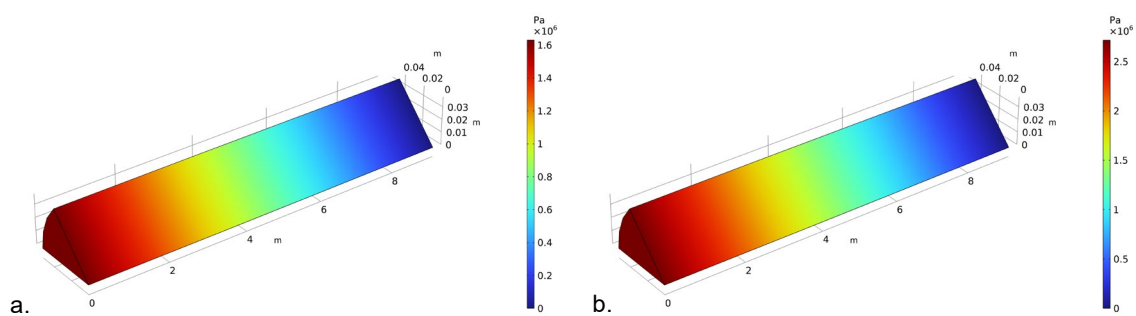


Figure 5: The pressure drop variation at different fluid velocities a.  $u = 0.92 \text{ m/s}$ , b.  $u = 1.23 \text{ m/s}$

#### 4. Conclusions

In this work, a multiscale heterogeneous dynamic 3D model for the biogas steam reforming process was developed using COMSOL Multiphysics and validated with literature data. The study included sensitivity analyses to investigate the impact of fluid velocity on system pressure and the main product quantity, as well as the influence of biogas composition (depending on the source of origin) on hydrogen concentration. Ongoing

research will focus on examining additional parameters to determine the optimal conditions for this process, in order for it to become a feasible and easily approachable alternative in the ammonia-based fertilizer industry.

### Nomenclature

a, b, c – kinetic variables	$p_i$ – partial pressure of component $i$ , bar
$c_{pe,j}$ – concentration of component $j$ in the microscale, $\text{kmol}/\text{m}^3$	$P_g$ – gas pressure, bar
$D_i$ – component $i$ diffusion coefficient, $\text{m}^2/\text{s}$	$r$ – radial coordinate, -
$D_{pe,i}$ – component $i$ effective diffusion coefficient inside the pellet, $\text{m}^2/\text{s}$	$R_{pe,i}$ – reaction rate of reaction $i$ , $\text{kmol}/(\text{m}^3 \cdot \text{h})$
$D_p$ – particle diameter, m	$r_{pe}$ – pellet radius, m
$D_t$ – tube diameter, m	$t$ – time, h
$F$ – molar flow rate for one tube, $\text{kmol}/\text{h}$	$T_c$ – temperature of catalyst particle, K
$F_{vol,total}$ – total volumetric flow rate, $\text{m}^3/\text{day}$	$T_g$ – temperature of gas mixture in the reactor, K
$\kappa$ – permeability of the model, -	$u$ – Velocity field, -
$k_1, k_2, k_3$ – rate coefficients, $\text{kmol} \cdot \text{kPa}^{0.5}/(\text{kg} \cdot \text{h})$ , $\text{kmol} \cdot \text{kPa}^{-1}/(\text{kg} \cdot \text{h})$ , $\text{kmol} \cdot \text{kPa}^{0.5}/(\text{kg} \cdot \text{h})$	$x_i$ – mole fraction of species $i$ , -
$K_1, K_2, K_3$ – equilibrium constants, -	$X_t$ – tube wall thickness, m
$K_i$ – absorption constant of component $i$ , -	$Q_m$ – total discharge, -
$L_{cat}$ – catalyst layer height, m	$\Delta H^\circ_T$ – enthalpy of reaction, J/mol
$N$ – number of pellets per unit volume of bed, -	$\epsilon_{pe}$ – bed porosity, -
$N_{tube}$ – total number of tubes contained in the reactor, -	$\mu_i$ – Dynamic viscosity of component $i$ , $\text{N} \cdot \text{s}/\text{m}^2$
	$\rho_c$ – catalyst density, $\text{kg}/\text{m}^3$
	$\rho_g$ – gas mixture density, $\text{kg}/\text{m}^3$

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