

CATALYTIC STEAM REFORMING OF TOLUENE POST-GASIFICATION USING AS MODEL COMPOUND OF TAR PRODUCED BY BIOMASS GASIFICATION

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ABSTRACT-The study presents a mathematical model to analyze the dynamic evolution of molar concentrations of toluene (C_7H_8), water vapor (H_2O) carbon monoxide (CO), hydrogen (H_2), methane (CH_4) and carbon dioxide (CO_2) in a catalytic reactor of fixed bed. 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 (ODEs). The system of ODEs has been solved by the implementation of the method of 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 catalytic fixed bed 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 chemical species C_7H_8 , H_2 , CO , H_2 , CH_4 and CO_2 was studied.

1. INTRODUCTION

The global interest 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 productions. 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, the gas produced into the fixed bed or fluidized gasifiers contains about 10% to 20% of tar with 14.2 % toluene, 13.9 % of hydrocarbon with one aromatic ring, 9.6% naphthalene, 7.8% of hydrocarbons with two aromatic rings, 3.6 % of hydrocarbons with three aromatic rings, 0.8 % of hydrocarbons with four aromatic rings, 4.6 % of phenolic compounds, 6.5 % of heterocyclic

compounds 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 modelling of steam reforming of toluene (SRT) in a catalytic reactor of fixed bed (LF).

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

The mathematical modelling and computer simulation for the catalytic reactors of LF are in continuous development, aiming to improve knowledge of the phenomenological processes of this equipment. As its applications, the catalytic reactors of LF are applied in the process of the chemical, biochemical, petrochemical and oil refineries to process hydrosulfurization, 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 of 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 chemical species (C_7H_8 , H_2 , CO, H_2 , CH_4) were studied as well as the concentrations for chemical species (C_7H_8 , H_2 , CO, H_2 , CH_4 and CO_2).

2. MATERIALS AND METHODS FOR THIS RESEARCH

A conceptual schematic of the catalytic reactor of LF was developed to investigate the SRT according to the Figure 1. For this work, toluene was selected as one tar model compound which will be analyzed at different temperatures ($750\text{-}900^\circ\text{C}$).

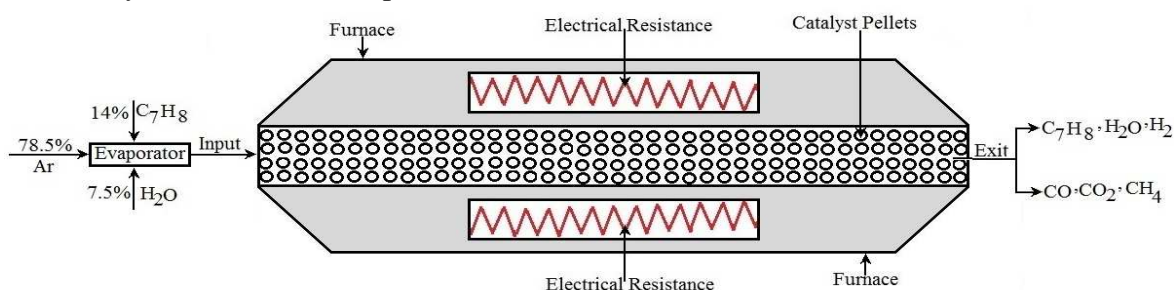
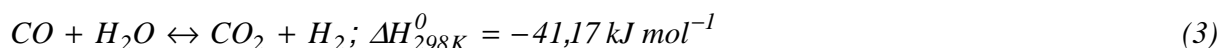
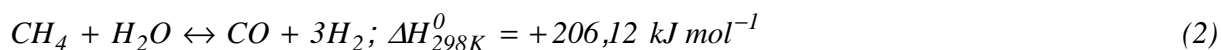
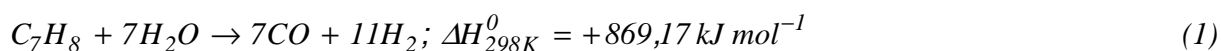


Figure 1: schematic of the CFBR for the SRT

2.1. Kinetic Mechanism

The kinetic models treat the mechanisms, rates of chemical reactions and the resulting concentrations of chemical species at any point in time and space of a system. These models are generally related to specific processes, providing important considerations for relating 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 (1) is the steam reforming of toluene, the reaction (2) presents the partial steam reforming reaction of methane and (3) shows the reaction water-gas Shift. The reaction (1) is an irreversible reaction, while the reactions (2) and (3) are reversible (equilibrium) as follows.



Thermodynamically, the reactions (1) and (2) are endothermic and the reaction (3) is exothermic. The components of these reaction 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 model components 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

2.2. Kinetic Modelling

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

$$R_1 = 8.723 \times 10^9 C_{C_7H_8}; (\text{kg}_{\text{cat}} \text{ s})^{-1} \quad (4)$$

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

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

The net rates, r_i , for each component type of the reactions (1), (2) and (3) have been obtained using the following equation (Oliveira and Silva, 2012).

$$r_i = \sum_{j=1}^n \nu_{ij} R_j \quad (7)$$

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

- net rate of C_7H_8 ;

$$r_{C_7H_8} = -R_1 \quad (8)$$

- net rate of H_2O ;

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

- net rate of CO ;

$$r_{CO} = 7R_1 + R_2 - R_3 \quad (10)$$

- net rate of H_2 ;

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

- net rate of CH_4 ;

$$r_{CH_4} = -R_2 \quad (12)$$

- net rate of CO_2 ;

$$r_{CO_2} = +R_3 \quad (13)$$

2.3. MODEL FOR THE CATALYTIC REACTOR OF LF

The mathematical modelling can act significantly to explain the evolution of model components of chemical reactions (1), (2) and (3) in catalytic reactor of 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 net rates of model component in the work reactions considered for the process (Oliveira and Silva, 2012). Based on these assumptions, a simplified mathematical model for the catalytic reactor of LF is formulated by the simplified equations of model components which describe the dynamic behavior. In the reaction

zone of the catalytic reactor of LF, the mass balance equations of the model components of the reactions (1), (2) and (3) (reactants and products) have been described as follows.

- Mass balance of the model components

$$\varepsilon_g \frac{\partial C_i}{\partial t} + \varepsilon_g \frac{4Q_g}{\pi d_c^2} \frac{\partial C_i}{\partial z} = \varepsilon_g D_i \frac{\partial^2 C_i}{\partial z^2} + (1 - \varepsilon_s) \sum_{j=1}^3 \sum_{i=1}^6 \eta_j r_i \quad (14)$$

- Initial and boundary conditions of the model components;

$$C_i|_{t=0} = C_{i,0}; \text{ for all } z \quad (15)$$

$$D_i \frac{\partial C_i}{\partial z} \Big|_{z=0^+} = \frac{4Q_g}{\pi d_c^2} [C_i|_{z=0^+} - C_{i,0}]; \text{ for } t \geq 0 \quad (16)$$

$$\frac{\partial C_i}{\partial z} \Big|_{z=L^+} = 0; \text{ for } t \geq 0 \quad (17)$$

Where $i = C_7H_8, H_2O, CO, H_2, CH_4$ and CO_2 , $j = 1, 2$ and 3 (reactions).

3. RESULTS

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

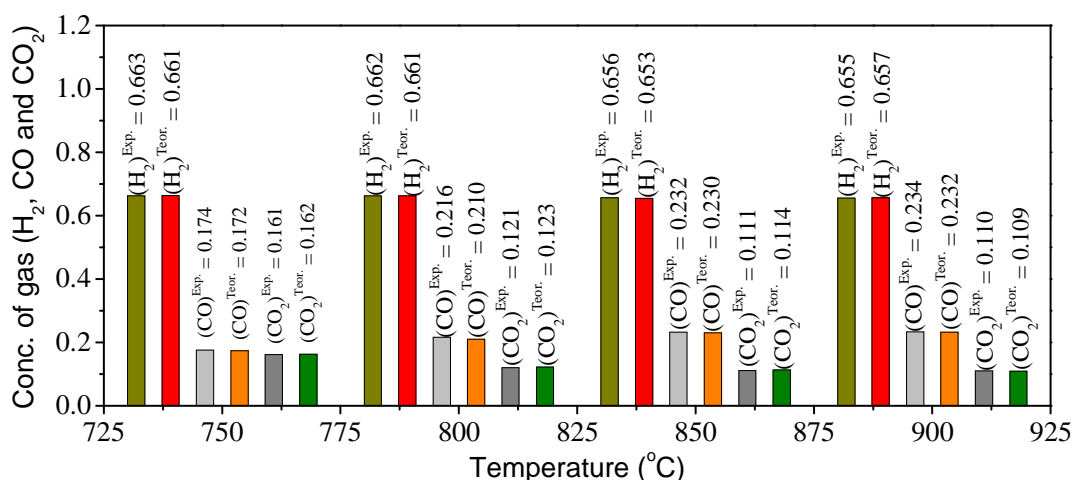


Figure 2: Comparison between experimental data of Zhao et al.(2010) and the results of this optimized study for four different temperatures (750°C, 800°C, 850°C and 900°C) with $Q_g = 2.367 \times 10^{-2} \text{ m}^3 \text{ s}^{-1}$, $Q_v = 2.561 \times 10^{-2} \text{ m}^3 \text{ s}^{-1}$ and $z = 1 \text{ m}$ at the output of the LF

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 .

Table 2: Operating conditions, properties of the gas and solid phases used in the simulation were extracted of the following references (Silva, 2012; Zhao et al, 2010; Yao et al. 2007)

Categories	Properties	Numerical Values
Operation Conditions	Operation temperature of the gas phase, T_g °C	400
	Operation temperature of the solid phase, T_s °C	400
	Operation pressure, P_{op} atm	1.011
	Gas flow rate, Q_g m ³ s ⁻¹	2.367×10^{-2}
	Flow of water vapor, Q_v m ³ s ⁻¹	2.561×10^{-4}
	Initial concentration of C_7H_8 , $C_{C_7H_8,0}$ kg m ⁻³	0.145
	Initial concentration of H_2O , $C_{H_2O,0}$ kg m ⁻³	0.052
	Initial concentration of CO, $C_{CO,0}$ kg m ⁻³	0.000
	Initial concentration of H_2 , $C_{H_2,0}$ kg m ⁻³	0.000
	Initial concentration of CH_4 , $C_{CH_4,0}$ kg m ⁻³	0.100
	Initial concentration of CO_2 , $C_{CO_2,0}$ 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 , $D_{C_7H_8}$ m ² s ⁻¹	1.571×10^{-5}
	Diffusion coefficient of H_2O , D_{H_2O} m ² s ⁻¹	2.113×10^{-5}
	Diffusion coefficient of CO, D_{CO} m ² s ⁻¹	1.567×10^{-5}
	Diffusion coefficient of H_2 , D_{H_2} m ² s ⁻¹	6.915×10^{-6}
	Diffusion coefficient of CH_4 , D_{CH_4} m ² s ⁻¹	3.337×10^{-5}
	Diffusion coefficient for CO_2 , D_{CO_2} m ² s ⁻¹	8.987×10^{-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	1.250×10^3
	Solid particle diameter, d_p m	0.00046
Heat of reactions effectiveness factor	Heat of react. for react. (1), $\Delta H_{r,1}$ 850 °C, kJ mol ⁻¹	$+ 639.291 \times 10^3$
	Heat of react. for react. (2), $\Delta H_{r,2}$ 850 °C, kJ mol ⁻¹	$+ 206.191 \times 10^3$
	Heat of react. for react. (3), $\Delta H_{r,3}$ 850 °C, kJ mol ⁻¹	$- 89.231 \times 10 \times 10^3$
	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

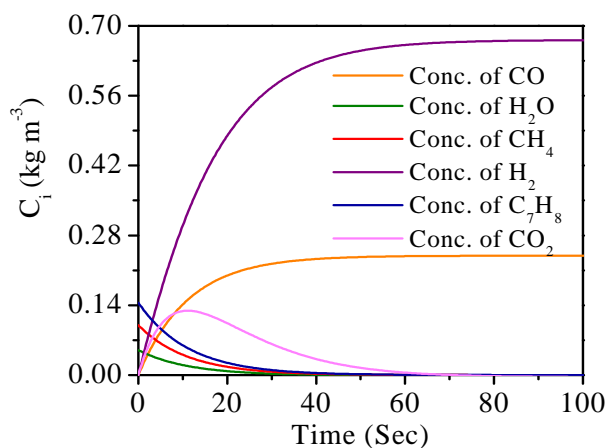


Figure 3: Profiles of the concentrations of species C_7H_8 , H_2O , H_2 , CH_4 , CO and CO_2 in function of time at the exit of the CFBR on the conditions: $z = 1$ m, $Q_g = 6.87 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$ and at $t = 8$ sec of computer time

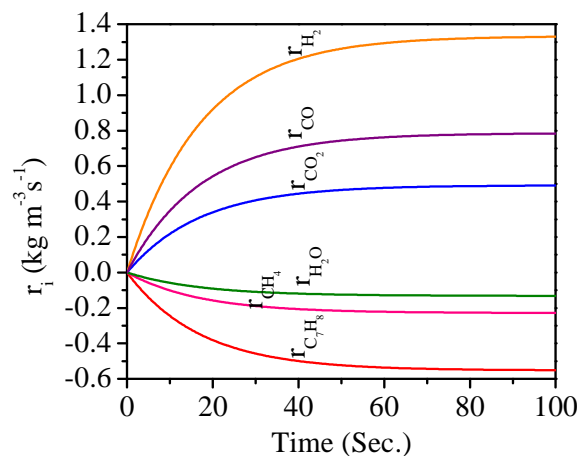


Figure 4: Profiles of net rates of species C_7H_8 , H_2O , H_2 , CH_4 , CO and CO_2 in function of time at the exit of the CFBR under the following conditions: $z = 1$ m, $Q_g = 6.87 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$ and at $t = 8$ sec of computer time

Figure 3 reports the evolution of C_7H_8 , H_2O , CO , H_2 , CH_4 , and CO_2 versus the time variable at the output of the LF. Chemical species CO , CO_2 and H_2 are produced from the initial values of $C_{CO} = 0.00$, $C_{H_2} = 0.00$ and $C_{CO_2} = 0.00$ 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 $Y_{C_7H_8} = 0.148$, $Y_{H_2O} = 0.052$ and $Y_{CH_4} = 0.101$. 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 sec. For chemical species C_7H_8 , H_2O and CH_4 , it is observed that they were completely consumed between (20-40) sec.

The Figure 4 shows the net rates of each chemical species relative to the time variable at the output of the LF. The net rates r_{H_2} , r_{CO} , r_{CO_2} reported an increase between 0.00 sec. to 100 sec. due to increased production of chemical species H_2 , CO and CO_2 at 800°C . The net rates $r_{C_7H_8}$, r_{CH_4} and r_{H_2O} suffer because of decreasing consumption of chemical species C_7H_8 , CH_4 and H_2O at 800°C .

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 of the process in isothermal catalytic reactor of LF. In conditions allowed for this research, the method of Runge-Kutta Gill was used to predict chemical species (C_7H_8 , H_2O , CO , H_2 , CH_4 , and CO_2). The development of computer code to process and analyze the behavior of the variables in this research allowed the following conclusions:

- 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 optimized 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.
- The net rates ($r_{C_7H_8}$, r_{H_2O} , r_{CO} , r_{H_2} , r_{CH_4} and r_{CO_2}) of each chemical species were calculated. Since the net rates r_{CO} , r_{H_2} and r_{CO_2} showed in the Figure 1 increases, while the net rates $r_{C_7H_8}$, r_{CH_4} and r_{H_2O} reported in the Figure 1 decrease;

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