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Mathematical Modelling of the Steam Reforming of Toluene for Fuel Gas Production in a Fixed Bed Catalytic Reactor

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The study presents a mathematical model to analyze the dynamic evolution of molar concentrations for toluene (C_7H_8), water vapor (H_2O) carbon monoxide (CO), hydrogen (H_2), methane (CH_4) and carbon dioxide (CO_2) in fixed bed catalytic reactor. The mathematical model was discretized using the method of lines (MDLs) to transform the system of partial differential equations (PDEs) in a system of ordinary differential equations (ODE). The system of ODEs has been solved by the implementation of the Runge-Kutta Gill to estimate the chemical species C_7H_8, H_2, CO, H_2, CH_4 and CO_2.The estimation allows the quantification of individual forecasts of the variables presented in this study. However, valuable information can be obtained from the estimated behaviors in fixed bed catalytic reactor. The model has allowed the validation of chemical species (H_2, CO and CO_2) by comparing the optimized values. Additionally, the concentrations for the chemical species C_7H_8, H_2, CO, H_2, CH_4 and CO_2 was studied.

1. Introduction

The global concern with the depletion of fossil fuels and rising environmental problems associated with the use of these sources has attracted the attention of researchers to develop new processes for power generation based on renewable sources. Biomass has been considered a renewable energy source. Alternatively, the biomass can be converted into gaseous fuel through gasification technology. The gasification of biomass is a promising technology for power generation and chemical production. A major problem for commercialization of biomass gasification is the quality of the gas produced (post-gasification gas). Among the impurities present in the post-gasification gas, tar is a serious problem for the gas produced from biomass.

Normally, gas produced into the fixed bed or fluidized gasifiers contains about 10 % to 20 % of tar with 14.2 % toluene, 13.9 % of an aromatic hydrocarbon, 9.6 % naphthalene, 7, 8 % for hydrocarbons two aromatic rings, 3.6 % hydrocarbon three aromatic rings, 0.8 % four ring aromatic hydrocarbons, 4.6 % of phenolic compounds, heterocyclic compounds 6.5 % and 1 % others. The removal or destruction of tar is seen as one of the major technical challenges to be overcome for the commercial success of advanced gasification technologies. According Bona et al., (2008), the catalytic reforming of tar increases the calorific value of the gas produced and the overall efficiency of the thermochemical conversion process. Toluene being the main component of tar, the present work has been focused on modeling of steam reforming of toluene in a catalytic reactor of Fixed Bed (LF).

A complete description of the process of mixing the vapor (H_2O + toluene) in diluent gas (Ar) of solid catalytic particles in catalytic reactors (LF), involves hydrodynamic aspects of this mixture. Among these aspects, there is heat transfer from the gas-solid interphase, interphase mass transfer of gas-solid diffusion of chemical components into the pores of the catalyst and the gas-solid interactions such as adsorption, desorption and reaction. Emphasizing the modelling of catalytic reactors (LF), refers to the application of dynamic models able to describe the phenomenology of realistic transient and stationary regimes, enabling secure and reliable reviews on control and process optimization (Silva and Abreu, 2012).

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The mathematical modelling and computer simulation for catalytic reactors (LF) are in continuous development, aiming to improve knowledge of the phenomenological processes of this equipment. As its applications, catalytic reactors (LF) are applied in the process of the chemical, biochemical, petrochemical and oil refineries to process hydrodesulfurization, hydrotreatment and hydrocracking (Silva, 2012).

The main objective of this paper was the development of a dynamic mathematical model to study isothermal steam reforming of toluene in a catalytic reactor (LF). The model has allowed a validation of chemical species (H_2, CO and CO_2) by comparing the optimized values. Additionally, the net rates of the chemical species C_7H_8, H_2, CO, H_2, CH_4 were studied as well as the concentrations for the chemical species C_7H_8, H_2, CO, H_2, CH_4 and CO_2.

1.1 Kinetic mechanism for this search

The kinetic models treat the mechanisms, rates of chemical reactions and the resulting concentrations of species at any point in time and space of a system. These models are generally related to specific processes, providing important considerations relating to the mechanisms of reactions and ways to increase the rate of a reaction or process. The process discussed here has involved the main reactions of steam reforming of toluene. In normal operation, the reaction (I) is the steam reforming of toluene, the reaction (II) presents the partial steam reforming reaction of methane and (III) shows the reaction gas Shift. Reaction (I) is an irreversible reaction, while reactions (II) and (III) are reversible (equilibrium) as follows.

$$C_7H_8 + 7H_2O \rightarrow 7CO + 11H_2;\ \Delta H^0_{298K} = +869{,}17\,kJ\,mol^{-1} \qquad (1)$$

$$CH_4 + H_2O \leftrightarrow CO + 3H_2;\ \Delta H^0_{298K} = +206{,}12\ kJ\,mol^{-1} \qquad (2)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2;\ \Delta H^0_{298K} = -41{,}17\,kJ\,mol^{-1} \qquad (3)$$

Thermodynamically, reactions (I) and (II) are endothermic and enough diet (III) is exothermic. The components of these reactions models are defined as toluene (C_7H_8), water (H_2O), carbon monoxide (CO), hydrogen (H_2), methane (CH_4) and carbon dioxide (CO_2). The stoichiometric coefficients for these components models have been presented in Table 1.

Table 1: Stoichiometric coefficients ν_{ij} of the components of the reactions

Reactions	C_7H_8	H_2O	CO	H_2	CH_4	CO_2
1	-1	-7	+7	+11	0	0
2	0	-1	+1	+3	-1	0
3	0	-1	-1	+1	0	+1

1.2 Mathematical Modeling Study on Kinetic Process

The kinetic mathematical model presented here considers only three homogeneous reactions according to the reactions (I), (II) and (III) for the reform of toluene. The overall rates for chemical reactions (1), (2) and (3) are presented below with their respective kinetic parameters.

$$R_1 = 8.723x10^9\ C_{C_7H_8}\ ;\ (kg_{cat}\,s)^{-1} \qquad (4)$$

$$R_2 = 3.101exp\left(-\frac{15.000}{T_g}\right)\left[C_{CH_4}C_{H_2O} - \frac{C_{CO}C_{H_2}^2}{0.0265exp\left(\frac{32.900}{T_g}\right)}\right];\ (kg_{cat}\,s)^{-1} \qquad (5)$$

$$R_3 = 250.000exp\left(-\frac{138.000}{T_g}\right)\left[C_{CO}C_{H_2O} - \frac{C_{CO_2}C_{H_2}}{0.0265exp\left(\frac{3966.000}{T_g}\right)}\right];\ (kg_{cat}\,s)^{-1} \qquad (6)$$

The rates of liquid intake and training, r_i, for each component type of the reactions (I), (II) and (III) have been obtained using the following equation (Xiu et al, 2002).

$$r_i = \sum_{j=1}^{n} \nu_{ij} R_j \tag{7}$$

Where, $r_i \rightarrow$ net rate of component I, $\nu_{ij} \rightarrow$ stoichiometric coefficient of the reaction and $R_j \rightarrow$ Reaction rate.

From the Eq. *(7)*, we get to obtain $r_{C_7H_8}$, r_{H_2O} , r_{CO} , r_{H_2} , r_{CH_4} and r_{CO_2} as fallows:

-net rate of C_7H_8;

$$r_{C_7H_8} = -R_1 \tag{8}$$

-net rate of H_2O;

$$r_{H_2O} = -(7R_1 + R_2 + R_3) \tag{9}$$

-net rate of CO;

$$r_{CO} = 7R_1 + R_2 - R_3 \tag{10}$$

-net rate of H_2;

$$r_{H_2} = (11R_1 + 3R_2 + R_3) \tag{11}$$

-net rate of CH_4;

$$r_{CH_4} = -R_2 \tag{12}$$

-net rate of CO_2;

$$r_{CO_2} = +R_3 \tag{13}$$

2. Simplified Mathematical Model for a Catalytic Reactor

The mathematical modelling can act significantly to explain the evolution of model components of chemical reactions 1, 2 and 3 in catalytic reactor (LF). For this work, the equations of the model components involved terms of chemical species accumulation, convection of chemical species, dispersions of chemical species and the rates of component templates in reactions considered for the process (Oliveira and Silva, 2012). Based on these assumptions, a simplified mathematical model for LF is formulated by the simplified equations of model components which describe the dynamic behavior. In the reaction zone of the LF, the mass balance equations of the components of the reactions 1, 2 and 3 (reactants and products) have been described in the following sequence C_7H_8, H_2O, CO, H_2, CH_4 and CO_2 as follows.

- Mass balance of the model components

$$\varepsilon_g \frac{\partial C_i}{\partial t} + \varepsilon_g \frac{4\,Q_g}{\pi\, d_c^2} \frac{\partial C_i}{\partial z} = \varepsilon_g\, D_i \frac{\partial^2 C_i}{\partial z^2} + (1-\varepsilon_s)\left(\sum_{j=1}^{3} \eta_j\right) r_i \tag{10}$$

- Initial and boundary conditions of the model components;

$$Ci\big|_{t=0} = C_{i,0} \text{ ; for all z} \tag{11}$$

$$D_i \left.\frac{\partial C_i}{\partial z}\right|_{z=0^+} = \frac{4\,Q_g}{\pi\, d_c^2}\left[C_i\big|_{z=0^+} - C_{i,0}\right] \text{ ; for t > 0} \tag{12}$$

$$\left.\frac{\partial C_i}{\partial z}\right|_{z=L^+} = 0 \text{ ; for t > 0} \tag{13}$$

Where i = C_7H_8, H_2O, CO, H_2, CH_4 and CO_2; $\sum_{j=1}^{3} \eta_j$, j = 1, 2 and 3 (reactions)

3. Results

The mathematical model was developed to analyze the molar concentrations of chemical species for C_7H_8, H_2O, CO, H_2, CH_4 and CO_2. The proposed model for this study was used to analyze the evolution of chemical species over time variable (t) at the output of this reactor. In the simulation, the Computational code has been fed with parameters shown in Table 2. In this table, it was shown the operational parameters in the reaction region of the LF mass transfer coefficients and physical properties of the gaseous phase. The parameters of Table 2 have been admitted as fixed values.

Table 2: Input values of operating conditions, properties of the gas and solid phases used in the simulation – extracted from the following sources (Silva, 2012; Zhao et al, 2010; Yao et al. 2007)

Categories	Properties	Numerical Values
Operation Conditions	Operation temperature of the gas phase, Tg ^oC	400
	Operation temperature of the solid phase, Ts ^oC	400
	Operation pressure, P_{op} atm	1.011
	Gas flow rate, Q_g m^3 s^{-1}	$2.367 x 10^{-2}$
	Flow of water vapor, Q_v m^3 s^{-1}	$2.561 x 10^{-4}$
	Initial concentration of C_7H_8, $C_{C7H8,0}$ kg m^{-3}	0.145
	Initial concentration of H_2O, $C_{H2O,0}$ kg m^{-3}	0.052
	Initial concentration of CO, $C_{CO,0}$ kg m^{-3}	0.000
	Initial concentration of H_2, $C_{H2,0}$ kg m^{-3}	0.000
	Initial concentration of CH_4, $C_{CH4,0}$ kg m^{-3}	0.100
	Initial concentration of CO_2, $C_{CO2,0}$ kg m^{-3}	0.000
	Catalytic reactor diameter, d_r m	0.032
Gas properties	Void fraction of the gaseous phase, ε_g (-)	0.360
	Density of the gaseous phase, ρ_g kg m^{-3}	0.0756
	Diffusion coefficient of C_7H_8, D_{C7H8} m^2 s^{-1}	$1.571 x 10^{-5}$
	Diffusion coefficient of H_2O, D_{H2O} m^2 s^{-1}	$2.113 x 10^{-5}$
	Diffusion coefficient of CO, D_{CO} m^2 s^{-1}	$1.567 x 10^{-5}$
	Diffusion coefficient of H_2, D_{H2} m^2 s^{-1}	$6.915 x 10^{-6}$
	Diffusion coefficient of CH_4, D_{CH4} m^2 s^{-1}	$3.337 x 10^{-5}$
	Diffusion coefficient for CO_2, D_{CO2} m^2 s^{-1}	$8.987 x 10^{-6}$
Properties of the solid phase	Void fraction of the solid phase, ε_s (-)	0.614
	Density of the solid phase, ρ_s kg m^{-3}	$1.250 x 10^3$
	Solid particle diameter, d_p m	0.00046
Heat of reactions and effectiveness factor	Heat of reaction for reaction (1), $\Delta H_{r,1}$ 850 ^oC, kJ mol^{-1}	+ $639.291 x 10^3$
	Heat of reaction for reaction (2), $\Delta H_{r,2}$ 850 ^oC, kJ mol^{-1}	+ $206.191 x 10^3$
	Heat of reaction for reaction (3), $\Delta H_{r,3}$ 850 ^oC, kJ mol^{-1}	- $89.231 x 10 x 10^3$
	Effectiveness factor of reaction (1), η_1	0.067
	Effectiveness factor of reaction (2), η_2	0.073
	Effectiveness factor of reaction (3), η_3	0.573

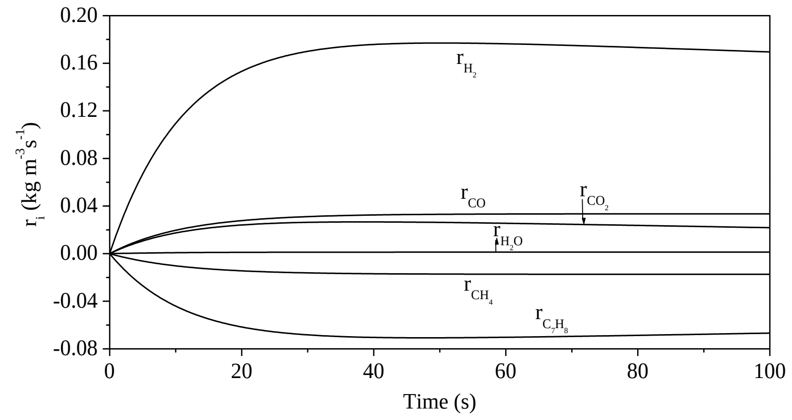

Figure1: Profiles of net chemical species for C_7H_8, H_2O, CO, H_2, CH_4, CO_2 versus the time variable in the output of the LF: z = 1m, $Q_g = 2.367 x 10^{-2}$ m^3 s^{-1}, $Q_v = 2.561 x 10^{-2}$ m^3 s^{-1}, $T_g = 400$ ^oC and $T_s = 400$ ^oC

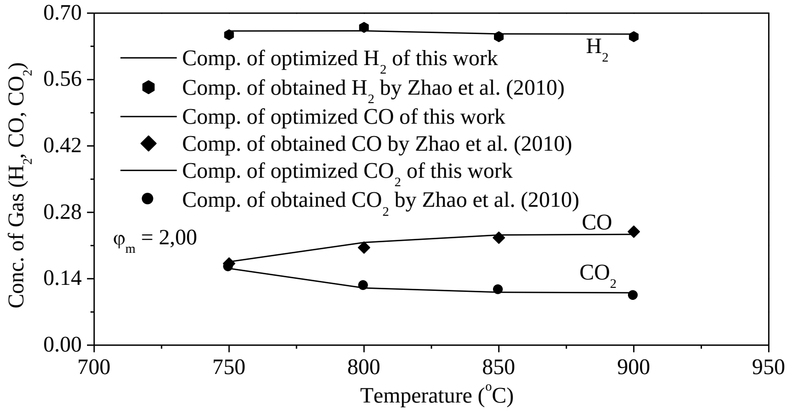

Figure 2: Comparison between experimental data of Zhao et al. and the results of this study optimized for four temperatures with $Q_g = 2.367 x10^{-2} m^3 s^{-1,} Q_v = 2.561 x 10^{-2} m^3 s^{-1}$

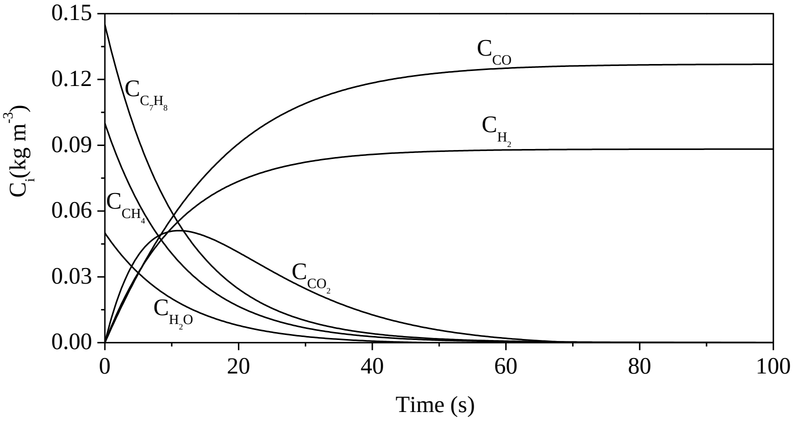

Figure 3: Profiles of the concentrations of chemical species H_2, CO, CO_2, $C_7 H_8$, CH_4 e H_2O *time variable at the output of LF under the following conditions: z = 1m, $Q_g = 2.367 x 10^{-2} m^3 s^{-1,}$ T_g = 400 °C, T_s = 400 °C and at = 8 s. of* computer time.

Figure 1 shows the net rates of each chemical species relative to the time variable at the output of the LF. The net rates r_{H2}, $r_{CO,}$ r_{CO2} reported an increase between 0.00 s. to 100 s. due to increased production of chemical species $H_{2,}$ CO and CO_2 800 °C. The net rates $r_{C7H8,}$ r_{CH4} and r_{H2O} suffer because of decreasing consumption of chemical species $C_7H_{8,}CH_4$ and H_2O at 800 °C.

Figure 2 shows the comparative experimental data of the literature and data of the present study optimized. The comparison shows a good fit of the experimental and optimized for the gases $H_{2,}$ CO and CO_2.

Figure 3 reports the evolution of C_7 H_8, H_2O, CO, H_2, CH_4, and CO_2 versus the time variable in the exit of the LF. Chemical species CO, CO_2 and H_2 are produced from the initial values of $C_{CO} = 0.00$, $C_{H2} = 0.00$ and $C_{CO2} = 0.00$ until reaching a maximum value at the operating conditions adopted, while chemical species C_7H_8, H_2O and CH_4 have been consumed from the initial values $Y_{C7H8} = 0.148$, $Y_{H2O} = 0.052$ and $Y_{CH4} = 0.101$. The chemical species H_2 and CO in ± 80 s. reached steady state, while the chemical species CO_2 reached a maximum and then decreases reaching a steady state at ± 70 s. Regarding chemical species C_7H_8, H_2O and $CH_{4,}$ it is observed that they were completely between (40-60) s.

4. Conclusions

Conducted in the context of reform of the line of aromatic components, this research will resort numerical methodology in order to carry out the development process in isothermal catalytic reactor operating dynamics of LF. In conditions allowed for this research, the method of Runge-Kutta Gill was used to predict a chemical species H_2, CO, CO_2, C_7 H_8, CH_4 e H_2O. The development of computer code to process and analyze the behavior of the variables in this research allowed the lead the following conclusions:

- The net rates (r_{C7H8}, r_{H2O}, r_{CO}, r_{H2}, r_{CH4} and r_{CO2}) of each chemical species were calculated. Since the net rates r_{CO}, r_{H2} and r_{CO2} showed in the Figure 1 increases, while the net rates r_{C7H8}, r_{CH4} and r_{H2O} reported in the Figure 1 decrease;
- The model developed for the LF led to calculations of optimized concentrations of chemical species H_2, CO and CO_2, validation confirmed by comparing the results of this research and the results obtained by Zhao et al., (2010);
- Consumption and production have shown the evolution of chemical species of C_7H_8, H_2, CO, H_2, CH_4, and CO_2 versus time.

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