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## THERMAL ANALYSIS OF THE ENDOTHERMIC REACTION OF THE STEAM REFORMING OF METHANE IN A FIXED BED REFORMER: NUMERICAL MODELLING AND COMPUTER SIMULATION

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**Abstract.** Thermochemical Packed-Bed (TPB) reformer has been substantially studied in the past years as a promising equipment to investigate the thermochemical conversion of methane ( $\text{CH}_4$ ). This work has as main objective a theoretical modelling to describe the process variables of Steam Reforming of Methane (SRM) method in the TPB reformer. The TPB reformer is filled with  $\beta$ -SiC open-cell foam where the thermochemical conversion of  $\text{CH}_4$  is carried out. The model variables describe the specific aims of work and these objectives can be identified from each equation of the developed mathematical model. This work has been proposed to study two specific aims as (i) The effective thermal conductivity's effect of the solid phase ( $\lambda_{s,eff}$ ) and (ii) molar flows of chemical components. The endothermic reaction temperature's profiles are notably increased as the numeral value of  $\lambda_{s,eff}$  is risen. The Steam Reforming of Methane (SRM) method is suggested to improve the Production Rate (PR) of  $\text{H}_2$  regarding the PR of CO. As results, the PR of  $\text{H}_2$  is of 29.48% while the PR of CO is of 2.76%.

**Keywords:**  $\beta$ -SiC open-cell foam, TPB reformer, reaction temperature, SRM method, mathematical model

### 1. INTRODUCTION

The production of hydrogen ( $\text{H}_2$ ) can be carried out from different methods such as thermochemical method (heat and chemical reactions to produce  $\text{H}_2$ ), Reforming of hydrocarbons, biomass gasification, coal gasification, electrolytic method, and biological method (Lima et al., 2020; Anjos et al., 2020). The production of  $\text{H}_2$  in packed bed reformers is still attracting the interest of researchers and engineers. Up to date, several works have been published in the literature dealing with reforming method to produce  $\text{H}_2$  on different commercial catalyst (Silva and Abreu, 2017; Fuqiang et al., 2015; Yu et al., 2017). This work has as novelty the thermochemical conversion of  $\text{CH}_4$  on a  $\beta$ -SiC open-cell foam in a Thermochemical Packed Bed (TPB) reformer.  $\beta$ -SiC open-cell foams have been considered as potential candidates for catalyst support in the heterogeneous catalysis field due to their high external surface area combined with a low pressure drop (Chen et al., 2018). On the other hand, foam-based packed bed reformers offer great potential advantages for the thermal energy storage due to bed's high porosity.

The hydrodynamic characterization of the Steam Reforming of Methane (SRM) through  $\beta$ -SiC open-cell foam in a packed bed configuration in the TPB reformer is performed by reacting Methane ( $\text{CH}_4$ ) with water steam ( $\text{H}_2\text{O}$ ). A physical-mathematical modelling is important to design and optimize the SRM method in the TPB reformer. Usually, the SRM method's application through  $\beta$ -SiC foam bed improves the heat transfer and mass transfer due to high porosity and surface area of the  $\beta$ -SiC foam (Vanhaecke et al., 2012). Mass, energy and momentum balance's equations for the gas phase as well as mass, energy and momentum balance's equations to the solid phase are described through mathematical models (Ma et al., 2016; Hussain et al., 2006). Here, a Non-isothermal Pseudo-Homogeneous mathematical (NIPHM) model is used to model the SRM method in the TPB reformer. The NIPHM model is described by a system of Nonlinear Partial Differential Equations (NPDEs) in together with a developed kinetic model for reforming reactions.

With the purpose to reduce the research cost and project time, the mathematical modelling and computer simulation are extensively used to obtain a better understanding of design parameters in reformers. The approach and solution of physical-mathematical models are still a novelty of TPB reformers and thus the topic is a very actual in accessible literature. The novelty of this work lies in the application of open-cell foam ( $\beta$ -SiC) bed for the SRM method. A numerical analysis has been driven to investigate the molar flows of chemical components i on the SRM method of the

TPB reformer. In addition, the profiles of the endothermic reaction temperature were also analyzed for the SRM method in the TPB reformer.

## 2. PHYSICAL-MATHEMATICAL MODELLING

### 2.1 Physical model

A schematic setup is used to study the thermochemical conversion of the SRM method in TPB reformer according to Fig. 1. The physical model from TPB reformer is shown in Fig. 1 below.

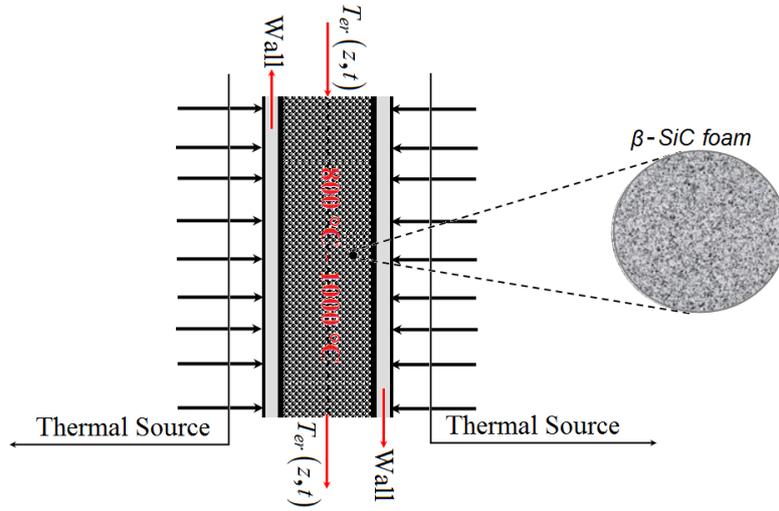
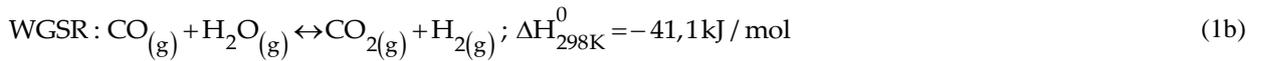
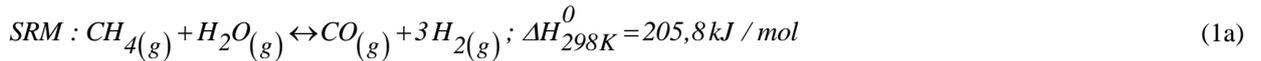


Figure 1. Schematic setup of the physical model from TPB reformer to study the SRM method on the  $\beta$ -SiC foam

### 2.2 Thermochemical kinetic model

The reforming reaction of  $\text{CH}_4$  is used to produce syngas ( $\text{H}_2$  e  $\text{CO}$ ) and it is highly endothermic (Cruz and Silva, 2017). The SRM process has a limited equilibrium and can be described by the following reforming reaction:



The reforming reaction, Eq. (1), is a highly endothermic reaction and it needs to high temperatures to obtain great  $\text{H}_2$  productivity. The overall rate equation of the reaction, Eq. (1), is based on the Langmuir-Hinshelwood kinetic model (Cruz and Silva, 2017). The kinetic rate from Eq. (1) is considered more general for nickel (Ni) catalyst and, therefore, the equation of the SRM process is reported as:

$$R_{\text{SRM}} = \frac{\frac{k_{\text{SRM}}}{P_{\text{H}_2}^{2.5}} \left( P_{\text{CH}_4} P_{\text{H}_2\text{O}} - \frac{P_{\text{H}_2}^3 P_{\text{CO}}}{K_{\text{SRM}}} \right)}{\left( 1 + \frac{F_{\text{H}_2\text{O},0}}{F_{\text{CH}_4,0}} + \frac{F_{\text{H}_2,0}}{F_{\text{CH}_4,0}} + K_{\text{CO}} P_{\text{CO}} + K_{\text{H}_2} P_{\text{H}_2} + K_{\text{CH}_4} P_{\text{CH}_4} + \frac{K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}}}{P_{\text{H}_2}} \right)^2} \quad (2a)$$

$$R_{\text{WGSR}} = \frac{\frac{k_{\text{WGSR}}}{P_{\text{H}_2}} \left( P_{\text{CO}} P_{\text{H}_2\text{O}} - \frac{P_{\text{H}_2} P_{\text{CO}_2}}{K_{\text{WGSR}}} \right)}{\left( 1 + \frac{F_{\text{H}_2\text{O},0}}{F_{\text{CH}_4,0}} + \frac{F_{\text{H}_2,0}}{F_{\text{CH}_4,0}} + K_{\text{CO}} P_{\text{CO}} + K_{\text{H}_2} P_{\text{H}_2} + K_{\text{CH}_4} P_{\text{CH}_4} + \frac{K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}}}{P_{\text{H}_2}} \right)^2} \quad (2b)$$

The partial pressures of chemical components  $i$ ,  $i = \text{CH}_4, \text{H}_2\text{O}, \text{CO}, \text{CO}_2$  and  $\text{H}_2$ , from Eqs. (2a)-(2b) are computed using the Eqs. (2c)-(2e) below

$$P_{\text{CH}_4} = \frac{1 - \left(1 - \frac{F_{\text{CH}_4}}{F_{\text{CH}_4,0}}\right)}{1 + \sum_j^4 \frac{F_{j,0}}{F_{\text{CH}_4,0}}} P_{op.}; P_{\text{H}_2\text{O}} = \frac{\frac{F_{\text{H}_2\text{O},0}}{F_{\text{CH}_4,0}} - \left(1 - \frac{F_{\text{CH}_4}}{F_{\text{CH}_4,0}}\right) - \left(\frac{F_{\text{CO}_2}}{F_{\text{CH}_4,0}}\right)}{1 + \sum_j^4 \frac{F_{j,0}}{F_{\text{CH}_4,0}}} P_{op.} \quad (2c)$$

$$P_{\text{CO}} = \frac{\frac{F_{\text{CO},0}}{F_{\text{CH}_4,0}} + \left(1 - \frac{F_{\text{CH}_4}}{F_{\text{CH}_4,0}}\right) - \left(\frac{F_{\text{CO}_2}}{F_{\text{CH}_4,0}}\right)}{1 + \sum_j^4 \frac{F_{j,0}}{F_{\text{CH}_4,0}}} P_{op.}; P_{\text{CO}_2} = \frac{\frac{F_{\text{CO}_2,0}}{F_{\text{CH}_4,0}} + \left(\frac{F_{\text{CO}_2}}{F_{\text{CH}_4,0}}\right)}{1 + \sum_j^4 \frac{F_{j,0}}{F_{\text{CH}_4,0}}} P_{op.} \quad (2d)$$

$$P_{\text{H}_2} = \frac{\frac{F_{\text{H}_2,0}}{F_{\text{CH}_4,0}} + 3 \left(1 - \frac{F_{\text{CH}_4}}{F_{\text{CH}_4,0}}\right) - \left(\frac{F_{\text{CO}_2}}{F_{\text{CH}_4,0}}\right) - \frac{F_{\text{H}_2}}{F_{\text{CH}_4,0}}}{1 + \sum_j^4 \frac{F_{j,0}}{F_{\text{CH}_4,0}}} P_{op.}, j = \text{H}_2\text{O}, \text{CO}, \text{CO}_2 \text{ and } \text{H}_2 \quad (2e)$$

For the purpose of obtaining the net rates ( $r_i$ ) to each chemical component  $i$  ( $i = \text{CH}_4, \text{H}_2\text{O}, \text{CO}, \text{CO}_2$  and  $\text{H}_2$ ), an expression is used to compute these net rates as follows.

$$r_i = \sum_{i=1}^5 \sum_{j=1}^2 \eta_j \sigma_{ij} R_j; j = \text{SRM}, \text{WGSR} \quad (2f)$$

In relation to the net rates, Eq. (2f) is used to describe the net rate of each chemical component  $i$  of Eqs. (1a) and (b) as follows.

$$r_{\text{CH}_4} = -\eta_{\text{SRM}} R_{\text{SRM}}; r_{\text{H}_2\text{O}} = -(\eta_{\text{SRM}} R_{\text{SRM}} + \eta_{\text{WGSR}} R_{\text{WGSR}}); r_{\text{CO}} = \eta_{\text{SRM}} R_{\text{SRM}} - \eta_{\text{WGSR}} R_{\text{WGSR}} \quad (3a)$$

$$r_{\text{H}_2} = 3\eta_{\text{SRM}} R_{\text{SRM}} + \eta_{\text{WGSR}} R_{\text{WGSR}}; r_{\text{CO}_2} = \eta_{\text{WGSR}} R_{\text{WGSR}} \quad (3b)$$

The kinetic constants, equilibrium constants and adsorption equilibrium constants for the calculations of reaction rates are described as a function of operating temperature (Cruz and Silva, 2017).

$$k_{\text{SRM}} = 2.636 \times 10^{13} \exp\left(-\frac{240.10}{R_u T_{op.}}\right), \left(\text{mol}(\text{kPa})^{0.5} / \text{kg}_{cat.} \text{sec.}\right) \quad (4a)$$

$$K_{\text{SRM}} = 1.0267 \times 10^4 \exp\left(-\frac{26830.0}{T_{op.}}\right) + 30.114, (\text{kPa}^2) \quad (4b)$$

$$k_{\text{WGSR}} = 12.194 \exp\left(-\frac{240.10}{R_u T_{op.}}\right), \left(\text{mol}(\text{kPa})^{-1} / \text{kg}_{cat.} \text{sec.}\right); K_{\text{WGSR}} = \exp\left(-\frac{26830.0}{T_{op.}}\right) - 4.063, (-) \quad (4c)$$

$$K_{\text{CH}_4} = 6.650 \times 10^{-6} \exp\left(-\frac{38.28}{R_u T_{op.}}\right), (\text{kPa}^{-1}); K_{\text{H}_2\text{O}} = 1.770 \times 10^5 \exp\left(-\frac{88.68}{R_u T_{op.}}\right), (-) \quad (4d)$$

$$K_{\text{H}_2} = 6.120 \times 10^{-11} \exp\left(\frac{82.90}{R_u T_{op.}}\right), (\text{kPa}^{-1}); K_{\text{CO}} = 8.230 \times 10^{-7} \exp\left(\frac{70.65}{R_u T_{op.}}\right), (\text{kPa}^{-1}) \quad (4e)$$

### 2.3 TPB reformer's mathematical modelling

The thermochemical modelling from TPB reformer are described by a NIPHM model. The development of the NIPHM model takes into account the following assumptions: (1) the NIPHM model is described under non-isothermal condition, (2) the NIPHM model from TPB reformer is plug-flow with axial dispersion under transient condition, (3) the radial dispersion is negligible inside TPB reformer, (4) the gaseous mixture has constant density in TPB reformer, (5) the molar flow rates inside TPB reformer are constant, (6) the deposition effect of carbon at the surface of catalytic

particles has been neglected, (7) the gas behavior inside TPB reformer was considered as an ideal gas mixture, (8) the bed porosity in axial direction is considered constant, (9) the heaviest hydrocarbons than methane haven't been considered in this work, and (10) chemical reactions as assumed to take place at the surface of catalyst particles. These premises are used to build the governing equations of the NIPHD model inside TPB reformer as follows.

## 2.4 Gas phase's energy balance

A governing equation is described to study the heat distribution on the gas phase inside TFB reformer. The proposed equation provides clear information to drive the temperature distribution on the gas phase under open-cell foam ( $\beta$ -SiC) bed. Therefore, an one-dimensional dynamic equation is developed for the gas phase's temperature as follows.

$$\rho_{g,mix}.C_{p,g,mix} \left( \frac{\partial T_g}{\partial t} + \frac{4q_g}{\pi d_{refor}^2} \frac{\partial T_g}{\partial z} \right) = \lambda_{g,eff} \frac{\partial^2 T_g}{\partial z^2} - h_{gs} \frac{(1-\varepsilon_b)}{\varepsilon_b} \frac{6}{d_p} (T_g - T_{er}) \quad (5a)$$

The effective thermal conductivity of the gas phase is defined as a function of the gas thermal conductivity as follows.

$$\lambda_{g,eff} = \varepsilon_b \lambda_{g,mix}; \lambda_{g,mix} = 1.52 \times 10^{-11} T_{g,0}^3 - 4.86 \times 10^{-8} T_{g,0}^2 + 1.02 \times 10^{-4} T_{g,0} - 3.93 \times 10^{-3} \quad (5b)$$

The suitable initial and boundary conditions from Eq. (4a) are given as follows.

$$T_g \Big|_{t=0} = T_{g,0}; 0 \leq z \leq L; \frac{\partial T_g}{\partial z} \Big|_{z=0^+} = \frac{\rho_{g,mix}.C_{p,g,mix}}{\lambda_{g,mix}} \frac{4q_g}{\pi d_{ref.}^2} \left( T_g \Big|_{z=0^+} - T_{g,\infty} \right); t \geq 0 \quad (5c)$$

$$\frac{\partial T_g}{\partial z} \Big|_{z=L} = \frac{h_{gs,eff}}{\lambda_{g,eff}} \left( T_{g,\infty} - T_g \Big|_{z=L} \right); t \geq 0 \quad (5d)$$

## 2.5 Solid phase's energy balance

The reactive packed-bed has been filled with  $\beta$ -SiC open-cell foams. The energy balance equation is built at the surface of  $\beta$ -SiC open-cell foams where take place the endothermic reaction of  $\text{CH}_4$ . The thermal storage takes place on the  $\beta$ -SiC open-cell foams to ensure sufficient energy to process the SRM's endothermic reaction. However, the energy balance for the SRM's temperature at the surface of  $\beta$ -SiC open-cell foams is given as follows.

$$\rho_s C_{p,s} \frac{\partial T_{er}}{\partial t} = \lambda_{s,eff} \frac{\partial^2 T_{er}}{\partial z^2} + h_{sg} \frac{6}{d_p} \frac{(1-\varepsilon_b)}{\varepsilon_b} (T_g - T_{er}) + \rho_s \frac{(1-\varepsilon_p)}{\varepsilon_p} \sum_{j=1}^2 \pm \Delta H_j \eta_j R_j \quad (6a)$$

The solid phase's thermal conductivity is defined as a function of the gaseous mixture's thermal conductivity according to Eq. (6a) below.

$$\lambda_{s,eff} = (1-\varepsilon_b) \lambda_{g,mix} \quad (6b)$$

The suitable initial and boundary conditions from Eq. (6a) are given as follows.

$$T_{er} \Big|_{t=0} = T_{er,0}; 0 \leq z \leq L; \frac{\partial T_{er}}{\partial z} \Big|_{z=0^+} = \frac{q_h}{\lambda_s}; t \geq 0; \frac{\partial T_{er}}{\partial z} \Big|_{z=L} = \frac{h_{sg,eff}}{\lambda_{s,eff}} \left( T_{er,\infty} - T_{er} \Big|_{z=L} \right); t \geq 0 \quad (6c)$$

## 2.6 Transport equation of chemical components

In Section 2.3, it was approached some assumptions that can be used to build the proposed problem's modelling. However, the transport equations for chemical components  $i$  ( $i = \text{CH}_4, \text{H}_2\text{O}, \text{CO}, \text{CO}$  and  $\text{H}_2$ ) are presented as follows.

$$\frac{u_{sg}}{g} \frac{\partial F_i}{\partial t} + \frac{4q_g}{S_{sp}\pi d_{ref}^2} \frac{\partial F_i}{\partial z} = \frac{D_{ax,i}}{S_{sp}} \frac{\partial^2 F_i}{\partial z^2} + \rho_s r_{ref}^2 L(1-\varepsilon_b) r_i; 0 < z < L \quad (7a)$$

The suitable initial and boundary conditions from Eq. (7a) are presented as follows.

$$F_i|_{t=0} = F_{i,0}; 0 \leq z \leq L; \varepsilon_b \frac{D_{ax,i}}{L} \frac{\partial F_i}{\partial z} \Big|_{z=0^+} = u_{sg} \left( F_i|_{z=0^+} - F_{i,\infty} \right); t \geq 0; \quad (7b)$$

$$\varepsilon_b \frac{D_{ax,i}}{L} \frac{\partial F_i}{\partial z} \Big|_{z=L} = k_{gs,eff} \left( F_i|_{z=L} - F_{i,\infty} \right); t \geq 0 \quad (7c)$$

## 2.7 Proposed model's solution by the CIEA

The CIEA's method can be employed as a good technique for studying the performance from TPB reformers (Dias and Silva, 2020). The CIEA's methodology has been used to transform the PDE system (Eqs. (5a), (6a), and (7a)) into an ODE system using the boundary conditions (Eqs. (5d), (5e), (6d), (6e), (7c), and (7d)) of each PDE. Thus, the system of ODEs is reported as follows.

$$\alpha_{g,1} \frac{d\bar{T}_g(t)}{dt} = \left( \alpha_{g,2} - \lambda_{g,eff} \cdot \alpha_{g,4} \right) T_g(0,t) - \left( \alpha_{g,2} + \lambda_{g,eff} \cdot \alpha_{g,5} \right) T_g(L,t) - \alpha_{g,3} \left( \bar{T}_g(t) - \bar{T}_s(t) \right) + \lambda_{g,eff} \cdot T_{g,\infty} \left( \alpha_{g,4} + \alpha_{g,5} \right) \quad (8a)$$

$$\frac{d\bar{T}_{er}(t)}{dt} = \beta_{s,5} \left( \bar{T}_g(t) - \bar{T}_{er}(t) \right) + \sum_{j=1}^3 \Delta H_j \eta_j \bar{R}_j(t) - \beta_{s,1} \beta_{s,5} T_{er}(L,t) + \beta_{s,1} \left( \beta_{s,5} T_{er,\infty} - \beta_{s,4} \right) \quad (8b)$$

$$\frac{d\bar{F}_i(t)}{dt} = \left( \varphi_{f,2} \varphi_{f,5} - \varphi_{f,1} \right) F_i(L,t) - \left( \varphi_{f,2} \varphi_{f,4} - \varphi_{f,1} \right) F_i(0,t) + \varphi_{f,3} \bar{r}_i(t) + \varphi_{f,2} F_{i,\infty} \left( \varphi_{f,4} - \varphi_{f,5} \right) \quad (8c)$$

All coefficients from Eqs. (8a)-(8c) are presented in Appendices A, B and C, respectively

## 2.8 Full solution

Several numerical methods have been proposed to solve systems of PDEs. The numeric methodology's choice is limited to the desired accuracy on the consistency and robustness of PDE system's numerical data. In relation to ODEs, Eqs. (8a)-(8c), they were solved by Runge-Kutta Gill method. On the other hand, the full solutions are approximated as follows.

$$T_g(z,t) = \frac{1}{2} T_g(z,t) \Big|_{t=0} + \sum_{k=1}^{\infty} \bar{T}_g(t_k) \sin\left(\frac{k\pi z}{L}\right); T_{er}(z,t) = \frac{1}{2} T_{er}(z,t) \Big|_{t=0} + \sum_{k=1}^{\infty} \bar{T}_{er}(t_k) \sin\left(\frac{k\pi z}{L}\right) \quad (8d)$$

$$F_i(z,t) = \frac{1}{2} F_i(z,t) \Big|_{t=0} + \sum_{k=1}^{\infty} \bar{F}_i(t_k) \sin\left(\frac{k\pi z}{L}\right) \quad (8e)$$

## 3. RESULTS AND DISCUSSIONS

In section 2, a physical-mathematical modelling has been developed to investigate the SRM method in the TPB reformer. A computational algorithm using the FORTRAN 95 has been elaborated by authors to compute the SRM method's variables in the TPB reformer.

### 3.1 Kinetic parameters

In Section 2.1, kinetic model's equations were presented. The kinetic model's parameters are used to feed the computational algorithm in combination with hydrodynamic model's parameters from the TPB reformer. The numerical values of the kinetic model's parameters are shown in Table 1 below.

Table 1. Kinetic parameters, equilibrium constants of reactions and equilibrium constants

Parameters kinetic, equilibrium, and adsorption	Values	Sources
$k_{SRM} (\text{mol (kPa)}^{0.5}/\text{kg}_{\text{cat.}} \text{ sec.})^{(1)}$	$2.015 \times 10^{11}$	Eq. (4a)
$K_{SRM} (\text{kPa})^{2(1)}$	$2.135 \times 10^7$	Eq. (4b)
$K_{WGSR} (\text{mol (kPa)}^{-1}/\text{kg}_{\text{cat.}} \text{ sec.})^{(1)}$	$1.218 \times 10^3$	Eq. (4c)
$K_{WGSR} (-)^{(1)}$	13.015	Eq. (4c)
$K_{CH_4} (\text{kPa})^{-1(1)}$	$8.974 \times 10^{-7}$	Eq. (4d)
$K_{H_2O} (-)^{(1)}$	$3.701 \times 10^4$	Eq. (4d)
$K_{H_2} (\text{kPa})^{-1(1)}$	$8.987 \times 10^{-12}$	Eq. (4e)
$K_{CO} (\text{kPa})^{-1(1)}$	$5.671 \times 10^{-6}$	Eq. (4e)
$\eta_{SRM} (-)^{(1)}$	0.021	Cruz and Silva, 2017
$\eta_{WGSR} (-)^{(1)}$	0.0169	Cruz and Silva, 2017

<sup>(1)</sup> Computed at 900°C

### 3.2 TFB reformer's hydrodynamic parameter

In Section 2.2, hydrodynamic model's equations have been described. Hydrodynamic model's parameters are used to feed the computational algorithm and these parameters are reported in Table 2 below.

Table 2. Model parameters and inlet operating conditions of the SRM method in the TPB reformer.

Model parameters	Values	Sources
L (m)	0.60	Estimated
$d_p$ (m)	$3.4 \times 10^{-4}$	Estimated
$d_{\text{refor.}}$ (m)	$3.2 \times 10^{-3}$	Estimated
$T_{g,0}$ (K)	673	Estimated
$T_{\text{er},0}$ (K)	673	Estimated
$P_{\text{op.}}$ (kPa)	600	Estimated
$\rho_{g, \text{mix.}}$ (kg/m <sup>3</sup> )	0.1692	Silva and Abreu, 2016
$C_{p, g, \text{mix.}}$ (kJ/kg K)	127.09	Dias and Silva, 2020
$q_g$ (m <sup>3</sup> /sec.)	$1.201 \times 10^{-6}$	Estimated
$g$ (m/sec <sup>2</sup> )	9.81	Estimated
$S_p$ (sec <sup>-1</sup> )	$3.53 \times 10^7$	Cruz and Silva, 2017
$\lambda_{g, \text{eff}}$ (W/m K)	1.078	Eq. (5b)
$h_{\text{gs}}$ (W/m <sup>2</sup> K)	1.902	Dias and Silva, 2020
$\varepsilon_b$ (m <sup>3</sup> gas/m <sup>3</sup> reformer)	0.39	Dias and Silva, 2020
$\varepsilon_p$ (m <sup>3</sup> gas/m <sup>3</sup> reformer)	0.87	Voltolina et al., 2017
$C_{p, s}$ (J/kg K)	336.00	Dias and Silva, 2020
$\lambda_{s, \text{eff}}$ (W/m K)	0.501	Eq. (6b)
$F_{CH_4,0}$ (mol/sec.)	0.25	Silva and Abreu, 2016
$F_{H_2O,0}$ (mol/sec.)	0.75	Silva and Abreu, 2016
$F_{H_2,0}$ (mol/sec.)	$7.62 \times 10^{-5}$	Silva and Abreu, 2016
$F_{CO,0}$ (mol/sec.)	$3.2 \times 10^{-5}$	Silva and Abreu, 2016
$F_{CO_2,0}$ (mol/sec.)	$6.32 \times 10^{-5}$	Silva and Abreu, 2016
$D_{\text{ax, CH}_4}$ (m <sup>2</sup> /sec.) <sup>(1)</sup>	$289 \times 10^{-3}$	Cruz and Silva, 2017
$D_{\text{ax, H}_2O}$ (m <sup>2</sup> /sec.) <sup>(1)</sup>	$3.79 \times 10^{-3}$	Cruz and Silva, 2017
$D_{\text{ax, H}_2}$ (m <sup>2</sup> /sec.) <sup>(1)</sup>	$2.01 \times 10^{-3}$	Cruz and Silva, 2017
$D_{\text{ax, CO}}$ (m <sup>2</sup> /sec.) <sup>(1)</sup>	$3.41 \times 10^{-3}$	Cruz and Silva, 2017
$D_{\text{ax, CO}_2}$ (m <sup>2</sup> /sec.) <sup>(1)</sup>	$1.89 \times 10^{-3}$	Cruz and Silva, 2017

<sup>(1)</sup> Computed at 900°C

### 3.3 Validation by comparison against published data

To ensure the validity of the proposed model, authors have made a comparison of simulated results with published data of the literature. The simulating results are computed from a computer code developed by authors. Slight differences can be found due to the deviation between the literature results and simulating results. An average relative error (ARE), Eq. (9a), was used to compute the consistency criterion and therefore, the ARE is given as follows.

$$ARE = \left| \frac{F_i^{Chompupun\ et\ al.,\ 2018} - F_i^{Simulating\ results}}{F_i^{Chompupun\ et\ al.,\ 2018}} \right| \times 100; i = CH_4, H_2O, H_2, CO\ and\ CO_2 \quad (9a)$$

Fig. 2 compares the literature results and simulated results of molar flows of chemical components  $i$  at the outlet of the TPB reformer. The good agreement between the simulated results and literature data reports that the developed model is acceptable. As it can be seen in Fig. 2, the simulated results against the experimental results from literature (Chompupun et al., 2018) have presented a good agreement, resulting in AREs of 9.28%, 0.81%, 1.29%, 9.74%, and 2.13%. These AREs should be due to the incompatibility between the simulating results and experimental results.

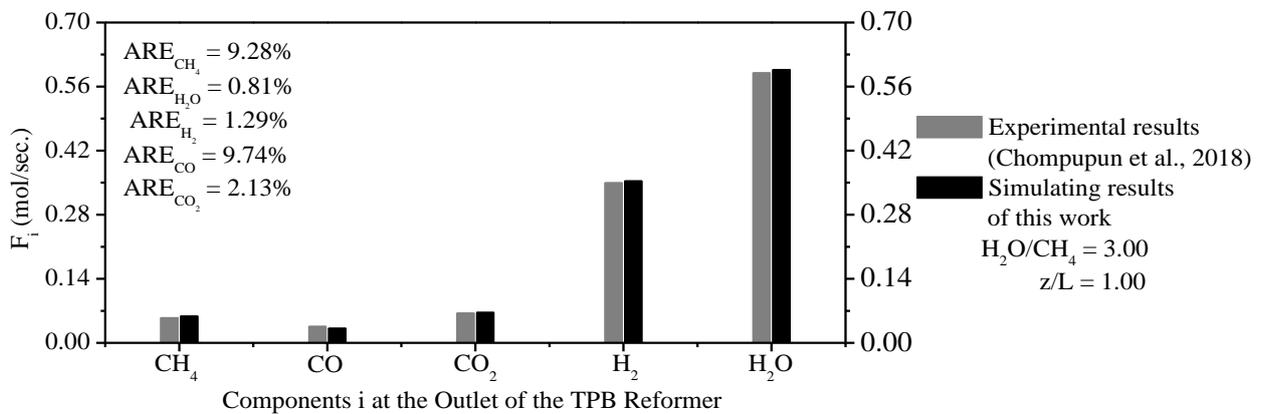


Figure 2. Comparison between molar flows of chemical components  $i$  at the outlet of TPB reformer.

### 3.4 Endothermic reaction temperature's numerical experiments

The profiles of the Endothermic Reaction Temperature (ERT) were computed from Eq. (6a) for the SRM method in the TPB reformer. In Fig. 3, it is checked the dynamic region and stationary region along the TPB reformer's length. The dynamic region occurs up to  $\pm 0.18$  m, after that the stationary state is kept until 0.60 m. It was reported that the profiles of the endothermic reaction temperature tend to assume an inflection point at minimum values because of the endothermic reaction's effect. The range of the  $\lambda_{s,eff}$  has a pertinent effect on the ERT's profiles in TFB reformer. Three different values of the  $\lambda_{s,eff}$  have been used to check the ERT's sensibility to the  $\lambda_{s,eff}$ . As results, when the  $\lambda_{s,eff}$  is higher ( $\lambda_{s,eff} = 129.23$ ), the heat absorption in TFB reformer is notably increased and therefore, the ERT's profile is favoured. On the other hand, when the  $\lambda_{s,eff}$  is lower ( $\lambda_{s,eff} = 107.26$ ), the heat absorption in TFB reformer is remarkably decreased and thus, the ERT's profile is reduced.

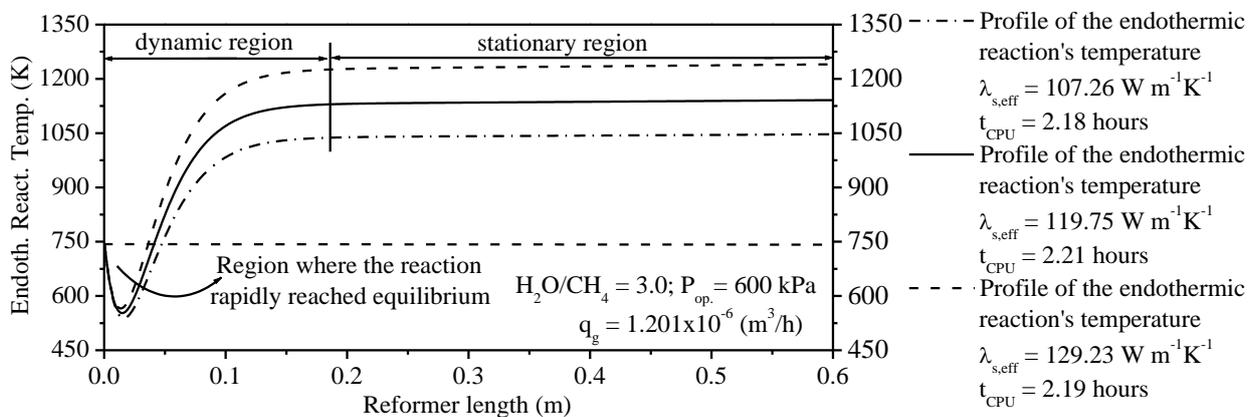


Figure 3. Endothermic reaction temperature's profiles along of the TPB reformer's length on  $\beta$ -SiC foam.

Fig. 4 shows the profiles of the molar flow of each chemical component  $i$  of the SRM method at the following operating conditions:  $H_2O/CH_4 = 3.00$ , 500 kPa, 1173 K, and  $1.201 \times 10^{-6}$  ( $m^3/sec.$ ). In this figure, the profiles of the molar flows from the consumed reactants ( $H_2O$  and  $CH_4$ ) and produced products ( $CO$ ,  $CO_2$  and  $H_2$ ) are reported in the TPB reformer. After reaching the stable state, only 18.67% of  $H_2O$  was consumed. On the other hand, after achieving the stable state, 97.26% of  $CH_4$  was consumed. After reaching the stable state, 29.48% of  $H_2$ , 14.23% of  $CO_2$ , and 2.76% of  $CO$  were produced for the SRM method in the TPB reformer.

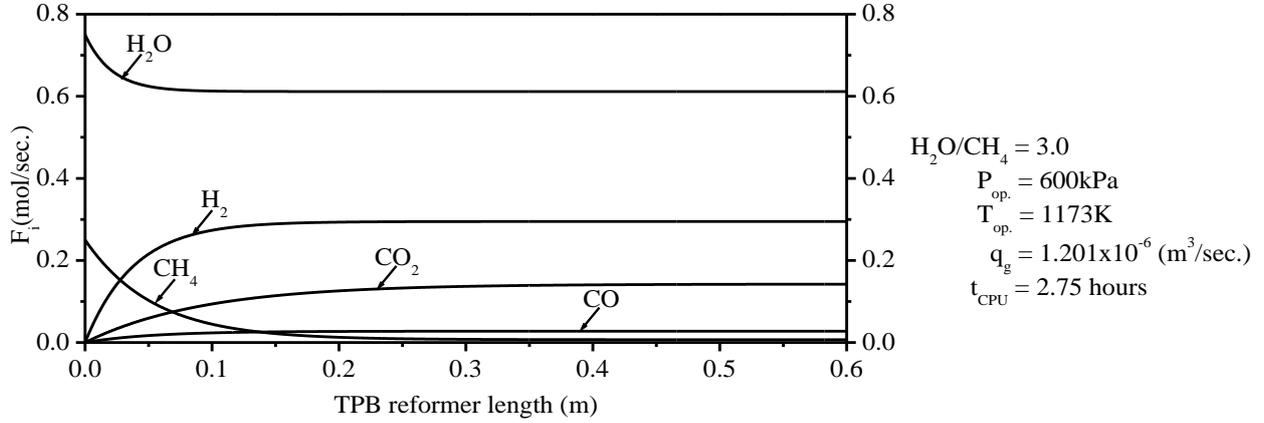


Figure 4. Molar flows of each chemical component  $i$  along of the TPB reformer's length on  $\beta$ -SiC foam.

#### 4. CONCLUSIONS

A non-isothermal pseudo-homogeneous mathematical model which includes the thermal energy transfer on the endothermic thermochemical conversion and mass transfer coupled with a thermochemical kinetic model was developed and validated against published data of the literature for a FBR reformer. After validating the numerical model, such model can be used like a process simulator. Therefore, the major conclusions are listed as follows.

1. The simulating results of molar flows are similar to experimental results of molar flows under same operating conditions. The validating results have driven a good agreement against the literature data for molar flows at the outlet from FBR.
2. When the  $\lambda_{s, eff.}$  is notably increased, the ERT's profile is risen. On the other hand, when the  $\lambda_{s, eff.}$  is remarkably reduced, the ERT's profile is decreased.
3. Under the prescribed operating conditions, 18.67% of  $H_2O$  and 97.26% of  $CH_4$  were consumed while 29.48% of  $H_2$ , 14.23% of  $CO_2$ , and 2.76% of  $CO$  were produced.

#### 5. ACKNOWLEDGEMENTS

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#### Appendix A: Parameters from Eq. (8a)

$$\alpha_{g,1} = \rho_{g,mix} \cdot C_{p,g,mix}; \alpha_{g,2} = \rho_{g,mix} \cdot C_{p,g,mix} \cdot \frac{4q_g}{\pi d_{rz}^2}; \alpha_{g,3} = h_{gs} \frac{(1-\varepsilon_b)}{\varepsilon_b} \frac{6}{d_p} \quad (10a)$$

$$\alpha_{g,4} = \frac{\rho_{g,mix} \cdot C_{p,g,mix}}{\lambda_{g,mix}}; \alpha_{g,5} = \frac{h_{gs,eff.}}{\lambda_{g,eff.}}; \alpha_{g,6} = L(6 + L\alpha_{g,4}) - \frac{L(6 + L\alpha_{g,5})(1 + 0.5L\alpha_{g,4})}{1 + 0.5L\alpha_{g,5}} \quad (10b)$$

$$\alpha_{g,7}(t) = 12\bar{T}_g(t) + L^2 \left( \alpha_{g,4} T_{g,\infty}^{Up.} + \alpha_{g,5} T_{g,\infty}^{Bot.} \right) \left[ 1 + \frac{0.5(6 + L\alpha_{g,5})}{1 - 0.5L\alpha_{g,5}} \right] \quad (10c)$$

$$T_g(0,t) = \frac{\alpha_{g,7}(t)}{\alpha_{g,6}}; T_g(L,t) = \frac{1}{1 - 0.5L\alpha_{g,5}} \left[ 0.5LT_{g,\infty}(\alpha_{g,4} + \alpha_{g,5}) - (1 + 0.5L\alpha_{g,4}) \frac{\alpha_{g,7}(t)}{\alpha_{g,6}} \right] \quad (10d)$$

### Appendix B: Parameters from Eq. (8b)

$$\beta_{er,1} = \frac{\lambda_{s,eff.}}{\rho_s C_{p,s}}; \beta_{er,2} = h_{sg} \frac{6}{d_p} \frac{1}{\rho_s C_{p,s}} \frac{(1-\varepsilon_b)}{\varepsilon_b}; \beta_{er,3} = \frac{(1-\varepsilon_p)}{\varepsilon_p} \quad (11a)$$

$$\beta_{er,4} = \frac{qh}{\lambda_s}; \beta_{er,5} = \frac{h_{sg,eff.}}{\lambda_{s,eff.}}; \beta_{er,6} = 2L \left[ 3 - \frac{(6 + L\beta_{s,5})}{2 + L\beta_{s,5}} \right] \quad (11b)$$

$$\beta_{er,7}(t) = 12\bar{T}_{er}(t) - L^2 (\beta_{er,4} - \beta_{er,5} T_{er,\infty}) - \frac{L^2 (6 + L_z \beta_{er,5}) (\beta_{er,4} + \beta_{er,5} T_{er,\infty})}{2 + L\beta_{er,5}} \quad (11c)$$

$$T_{er}(0,t) = \frac{\beta_{er,7}(t)}{\beta_{s,6}}; T_{er}(L,t) = \frac{1}{2 + L\beta_{er,5}} \left[ L_z (\beta_{er,4} + \beta_{er,5} T_{er,Bot.}) + 2 \frac{\beta_{er,7}(t)}{\beta_{er,6}} \right] \quad (11d)$$

### Appendix C: Parameters from Eq. (8c)

$$\varphi_{f,1} = \frac{4q_g}{S_{sp} \pi d_{rz}^2} \frac{g}{u_{sg}}; \varphi_{f,2} = \frac{g}{u_{sg}} \frac{D_{ax,i}}{S_{sp}}; \varphi_{f,3} = \frac{g}{u_{sg}} \rho_s r_{rz}^2 L(1-\varepsilon_b); \varphi_{f,4} = \frac{L}{\varepsilon_b} \frac{u_{sg}}{D_{ax,i}} \quad (12a)$$

$$\varphi_{f,5} = \frac{L}{\varepsilon_b} \frac{k_{sg}}{D_{ax,i}}; \varphi_{f,6} = L(6 + L\varphi_{f,4}) - \frac{L(6 - L\varphi_{f,5})}{2 - L\varphi_{f,5}} (2 + L\varphi_{f,4}) \quad (12b)$$

$$\varphi_{f,7}(t) = 12\bar{F}_i(t) - L^2 F_{i,\infty} (\varphi_{f,5} - \varphi_{f,4}) - \frac{L^2 F_{i,\infty} (6 - L\varphi_{f,5}) (\varphi_{f,4} + \varphi_{f,5})}{2 - L\varphi_{f,5}} \quad (12c)$$

$$F_i(0,t) = \frac{\varphi_{f,7}(t)}{\varphi_{f,6}}; F_i(L,t) = \frac{1}{2 - L\varphi_{f,5}} \left[ (2 + L\varphi_{f,4}) \frac{\varphi_{f,7}(t)}{\varphi_{f,6}} - L F_{i,\infty} (\varphi_{f,4} + \varphi_{f,5}) \right] \quad (12d)$$

## 6. LIST OF SYMBOLS

$C_{p,g,mix.}$	Molar heat capacity at constant pressure of the gas mixture (kJ/kg K)
$C_{p,s}$	Heat capacity pressure of the solid phase (kJ/kg K)
$D_{ax,i}$	Dispersion coefficients of each component i (m <sup>2</sup> /sec.)
$d_p$	Diameter of the solid particles (m)
$F_i$	Molar flow of components i (kmol/sec.)
$F_{j,0}$	Initial molar flows of components j
$g$	Gravity acceleration (m/sec. <sup>2</sup> )
$h_{gs}$	Gas-solid heat transfer coefficient (W/m <sup>2</sup> K)
$k_{SRM}$	Reaction constant of the $R_{SRM}$ (kmol kPa <sup>0.5</sup> /kg <sub>cat.</sub> sec.)
$k_{WGSR}$	Reaction constant of the $R_{WGSR}$ (kmol kPa <sup>-1</sup> /kg <sub>cat.</sub> sec.)
$K_{SRM}$	Equilibrium constant of the $R_{SRM}$ (kPa <sup>2</sup> )
$K_{WGSR}$	Equilibrium constant of the $R_{WGSR}$ (-)
$K_i$	Adsorption constants of components i, i = CO, H <sub>2</sub> and CH <sub>4</sub> , (kPa <sup>-1</sup> )
$K_j$	Adsorption constant of components j, j = H <sub>2</sub> O, (-)
$L$	TPB reformer length (m)
$P_i$	Partial pressures of components i, i = CH <sub>4</sub> , H <sub>2</sub> O, CO, CO <sub>2</sub> and H <sub>2</sub> , (kPa)
Pop.	Operating pressure (kPa)
$q_g$	Gas phase's flow rate (m <sup>3</sup> /sec.)
$r_i$	Net rates of components i (i = CH <sub>4</sub> , H <sub>2</sub> O, CO, CO <sub>2</sub> and H <sub>2</sub> ) (kmol/kg <sub>cat.</sub> sec.)
$R_j$	Overall rates of the reforming reactions j, j = 1 and 2, (kmol/kg <sub>cat.</sub> sec.)
$S_{sp}$	Spatial velocity (sec <sup>-1</sup> )
$t$	Iteration time (sec.)
$T_{er,0}$	Initial temperature of the endothermic reaction (K)
$T_{er}$	Temperature of the endothermic reaction (K)

$T_{g,0}$	Gas phase's initial temperature (K)
$T_g$	Gas phase's temperature (K)
$u_{sg}$	Gas superficial velocity (m/sec)
$z$	Axial coordinate (m)

## 7. GREEK LETTERS

$\varepsilon_b$	Packed-bed porosity ( $m^3_{\text{gas}}/m^3_{\text{reformer}}$ )
$\varepsilon_p$	Particle porosity ( $m^3_{\text{particle}}/m^3_{\text{reformer}}$ )
$\eta_j$	Effectiveness factors of reforming reactions $j$ ( $j = \text{SRM and WGSR}$ )
$\lambda_{g, \text{mix.}}$	Gaseous mixture's thermal conductivity (W/m K)
$\lambda_{g, \text{eff.}}$	Gas phase's effective thermal conductivity (W/m K)
$\lambda_{s, \text{eff.}}$	Solid phase's effective thermal conductivity (W/m K)
$\rho_{g, \text{mix.}}$	Gas mixture density of components $i$ ( $kg/m^3$ )
$\rho_s$	Solid phase density ( $kg/m^3$ )

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