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NUMERICAL ANALYSIS OF THE STEAM REFORMING OF TOLUENE TO PRODUCE HYDROGEN IN A FIXED BED CATALYTIC REACTOR

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Abstract. *The biomass can be used as a renewable source with huge potential to cope with environmental concerns derived from the large dependence on fossil fuels and reduce the greenhouse gas emissions. However, within the process of biomass gasification there is the formation of tar, which is a serious impediment among the impurities present in the synthesis produced. The steam reform is a widely known technique for the removal of tar, avoiding equipment damage, and can produce hydrogen fuel that is component is a relevant alternative for reducing environmental impact, which is usually caused by greenhouse gas emissions from fossil fuel use since it is produced sustainably from renewable energy sources. In this sense, this paper presents a numerical analysis of the steam reforming using toluene as model Compound to produce hydrogen in a fixed bed catalytic reactor. In order to carry out a dynamical analysis of the behavior of this reactor, the analysis of a mathematical model was developed to investigate the dynamic evolution of the temperatures and chemical species present in the reactions of reforming. This model is described by a system of Partial Differential Equations (PDEs). In addition, to solve these PDEs, it was used the technique Coupled Integral Equation Approach (CIEA) and with a code in FORTRAN 95 language, that allowed obtaining data about the temperatures profiles and H_2 production.*

Keywords: *hydrogen, mathematical model, fixed bed catalytic reactor*

1. INTRODUCTION

The biomass can be used as a renewable source with huge potential to cope with environmental concerns over fossil fuel usage and reduce the greenhouse gas emissions. Biomass gasification is a promising technology for production of sustainable fuels, like hydrogen, as it converts the low-value feedstock to high-quality combustible gases (syngas), which can be directly combusted for power generation or turned into chemical fuels (Xiao*et al.*,2017). In addition, Processes based on the thermochemical conversion of biomass are nowadays of paramount importance, since they present higher energy efficiency than the direct combustion.

The gasification of biomass is very advantageous for the environment, however, there is the formation of tar, which is a serious impediment among the impurities present in the synthesis produced and may damage equipment. Biomass-derived syngas produced in the fixed bed contains about 10% to 20% of tar with 14.2 % toluene, 13.9 % of other one-ring aromatic hydrocarbons, 9.6% naphthalene, 7.8% other two-ring aromatic hydrocarbons, 3.6% three-ring aromatic hydrocarbons, 0.8% other four-ring aromatic hydrocarbons, 4.6% phenolic compounds, 6.5% heterocyclic compounds and 1 % others (Oliveira, 2012). The removal or decomposition of tar is considered as one of the major technical challenges to be overcome for the commercial success of advanced gasification technologies (Virgine *et al*., 2010).

To investigate the decomposition behavior of the tar, several typical aromatics have been adopted as model biomass tar compounds, such as phenol and toluene. Moreover, several researchers study the reforming of hydrocarbons, provided that this process can reduce the tar and produce hydrogen fuel. Bona *et al.*(2008), investigated experimentally the catalytic reforming of tar to analyze the calorific value of the gas produced and the overall efficiency of the thermochemical conversion process. Ashok and Kawi(2013), studied the steam reforming of toluene like a biomass tar model consisting of Ni supported CaO-AℓO_3 (Ca-Aℓ) and CeO_2 promoted CaO-AℓO_3 to analyze promotional effect CeO_2 on Ca-Aℓ support. Wu *et al.*(2013), analyzed hydrogen production from catalytic steam reforming of toluene over experimental nature. Silva and Abreu(2016), modeled and simulated the steam methane reforming in the conventional

fixed bed reactor (FBR) and fixed-bed membrane reactors. Swierczynski *et al.*(2008) studied of steam reforming of toluene used as a model composed of tar, through natural olivine improved by adding Ni catalyst. In this work, toluene is chosen as the model compound of biomass gasification because it exists as a tar component in a significant high quantity and represents a stable aromatic structure apparent in tar forming processes.

Among the advantages of the steam reform is the cost-effective way to produce hydrogen. This component is a relevant alternative for reducing environmental impact, which is usually caused by greenhouse gas emissions from fossil fuel use since it is sustainably produced from renewable energy sources. Moreover, the catalytic steam reforming is the most common process to obtain hydrogen, which is usually chosen due to its high efficiency.

Therefore, in order to study alternatives to the energy fuel, this work carried out a numerical analysis of the steam reforming of toluene to produce hydrogen in a Fixed Bed Reactor (FBR). Thus, based on the energy and mass balances of chemical species, a system of partial differential equations (PDE) was obtained for describing governing equations of the energy and mass balances. Applying the methodology of the Coupled Integral Equation Approach (CIEA) it was possible to transform the PDE into Ordinary Differential Equations (ODE) and to obtain the graphs of the temperatures, referring to the energy balance, and the concentrations of the chemical compounds present in the mathematical model.

2. PROBLEM FORMULATION

To do the mathematical modeling, a detailed one-dimensional model is formulated by using the mass and energy balance equations for a fixed bed reactor. A set of assumptions for the energy balance are made, i.e: (i) temperature gradients in the axial direction of the FBR, (ii) temperature gradients in the radial direction of the particle, (iii) in the proposed model, only thermal effects are considered in both phases, (iv) the wall temperature of the FBR is considered constant and (v) the particle size is uniform. In addition, the mass balance equations take the following assumptions into account: (i) the term of accumulation, (ii) convection and (iii) dispersion of the chemical species in the process have been considered (iv) and the rates of the component templates of the reactions also have been considered. Based on these assumptions, a simplified mathematical model for FBR is formulated by the simplified equations of mass and energy balances to describe the dynamic behavior. In addition, the initial and boundary conditions for the mass and energy balance are given in table 1.

-Energy balance for the gas-liquid phase (01) and solid phase (02) and mass balance (03);

$$\phi_{g\ell}\frac{\partial T_{g\ell}(z,t)}{\partial t}+\vartheta_{g\ell}\frac{\partial T_{g\ell}(z,t)}{\partial z}=\mu_{g\ell}\frac{\partial^2 T_{g\ell}(z,t)}{\partial z^2}-h_{fp}\frac{3}{r_p}(1-\varepsilon_b)\left[T_{g\ell}(z,t)-\mathrm{T_s}(r,t)|_{r=R}\right] \tag{1}$$

Where, $\varphi_{g\ell}$ (Kj/m^{3}K) is the coefficient of the term of thermal accumulation, T_{gl} (K) is the fluid temperature, $\vartheta_{g\ell}$ (kJ/m^{3}K h) is the coefficient of the term of thermal convection, t (h) is the time, z (m) é a coordinate in the axial direction respectively, $\mu_{g\ell}$ (kJ/m^{3}K h) is the coefficient of the term of thermal dispersion and ε_s(-) is the void fraction of bed.

$$\rho_s C_{p,s}\frac{\partial T_s(r,t)}{\partial t}=\frac{\lambda_s}{R^2}\frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial T_s(r,t)}{\partial r}\right]\pm\rho_S\left(\Delta H_R\right)R_{tol} \tag{2}$$

Where, ρ_s(kg/m^3) is the density of the solid phase, $C_{p,s}$(kJ/kg·K) is the heat capacity of the solid phase, respectively; λ_s (kJ/m K h) is the thermal conductivity for the solid phase, R (m) is the superficial radius of the solid phase, r (m) is the particle radius, R_{tol} is the global rate of toluene, detailed in *Silva and Abreu, (2016).*

$$\varepsilon_g\frac{\partial C_i(z,t)}{\partial t}+\varepsilon_g\frac{4Q_g}{\pi d_c^2}\frac{\partial C_i(z,t)}{\partial z}=\varepsilon_g D_i\frac{\partial^2 C_i(z,t)}{\partial z^2}+\left(1-\varepsilon_s\right)r_i \tag{3}$$

Where i = toluene (C_7H_8), water (H_2O), carbon monoxide (CO), hydrogen (H_2), methane (CH_4) and carbon dioxide (CO_2), ε_g(-) is the void fraction of the gas phase, C_i(kg m^{-3}) is the concentration of components, Q_g(m^3/h) is the gas flow rate, d_c(m) is the catalytic reactor diameter, D_i (m²/h) is the diffusion coefficient of the components and r_i(kg m^{-3} h) is the rate of liquid for each component, detailed in *Silva and Abreu* (2016).

Table 1 -The initial and boundary conditions for the mass and energy balance

For Fluid Phase	For Solid Phase	For mass balance
$\left.\frac{\partial T_{g\ell}}{\partial z}\right\|_{z=0^+} = \frac{\vartheta_{g\ell}}{\mu_{g\ell}}\left[T_{g\ell}\right\|_{z=0^+} - T_{g\ell}\right]$	$\left.\frac{\partial T_s}{\partial r}\right\|_{r=R} = \frac{h_{sc}}{\lambda_s}\left[T_{g\ell} - T_s\right\|_{r=R}\right]$	$\left.\frac{\partial C_i}{\partial z}\right\|_{z=0^+} = \frac{4Q_g}{\pi d_c^2 D_i}\left[C_i\right\|_{z=0^+} - C_i\right]$
$\left.\frac{\partial T_{g\ell}}{\partial z}\right\|_{z=L} = 0$	$\left.\frac{\partial T_s}{\partial r}\right\|_{r=0} = 0$	$\left.\frac{\partial C_i}{\partial z}\right\|_{z=L} = 0$

3. SOLUTION METHODOLOGY

This paper presents a CIEA-based analytical technique for solving Eqs.1, 2 and 3. This method has the main goal to simplify the expressions for the Energy and Mass Balances of the reactor.

The basis for the CIEA is the Hermite approximation of an integral. The Hermite approximation is to approximate an integral through a linear combination of integrand values and their derivatives. It was originally developed by Hermite (1878) and first presented by Menning *et al.*(1983). These approximations allow a complex problem to be simplified, so that it can be solved with much less effort, as well as in many cases using analytical methods. The advantage of this technique, when compared to other traditional methods of approximations is that a smaller error is obtained providing more accurate results. This technique has been used elsewhere as reported by Anjos *et al.*(2017), Cardoso *et al.* (2014), Knupp *et al.*(2012), An and Su (2011), Corrêa and Cotta (1998. This technique is represented by the general expression:

$$\int_{x_{i-1}}^{x_i} y(x)dx \cong \sum_{v=0}^{\alpha} C_v(\alpha,\beta) h_i^{v+1} y_{i-1}^{(v)} + \sum_{v=0}^{\beta} C_v(\alpha,\beta)(-1)^v h_i^{v+1} y_i^{(v)} + O(h_i^{\alpha+\beta+3}) \tag{4}$$

Where,

$$h_i = x_i - x_{i-1} \tag{5}$$

$$C_v(\alpha,\beta) = \frac{(\alpha+1)!(\alpha+b+1-v)!}{(v+1)!(\alpha-v)!(\alpha+\beta+2)!} \tag{6}$$

and y(x) and its derivatives $y^{(v)}(x)$ are defined for all $x \in (x_{i-1},x_1)$. Furthermore, it is assumed that the numerical values of $y^{(v)}(x_{i1}) \equiv y_{i-1}^{(v)}$ for v = 0,1,2,3...,α and $y^{(v)}(x_i) \equiv y_i^{(v)}$ para v = 0,1,2,3,..., β are available at the end points of the interval.

This integration formula can provide different approximation levels, from the classical lumped system analysis to improve lumped-differential formulations ($H_{0,0}$, $H_{1,1}$, $H_{2,2}$,…). Since approximations of order higher than $H_{1,1}$ involve derivatives of order higher than one, these are avoided for the sake of simplicity of the technique. Hence, only the two different approximations below are considered:

$$H_{0,0} \rightarrow \int_0^L f(t)dt \cong \frac{L}{2}[f(0,t) + f(L,t) \tag{7}$$

$$H_{1,1} \rightarrow \int_0^L f(t)dt \cong \frac{L}{2}[f(0,t) + f(L,t) + \frac{L^2}{12}\left[\left.\frac{\partial f}{\partial s}\right|_{s=0} - \left.\frac{\partial f}{\partial s}\right|_{s=L}\right] \tag{8}$$

4. RESULTS

The energy and mass balance equations are numerically solved with the Euler method, implemented in Fortran PowerStation 4.0. The proposed model was used to provide support to analyze the evolution of chemical species over time at the output of the reactor, and the variations of the temperature up to the stabilization time. Moreover, the Table 2 shows the parameter of entry for the simulation.

Table 2 - Entry data for the simulation

Categories	Symbol	Number value	Categories	Symbol	Number value
Condition of Operations	$T_{gf,0}$	400	Properties of Liquid phase	$C_{p,l}$	2.001
	$T_{s,0}$	400		h_f	0.791
	L	1.0		$V_{s,f}$	2.01
	ε_s	0.59		λ_l	$1.80x10^{-2}$
	r_p	$3.2x10^{-4}$		ρ_L	$1.01x10^{-2}$
	R	1.0			
Properties of Gaseous phase	$C_{p,g}$	$2.101x10^{-1}$	Properties of Solid phase	$C_{p,s}$	$2.00x10^{3}$
	h_g	0.80		h_{fp}	$2.635x10^{-2}$
	$V_{s,g}$	$29.46x10^{-1}$		λ_s	$1.559x10^{+2}$
	λ_g	0.0547		ρ_s	$1.08x10^{-1}$
	ε_g	0.47			
Initial Concentration	C^0_{C7H8}	0.20	Diffusion Coefficient	D_{C7H8}	$5.566x10^{-2}$
	C^0_{CH4}	0.36		D_{CH4}	$5.005x10^{-2}$
	C^0_{H2O}	0.60		D_{H2O}	$7.061x10^{-1}$
	C^0_{CO}	0.00		D_{CO}	$3.982x10^{-1}$
	C^0_{CO2}	0.00		D_{CO2}	$3.000x10^{-2}$
	C^0_{H2}	0.00		D_{H2}	$0.143x10^{-1}$

Figure 1 shows the evolution of temperatures throughout the process in the reactor. The left-hand side of Figure 1 shows the temperature of the fluid phase with sensitivity analysis of the h_{fp} parameter. In additions, is observed that the smaller variations of the h_{fp}, the higher temperature variations. The right-hand side of Figure 1 shows the temperature of the solid phase. Moreover, a dashed region is enlarged to show the energy transference that occurs in this phase, being considered a common behavior in this process of hydrocarbon reforming, as reported in *Silva and Abreu(2016)*. It is also possible to observe that the temperatures stabilize after approximately 16 hours, being this information important for better control of the reactor.

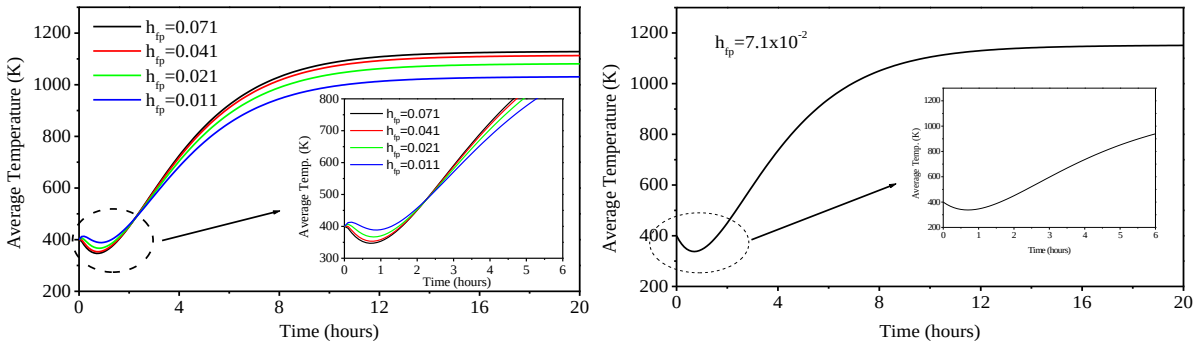

Figure 1 – Evolution of the fluid phase temperature with sensible analysis of the h_{fp} parameter (left) and the behavior of the solid phase temperature (right), versus time.

The leff-hand side of Figure 2~~,~~ shows the dynamic evolution of the reactor temperature. Note that over the course of 20 hours the temperatures follow the same behavior and present values closely each other~~.~~ This is important because the reactor has almost the same temperature and becomes easier to control and to operate the equipment. Table 3 shows in detail the temperature difference in five-time intervals, and it is observed that after 12 hours the model reaches the steady-state. The right-hand side of Figure 2~~,~~ shows that the dynamics evolutions of the product gas distribution reach to stable levels immediately after introducing the feed. Usually, it can be noticed that 16h approximately after starting the FBR from initial conditions, all curves describing the product gas distribution achieves to steady-state. During the transient period, it is remarked that as the operation proceeds, methane and toluene are consumed with water available in inlet gas mixture (steam reforming). Under the prescribed operating conditions, the product gas temperature is about 1128K steady-state, the wet basis products contain about 0.60 kmol/h of H_2, 0.10 kmol/h of CO, 0.22 kmol/h of CO_2, 0.019 kmol/h of CH_4, 0.015 kmol/h of C_7H_8 and 0.48 kmol/ of H_2O.

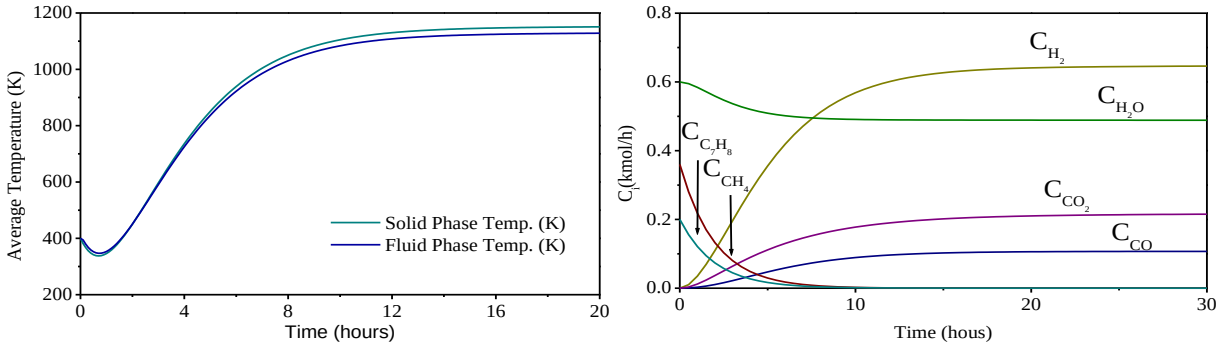

Figure 2 – Dynamic evolutions of the reactor temperatures (left) and dynamic behavior of the components of reaction (right).

Table 3. Results of the T_s and T_{gl} after 20hours in the FBR.

Time (hours)	T_s(K)	T_{gl} (K)	T_s(K) – T_{gl}(K)
04	589.30	579.24	10.06
08	827.47	811.17	16.30
12	1130.11	1108.07	22.04
16	1146.86	1124.38	22.51
20	1150.85	1128.26	22.56

4.1 Yield of Hydrogen

Obtaining yield of hydrogen (ψ) is essential in the reform process to analyze reactor performance. As in the studied reactor, the steam reforming reactions of toluene and the partial methane reforming are present, the yield of hydrogen was calculated based on each compound. Moreover, the following definitions, given in Silva and Abreu, 2017, are used to describe this process:

$$\psi_{H_2,Tol} = \left| \frac{C^K_{H_2}}{C^0_{C_7H_8} - C^K_{C_7H_8}} \right| \tag{9}$$

$$\psi_{H_2,CH_4} = \left| \frac{C^K_{H_2}}{C^0_{CH_4} - C^K_{CH_4}} \right| \tag{10}$$

Where C^K_j is the concentration of compound "j" throughout the process, j =H_2, C_7H_8, CH_4 C^0_i is the initial concentration of compound "I" throughout the process, i= C_7H_8, CH_4

The solutions to Eqs. 9 and 10 are represented in Figure 3. The left-hand side of Figure 3, represents the yield of the hydrogen produced being the component of feedstock toluene, whereas the right-hand side of figure has the raw material methane, both compounds present in the chemical reactions and kinetic process studies. In addition, it is necessary to emphasize that with the toluene the yield of hydrogen is greater, stabilizing at 3.2.

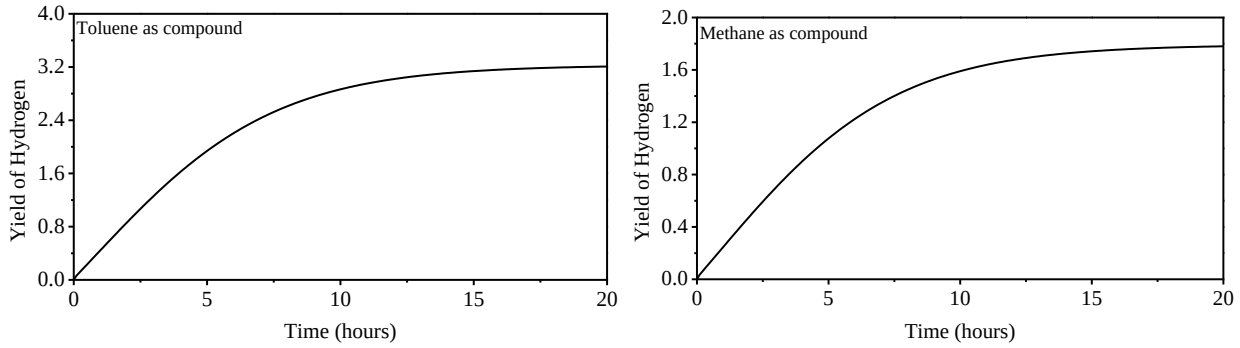

Figure 3 – Dynamic evolution of the Yield of Hydrogen with toluene (left) and methane (right) as compound.

5. CONCLUSION

A one-dimensional mathematical model was used to report the dynamics analysis of the catalytic toluene steam reforming using an FBR reactor.

For this purpose, two numerical methods (coupled integral equation approach and Euler Method) have been used to solve the developed mathematical models FBR reactor. A computer code to process and analyze the performance of the operating variables allowed the following conclusions:

- In the FBR model, the solid phase temperature reaches higher values compared to the fluid phase temperature;
- At the end of process, the reactor temperature is almost the same in both phases;
- The developed model allowed the analysis of the fluid temperature with the variation of the coefficient of heat transfer. In addition, this coefficient presented huge influence on the temperature, the higher your value the higher the temperature;
- The dynamic behavior of the components of reactions was obtained. H2, CO, and CO2 are produced and C7H8, CH4 and H2O are consumed.
- The yield of hydrogen from toluene and methane was calculated and studied as a function of time
- Almost all toluene and methane are consumed in the reaction.

6. ACKNOWLEDGEMENTS

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7. REFERENCES

An, C., Su, J., (2011) “Improved lumped models for transient combined convective and radiative colling of multi-layer composite”. *Applied Thermal Engineering*, vol. 31, pp. 2508-2517.

Anjos E., Silva J., Carvalho J., 2017. “Dynamic Analysis of a Three-Phase Reactor of Fixed Bed for Petroleum and Petrochemical Industry”. Prec. of 24th ABCM International Congress of Mechanical Engineering.

Ashok, J., Kawi, S., 2013. “Steam reforming of toluene as a biomass tar model compound over CeO_2 promoted Ni/CaO-Aℓ_2O_3 catalytic systems”. *Int. J. of Hydrogen Energy*, vol. 38, pp. 13938-13949.

Bona, S., Guillén, P. J., Alcalte, G., García, L., Bilbao, R., 2008. “Toluene steam reforming using coprecipitated Ni/Al catalysts modified with lanthanum or cobalt”. *Chemical Engineering Journal*, 137 (2008) 587-597.

Cardoso, S.A., Macêdo, E.N. and Quaresma, J.N.N., 2014. “Improved lumped solutions for mass transfer analysis in membrane separation process of metals”. *Int. J. of Heat and Mass Transfer*, vol. 68, p. 599-611.

Côrrea, E.J., Cotta, R.M., 1998. “Enhanced Lumped-Differential Formulations of Diffusion Problems”. *Applied Mathematical Modelling*, vol. 22, pp.137-152.

Hermite, M.Ch., 1878. “Sur la Formuled’Interpolation de Lagrange”, *J Crelle*.

Knupp, D.C., Naveira-Cotta, C.P., Ayres, J.V.C, Cotta R.M. and Orlande, H.R.B. 2012. “Theoretical experimental analysis of heat transfer in nonhomogeneous solids via improved lumped formulation, integral transforms and infrared thermography”. *Int. J. of Thermal Sciences*, vol. 46, p. 878-889.

Menning, J., Auerbach, T., Halg,W., 1983. “Two Point Hermite approximations For the Solution of Linear Initial Value and Boundary Value Problems”. *Computer Methods in Applied Mechanics and Engineering*, vol 39, pp. 199- 224.

Oliveira, A. N.,2012. “Mathematical Modelling of the Steam Reforming of Toluene for Fuel Gas Production in a Fixed Bed Catalytic Reactor”. (PhD Thesis), University of Pernambuco, Recife, Brazil.

Wu, C.,Huang, J.,Williams, P.T., 2013.“Carbon nanotubes and hydrogen production from the reforming of toluene”.*International Journal of Hydrogen Energy*, vol. 38, pp. 8790-8797.

Silva, J.D., Abreu., C.A.M., 2016. “Modelling and simulation in conventional fixed-bed and fixed-bed membrane reactors for the steam reforming of methane”. *Int. J. of Hydrogen Energy*, vol. 41, pp.11660-11674.

Swierczynski, D.,Courson, C.,Kiennemann. A., 2008.“Study of steam reforming of toluene used as model compound of tar produced by biomass gasification”. *Chem. Eng. Process. Process Intensif*, vol. 47, pp.508-513.

Virgine, M., Courson, C., Niznansky, D., Chaoui, N., Kiennemann, A., 2010. “Characterization and reactivity in toluene reforming of a Fe/olivine catalyst designed for gas cleanup in biomass gasification”. *Applied Catalysis B: Environmental*, vol. 101, pp. 90-100.

Xiao, X., Liu, J., Gao, A., Zhouyu, M., Liu, B., Gao, M.,Zhang, X.,Lu, Q.,Dong, C., 2017."The performance of nickel-loaded lignite residue for steam reforming of toluene as the model compound of biomass gasification tar". *J. of Energy Institute*.

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