Cleiseano Emanuel da Silva Paniagua
(Organizador)

ENGENHARIA QUÍMICA:

Desenvolvimento de novos processos e produtos

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APRESENTAÇÃO

O e-book: “Engenharia química: Desenvolvimento de novos processos e produtos” é constituído por nove capítulos de livros que apresentaram estudos aplicados a diferentes segmentos industriais e ambientais.

O primeiro capítulo avaliou as propriedades e capacidade de escoabilidade de materiais pulverulentos a base de celulose e lactose na fabricação de medicamentos na forma de comprimidos ou cápsulas, os resultados foram satisfatórios e possibilita a substituição da lactose pela celulose. O segundo trabalho avaliou o processo de cavitação no canal do bico injetor ao se substituir o tipo de combustível em motores que operam a diesel, a viscosidade do combustível e a pressão de injeção foram os fatores que mais influenciaram na cavitação. O terceiro capítulo avaliou diferentes modificações químicas no óleo de soja refinado a partir da reação de inúmeras reações com o intuito de melhorar as características lubrificantes, obtendo-se um lubrificante biodegradável a partir do óleo de soja. O capítulo 4 apresenta o estudo da incorporação do extrato de frutos – cupuaçu – e do mesocarpo do coco de babaçu a fim de conferir atividade antioxidante para biofilmes com potencial utilização em biopolímeros.

O capítulo 5 realizou uma análise bibliográfica de catalisadores e suas propriedades que viabilizam reações de transesterificação heterogênea a fim de obter biocombustíveis. Já o capítulo 6 realizou um estudo apresentando a importância da Espectroscopia Raman como técnica de caracterização de óxidos com propriedades catalíticas. O capítulo 7 apresentou um estudo de desenvolvimento de uma planta pirolítica de baixo custo utilizando resíduos de colheita de Eucalipto como biomassa para a combustão. O capítulo 8 apresentou uma técnica de conversão integral de gás metano em gás carbônico em um reator de leito fixo. Por fim, o estudo de potencialidade de biorremediação utilizando a biomassa de *Chlorella Vulgaris* em processos de tratamento de águas residuárias.

Nesta perspectiva, a Atena Editora vem trabalhando de forma a estimular e incentivar cada vez mais pesquisadores do Brasil e de outros países a publicarem seus trabalhos com garantia de qualidade e excelência em forma de livros, capítulos de livros e artigos científicos.

Cleiseano Emanuel da Silva Paniagua

SUMÁRIO

CAPÍTULO 8

GENERALIZED INTEGRAL TRANSFORM TECHNIQUE APPLIED IN METHANE REFORMING PROCESS WITH CARBON DIOXIDE IN FIXED BED REACTOR

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ABSTRACT: In this work, a one-dimensional transient pseudo-heterogeneous mathematical model with axial dispersion was used to quantify components concentration profiles in the methane reforming process with carbon dioxide, taken into account, reaction mechanism of three elementary reactions, including the decomposition of methane, shift and reverse Boudouard reactions. The model was obtained on the basis of differential mass balance, including a reaction rate for methane according to the Langmuir-Hinshelwood model and the rates of both homogenous and heterogeneous reactions for carbon dioxide. For the solid phase of nickel based catalyst ($Ni/\gamma\text{-}Al_2O_3$), was assumed that it is composed by small spherical particles, allowing an average process in the radial coordinate of the particle transport equation to eliminate the radial dependence of these equations. This average process is based on the technique of Coupled Integral Equations Approach (CIEA) that incorporates boundary conditions to the resulting partial differential equations (PDEs). After this average process, the Generalized Integral Transform Technique (GITT) was used in the resulting PDEs, obtaining a new system of Ordinary Differential Equations (ODEs) in time. The reduced model was solved numerically using the routine DIVPAG of IMSL Library. The results were compared with some available in the literature on the basis of model parameters, such as the axial dispersion coefficient, effective diffusion, mass transfer and kinetic constants.

KEYWORDS: Methane reforming, Nickel, Generalized Integral Transform Technique.

RESUMO: Neste trabalho, um modelo matemático pseudo-heterogêneo unidimensional transiente, do tipo dispersivo foi usado para a quantificação dos perfis de concentração dos componentes do processo de reforma do metano com dióxido de carbono, tendo como base o mecanismo e a cinética de três etapas reacionais, incluindo a decomposição do metano e as reações reversas de Boudouard e de shift. O modelo foi obtido com base no balanço diferencial de massa, incluindo a taxa de reação para o metano segundo o modelo de Langmuir-Hinshelwood e as taxas de reação homogênea e heterogênea para o dióxido de carbono. Considerando que a fase sólida, catalisador de Níquel (Ni/ -Al2O3), é composta por partículas esféricas pequenas, um processo de média na coordenada radial das equações de transporte na partícula foi utilizado para eliminar a dependência radial dessas equações. Tal processo de média é baseado na Técnica das Equações Integrais Acopladas (CIEA) e incorpora, nas EDPs resultantes, informações das condições de contorno. Após este processo, foi empregado a Técnica da Transformada Integral Generalizada (GITT) no sistema diferencial parcial resultante, obtendo-se, neste caso, um sistema de equações diferenciais ordinárias (EDOs) no tempo. Os modelos reduzidos foram, então, solucionados numericamente usando-se a rotina DIVPAG da biblioteca IMSL. Os resultados obtidos são comparados com alguns disponíveis na literatura, em função dos parâmetros do modelo, como a dispersão axial, difusividade efetiva, coeficiente de transferência de massa e constantes cinéticas.

PALAVRAS-CHAVE: Reforma do metano, Níquel, Técnica da Transformada Integral Generalizada.

NOMENCLATURE

Bi_m,i	Mass transfer Biot number of specie *i*, (-)
C_{ie}	Fluid phase concentration for the specie *i* in z=0, (mol.m^{-3})
C_T	Fluid phase total concentration (C_{1e} + C_{2e}), (mol.m^{-3})
D_{ax}	Axial dispersion coefficient, (m^2/s)
$D_{i,ef}$	Effective diffusivity for the component *i* in Air, (m^2/s)
k_1	Kinetic constant of methane decomposition reaction, (mol/g$_{cat}$.s)
k_2	Kinetic constant in the forward direction of shift reaction, ((m^3)^2/g$_{cat}$.s.mol)
k_{-2}	Kinetic constant in the reverse direction of shift reaction, ((m^3)^2/g$_{cat}$.s.mol)
k_3	Kinetic constant of reverse Bourdouard reaction, (m^3/g$_{cat}$.s)
k_{CH4}	Equilibrium adsorption constant of methane, (m^3/mol)
K_{eq}	Equilibrium constant of reverse shift reaction, (-)
R_p	Radius of the particle, (m)

u_0	Superficial velocity, (m/s)
u	Interstitial velocity, (m/s)
ε_b	Bed porosity, (-)
ε_p	Particle porosity, (-)

1 | INTRODUCTION

Natural gas is a very attractive fossil energy source, due to the large worldwide reserves and its lower carbon emissions compared to coal and oil (U. S. Energy Information Administration, 2013). In addition, is expected that Brazil will increase natural gas production due to reserves associated with presalt basins (U. S. Energy Information Administration, 2014), which offer great opportunities to meet future energy needs of this country. From natural gas, hydrogen can be obtained by steam reforming, carbon dioxide reforming, partial oxidation, autothermal reforming or catalytic decomposition of methane. Hydrogen is an important commodity for the chemical industry and petroleum refining and can be considered as a source of energy for store and produce electricity from fuel cell systems (Tuza and Souza, 2016). Carbon dioxide reforming of methane could convert two greenhouse gases (CH_4 and CO_2) into syngas, which could be further employed to synthesize high-value added products (Yang *et al.*, 2016). Currently, studies on the catalysts used in CH_4 e CO_2 reforming are mainly focused on the noble metals and transition metals used. However, the noble metals are expensive and these resources are limited. And the transition metals are easily deactivated due to carbon deposition, so it has become the bottleneck of its industrial application (Guo *et al.*, 2013).

2 | MATHEMATICAL ANALYSIS

As was done by Pacífico (2004), the present work modeled the kinetics of methane reforming reaction with CO_2 using the reactions of reverse water-gas-shift, reverse Boudouard and decomposition of methane, determining the kinetics and adsorption parameters from an optimization with the experimental data of a differential bed reactor. A Langmuir-Hinshelwood model was used to represent the methane reaction rate. In addition, to the reaction conditions it was considered that reverse-Boudouard is almost irreversible and the reverse shift reaction is homogeneous, meaning that CO_2 does not adsorb on the metal surface of the catalyst (Pacífico, 2004). The model reactions can be represented as in Table 1. The fixed bed reactor used for dry reforming process operated with a structure composed of 3 zones: the first composed of ceramic balls was identified as the pre-heating zone and distribution of the gas mixture; the second is composed by the catalytic bed and the third zone composed of another bed of ceramic balls, to support the catalytic bed, as shown in Figure 1.

Reaction	Kind
$CH_4 \xrightarrow{k_1, K_{CH4}} C + 2H_2$	Catalytic
$CO_2 + H_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CO + H_2O;\ K_{eq} = k_2 / k_{-2}$	Homogeneous
$C + CO_2 \xrightarrow{k_3} 2CO$	Non-catalytic heterogeneous

Table 1 - Set of reactions realized by Pacífico (2004).

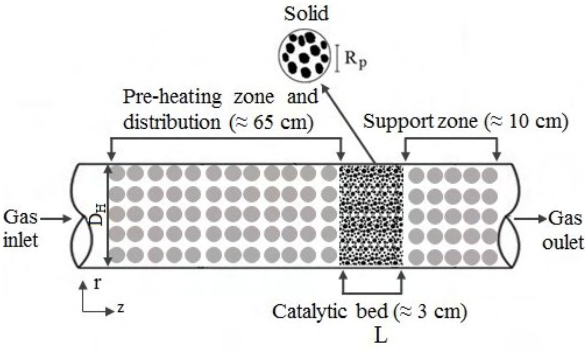


Figure 1 - Is the geometry of the problem, similar to that used by Souto (2005).

Thus, were adopted the following assumptions:

- The matrix is a porous solid, where the oil is uniformly distributed;
- The solid particles are considered uniform and spherical;
- The process of mass transfer in the bed is one-dimensional transient $C_i(t,z)$;
- The process of mass transfer on the particle is one-dimensional transient $C_{pi}(t,r)$;
- The fluid velocity does not change in any spatial coordinates;
- The system is isothermal and isobaric;
- The physical properties of the fluid are constant;
- The length of the control volume is sufficiently large, so that the condition $(\partial C_i/\partial z)_{z=L}=0$, can be satisfied.

2.1 Model Description

Based on the above assumptions and differential mass balance (Pacífico, 2004), the following model, with their initial and contours conditions, it was proposed to describe the methane reforming process with CO_2. Considering the following index: (CH_4 = 1, CO_2 = 2, H_2 = 3, CO = 4 and H_2O =5). For the fluid phase:

$$\frac{\partial C_1}{\partial t} + \frac{u_0}{\varepsilon_b}\frac{\partial C_1}{\partial z} = D_{ax}\frac{\partial^2 C_1}{\partial z^2} - R_{f1}; \qquad 0 < z < L; \quad t > 0;$$

$$\frac{\partial C_2}{\partial t} + \frac{u_0}{\varepsilon_b}\frac{\partial C_2}{\partial z} = D_{ax}\frac{\partial^2 C_2}{\partial z^2} - R_{f2}; \qquad 0 < z < L; \quad t > 0;$$

$$\begin{aligned}
&\frac{\partial C_3}{\partial t}+\frac{u_0}{\varepsilon_b}\frac{\partial C_3}{\partial z}=D_{ax}\frac{\partial^2 C_3}{\partial z^2}+R_{f3}; \quad 0<z<L; \quad t>0;\\
&\frac{\partial C_4}{\partial t}+\frac{u_0}{\varepsilon_b}\frac{\partial C_4}{\partial z}=D_{ax}\frac{\partial^2 C_4}{\partial z^2}+R_{f4}; \quad 0<z<L; \quad t>0;\\
&\frac{\partial C_5}{\partial t}+\frac{u_0}{\varepsilon_b}\frac{\partial C_5}{\partial z}=D_{ax}\frac{\partial^2 C_5}{\partial z^2}+R_{f5}; \quad 0<z<L; \quad t>0;\\
&C_i=C_{i0} \quad \text{for } \mathrm{t}=0\\
&-D_{ax}\frac{\partial C_i}{\partial z}=u(C_{ie}-C_i) \quad \text{for } \mathrm{z}=0; \quad i=1,2,\ldots,5\\
&\frac{\partial C_i}{\partial z}=0 \quad \text{for } \mathrm{z}=\mathrm{L}
\end{aligned} \tag{1-8}$$

Where:

$$\begin{aligned}
&R_{f1}=\frac{(1-\varepsilon_b)}{\varepsilon_b}\rho_{cat}\eta_1 R_{fa}; \quad R_{f2}=\frac{(1-\varepsilon_b)}{\varepsilon_b}\rho_{cat}\eta_2 R_{fb}+\rho_{gas}R_{fc};\\
&R_{f3}=\frac{2(1-\varepsilon_b)}{\varepsilon_b}\rho_{cat}\eta_1 R_{fa}-\rho_{gas}R_{fc}; \quad R_{f4}=\frac{2(1-\varepsilon_b)}{\varepsilon_b}\rho_{cat}\eta_2 R_{fb}+\rho_{gas}R_{fc};\\
&R_{f5}=\rho_{gas}R_{fc}
\end{aligned} \tag{9-13}$$

Where:

$R_{fa}=\dfrac{k_1 K_{CH4} C_{p1}}{1+K_{CH4}C_{p1}}$: Reaction rate for methane;

$R_{fb}=k_3 C_{p2}$: Heterogeneous reaction rate for carbon dioxide;

$R_{fc}=k_2\left(C_2C_3-\dfrac{C_4C_5}{K_{eq}}\right)$: Homogeneous reaction rate for carbon dioxide.

The terms η_1 and η_2 represents the effectiveness factor for CH_4 and CO_2, respectively, given by Equations (14, 15). The factors represent diffusive and chemical effects, or if the diffusion effects are very strong, the effectiveness factor tends to zero and the reaction takes place in a thin layer of the catalyst grain. However, if chemical state occurs, almost all of the catalyst surface area is utilized (Souto, 2005).

$$\eta_1=\frac{3D_{CH_4,ef}\left(\dfrac{\partial C_{p1}}{\partial r}\right)_{R_p}}{R_p\rho_{cat}R_{fa}},; \quad \eta_2=\frac{3D_{CO_2,ef}\left(\dfrac{\partial C_{p2}}{\partial r}\right)_{R_p}}{R_p\rho_{cat}R_{fb}} \tag{14, 15}$$

For the porous phase:

$$\frac{\partial C_{p1}}{\partial t}=\frac{D_{1,ef}}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_{p1}}{\partial r}\right)-R_{p1}; \quad 0<r<R_p; \quad t>0;$$

$$
\begin{aligned}
&\frac{\partial C_{p2}}{\partial t} = \frac{D_{2,ef}}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_{p2}}{\partial r}\right) - R_{p2}; \quad 0<r<R_p; \quad t>0;\\
&\frac{\partial C_{p3}}{\partial t} = \frac{D_{3,ef}}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_{p3}}{\partial r}\right) + R_{p3}; \quad 0<r<R_p; \quad t>0;\\
&\frac{\partial C_{p4}}{\partial t} = \frac{D_{4,ef}}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_{p4}}{\partial r}\right) + R_{p4}; \quad 0<r<R_p; \quad t>0;\\
&\frac{\partial C_{p5}}{\partial t} = \frac{D_{5,ef}}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_{p5}}{\partial r}\right) + R_{p5}; \quad 0<r<R_p; \quad t>0;\\
&C_{pi} = C_{pi0} \quad \text{for } t=0\\
&\frac{\partial C_{pi}}{\partial r} = 0 \quad \text{for } r=0; \quad i=1,2,\ldots,5\\
&\frac{\partial C_{pi}}{\partial r} = D_{i,ef}h_m(C_i - C_{pi}) \quad \text{for } r=R_p
\end{aligned}
\tag{16-23}
$$

Where:

$$
\begin{aligned}
&R_{p1} = \frac{(1-\varepsilon_b)}{\varepsilon_b}\rho_{cat}\eta_1 R_{pa}; \quad R_{p2} = \frac{(1-\varepsilon_b)}{\varepsilon_b}\rho_{cat}\eta_2 R_{pb} + \rho_{gas}R_{pc}\\
&R_{p3} = \frac{2(1-\varepsilon_b)}{\varepsilon_b}\rho_{cat}\eta_1 R_{pa} - \rho_{gas}R_{pc}; \; R_{p4} = \frac{2(1-\varepsilon_b)}{\varepsilon_b}\rho_{cat}\eta_2 R_{pb} + \rho_{gas}R_{pc};\\
&R_{p5} = \rho_{gas}R_{pc}
\end{aligned}
\tag{24-28}
$$

Where:

$$
R_{pa} = R_{fa}; \quad R_{pb} = R_{fb}; \quad R_{pc} = R_{fc} \tag{29.a-c}
$$

2.2 Dimensionless Equations

The dimensionless equations governing the mass transfer, as well as the initial conditions and contours, are made from the following dimensionless groups:

$$
Y_i = \frac{C_i}{C_T}; \; Y_{ie} = \frac{C_{ie}}{C_T}; \; X_i = \frac{C_{pi}}{C_T}; \; X_{i0} = \frac{C_{pi0}}{C_T}; \; \tau = \frac{u_0 t}{L}; \; \eta = \frac{r}{R_p}; \; Pe = \frac{uL}{D_{ax}}; \; Z = \frac{z}{L} \tag{30.a-h}
$$

$$
\alpha_0 = \frac{(1-\varepsilon_b)}{\varepsilon_b}; \; \mathbb{R}_{fi} = \frac{R_{fi}C_T u_0}{L}; \; \alpha_p = \frac{(1-\varepsilon_p)}{\varepsilon_p}; \; \gamma_i = \frac{LD_{i,ef}}{u_0 R_p^2}; \; Bi_m, i = \frac{h_m R_p}{D_{i,ef}} \tag{31.a-e}
$$

$$
a = C_T K_{CH_4}; \; \mathbb{R}_{pi} = \frac{R_{pi}C_T u_0}{L}; \; \mathbb{k}_1 = \frac{\rho_{cat}Lk_1}{u_0 C_T}; \; \mathbb{k}_2 = \frac{\rho_{gas}Lk_2 C_T}{u_0}; \; \mathbb{k}_3 = \frac{\rho_{cat}Lk_3}{u_0} \tag{32.a-e}
$$

In this way, the dimensionless model will be as follows, for the fluid phase:

$$
\begin{aligned}
&\frac{\partial Y_i}{\partial \tau}+\frac{1}{\varepsilon_b}\frac{\partial Y_i}{\partial Z}=\frac{1}{Pe}\frac{\partial^2 Y_i}{\partial Z^2}\pm\mathbb{R}_{fi};\ 0<Z<1;\ \tau>0\\
&Y_i=Y_{i0}\quad \text{for } \tau=0\\
&\frac{\partial Y_i}{\partial Z}=Pe(Y_i-Y_{ie})\quad \text{for } Z=0;\quad i=1,2,\ldots,5\\
&\frac{\partial Y_i}{\partial Z}=0\quad \text{for } Z=1
\end{aligned}
\tag{33.a-d}
$$

Where:

$$
\begin{aligned}
&\mathbb{R}_{f1}=\alpha_0\eta_1\mathbb{R}_{fa};\quad \mathbb{R}_{f2}=\alpha_0\eta_2\mathbb{R}_{fb}+\mathbb{R}_{fc};\quad \mathbb{R}_{f3}=2\alpha_0\eta_1\mathbb{R}_{fa}-\mathbb{R}_{fc}\\
&\mathbb{R}_{f4}=2\alpha_0\eta_2\mathbb{R}_{fb}+\mathbb{R}_{fc};\quad \mathbb{R}_{f5}=\mathbb{R}_{fc}
\end{aligned}
\tag{34.a-e}
$$

Where:

$$
\mathbb{R}_{fa}=\frac{\Bbbk_1 aX_1}{1+aX_1};\quad \mathbb{R}_{fb}=\Bbbk_3X_2;\quad \mathbb{R}_{fc}=\Bbbk_2\left(Y_2Y_3-\frac{Y_4Y_5}{K_{eq}}\right)
\tag{35.a-c}
$$

For the porous phase:

$$
\begin{aligned}
&\frac{\partial X_i}{\partial \tau}=\frac{\gamma_i}{\eta^2}\frac{\partial}{\partial \eta}\left(\eta^2\frac{\partial X_i}{\partial \eta}\right)\pm\mathbb{R}_{pi};\ 0<\eta<1;\ \ \tau>0\\
&X_i=X_{i0}\quad \text{for } \tau=0\\
&\frac{\partial X_i}{\partial \eta}=0\quad \text{for } \eta=0;\quad i=1,2,\ldots,5\\
&\frac{\partial X_i}{\partial \eta}=Bi_m,i(Y_i-X_i)\quad \text{for }\ \eta=1
\end{aligned}
\tag{36.a-d}
$$

Where:

$$
\begin{aligned}
&\mathbb{R}_{p1}=\alpha_p\mathbb{R}_{pa};\qquad \mathbb{R}_{p2}=\alpha_p\mathbb{R}_{pb}+\mathbb{R}_{pc};\qquad \mathbb{R}_{p3}=2\alpha_p\mathbb{R}_{pa}-\mathbb{R}_{pc}\\
&\mathbb{R}_{p4}=2\alpha_p\mathbb{R}_{pb}+\mathbb{R}_{pc};\qquad \mathbb{R}_{p5}=\mathbb{R}_{pc}
\end{aligned}
\tag{37.a-e}
$$

Where:

$$
\mathbb{R}_{pa}=\mathbb{R}_{fa};\quad \mathbb{R}_{pb}=\mathbb{R}_{fb};\quad \mathbb{R}_{pc}=\mathbb{R}_{fc}
\tag{38.a-c}
$$

2.3 Model Parameters

The parameters involved in the model are the coefficient of mass transfer to the fluid (h) the axial dispersion coefficient (D_{ax}), the coefficient of effective diffusivity (D_{ef}). The parameters were estimated from the following correlations. The method adopted to calculate the diffusivity of A in B was from Wilke e Lee (Poling, Prausnitz and O'Connell, 2001), represented by Equation (39):

$$D_{ab} = \frac{\left(3.03 - \left(0.98 / M_{ab}\right)\right) \times 10^{-3} \times T^{3/2}}{P \times M_{ab} \times \sigma_{ab}^{2} \times \Omega_D} \tag{39}$$

Where:

Ω_D = Collision integral;

M_{ab}= Average molar mass of the components, g/mol;

σ_{ab} = Average characteristic length, m.

For the effective diffusivity, following the methodology of Souto (2005), was used the model proposed by Wheeler (Figueiredo and Ribeiro, 1989) to calculate diffusion in porous media:

$$D_{ef} = \frac{\varepsilon_p}{\tau_\tau} \frac{1}{\dfrac{1}{D_{ka}} + \dfrac{1}{D_{ab}}} \tag{40}$$

Where:

τ_τ = Tortuosity of porous particle.

The Knudsen diffusivity (D_{ka}) predominates the process when the mean free path of the molecules is much larger than the pore radius and the diffusion resistance occurs by collisions of the molecules with the walls. This coefficient is defined by Equation (41):

$$D_{ka} = 9700 R_p \sqrt{\frac{T}{M_a}} \tag{41}$$

The mass transfer coefficient was calculated with the aid of the correlation proposed by Frössling (Fogler, 1999) and shown in Equation (42) to calculate the Sherwood number for packed beds.

$$Sh = 2 + 0.6 Sc^{1/3} Re^{1/2} \tag{42}$$

Where the dimensionless groups Reynolds (*Re*), Schmidt (*Sc*) and Sherwood (*Sh*) are defined by:

$$Re = \frac{\rho_{gas} u d_p}{\mu} \tag{43}$$

$$Sc = \frac{\nu}{D_{ab}} \tag{44}$$

$$Sh = \frac{d_p h}{D_{ab}} \tag{45}$$

The axial dispersion coefficient was calculated with the relationship proposed by Ruthven (1984), given by:

$$\frac{D_{ax}}{u.d_p} = \frac{20}{\varepsilon_b}\left(\frac{D_{ab}}{u.d_p}\right) + \frac{1}{2} \tag{46}$$

3 I SOLUTION METHODOLOGY

For the proposed solution methodology, was applied an average process to the particle concentration (average in the radial direction) which together with the CIEA gave a simplified formulation, so the five partial differential equations for concentration in the particle were reduced into differential equations in function of time. The technique of the coupled integral equations approach (CIEA) was used in the Equations (36.a-d) that describes the solid phase and GITT (Cotta, 1993) was applied on the resulting partial differential system.

3.1 Coupled Integrals Equation Approach (CIEA)

The CIEA seeks to reduce the number of independent variables through an averaging process, followed by integration of all partial differential equation, carrying out information of the boundary conditions. So, it is possible to develop a simplified formulation for the partial differential equation by eliminating the spatial dependence of the radius of the particle. That is, the particles are considered to be small, what allows the approximation $X_i(\tau,\eta) \cong \tilde{X}_i(\tau)$. Considering the small particles, an average potential was set to the variable Xi:

$$\tilde{X}_i(\tau) = \frac{\int_V X_i(\tau,\eta)dV}{\int_V dV} \Rightarrow \tilde{X}_i(\tau) = 3\int_0^1 \eta^2 X_i(\tau,\eta)d\eta \tag{47}$$

Considering the average potential defined by multiplying η^2 in the Equation (36.a), integrating in the domain of validity ($0 \leq \eta \leq 1$) and making use of the average process and boundary conditions, were determined the following ODEs:

$$\begin{gathered} \frac{\partial \tilde{X}_i}{\partial \tau} = 3\gamma_i Bi_m,i\left(Y_i - X_i(\tau,1)\right) \pm \tilde{\mathbb{R}}_{pi}; \quad \tau > 0; \quad i = 1,2,\ldots,5 \\ \tilde{X}_i = \tilde{X}_{i0} \quad \text{for} \quad \tau = 0 \end{gathered} \tag{48.a, b}$$

Where:

$$\begin{gathered} \tilde{\mathbb{R}}_{p1} = \alpha_p \frac{\Bbbk_1 a \tilde{X}_1}{1 + a\tilde{X}_1}; \; \tilde{\mathbb{R}}_{p2} = \alpha_p \Bbbk_3 \tilde{X}_2 + \Bbbk_2\left(\tilde{Y}_2\tilde{Y}_3 - \frac{\tilde{Y}_4\tilde{Y}_5}{K_{eq}}\right); \\ \tilde{\mathbb{R}}_{p3} = 2\alpha_p \frac{\Bbbk_1 a \tilde{X}_1}{1 + a\tilde{X}_1} - \Bbbk_2\left(\tilde{Y}_2\tilde{Y}_3 - \frac{\tilde{Y}_4\tilde{Y}_5}{K_{eq}}\right); \; \tilde{\mathbb{R}}_{p4} = 2\alpha_p \Bbbk_3 \tilde{X}_2 + \Bbbk_2\left(\tilde{Y}_2\tilde{Y}_3 - \frac{\tilde{Y}_4\tilde{Y}_5}{K_{eq}}\right); \\ \tilde{\mathbb{R}}_{p5} = \Bbbk_2\left(\tilde{Y}_2\tilde{Y}_3 - \frac{\tilde{Y}_4\tilde{Y}_5}{K_{eq}}\right) \end{gathered} \tag{49.a-e}$$

A simplified formulation for the differential equations can be developed by eliminating the spatial dependence, making use of average potentials terms, such a consideration is well accepted because the catalyst particle is small, which means that the concentration over the spatial variable do not vary significantly, turning able to make a classical approach $\left[X_i(\tau,1)\equiv\tilde{X}_i(\tau)\right]$, where the average potential is equal to the potential on the surface. In this way, the model for the pore phase reduces to:

$$\begin{aligned}
&\frac{\partial\tilde{X}_i}{\partial\tau}=3\gamma_i f_i\pm\tilde{\mathbb{R}}_{pi};\quad \tau>0;\quad i=1,2,\dots,5\\
&\tilde{X}_i=\tilde{X}_{i0}\ \text{ for }\ \tau=0\\
&f_i=Bi_m,i\left(Y_i-\tilde{X}_i\right)
\end{aligned}\tag{50.a-c}$$

3.2 Generalized Integral Transform Technique (GITT)

To obtain a general solution of the CIEA to the $Y_i(Z,\tau)$ simplified model a solution is proposed to this potential in the following way, to make the non-homogeneous original problem in a homogeneous problem.

$$\theta_i(Z,\tau)=Y_i(Z,\tau)-Y_{ie}\tag{51}$$

Isolating $Y_i(Z,\tau)$ and substituting in the reduced model we have:

$$\begin{aligned}
&\frac{\partial\theta_i}{\partial\tau}+\frac{1}{\varepsilon_b}\frac{\partial\theta_i}{\partial Z}=\frac{1}{Pe}\frac{\partial^2\theta_i}{\partial Z^2}\pm\mathbb{R}_{fi};\quad 0<Z<1;\quad \tau>0;\quad i=1,2,\dots,5\\
&\frac{\partial\tilde{X}_i}{\partial\tau}=3\gamma_i f_i\pm\tilde{\mathbb{R}}_{pi};\quad \tau>0\\
&\tilde{X}_i=\tilde{X}_{i0}\ ;\ \theta_i=\theta_{i0}\ \text{ for }\ \tau=0\\
&\frac{\partial\theta_i}{\partial Z}=\theta_i Pe\ \text{ for }\ Z=0\\
&\frac{\partial\theta_i}{\partial Z}=0\ \text{ for }\ Z=1
\end{aligned}\tag{52-56}$$

Due to homogeneous characteristics of boundary conditions, the auxiliary problem for the potentials of θ_i and $\tilde{X}_i$, assuming equilibrium for them, is described by Equations (57-59):

$$\begin{aligned}
&\frac{d^2\psi_l}{dZ^2}+\mu_l^2\psi_l=0;\quad 0<Z<1\\
&-\frac{d\psi_l}{dZ}+Pe\psi_l=0\ \text{ for }\ Z=0\\
&\frac{d\psi_l}{dZ}=0\ \text{ for }\ Z=1
\end{aligned}\tag{57-59}$$

Which is solved analytically to provide the eigenfunctions, eigenvalues and norm, respectively:

$$\psi_l(Z) = Cos\left[\mu_l(1-Z)\right]$$
$$\mu_l Sen(\mu_l) = PeCos(\mu_l), \quad l=1,2,3,.... \tag{60.a-c}$$
$$N_l = \frac{1}{2}\frac{\mu_l^2 + Pe^2 + Pe}{\mu_l^2 + Pe^2}$$

Where ψ_l, μ_l and N_l are respectively the eigenfunctions, eigenvalues and the integral normalization of the problem (57-59), which satisfies the following orthogonality property:

$$\int_0^1 \tilde{\psi}_l \tilde{\psi}_j d\eta = \begin{cases} 0, & if \;\; l \neq j \\ 1, & if \;\; l = j \end{cases} \tag{61}$$

The normalized eigenfunction ($\tilde{\psi}_l$) is given by:

$$\tilde{\psi}_l = \frac{\psi_l}{\sqrt{N_l}} \tag{62}$$

The problem (57-59) allows a definition of pairs of inverse-transform to the potentials θ_i and $\tilde{X}_i$:

$$\bar{\theta}_{i\,l}(\tau) = \int_0^1 \tilde{\psi}_l(Z)\theta_i(Z,\tau)d\eta \quad \text{transform}$$
$$\theta_i(Z,\tau) = \sum_{i=1}^{\infty} \tilde{\psi}_l(Z)\bar{\theta}_{i\,l}(\tau) \quad \text{inverse} \tag{63.a, b}$$

$$\bar{\tilde{X}}_{i\,l}(\tau) = \int_0^1 \tilde{\psi}_l(Z)\tilde{X}_i(Z,\tau)dZ \quad \text{transform}$$
$$\tilde{X}_i(Z,\tau) = \sum_{i=1}^{\infty} \tilde{\psi}_l(Z)\bar{\tilde{X}}_{i\,l}(\tau) \quad \text{inverse} \tag{64.a, b}$$

The integral transform process for the partial differential equations representing the problem, starts utilizing the respective integral operator in differential equations together with the original boundary conditions and with the use of the orthogonality properties and inversion formulas, resulting in ordinary differential equations for the potentials $\bar{\theta}_{i\,l}(\tau)$ and $\bar{\tilde{X}}_{i\,l}(\tau)$. Multiplying the set of originals PDEs for $\tilde{\psi}_l(Z)$ and integrating in the domain Z=0 to Z=1:

$$\int_0^1 \tilde{\psi}_l(Z)\left\{\frac{\partial\theta_i}{\partial\tau} + \frac{1}{\varepsilon_b}\frac{\partial\theta_i}{\partial Z} = \frac{1}{Pe}\frac{\partial^2\theta_i}{\partial Z^2} \pm \mathbb{R}_{fi}\right\}dZ$$
$$\int_0^1 \tilde{\psi}_l(Z)\left\{\frac{\partial\tilde{X}_i}{\partial\tau} = 3\gamma_i f_i \pm \tilde{\mathbb{R}}_{pi}\right\}dZ \tag{65.a-c}$$
$$f_i = Bi_m,i\left(\theta_i + Y_{ie} - \tilde{X}_i\right)$$

Resulting in the following coupled and infinite ordinary differential system:

$$\frac{d\overline{\theta}_{i\,l}}{d\tau}+\frac{1}{\varepsilon_b}\sum_{j=1}^{\infty}A_{l\,j}\overline{\theta}_{i\,j}=-\frac{\mu_l^2}{Pe}\overline{\theta}_{i\,l}\pm\overline{q}_{i\,l};\quad \tau>0$$

$$\frac{d\overline{\tilde{X}}_{i\,l}}{d\tau}=3\gamma_i\overline{f}_{i\,l}\pm\overline{p}_{i\,l};\quad \tau>0 \tag{66.a-d}$$

$$\overline{\theta}_{i\,l}=\theta_{i0}D_l;\ \overline{\tilde{X}}_{i\,l}=\tilde{X}_{i0}F_l\ \text{ for }\ \tau=0$$

Where non-transformable terms turn into infinity summations with the system coefficients defined by:

$$A_{l\,j}=\int_0^1\tilde{\psi}_l(Z)\tilde{\psi}'_j(Z)dZ;\ \overline{f}_{i\,l}=Bi_m,i\left(\sum_{j=1}^{\infty}\int_0^1\left(\tilde{\psi}_l(Z)\tilde{\psi}_j(Z)dZ\right)\tilde{\theta}_{i\,j}-\overline{\tilde{X}}_{i\,l}+Y_{ie}F_l\right) \tag{67.a-f}$$

$$F_l=D_l=\int_0^1\tilde{\psi}_l(Z)dZ;\ \overline{q}_{i\,l}=\int_0^1\tilde{\psi}_l(Z)\mathbb{R}_{fi}dZ;\ \overline{p}_{i\,l}=\int_0^1\tilde{\psi}_l(Z)\tilde{\mathbb{R}}_{pi}dZ$$

The integral coefficients formed by Equations (67.a-d) were solved analytically by the software *Mathematica* (Wolfram, 2005) and the resulting solution was incorporated into the algorithm used. The coefficients formed by equations (67.e, f) require the computation of integrals involving the eigenfunctions. On a few occasions, some of these could be evaluated analytically; however, often this is not the case and numerical integration is usually required. The use of a general-purpose numerical integration scheme can present some drawbacks, especially for larger eigenvalues due to the highly oscillatory nature of the eigenfunctions. Therefore, in order to offer an alternative, a semi-analytical integration approximation scheme is proposed (Sphaier *et al.*, 2011). Noting that the calculation of $\bar{q}_{i\,l}$ and $\bar{p}_{i\,l}$ are in the form:

$$\overline{q}_{i\,l}=\int_0^1\tilde{\psi}_l(Z)\mathbb{R}_{fi}dZ=\sum_{k=1}^{NIQ}\int_{Z_{k-1}}^{Z_k}\tilde{\psi}_l(Z)\mathbb{R}_{fi}dZ;$$

$$\overline{p}_{i\,l}=\int_0^1\tilde{\psi}_l(Z)\tilde{\mathbb{R}}_{pi}dZ=\sum_{k=1}^{NIQ}\int_{Z_{k-1}}^{Z_k}\tilde{\psi}_l(Z)\tilde{\mathbb{R}}_{pi}dZ \tag{68.a, b}$$

Where:

$$\mathbb{R}_{fi}=a_kZ+b_k;\quad \tilde{\mathbb{R}}_{pi}=\tilde{a}_kZ+\tilde{b}_k \tag{69.a, b}$$

$$a_k=\frac{\mathbb{R}_{fi,k}-\mathbb{R}_{fi,k-1}}{\Delta Z};\quad \tilde{a}_k=\frac{\tilde{\mathbb{R}}_{pi,k}-\tilde{\mathbb{R}}_{pi,k-1}}{\Delta Z} \tag{70.a, b}$$

$$b_k=\mathbb{R}_{fi,k}-a_kZ_k;\quad \tilde{b}_k=\tilde{\mathbb{R}}_{pi,k}-\tilde{a}_kZ_k;\quad \Delta Z=Z_k-Z_{k-1}=\frac{1}{NIQ} \tag{71.a-c}$$

Substituting equations (69.a, b) into equations (68.a, b) and integrating:

$$\bar{q}_{i\,l} = \sum_{k=1}^{NIQ} \left\{ \left(\int_{Z_{k-1}}^{Z_k} Z\tilde{\psi}_l(Z)dZ \right) a_k + \left(\int_{Z_{k-1}}^{Z_k} \tilde{\psi}_l(Z)dZ \right) b_k \right\} \tag{72}$$

$$\bar{p}_{i\,l} = \sum_{k=1}^{NIQ} \left\{ \left(\int_{Z_{k-1}}^{Z_k} Z\tilde{\psi}_l(Z)dZ \right) \tilde{a}_k + \left(\int_{Z_{k-1}}^{Z_k} \tilde{\psi}_l(Z)dZ \right) \tilde{b}_k \right\} \tag{73}$$

Where:

$$\begin{aligned} \int_{Z_{k-1}}^{Z_k} Z\tilde{\psi}_l(Z)dZ &= \left. \frac{Cos\left[\mu_l(1-Z)\right] - \mu_l Z Sen\left[\mu_l(1-Z)\right]}{\mu_l^2\sqrt{N_l}} \right|_{Z_{k-1}}^{Z_k} \\ \int_{Z_{k-1}}^{Z_k} \tilde{\psi}_l(Z)dZ &= -\left. \frac{Sen\left[\mu_l(1-Z)\right]}{\mu_l\sqrt{N_l}} \right|_{Z_{k-1}}^{Z_k} \end{aligned} \tag{74.a, b}$$

The ODE system formed by Equations (66.a-d) was solved numerically by DIVPAG routine library Imsl (IMSL, 1987) FORTRAN. In DIVPAG routine (routine for initial value problems) used the Gear method for rigid systems, with an error prescribed of 10^{-7} by the user.

3.3 Conversions and Yields

The experimental results obtained by Souto (2005) allows valuation the performance of the methane reforming process with carbon dioxide, which can be expressed in terms of conversions and the yield. Conversion and yield estimates for the reforming process are defined as follows, respectively:

$$X_i^{conv} = \frac{C_{ie} - C_i}{C_{ie}} \times 100,\ i = CH_4 \text{ and } CO_2 \tag{75}$$

$$R_i^{yield} = \frac{C_i}{C_{1e} + C_{2e}} \times 100,\ i = H_2,\ CO,\ CO + H_2 \tag{76}$$

3.4 Case Studies

For the phenomenon simulation the parameters presented in Table 2 were used. Parameters values shown are taken from Souto (2005) with the exception of axial dispersion, reaction constants and effectiveness factors which needed to be adjusted, given that the model proposed in this paper presents some corrections when compared with model Souto (2005).

Parameters	Values	
Temperature (°C)	750	850
Simulation time (s)	2.47	2.47
Length of the bed (m)	0.0325	0.0325
Diameter of the bed (m)	0.022	0.022
Particle diameter (m)	0.002	0.002
Bed porosity	0.67	0.67
Particle porosity	0.61	0.61
Volumetric flow rate (mL/min)	600	600
Axial dispersion (cm^2/s)	3.68×10^{-3}	3.68×10^{-3}
k_1 ($mol/g_{cat}.s$)	1.019	8.61×10^{-3}
k_2 ($m^6/g_{cat}.s.mol$)	9.89×10^{-6}	1.92×10^{-6}
k_3 ($m^3/g_{cat}.s$)	3.94×10^{-4}	3.30×10^{-4}
K_{CH4} (m^3/mol)	6.47×10^{-3}	1.12
K_{eq}	0.75	1.07
CH_4 concentration in feed (g/m^3)	18.18	16.56
CO_2 concentration in feed (g/m^3)	70.25	63.99
Specific weight of the catalyst (g/cm^3)	2.3	2.3

Table 2 - Parameters that were used in the simulation of methane reforming with CO_2 utilizing nickel (*Ni/y - Al_2O_3*) as catalyst at T = 750°C and 850ºC.

Source: Adapted from Souto (2005).

4 I RESULTS AND DISCUSSION

4.1 Convergence Analysis

Initially, a convergence analysis was done for the solution of ODEs system. The Tables 3 and 4 shows the mesh convergence results for the concentration of CH_4 and CO_2 in three instants of time. It is observed a convergence of at least four significant digits, with a tolerance of plus or minus one digit, around number of terms NT = 100. So, for other cases the ordinary differential system is solved keeping the NT = 100 and NIQ=160 (number of quadrature intervals) for the semi-analytical integration. Figure 2 is the profile for the CH_4 concentration, varying the NIQ to analyze if the semi-analytical integral interferes with the results. It is observed that maintaining the number of terms (NT) equal to 100 and NIQ =160 the results already are converged.

NT	t = 0.1 s		t = 0.93 s		t = 1.85 s	
	z=0.001m	z=0.033m	z=0.001m	z=0.033m	z=0.001m	z=0.033m
60	1.11054	0.00013	1.11209	0.52153	1.11117	0.52229
70	1.10958	0.00000	1.11198	0.52153	1.11139	0.52215
80	1.11007	0.00003	1.11177	0.52153	1.11137	0.52205
90	1.10987	0.00002	1.11132	0.52153	1.11104	0.52197
100	1.10996	0.00000	1.11085	0.52154	1.11064	0.52191
110	1.10993	0.00000	1.11060	0.52154	1.11044	0.52186
120	1.10994	0.00000	1.11057	0.52153	1.11045	0.52182
130	1.10993	0.00000	1.11064	0.52153	1.11053	0.52178

Table 3 - Convergence for the concentration of CH_4 (mol/m^3) at T=750ºC.

NT	t = 0.1 s		t = 0.93 s		t = 1.85 s	
	z=0.001m	z=0.033m	z=0.001m	z=0.033m	z=0.001m	z=0.033m
60	1.57591	0.00020	1.57744	0.82500	1.57664	0.82565
70	1.57442	0.00000	1.57725	0.82501	1.57675	0.82554
80	1.57543	0.00005	1.57699	0.82503	1.57665	0.82547
90	1.57490	0.00002	1.57657	0.82504	1.57633	0.82541
100	1.57528	0.00000	1.57618	0.82505	1.57600	0.82537
110	1.57514	0.00000	1.57597	0.82505	1.57584	0.82533
120	1.57525	0.00000	1.57595	0.82506	1.57584	0.82530
130	1.57522	0.00000	1.57598	0.82506	1.57588	0.82527

Table 4 - Convergence for the concentration of CO_2 (mol/m^3) at T=750ºC.

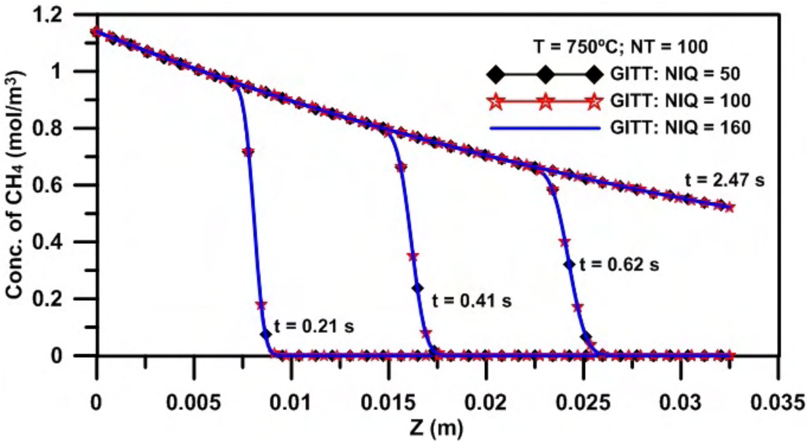
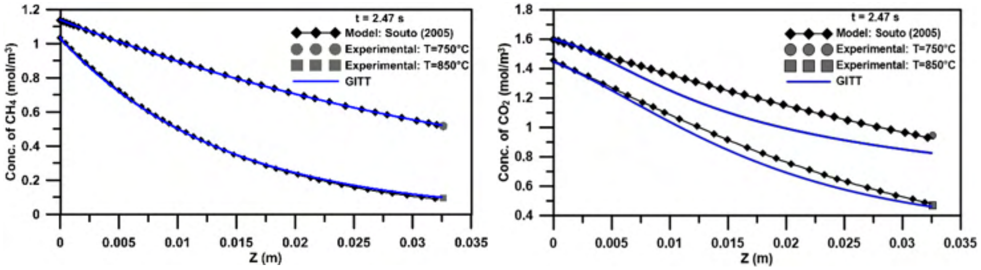


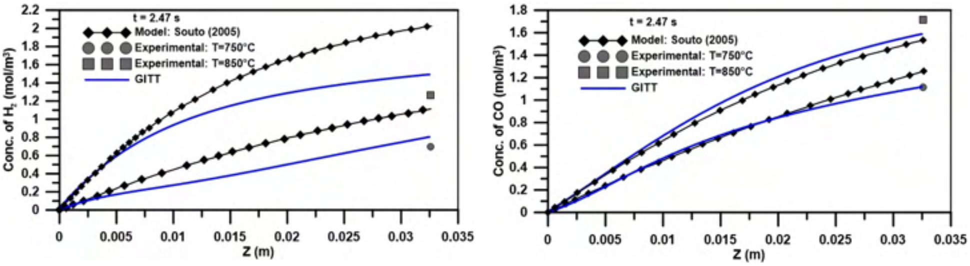
Figure 2 - Analysis of the number of terms in the semi-analytical integral. Conditions: P=1atm, T=750°C and Q=600mL/min.

4.2 Concentration Profile Analysis

The concentration profiles shown below correspond to the flow rate of 600 mL/min for all components involved in the process, at temperatures of 750°C and 850ºC. As observed by Souto (2005), with the experimental data of methane reforming process condition obtained at the outlet of the fixed bed reactor, it was possible to find validation for the model by comparing the estimated concentration levels for the discharge position in the reactor with those measured experimentally. In Figures 3 to 6, the experimental concentration values are prominent at points positioned at the reactor outlet, which are complementary profiles predicted by the model. The proposed model well establishes predictions for the reactants and products in the permanent regime (regime studied by Souto (2005)), with low deviations for carbon dioxide, carbon monoxide and hydrogen. However, these predictions were better than the results of Souto (2005) which may be due to corrections in some terms of the model that did not distinguish the phenomena occurring in particle (1-ε_b) and outside the particle (ε_b).



Figures 3 and 4 - Concentration profiles for CH_4 e CO_2 along the bed and in steady state. Conditions: P=1atm and Q=600mL/min.



Figures 5 and 6 - Concentration profiles for H_2 e CO along the bed and in steady state. Conditions: P=1atm and Q=600mL/min.

4.3 Analysis of Conversions and Yields

In Figure 7 it can be noticed, in terms of conversion at temperature of 750°C that there is an excellent predication for methane and a deviation for carbon dioxide, which were expected from analysis of Figures 4 and 5. Following this trend, in Figure 8, the deviation of predicted model concerning to H_2 generated a deviation for the synthesis gas (H_2 + CO), which also can be seen in Figures 5 and 6. It is noted that in Figure 9, in terms of conversion at temperature of 850°C, there is an excellent prediction for methane and carbon dioxide, which was expected from the analysis of Figures 4 and 5. In the same way for Figure 10, the deviation of predicted model with respect to H_2 and CO, generates a deviation to the synthesis gas, also suggesting the same conclusions for Figures 5 and 6.

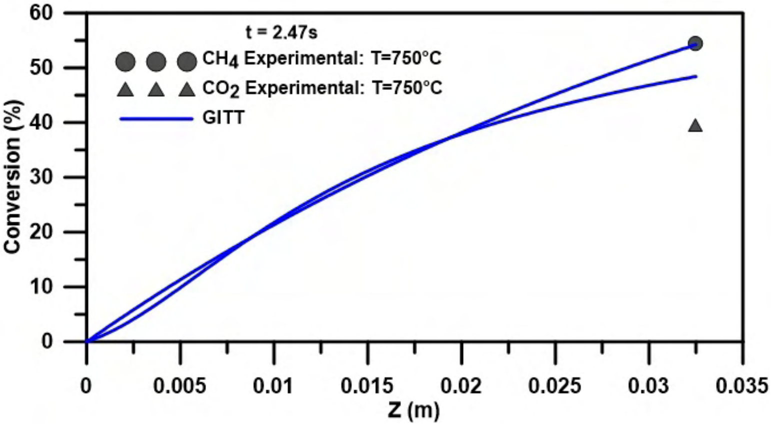


Figure 7 - Conversion for CH_4 and CO_2 along the bed in steady state. Conditions: P=1atm, T=750°C and Q=600mL/min.

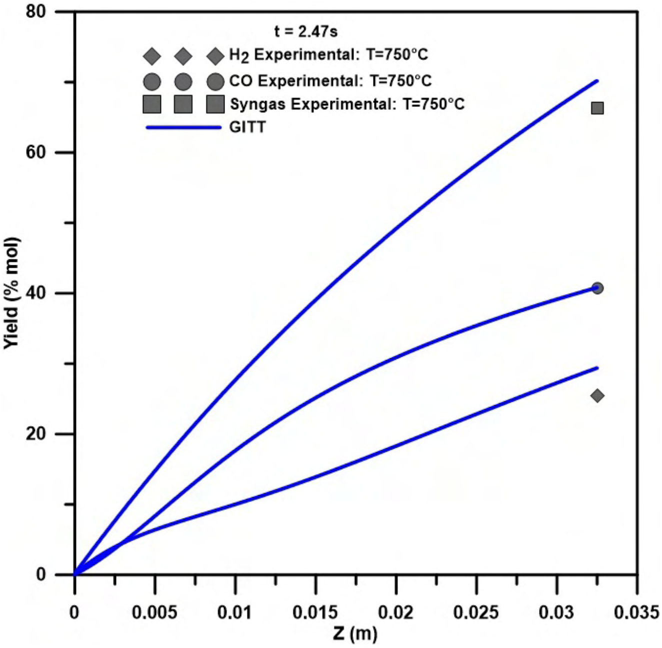


Figure 8 - Yields for CO, H_2 and syngas (CO + H_2) along the bed in steady state. Conditions: P=1atm, T=750°C and Q=600mL/min.

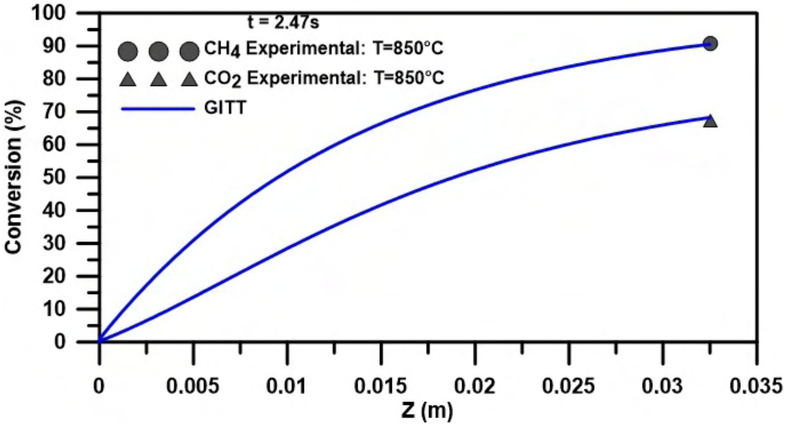


Figure 9 - Conversion for CH_4 and CO_2 along the bed in steady state. Conditions: P=1atm, T=850°C and Q=600mL/min.

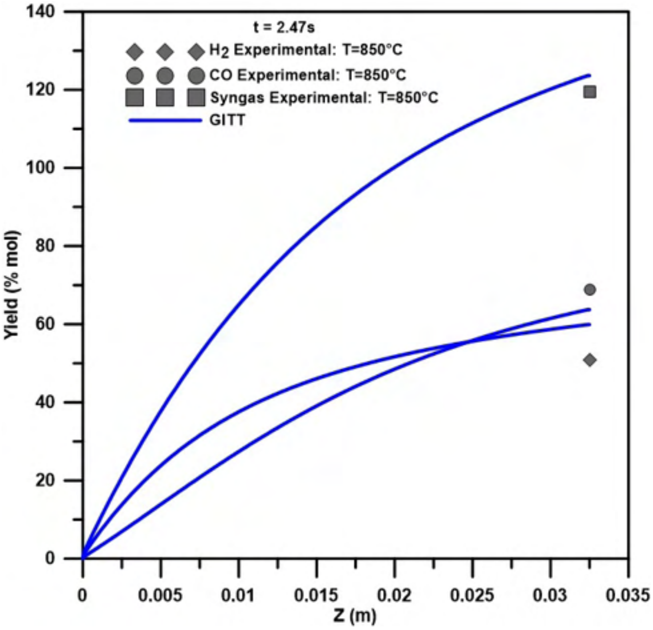


Figure 10 - Yields for CO, H_2 and syngas (CO + H_2) along the bed in steady state. Conditions: P=1atm, T=850°C and Q=600mL/min.

5 I CONCLUSIONS

The formulation used in this work shows that is unnecessary to study the distribution of particle concentration as a function of radius because the results were in excellent agreement with the numerical results and described well the experimental data. Even that the improved formulation eliminates the radial coordinate, it incorporates the mass transfer phenomena to the model on the particle surface. The mathematical model applied to the reforming of methane with carbon dioxide was able to describe the experimental results. The numerical solutions for the model, in function of four major process components, allowed simulations of these components concentration profiles. The improved mathematical formulation obtained by the utilization of CIEA together with GITT proved to be effective in solving the problem of mass transfer, since the results are in good agreement with the experimental data and the models in the literature.

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REFERENCES

Cotta, R. M. **Integral transforms in computational heat and fluid flow.** CRC Press, Boca Raton, Florida, 1993.

Figueiredo, J. L., Ribeiro, F. R. **Heterogeneous Catalysis**. Calouste Gulbenkian Foundation, Lisboa, 1989.

Fogler, H. S. **Elements of Chemical Reaction Engineering**. Prentice-Hall, 3rd edition, Englewood Cliffs, New Jersey, 1999.

Guo, F., Zhang, Y., Zhang, G., Zhao, H. **Syngas production by carbon dioxide reforming of methane over different semi-cokes**. J. Power Sources, v.231, n.1, p.82-90, 2013.

IMSL Library. **MATH/LIB**. Houston, Texas, 1987.

Pacífico, J. A. **Cinética do processo de reforma do metano com dióxido de carbono. Aplicação à modelagem e simulação da operação em reator de leito fluidizado**. Dissertação de Mestrado. Recife, Universidade Federal de Pernambuco, 2004.

Poling, B. E., Prausnitz, J. M., O'Connell, J. P. **The Properties of Gases and Liquids**. McGraw-Hill Co. Inc., 5rd edition, New York, 2001.

Ruthven, D. M. **Principles of Adsorption and Adsorption Process**. John Wiley & Sons, New York, 1984.

Souto, R, T. **Modelagem e validação experimental do processo de reforma do metano com dióxido de carbono em reator de leito fixo**, Dissertação de Mestrado. Recife, Universidade Federal de Pernambuco, 2005.

Sphaier, L. A., Cotta, R. M., Naveira-Cotta, C. P., Quaresma, J. N. N. **The UNIT algorithm for solving one-dimensional convection-diffusion problems via integral transforms**. Int. Comm. Heat & Mass Transfer, v. 38, n. 5, p. 565-571, 2011.

Tuza, P. V., Souza, M. M. V. M. **Steam reforming of methane over catalyst derived from ordered double perovskite: Effect of crystalline phase transformation**. Catal Letters, v. 146, p. 47-53, 2016.

U. S., Energy Information Administration. **International Energy Outlook**. http://www.eia.gov/forecasts/ieo/pdf/0484(2013).pdf (accessed May 15, 2018), 2013.

U. S., Energy Information Administration. **International Energy Outlook**. http://www.eia.gov/forecasts/ieo/pdf/0484(2014).pdf (accessed May 15, 2018), 2014.

Wolfram, S. **The Mathematica Book**. Cambridge, Wolfram Media, 2005.

Yang, W., Liu, H., Li, Y., Zhang, J., Wu, H., He, D. **Properties of yolk–shell structured Ni@SiO_2 nanocatalyst and its catalytic performance in carbon dioxide reforming of methane to syngas**. Catal Today, v. 259, n. 1, p. 438-445, 2016.

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