

Dynamic Analysis to Produce Hydrogen in a Fixed Bed Catalytic Reactor By the Steam Reforming of Toluene

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Hydrogen is considered as an essential fuel of the future, which can reduce the reliance on oil. It can be produced via the various chemical process including ion exchange membranes, biomass gasification, steam reforming. The use of biomass as alternative energy for fossil fuels has been attracting attention recently due to the rapid depletion of fossil fuel sources and the costly price tag of crude. However, one of the critical challenges in biomass gasification technology is the removal of tar, which contains oxygenated hydrocarbons and aromatic hydrocarbons which are difficult to degrade and can lead to a decrease in efficiency of the process operations and an increase in maintenance and operating costs. The steam reform is a widely known technique for the removal of tar, avoiding equipment damage, and can produce hydrogen fuel that is a relevant alternative for reducing environmental impact. In this sense, this paper presents a numerical analysis of the steam reforming using toluene as a model compound to produce hydrogen in a fixed bed catalytic reactor. The main objective of this paper was the development of a dynamic mathematical model to study non-isothermal steam reforming of toluene in a catalytic reactor. This model is described by a system of Partial Differential Equations (PDEs). Also, to solve these PDEs, it was using the technique Coupled Integral Equation Approach (CIEA) and with a code in FORTRAN 95 language that allowed obtaining data about the temperature profiles and H₂ production.

1. Introduction

Nowadays fossil fuels are used as the main energy source. However, the current fossil fuel sources are running, and new sources are difficult to find and use (Setiadjudi, 2018). The renewable, pollution-free green energy resources as a hotspot in the world energy field require a full development now and, in the future (Sun, 2018). Hydrogen is considered as an essential fuel of the future, which can reduce the reliance on oil. It can be produced via the various chemical process including ion exchange membranes, biomass gasification, steam reforming. The use of biomass as alternative energy for fossil fuels has been attracting attention recently due the to rapid depletion of fossil fuel sources and the costly price tag of crude.

The biomass gasification for producing syngas (H₂ + CO) is regarded as one of the most promising options. The gasification is defined as the thermochemical process which converts solid and liquid fuels into a combustible gas mixture of low or medium in the presence of a gasifying agent. However, one of the critical challenges in biomass gasification technology is the removal of tar, which contains oxygenated hydrocarbons and aromatic hydrocarbons which are difficult to degrade and can lead to a decrease in efficiency of the process operations and an increase in maintenance and operating costs. Tar is the inevitable by-product during the biomass gasification process and is a complex mixture of all organic compounds, among which toluene represents 24% from composition (Mitran et al., 2017).

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. Silva (2014), modeled and simulated one-dimensional isothermal modeling for the steam methane reforming in a fixed bed membrane reactor. Oliveira and Silva (2013), studied the steam

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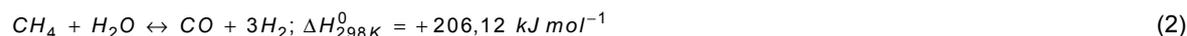
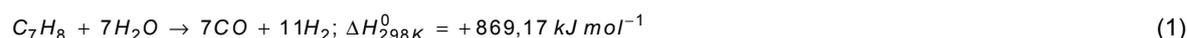
reforming of toluene in the isothermal modeling in a fixed bed reactor, Aydin et al. (2018) did a numerical and experimental investigation of hydrogen-rich syngas production via biomass and Wu et al. (2013), analyzed hydrogen production from the catalytic steam reforming of toluene over experimental nature. 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.

Therefore, the primary objective of this paper was the development of a dynamic mathematical model to study non-isothermal steam reforming of toluene in a catalytic reactor. 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

2.1 A kinetic mechanism for this search

The kinetic models specify the behavior, rates of chemical reactions as well as the resulting concentrations of species at any point in time and space of a system. These models generally refer to specific processes, providing relevant information of the reaction mechanisms and ways to control the rate of a reaction or process. Herein, the process consists of the primary reactions of the steam reforming of toluene. The reactions (1), (2) and (3) in operating conditions describe: the steam reforming reaction of toluene, the partial steam reforming reaction of methane, and the water gas shift reaction, respectively. Note that (1) is an irreversible reaction, while (2) and (3) are reversible (equilibrium) ones.



Thermodynamically, (1) and (2) are endothermic reactions and (3) is exothermic one. Chemical species of model reactions are known as toluene (C₇H₈), water (H₂O), carbon monoxide (CO), hydrogen (H₂), methane (CH₄) and carbon dioxide (CO₂).

2.2 Simplified Mathematical Model for a Catalytic Reactor

Figure 1 shows the schematic diagram of a Fixed-Bed Reactor (FBR). The model with fluid co-current, over particles, as illustrated in Figure 1, can be considered as an initial value problem. Thus, it is a useful tool, and it is possible to estimate the temperatures and the chemical species as a function of time. Mathematical models can be used to analyze reactor designs and their operating conditions. This work presents a one-dimensional model to predict the evolution of the temperatures in the gas-liquid and solid phases and evolution of chemical species during the steam reforming of toluene.

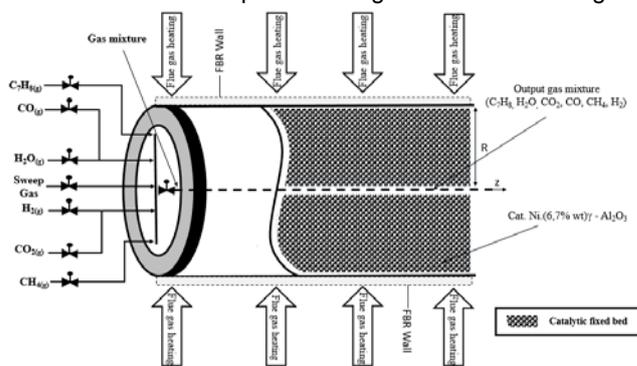


Figure 1: Schematic diagram of the FBR

The mathematical modeling can act significantly to explain the evolution of model components of chemical reactions Eq (1, 2 and 3) in FBR. The set of assumptions for the energy balance are: (i) temperature gradients in the axial direction of the FBR, (ii) temperature gradients in the radial direction of the particle, (iii) only thermal effects are considered in both phases of the proposed model, (iv) the wall temperature of the FBR is

deemed to be constant, and (v) the particle has a uniform size. Also, 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, and (iv) the net rate for each chemical compound have also been studied. Based on these assumptions, a simplified mathematical model for FBR is formulated by the mass and energy balance equations to describe the dynamic behavior. Table 1 contains the initial and boundary conditions of Eq (4,5 and 6).

- Energy balance for liquid-gas phase

$$\phi_{gt} \frac{\partial T_{gl}(z,t)}{\partial t} + \vartheta_{gt} \frac{\partial T_{gl}(z,t)}{\partial z} = \mu_{gt} \frac{\partial^2 T_{gl}(z,t)}{\partial z^2} - h_{fp} \frac{3}{r_p} (1-\varepsilon_b) [T_{gl}(z,t) - T_s(r,t)|_{r=R}] \quad (4)$$

Where, ϕ_{gt} (kJ/m³K) is the coefficient of the term of thermal accumulation, T_{gl} (K) is the gas-liquid phase temperature, ϑ_{gt} (kJ/m³K h) is the coefficient of the term of thermal convection, t (h) is the time, z (m) is the coordinate in the axial direction, μ_{gt} (kJ/m³K h) is the coefficient of the term of thermal dispersion, h_{fp} (kJ/m²K s) is the coefficient of heat transfer in fluid-particle, r_p (m) radius of particle, ε_b (m³ of fluid/m³ of reactor) is the bed porosity, T_s (K) is the solid phase temperature.

- Energy balance for Solid Phase

$$\rho_s C_{p,s} \frac{\partial T_s(r,t)}{\partial t} = \frac{\lambda_s}{R^2} \frac{1}{r^2} \frac{\partial}{\partial r} \left[r^2 \frac{\partial T_s(r,t)}{\partial r} \right] + \rho_s (\Delta H_R) R_{tol} \quad (5)$$

Where, ρ_s (kg/m³) is the solid phase density, $C_{p,s}$ (kJ/kg.K) is the heat capacity of the solid phase, λ_s (kJ/m K h) is the solid phase thermal conductivity, R (m) is the superficial radius of the solid phase, r (m) is the particle radius, ΔH_R (kJ/mol) is the enthalpy of reaction, and R_{tol} is the global rate of toluene, detailed discussion is given in *Oliveira and Silva (2013)*.

- Mass balance

$$\varepsilon_g \frac{\partial C_i(z,t)}{\partial t} + \varepsilon_g \frac{4Q_g}{\pi d_c^2} \frac{\partial C_i(z,t)}{\partial z} = \varepsilon_g D_i \frac{\partial^2 C_i(z,t)}{\partial z^2} + (1-\varepsilon_s) r_i \quad (6)$$

Where i is replaced by toluene (C₇H₈), water (H₂O), carbon monoxide (CO), hydrogen (H₂), methane (CH₄) and carbon dioxide (CO₂), ε_g (m³ of gas/m³ of the reactor) is the void fraction of the gas phase, C_i (kg m⁻³) is the concentration of components, Q_g (m³/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 net rate for each chemical compound, a further discussion is given in *Cruz and Silva (2017)*.

Table 1: Initial and boundary conditions

Liquid-Gas Phase	Solid Phase	Mass Balance
$\frac{\partial T_{gl}}{\partial z} \Big _{z=0^+} = \frac{\vartheta_{gl}}{\mu_{gl}} [T_{gl} _{z=0^+} - T_{gl}]$	$\frac{\partial T_s}{\partial r} \Big _{r=R} = \frac{h_{sc}}{\lambda_s} [T_{gl} - T_s _{r=R}]$	$\frac{\partial C_i}{\partial z} \Big _{z=0^+} = \frac{4Q_g}{\pi d_c^2 D_i} [C_i _{z=0^+} - C_i]$
$\frac{\partial T_{gl}}{\partial z} \Big _{z=L} = 0$	$\frac{\partial T_s}{\partial r} \Big _{r=0} = 0$	$\frac{\partial C_i}{\partial z} \Big _{z=L} = 0$

3. Numerical Solution

A mathematical model has been developed based on the mass and energy balance in the reactor. In order to solve the mathematical modeling of the energy and mass balance equations of the gas and solid phases together with the boundary conditions, the Coupled Integral Equations Approach (CIEA) method (Sousa, 2018; Anjos et al., 2017) was applied to transform the partial differential equations (PDEs) into ordinary differential equations (ODEs). This method was chosen because it is possible to reduce the number of independent variables without the minimum loss of information of the variable eliminated from the equation and by the simplicity when compared with traditional methods. The transformed equations are given next.

- The transformed equation of the gas-liquid phase energy balance

$$\frac{d\bar{T}_{gl}(t)}{dt} = \alpha_{5,gl}(T_{gl,0}) - \alpha_{7,gl}\bar{T}_{gl}(t) + \alpha_{6,gl}\bar{T}_s(t) \quad (7)$$

- The transformed equation of the solid phase energy balance

$$\frac{d\bar{T}_s(t)}{dt} = \beta_{6,s}\alpha_{4,gl}(T_{gl,0}) + \beta_{6,s}\alpha_{3,gl}\bar{T}_{gl}(t) - \beta_{7,s}\bar{T}_s(t) \quad (8)$$

- The transformed equation for component "i" in the mobile gas phase mass balance

$$\frac{d\bar{C}_i(t)}{dt} = \eta_{10}(C_{i,0}) + \eta_{11}\bar{C}_i(t) - \eta_{12}\bar{r}_i(t) \quad (9)$$

Where, $\alpha_{3,gl}, \alpha_{4,gl}, \alpha_{5,gl}, \alpha_{7,gl}, \alpha_{6,gl}, \beta_{6,s}, \beta_{7,s}, \eta_{10}, \eta_{11}$ and η_{12} are parameters obtained by the CIEA method.

4. Results and Discussion

The equations of the energy balance and mass balance are solved numerically by the Euler method, implemented in Fortran PowerStation 4.0. The proposed model for this study was used to analyze the evolution of chemical species throughout the processing time, and the variations of the temperature until the stabilization moment, which is essential to know the behavior of the reactor. Moreover, table 2 contains 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	$T_{gl,0}$	400	Properties of Liquid phase	$C_{p,l}$	2.001
	$T_{s,0}$	400		h_l	0.791
	L	1.0		$V_{s,l}$	2.01
	ε_s	0.59		λ_l	1.80×10^{-2}
	r_p	3.2×10^{-4}		ρ_L	1.01×10^{-2}
	R	1.0			
Properties of Gaseous phase	$C_{p,g}$	2.101×10^{-1}	Properties of Solid phase	$C_{p,s}$	2.00×10^3
	h_g	0.80		h_{fp}	2.635×10^{-2}
	$V_{s,g}$	29.46×10^{-1}		λ_s	$1.559 \times 10^{+2}$
	λ_g	0.0547		ρ_s	1.08×10^{-1}
	ε_g	0.47			
Initial Concentration	C_{C7H8}^0	0.20	Diffusion Coefficient	D_{C7H8}	5.566×10^{-2}
	C_{CH4}^0	0.36		D_{CH4}	5.005×10^{-2}
	C_{H2O}^0	0.60		D_{H2O}	7.061×10^{-1}
	C_{CO}^0	0.00		D_{CO}	3.982×10^{-1}
	C_{CO2}^0	0.00		D_{CO2}	3.000×10^{-2}
	C_{H2}^0	0.00		D_{H2}	0.143×10^{-1}

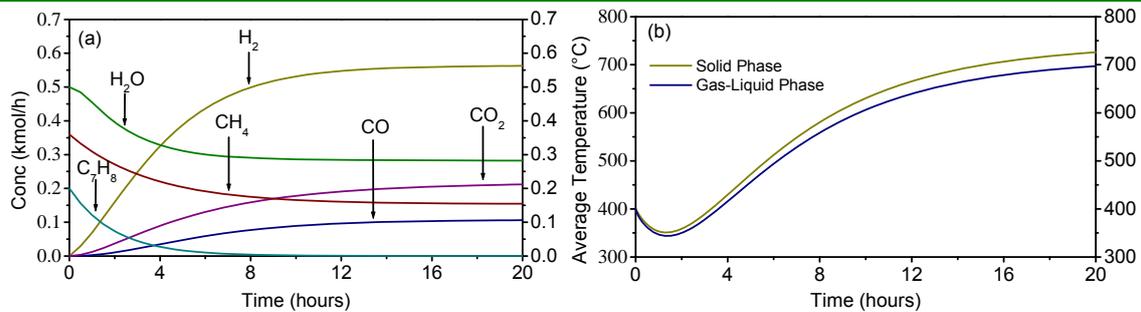


Figure 2: Concentration of chemical compounds (a) and Average Temperature at the outlet of the reactor (b).

Figure 2a shows that the dynamic evolutions of the product gas distribution reach stable levels hours after starting the operation. It can be observed that approximately 16 hours after beginning the FBR under initial conditions, all curves show the product gas distribution have achieved the steady-state. During the transient process, as the operation proceeds, methane and toluene are consumed with water available in an inlet gas mixture (steam reforming). The concentrations of CH_4 , H_2O , and C_7H_8 decrease continuously during the process while the concentrations of H_2 , CO_2 , and CO increase (behavior given by Eq (1-3)). Under the operating conditions, the reactor temperature had a range of 300K-800°C in regime dynamic, and the wet basis products in the same process contain about 0.62 kmol/h of H_2 , 0.10 kmol/h of CO , 0.22 kmol/h of CO_2 , 0.15 kmol/h of CH_4 , 0.015 kmol/h of C_7H_8 and 0.27 kmol/ of H_2O .

Figure 2b shows a comparison of the evolution of temperatures in each phase. It is observed that both curves represent a similar behavior, with slightly higher values in the solid phase compared to the gas-liquid phase. The differential between both temperatures reaches the steady-state after 20 hours. This slight variation of the temperatures shows that the operation takes place in a controlled way.

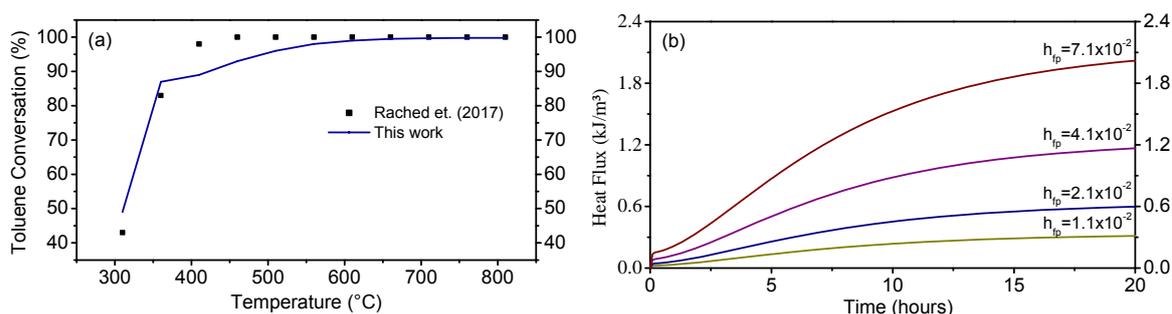


Figure 3: Comparison between the experimental data and the theoretical optimized data of the present study (a). Evolution of the heat flux throughout the processing time (b).

Figure 3a shows the comparison between the experimental data obtained by Rached et al. (2017) and the technical optimized data of the present study. The comparison was accomplished with points in the same temperature of both works and showed a good fit of the experimental and optimized for the toluene conversion.

Figure 3b shows the evolution of the heat flux throughout the processing time. The heat flux is obtained from the difference between the phases of the temperatures. A massive heat transfer is observed at the beginning of the operation, the influence of the parameter coefficient of heat transfer (h_{fp}) has also been seen. A significant increase of the heat flux occurs as the h_{fp} increases. However, after 0.5 hours a slight increase in heat flux is obtained reaching the steady-state in all cases. For instance, a large heat flux of 2.1 kJ / m^2 is received for a h_{fp} of 7.1×10^{-2} and the variation of temperature, in this case, it's already gone analyzed in figure 2b.

5. Conclusions

A one-dimensional mathematical model was used to report the dynamics analysis of the catalytic steam reforming of toluene 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 of FBR reactor. A computer code to process and analyze the performance of the operating parameters allowed the following conclusions:

- In the FBR model, the solid phase temperature reaches higher values compared to the gas-solid phase temperature;
- The higher the h_{fp} , the more significant the amount of heat flux. It is essential to consider this phenomenon because it allowed determining the total heat flux (a large heat flux of 2.1 KJ/m^2 is obtained for a h_{fp} of 7.1×10^{-2}) and was checked that hot spots not exist in this case;
- The dynamic behavior of the components of reactions was obtained. H_2 , CO , and CO_2 are produced, and C_7H_8 , CH_4 , and H_2O are consumed;
- The concentration of the chemical species C_7H_8 (toluene) was used to perform the validation of the comparative results of this study and the results obtained by Rached et al. (2017).
- Almost all toluene and methane are consumed in the reaction. Reaching the objective of the present paper to carry out steam reforming of toluene with the help of partial steam reforming of methane to avoid damages caused by biomass and to produce hydrogen to contribute to the study of renewable energies.

Acknowledgments

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