

Mathematical Model of Biomass Product Using Gasification Reactor

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ABSTRACT: *The aim of this study is to design a new mathematical model biomass product with the help of the gasification reactor. This design will help in describing most of the internal parameters inside this process. This research also aims to study and analyze the kinetic reaction, mass and heat transfer for four zones of the gasification reactor. It has been found that the char concentration from zone one is almost 42% consumption and from zone three to four, the consumptions have found to be 72.06%. It means that the char conversion depends on oxygen consumptions in all zones to produce volatility gases, methane, and hydrogen. The mathematical model will help in optimizing best possible conditions so as to give a high quality product of methane and hydrogen to 2.2 kmol/m³ and 3 kmol/m³ respectively. Thus, it appears to be important that important parameters of a chemical reaction are studied. Furthermore, all thermodynamic parameters of the reaction must be analyzed so as to optimize the best conditions through gasification reactor.*

KEYWORDS: *Mathematical model; Catalyst surface reaction; Gasification process' Biomass.*

INTRODUCTION

Nowadays the source of energy that is the most used comes from fossil fuel. Which are coal, natural gas and oil and this kind of source is shade as nonrenewable energy? Now to open our eyes to the truth the fossil fuel is depleting [1]. It causes the contribution to the world and global warming is one of its effects. To avoid and give a solution of those problems global research tried to find an alternative energy source to use instead of fossil fuel. The new resource is like expectancy to the human being.

The modern countries are starting using new techniques that are better to get energy with little impact on the environment to get a renewable source of energy such as gasification, combustion, Pyrolysis, hydrothermal

process and many other techniques. In Oman, these techniques are limited used and mainly does not popularly use. Comparing to modern countries like the USA, German, Japan, France, and many others are using gasification technique.

The idea of this mechanism is to convert the waste to friendly energy [2]. Biomass is a great selective to become a renewable source and it is biological material from living organism like agriculture residue, industrial waste, sewage sludge, polymer waste, and another type of waste[3-4]. Biomass can be transfer to benefit material like fuels, chemical (a mixture of gases which called syn gas or oil) and also electric energy. Gasification is useful

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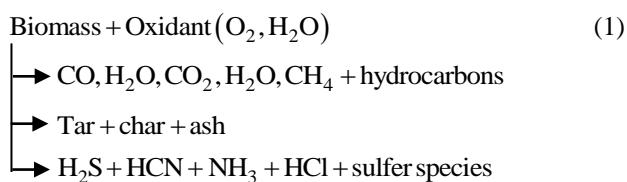
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the process to convert biomass because of the flexibility of applications which are thermal power generation, hydrogen production and synthesis of chemical.

In general, the gasification of biomass produces syn gas (H_2 and CO), carbon dioxide (CO_2), water (H_2O), methane (CH_4) and other light hydrocarbon compounds. This process also results in some material like dust (include ash and char), ammonia (NH_3), alkali (mostly potassium), sulfur, chloride, and tars [5]. The general equation of biomass gasification reaction is shown Equation (1a).



As shown in equation (1a) there is observing of tar in producer gas and that can cause several problems like cracking in the pores of filler, forming coke and plugging the fillers, and condensing in the cold spots and plugging the line, resulting in serious operational interruptions as shown in Table 1.

Tar can be removed physical process (like filtration), non-catalytic (e.g. thermal cracking) and catalytic tar removal process. The two first processes may be effective, but there is a block of this application and these processes have disadvantages one of it is the need of heating and cooling steps that will reduce the overall process efficiency. One other hand there is liquid scrubbing and it will cause an increasing amount of liquid waste and that require downstream treatment.

Catalytic steam reforming is the best way to remove tar [6,7]. The catalytic tar conversion is economically interesting for gas cleaning. It rises up the value of heat and the overall efficiency. There are several types of catalysts that are used for this purpose which are: mineral catalyst [34-37], transition metal [18-27] and nickel-based catalyst [9-19]. There are many side effects of using this catalyst fast inactivation by coke formation with using a nickel-based catalyst. Transition metal like Pt, Fe, and Rh are mostly expensive [8].

Our research to highlight about developing a new mathematical model and classification of the cheap catalyst which is more active for the steam reforming of biomass-derive tar compounds. The catalyst to be developed

Table 1: Typical composition of biomass gasification tar [7].

Compound	Percentage weight (%)
Benzene	37.9
Toluene	14.3
Other one-ring aromatic hydrocarbons	13.9
Naphthalene	9.6
Other two-ring aromatic hydrocarbons	7.8
Three-ring aromatic hydrocarbons	3.6
Four-ring aromatic hydrocarbons	0.8
Phenolic compounds	4.6
Heterocyclic compounds	6.5
Others	1.0

will use char as support catalyst instead of expensive traditional catalyst support like silica and alumina. The cheap catalyst will help to increase the commercialization of biomass gasification process as much as get lowers of operation cost and reduce the problems that happen by tar. Moreover, using char as a supported catalyst, getting rid of spent catalyst support (such as Al_2O_3 , SiO_2) would longer be a problem as char can be easily burnt to produce heat that can be used in a gasification system.

Gasification is a good way to get heat, energy, fuel and chemical form from biomass. However, the most effects cumbersome for commercialization of gasification are tar formation [28-33]. Tar can condense which gives a share in operational problems of downstream processes. The best to solve this problem by using catalytic steam reforming.

Several studies on the catalytic steam reforming of tar have been carried out using a natural catalyst and synthetic catalyst. Dolomite and olivine are non-metallic catalysts commonly used for tar conversion process but the catalyst is not enough for reforming to produce gas. Alkali metals based are very active but there is a disadvantage that due to the expensive improvement of catalyst. Most studies have been carried out using nickel-based catalyst because it is used broadly in the petroleum-based industrial steam reforming reactions. Nickel-based catalysts are usually supported on materials like alumina and silica. Theses support materials increase the cost of catalyst. It also suffers rapid deactivation by coke [8].

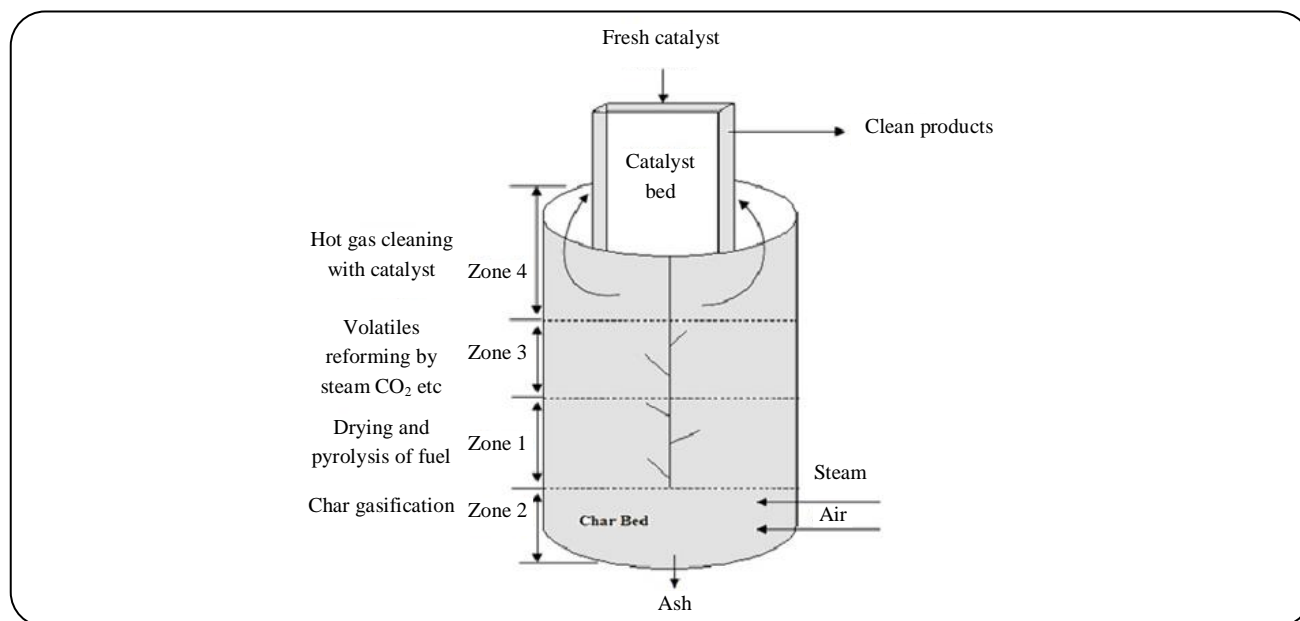


Fig. 1: Mathematical Model of Biomass Gasification.

The purpose of our research is to design a new mathematical model to be more close to the real state of the gasification reactor and specify all variables factors in all phases of the reactor.

Methodology

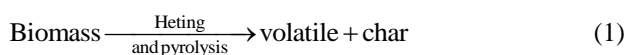
The methodology can be explained as shown in Fig. 1.

Formation of a mathematical model

By considering this process (gasification) behavior of biomass technology to be designed for four zones as follow:

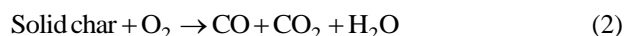
1. Zone 1: It represents drying and pyrolysis of fuel. Biomass particles enter the gasification reactor from the bottom and they will be heated up through their contact with the upcoming hot gas stream from zone 2. The pyrolysis of biomass would generate volatiles and char in zone 1 as shown in Fig. 1.

• Zone 1:



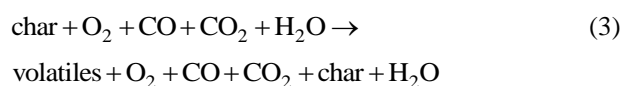
2. Zone 2: It represents the char gasification. The solid char particles formed from pyrolysis of biomass particles will descend by gravity inside the reactor and will meet with the incoming O_2 to form H_2O , CO , and CO_2 in the absence of volatile as shown in Fig. 1.

• Zone 2:



3. Zone 3: It represents volatiles reforming by steam. The hot gases from the second zone and char heterogeneous reactions will travel up inside the reactor to supply the heat required by pyrolysis and the volatile reforming reaction. The concentration of volatiles will increase mix with the upcoming hot gas stream like residual O_2 will take place in zone 3 as shown in Fig. 1.

• Zone 3:



4. Zone 4: It represents the catalyst zone. It is used to increase yield conversion product for the gases coming from zone 3 include char, tar, volatiles and other impurities such as HCN , NH_3 , CH_4 , inorganic, etc... The most active reaction in this zone is to produce hydrogen and the main reaction represents between Tar and Char with the steam of water and carbon dioxide, carbon monoxide with the steam of water and methane with the steam of water. These four parallel spontaneous reactions will be represented for the slow reaction of methane with the steam of water.

• Zone 4:

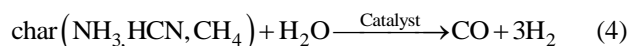
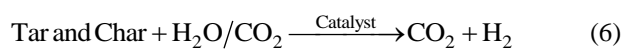
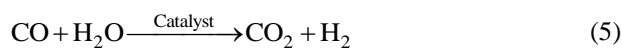


Table 2: List of model assumptions.

1	The gasification reactor includes two phases: gas and solid phases.
2	A chemical reaction occurs in four zones for gas and solid phases.
3	The air in excess of that required to satisfy a chemical condition to react with the solid phase of bio waste passes through the bottom of the reactor.
4	The gas phase is composed of volatiles gases, oxygen, carbon monoxide, carbon di oxide, and water vapor.
5	There are negligible radial temperature and concentration gradients in the reactor, due to the agitation produced by the up-flowing gas.
6	There is not negligible resistance to mass and heat transfers between gas and solid phases.
7	The dynamic of reactions are represented by the rates of adsorption, desorption, and reaction at the surface of catalysts (Fourth zone).
8	The tar and catalyst are separated from the product gas before leaving the reformer using the sand filter.



The model assumptions are listed in Table 2.

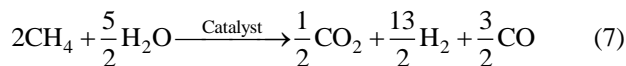
Mechanism of kinetic reaction

The kinetics of a chemical reaction is divided for four zones as follows:

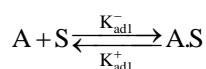
In zone-4, there are three mechanisms represented as follows:

1. Rate of adsorption.
2. Rate of surface reaction.
3. Rate of desorption.

We can organize the equations (4) to (6) as follow:

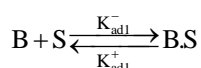


First, the rate of adsorption, there are two equations for adsorption rate. The first one is as follow:



$$r_{\text{ad1}} = \text{K}_{\text{ad1}}^+ \left[\text{P}_\text{A} \text{C}_\text{V} - \frac{\text{C}_{\text{A.S}}}{\text{K}_{\text{ad1}}^*} \right] \quad (8)$$

The second equation of the rate of adsorption is as follow:

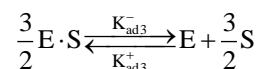
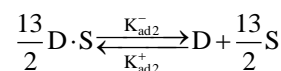
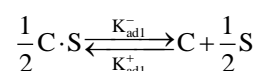


$$r_{\text{ad2}} = \text{K}_{\text{ad2}}^+ \left[\text{P}_\text{B} \text{C}_\text{V} - \frac{\text{C}_{\text{B.S}}}{\text{K}_{\text{ad2}}^*} \right] \quad (9)$$

Rate of surface reaction:

$$r_s = \text{K}_s^+ \left[\text{C}_{\text{A.S}} \cdot \text{C}_{\text{B.S}} - \frac{\text{C}_{\text{C.S}}^{1/2} \cdot \text{C}_{\text{D.S}}^{13/2} \cdot \text{C}_{\text{E.S}}^{3/2}}{\text{K}_s^*} \right] \quad (10)$$

Rate of desorption:



$$r_{\text{d1}} = \text{K}_{\text{d1}}^+ \left[\text{C}_{\text{C.S}}^{1/2} - \frac{\text{P}_\text{C} \cdot \text{C}_\text{V}^{1/2}}{\text{K}_{\text{d1}}^*} \right] \quad (11)$$

$$r_{\text{d2}} = \text{K}_{\text{d2}}^+ \left[\text{C}_{\text{D.S}}^{13/2} - \frac{\text{P}_\text{D} \cdot \text{C}_\text{V}^{13/2}}{\text{K}_{\text{d2}}^*} \right] \quad (12)$$

$$r_{\text{d3}} = \text{K}_{\text{d3}}^+ \left[\text{C}_{\text{E.S}}^{3/2} - \frac{\text{P}_\text{E} \cdot \text{C}_\text{V}^{3/2}}{\text{K}_{\text{d3}}^*} \right] \quad (13)$$

So, rate of surface reaction controls all rates of chemical mechanisms [5,8,17,43].

$$r_{\text{ad1}} = r_{\text{ad2}} = r_{\text{d1}} = r_{\text{d2}} = r_{\text{d3}} = 0$$

$$\text{C}_{\text{A.S}} = \text{P}_\text{A} \cdot \text{C}_\text{V} \cdot \text{K}_{\text{ad1}}^* \quad (14)$$

$$\text{C}_{\text{B.S}} = \text{P}_\text{B} \cdot \text{C}_\text{V} \cdot \text{K}_{\text{ad2}}^* \quad (15)$$

$$\text{C}_{\text{C.S}}^{1/2} = \frac{\text{P}_\text{C} \cdot \text{C}_\text{V}^{1/2}}{\text{K}_{\text{d1}}^*} \quad (16)$$

$$C_{DS}^{13/2} = \frac{P_D \cdot C_v^{13/2}}{K_{d2}^*} \quad (17)$$

$$C_{ES}^{3/2} = \frac{P_E \cdot C_v^{3/2}}{K_{d3}^*} \quad (18)$$

Substitute equation 14 to 18 in 10

$$r_s = K_s^+ \left[P_A \cdot C_v \cdot K_{ad1}^* \cdot P_B \cdot C_v \cdot K_{ad}^* - \right. \quad (20)$$

$$\left. \frac{P_C \cdot C_v^{1/2}}{K_{d1}^*} \frac{P_D \cdot C_v^{13/2}}{K_S^* K_{d2}^*} \frac{P_E \cdot C_v^{3/2}}{K_{d3}^*} \right]$$

$$C_T = C_{AS} + C_{BS} + C_{CS} + C_{DS} + C_{ES} + C_v \quad (21)$$

$$C_T = C_v \left[P_A K_{ad1}^* + P_B K_{ad2}^* + \frac{P_C^2}{(K_{d1}^*)^2} + \frac{P_D^{2/13}}{(K_{d2}^*)^{2/13}} + \frac{P_E^{2/3}}{(K_{d3}^*)^{2/3}} + 1 \right]$$

$$C_T = C_v K^* \quad (22)$$

$$r_s = K_s^+ \left(\frac{C_T}{K^*} \right)^2 \left[P_A \cdot K_{ad1}^* \cdot P_B \cdot K_{ad}^* - \right. \quad (23)$$

$$\left. \frac{P_C}{K_{a1}^*} \frac{P_D}{K_S^* K_{a2}^*} \frac{P_E}{K_{a3}^*} \left(\frac{C_T}{K^*} \right)^{15/2} \right]$$

The overall rate of reaction can be represented as a series chemical reaction start from zone-1 to zone 3 ($r_1 + r_2 + r_3$) and added zone 4 the slowest chemical reaction of surface reaction (r_s).

$$r_T = r_1 + r_2 + r_3 + r_s \quad (24)$$

$$r_T = -k_1 C_{Biomass} - k_2 C_{CO_2} C_{char} - k_3 C_{char} C_{O_2} C_{CO_2} C_{CO} +$$

$$K_s^+ \left(\frac{C_T}{K^*} \right)^2 \left[P_A \cdot K_{ad1}^* \cdot P_B \cdot K_{ad2}^* - \right.$$

$$\left. \frac{P_C}{K_{d1}^*} \frac{P_D}{K_{d2}^*} \frac{P_E \cdot C_v^{13/2}}{K_{d3}^*} \right]$$

This mechanism comprises of series and parallel elementary reactions as listed in Table 3.

$$C_{in-Biomass} - C_{Biomass} - \frac{V}{FAi} K_1 C_{Biomass} = \quad (25)$$

$$\frac{V}{FAi} \frac{dC_{Biomass}}{dt}$$

$$mc_p (T_i - T_1) - m \Delta H r_1 = mc_p \frac{dT_1}{dt} \quad (26)$$

Mass and heat balance for zone-2

$$C_{in-char} - \frac{V}{FAi} K_2 C_{char} C_{CO_2} = \frac{V}{FAi} \frac{dC_{char}}{dt} \quad (27)$$

$$mc_p (T_1 - T_2) - m \Delta H r_2 = mc_p \frac{dT_2}{dt} \quad (28)$$

$$C_{in-CO_2} - C_{CO_2} - \frac{V}{FAi} k_2 C_{CO_2} C_{char} = \frac{V}{FAi} \frac{dC_{CO_2}}{dt} \quad (29)$$

Mass and heat balance for zone-3

$$C_{in-char} - C_{char} - \frac{V}{FAi} K_3 C_{char} C_{O_2} C_{CO_2} C_{CO} C_{H_2O} = \quad (30)$$

$$\frac{V}{FAi} \frac{dC_{char}}{dt}$$

$$C_{in-CO} - C_{CO} - \frac{V}{FAi} K_3 C_{char} C_{O_2} C_{CO_2} C_{CO} C_{H_2O} = \quad (31)$$

$$\frac{V}{FAi} \frac{dC_{CO}}{dt}$$

$$C_{in-CO_2} - C_{CO_2} - \frac{V}{FAi} K_3 C_{char} C_{O_2} C_{CO_2} C_{CO} C_{H_2O} = \quad (32)$$

$$\frac{V}{FAi} \frac{dC_{CO_2}}{dt}$$

$$C_{in-H_2O} - C_{H_2O} - \frac{V}{FAi} K_3 C_{char} C_{O_2} C_{CO_2} C_{CO} C_{H_2O} = \quad (33)$$

$$\frac{V}{FAi} \frac{dC_{H_2O}}{dt}$$

$$C_{in-O_2} - C_{O_2} - \frac{V}{FAi} K_3 C_{char} C_{O_2} C_{CO_2} C_{CO} C_{H_2O} = \quad (34)$$

$$\frac{V}{FAi} \frac{dC_{O_2}}{dt}$$

Mass heat balance for zone-4

$$C_{in-CH_4} - C_{CH_4} \frac{V}{FAi} r_s = \frac{V}{FAi} \frac{dC_{CH_4}}{dt} \quad (35)$$

$$C_{in-H_2O} - C_{H_2O} \frac{V}{FAi} r_s = \frac{V}{FAi} \frac{dC_{H_2O}}{dt} \quad (36)$$

Table 3: Numerical values of the kinetic rate constants for chemical reactions in three zones, adsorption, surface and desorption reactions inside the catalyst layers.

Rate constant (s ⁻¹)	Value	Rate constant (s ⁻¹)	Value
k_1	1.05	K_s^+	0.0015
k_2	1.02	K_{d1}^+	0.0012
k_3	0.89	K_{d1}^*	0.002
K_{ad1}^+	0.003	K_{d2}^+	0.0011
K_{ad1}^*	0.005	K_{d2}^*	0.002
K_{ad2}^+	0.0025	K_{d3}^+	0.001
K_{ad2}^*	0.004	K_{d3}^*	0.0023
K_s^+	0.001		

Table 4: List of operating parameters [11,14].

Steam ratio	2
Gasification temperature	800 °C
Operating pressure	5 bar
Steam temperature	460 °C

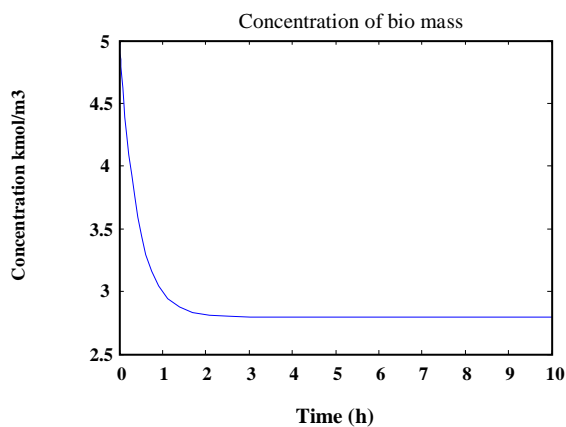


Fig. 2: Shows the Concentration of Bio Mass Changes with Time.

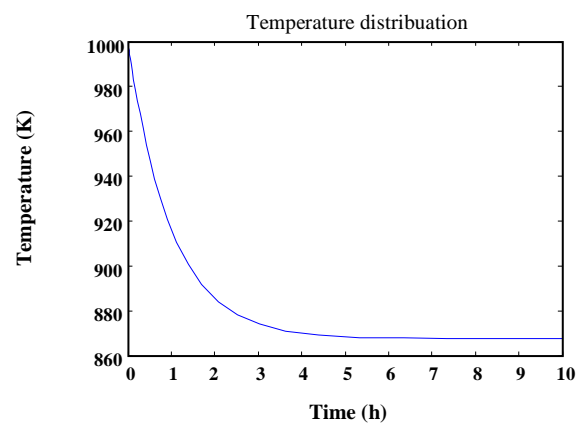


Fig. 3: Shows the Temperature in zone 1 Changes with Time.

RESULTS AND DISCUSSIONS

The operating parameters of the mathematical model can be represented in Table 4.

Results and discussions for zone-1

Fig. 2 provides the relation between the concentrations of bio mass with the time in the first zone. Due to the chemical reaction, the concentration of biomass is decreased until reached 2.8 kmol/m³ at 3 hours to produce volatile gases and solid char and be steady state as shown in Fig. 2. Fig. 3 explains the relation between the

temperature with the time in the first zone and because the endothermic reaction the temperature is going down from 1000 K to 870 K after 5 hours and be steady state.

Results and discussions for zone-2

Fig. 4 provides the relation between the concentrations of char with the time in the second zone. Due to the chemical reaction the concentration of char is decreased until reached 2kmol/m³ at 1 hour to produce monoxide, dioxide, water, and char and be steady state as shown in Fig. 4.

Fig. 5 provides the relation between the concentration of the oxygen in the second zone with the time. Due to the chemical reaction the concentration of oxygen is decreased until reached 2 kmol/m^3 at 1 hour and be a steady state as shown in Fig. 5.

Fig. 6 shows the relation change of the temperature with the time in the second zone. The temperature of the reaction is increased to 920 K due to the presence of a huge amount of oxygen. After one hour the oxygen will consume and heat transfer convection to the first zone the temperature will decrease 875 K to be steady state.

Results and discussions for zone-3

Fig. 7 provides the relationship between the temperature distribution and the time of the third zone. At the beginning of the reaction, the temperature is reached to a maximum value 907 K due to presence of oxygen that analysis from volatile gases with heat transfer convection from the second zone at 2 hours. Then, due to consumption, the reactant of oxygen with the char and heat transfer from the third zone to the fourth zone the temperature will decrease gradually with the time to be a steady state.

Relationship between the concentrations of CO and CO₂ with the time of the third zone. At the beginning of the reaction, the concentrations of CO and CO₂ were at the highest point (3 kmol/m^3), then it sharply decreased until it reached to the lower point (1.7 kmol/m^3) because of rate consumption for the reactants. Then, the concentrations of CO and CO₂ slightly increased until (1.8 kmol/m^3) due to produce extra amounts of volatile gases from analysis of char compound and remained constant until the end of reaction as shown in Figs. 8 and 9 respectively.

Relationship between the concentrations of char and oxygen with the time of the third zone. At the beginning of the reaction, the concentrations of char and oxygen were at the highest 2 kmol/m^3 , then it sharply decreased until it reached to the lower 0.8 kmol/m^3 because of rate consumption for the reactants and remained constant until the end of reaction as shown in Figs. 10 and 11 respectively.

Relationship between the concentration of water with the time of the third zone. At the beginning of the reaction, the concentration of water was at the highest value of 2 kmol/m^3 , then it sharply decreased until it reached

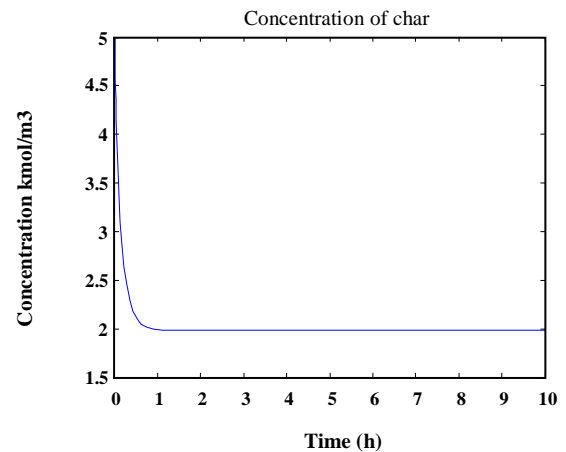


Fig. 4: Shows the Concentration of Char Changes with Time.

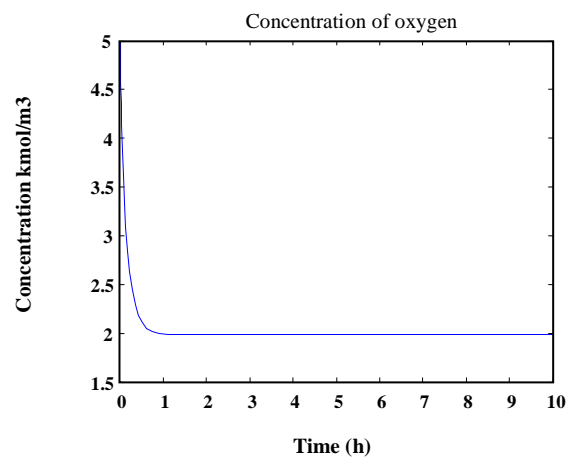


Fig. 5: Shows the Concentration of Oxygen Changes with Time.

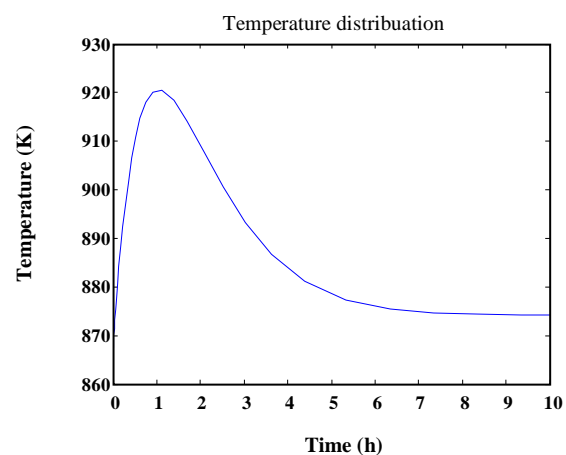


Fig. 6: Shows the Change of Temperature in Zone 2 with the Time.

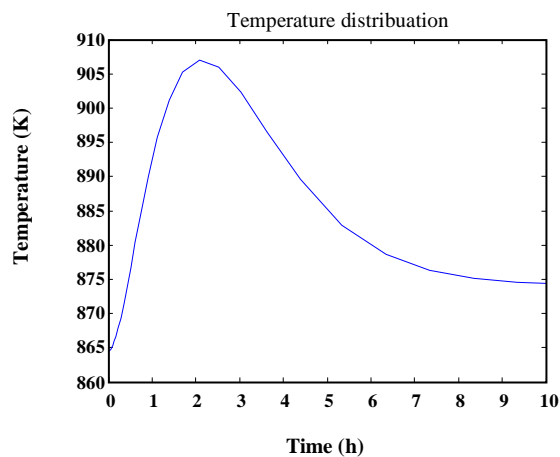


Fig. 7: Shows the Change of Temperature in Zone 3 with the time.

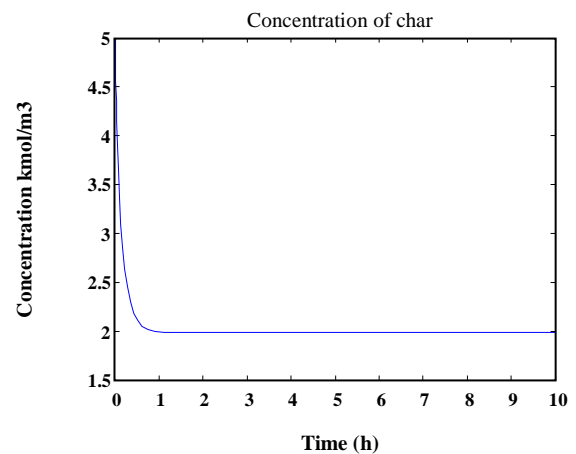


Fig. 9: Shows the temperature in zone 3 changes with time.

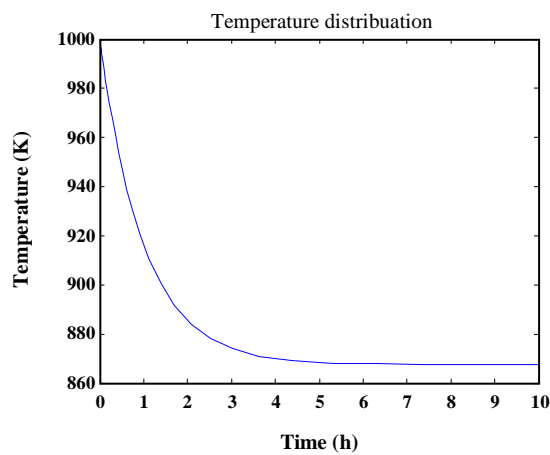


Fig. 8: Shows the temperature in zone 3 changes with time.

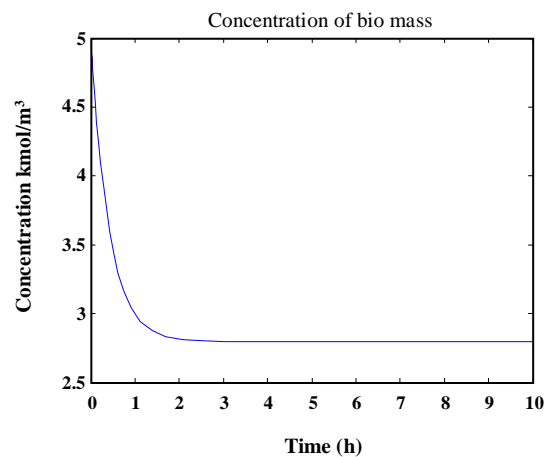


Fig. 10: Shows the concentration of bio mass changes with time.

to the lower value of 0.7 kmol/m^3 because of rate consumption for the reactants. Then, the concentrations of water slightly increased until (0.8 kmol/m^3) due to produce extra amounts of volatile gases from analysis of char compound and remained constant until the end of reaction as shown in Fig. 12.

Results and calculations for zone 4

Fig. 13 provides the relation between the temperature distributions with the time in the fourth zone. Due to the catalyst surface reaction the temperature is increased until it reached 899 K at 3 h and be steady state as shown in Fig. 13.

Fig. 14 shows the relation between the concentrations of methane and water with the time in the fourth zone.

The concentration of methane is increased until it reached 2.2 kmol/m^3 and the concentration of water is increased to 3 kmol/m^3 after 4 h and be steady state as shown in Figs. 14 and 15 respectively.

CONCLUSIONS

Mathematical model of gasification reaction can be used to evaluate and analyze most active parameters which affect the quality and quantity of production. This mathematical model is considered to evaluate and optimize the best kinetic conditions as it included all mechanisms in terms of the rates of adsorption, desorption and chemical surface reaction, which are specified in each zone. From the new mathematical model,

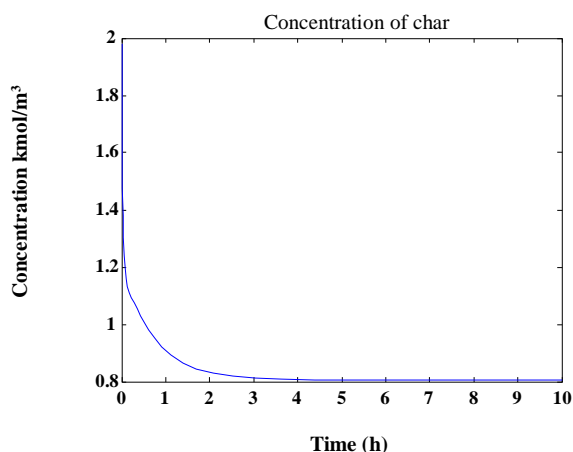


Fig. 11: Shows the Concentration of Char Changes with the Time.

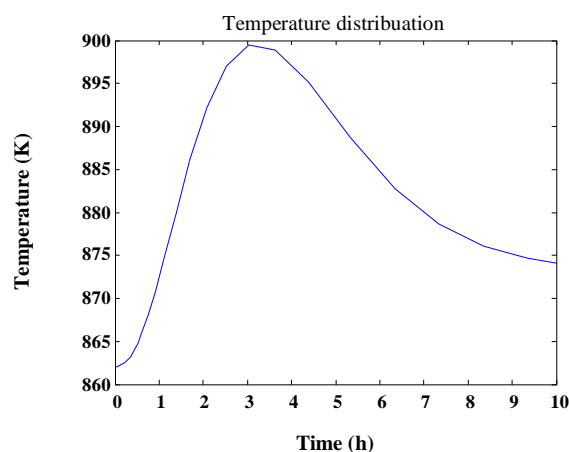


Fig. 13: Shows the Temperature of Zone 4 Changes with the Time.

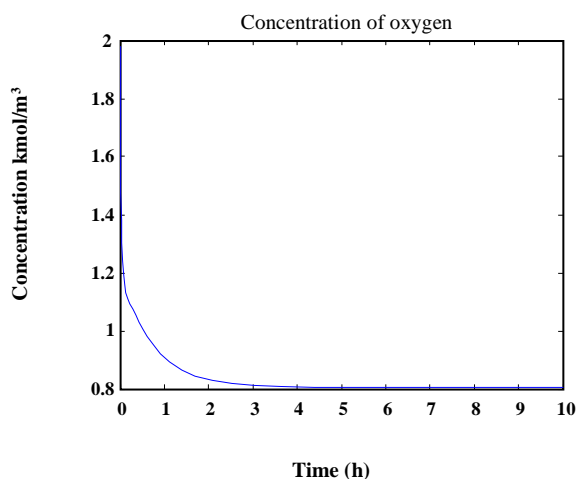


Fig. 12: Shows the Concentration of Oxygen Changes with the Time.

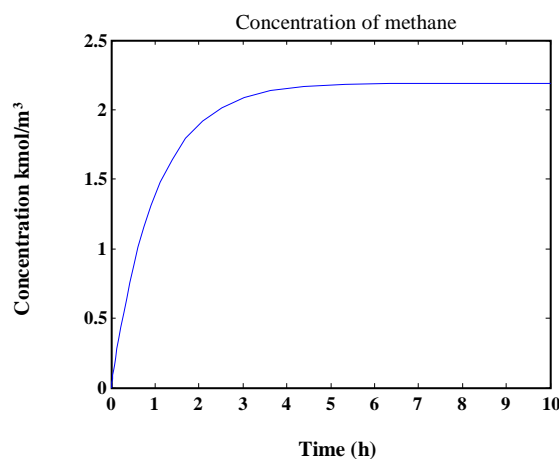


Fig. 14: Shows the Concentration of Methane Changes with the Time.

it is noticed that the temperature goes down from 1000 °C to approximately 874 °C due to the presence of a catalyst which helps in increasing the yield of production of methane and hydrogen to 2.2 kmol/m³ and 3 kmol/m³ respectively. Likewise, boiling down the temperature of the reaction. Hence, one of the most active parameters is the catalyst compound which has been employed in this procedure. The example developed here will also be used in model-based prediction, control to control the reactor, which is part of our future study.

Nomenclature

A Methane gas (CH₄)

B Water (H₂O)
 C Carbon Dioxide (CO₂)
 D Hydrogen gas (H₂)
 E Carbon Monoxide (CO)
 C_A Concentration of methane gas, mol/L
 C_B Concentration of water, mol/L
 C_C Concentration of carbon dioxide, mol/L
 C_D Concentration of hydrogen gas, mol/L
 C_E Concentration of carbon monoxide, mol/L
 C_V Vacant concentration of catalyst, mol/L
 P_A Partial pressure of methane gas, Pa
 P_B Partial pressure of water, Pa
 P_C Partial pressure of carbon dioxide, Pa

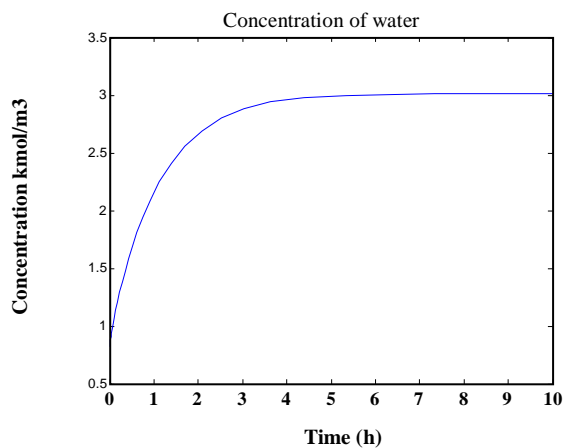


Fig. 15: Shows the Concentration of water Changes with the Time.

P_D	Partial pressure of hydrogen gas, Pa
P_E	Partial pressure of carbon monoxide, Pa
K_{ad}	Equilibrium constant of adsorption, Depends on the reaction order
K_d	Equilibrium constant of desorption Depends on the reaction order
K_s	Equilibrium constant of surface, Depends on the reaction order
r_{ad}	Rate of adsorption, M/sec
r_s	Rate of surface reaction, M/sec
r_d	Rate of desorption, M/sec
S	Catalyst
m	Mass, kg
C_p	Heat capacity, J/kg.K
T	Temperature, K
F	Volumetric flowrate, m ³ /sec
V	Volume, m ³
H	Heat enthalpy, kJ/kg

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