

## Mathematical Modeling of Biomass (Wood) Gasification

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### ABSTRACT:

The paper aims to work theoretical study by using three reactions for the wood burning analysis or (Wood Gasification). First, we suggested a general equation with molar balance modified for the burning. Results obtained, we solved multivariable nonlinear equations non-linear equations by means of Newton-Raphson method. Using the computer program Matlab, we calculated the degree of equilibriums heat for the reactions absolute (946 °k, 763 °k, and 67 °k). Also, we calculate thermodynamics functions for the reactions ( $\Delta G$ ,  $\Delta H$ , K) with two  $\Delta H^+$  (non-impulsive) and one  $\Delta H^-$  (impulsive).

**KEYWORDS:** Biomass, Gasification, wood, Combustion, Matlab program.

### الخلاصة:

يهدف البحث الى اجراء دراسة نظرية باستخدام تفاعلات ثلاثة لتحليل احتراق الوقود الحيوي (الخشب) او (تغويز الخشب)، اولاً تم اقتراح معادلة عامة للاحتراق و تم اجراء موازنة عادية ( موازنة مولية) للاحتراق. النتائج المستحصلة هو الحصول على اربعة معادلات رياضية تضم سبعة مجاهيل، بعدها تم احتساب عدد المولات باستخدام برنامج الماتلاب، حيث تم احتساب درجة حرارة الاتزان لكل تفاعل من التفاعلات الثلاثة باستخدام طريقة نيوتن - رافسون و كانت درجة حرارة الاتزان للتفاعلات الثلاثة التي حصلنا عليها (946 مطلقاً ، 763 مطلقاً و 67 مطلقاً). ايضاً تم احتساب الدوال الترموديناميكية ( $\Delta G$  ،  $\Delta H$  ، k) للتفاعلات الثلاثة حيث بينت النتائج ان التفاعل الاول و الثاني غير تلقائي و التفاعل الثالث تلقائي حيث كانت  $\Delta H$  سالبة.

الكلمات المفتاحية : الكتلة الحيوية، تغويز، الخشب، الاحتراق، برنامج ماتلاب.

### INTRODUCTION:

Gasification is a process used to generate energy that is cleaner and more efficient than traditional combustion processes. Gasification enables conversion of this material into combustible gas, mechanical and electrical power and synthetic fuels and chemicals (Babu and Sheth, 2006). Gasification is a process of conversion of solid carbonaceous fuel into combustible gas by partial combustion. Downdraft gasification is comparatively cheap method of gasification that can produce a product gas with very low tar content (Giltrap *et.al.*, 2003).

In this process, carbon-based materials are broken down into a high-energy gas by applying extreme temperatures in an environment containing limited oxygen supply. High temperatures and limited oxygen allows gasification to significantly reduce the harmful emissions. In addition, gasification has other advantages, including efficient use of waste for energy, effective method of reduction of waste volume, detoxification of hazardous materials, and the production of hydrogen (Smith *et.al.*, 2004). Gasification's main output is a clean synthetic gas called "synthesis gas" or "syngas" which is primarily a mixture of carbon monoxide (CO) and hydrogen (H<sub>2</sub>). Syngas has many commercial uses, including electricity generation, production of biofuels and chemicals, and powering hydrogen fuel cells. In general, a series of endothermic and exothermic reactions are followed in the gasification process to produce syngas (Jordon, J. Van Wylen, 2003).

Even with its many advantages, gasification has always been too expensive to gain a more wide-scale adoption. Continuous attempts by researchers are being made to develop efficient, flexible, and economic gasifiers for a variety of biomass feedstock in order to minimize the syngas pollution level and maximize the energy output (Nilson *et.al.*, 2001).

In the present study, first, been proposed general equation with molar balance modified for the wood burning. Results obtained, we solved multivariable nonlinear equations non-linear equations by means of Newton-Raphson method. Using the computer program Mat lab, we calculated the degree of equilibriums heat for the reactions Also; we calculate thermodynamics functions for the reactions ( $\Delta G$ ,  $\Delta H$ , K).

**Theoretical study:**

**1. Thermodynamic Equilibrium Model:**

Thermodynamic or chemical equilibrium calculation is independent of gasifier design and so is convenient for studying the influence of fuel and process parameters. Though chemical or thermodynamic equilibrium may not be reached within the gasifier, this model provides the designer with a reasonable prediction of the maximum achievable yield of a desired product. However, it cannot predict the influence of hydrodynamic or geometric parameters, like fluidizing velocity, or design variables, like gasifier height. Chemical stoichiometric equilibrium is based on the equilibrium constant as described in the following sub-sections:

**1.1 Assumptions**

1. It was assumed that all proposed reactions are perfect reactions.
2. It was taken into consideration the effect of humidity inside the wood.
3. It has been neglecting impurities within the wood.
4. It was considered that all the amount of wood to burn completely without waste.

**1.2 Biomass composition**

Starting from the ultimate analysis of the biomass and the mass fractions of the carbon, hydrogen and oxygen, the substitution fuel formula  $C_nH_aO_b$  can be calculated, assuming  $n = 1$ , with the following expressions:

$$a = \frac{H}{C} \quad \text{And} \quad b = \frac{O}{C}$$

Where  $a$  and  $b$  are the mole ratios of (H/C) and (O/C) determined from the ultimate analysis of the biomass.

From the substitution fuel formula, the general formula of solid biomass wood is  $CH_{1.44}O_{0.66} = CH_{0.2} (0.6H_2O)$ , and therefore the specific molecular weight of the biomass about 24 ( $M_{Biom}=24$ ). For 1 mole of biomass (wood) is being gasified in  $w$  moles of steam and  $m$  moles of air, the global gasification reaction is written as follows:



Where  $w$  is the amount of water per mol of biomass,  $m$  is the amount of oxygen per mol of biomass,  $n_1, n_2, n_3, n_4, n_5, n_6$  and  $n_7$  are the stoichiometric coefficients of the products (all stoichiometric coefficients in moles). All inputs on the left-hand side of Eq. (1) are defined at 25°C.

The molar quantity of water per mole of biomass ( $w$ ) can be determined as: Let, MC= moisture content per mole of biomass (wood)

$$MC = \frac{\text{Mass of water}}{\text{Mass of wet biomass}} \times 100\% = \frac{M_w w}{M_{Biom} + M_w w} \times 100\%$$

Therefore,  $w$  given by:

$$w = \frac{24MC}{18(1 - MC)} \quad (2)$$

### 1.3 Mass balance

From the global gasification reaction, there are seven unknowns  $n_1, n_2, n_3, n_4, n_5, n_7$  and  $m$ , representing the six unknown stoichiometric coefficients of the products and the oxygen content for the reaction, respectively. Therefore, seven equations are required, which are formulated based on the atom balance of the following:

$$\text{Carbon balance; C:} \quad 1 = n_2 + n_3 + n_5 + n_7 \quad (3a)$$

$$\text{Hydrogen balance; H:} \quad 1.44 + 2w = 2n_1 + 2n_4 + 4n_5 \quad (3b)$$

$$\text{Oxygen balance; O:} \quad 0.66 + w + 2m = n_2 + 2n_3 + n_4 \quad (3c)$$

The enthalpy balance equation includes the amount of electricity used in the plasma furnace:

$$\begin{aligned} \sum H_{f,Biom} + w(H_{f,H_2O(l)} + H_{H_2O(vap)}) + E_{Electricity} &= n_2 H_{f,CO}^o + n_3 H_{f,CO_2}^o + n_4 H_{f,H_2O(vap)}^o + n_5 H_{f,CH_4}^o \\ &+ n_7 H_{f,C}^o + \Delta T(n_1 C_{p,H_2} + n_2 C_{p,CO} + n_3 C_{p,CO_2} \\ &+ n_4 C_{p,H_2O} + n_5 C_{p,CH_4} + 3.76m C_{p,N_2} + n_7 C_{p,C}) \end{aligned} \quad (4)$$

Where the heat of formation are zero for all chemical elements at reference state (298 K, 1 atm) as:

$$H_{f,O_2}^o = H_{f,N_2}^o = H_{f,H_2}^o = 0$$

where  $H_{f,Biom}^o$  is the heat of formation of the biomass material,  $H_{f,H_2O(l)}^o$  is the heat of formation of liquid water,  $H_{H_2O(vap)}$  is the heat of formation of water vapor,  $H_{f,CO}^o, H_{f,CO_2}^o$  and  $H_{f,CH_4}^o$  are the heats of formation of the gaseous products,  $H_{f,C}^o$  is the heat of formation of solid carbon,

$C_{p,H_2}, C_{p,CO}, C_{p,CO_2}, C_{p,H_2O}, C_{p,CH_4}$  and  $C_{p,N_2}$  are the specific heats of the gaseous products and

$C_{p,C}$  is the specific heat of the solid carbon (soot) which is function of temperature ( $=f(T)$ ),  $T_2$  is the gasification temperature ( $\sim 1173$  K) and  $T_1$  is the ambient temperature (298 K), as

$\Delta T = T_2 - T_1$ . It is also mentioned that the  $E_{Electricity}$  value accounts for the energy required for the gasification reaction.

Eqn. (4) can be simplified to:

$$\begin{aligned} dH_{Biom} + wdH_{H_2O(l)} + E_{Electricity} &= n_1 dH_H + n_2 dH_{CO} + n_3 dH_{CO_2} + n_4 dH_{H_2O(vap)} \\ &+ n_5 dH_{CH_4} + 3.76mdH_{N_2} + n_7 dH_C \end{aligned} \quad (5)$$

Where:

$dH$  for any gas = heat of formation + enthalpy change

$$dH_{\text{gas}} = H_{f,\text{gas}}^{\circ} + \Delta H; \text{ while } dH_{\text{H}_2\text{O}(l)} = H_{f,\text{H}_2\text{O}(l)}^{\circ} + H_{\text{H}_2\text{O}(vap)}; \text{ and } dH_{\text{Biom}} = H_{f,\text{Biom}}^{\circ}$$

At constant pressure, the specific heat can be written as:

$$\Delta H = \int_{T_1}^{T_2} C_{p,mh} dT = C_{p,mh} \Delta T \quad (6)$$

Where  $C_{p,mh}$  is the average specific heat over the temperature change which is given by:

$$\frac{C_{p,mh}}{R} = A + BT_{am} + \frac{C}{3} (4T_{am}^2 - T_1 T_2) + \frac{D}{T_1 T_2} \quad (7)$$

Where  $T_{am}$  is the arithmetic mean temperature and given by:

$$T_{am} = \frac{T_1 + T_2}{2}$$

Also, A, B, C and D are the constants for the properties of the gases concerned (the values of the constants are given in Table 1) and R is the universal gas constant (8.314 J/mol.K).

The enthalpy of formation for solid biomass wood in reactant can be determined (De Souza-Santos, 2004) as:

$$H_{f,\text{Biom}}^{\circ} = \text{LHV}_{\text{Biom}} + \sum_{k=\text{prod}} n_k H_{f,k}^{\circ} \quad (8)$$

### 1.5 Equilibrium reactions

The three main independent equilibrium reactions are selected for the thermodynamics equilibrium calculations are shown below:

1.  $\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$  (Primary water gas-shift reaction— endothermic)
2.  $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$  (Methane decomposition—endothermic)
3.  $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$  (Water gas-shift reaction—exothermic)

For the model in this study, the thermodynamic equilibrium was assumed for all chemical for the model in this study, the thermodynamic equilibrium was assumed for all chemical reactions in the gasification zone. All gases were assumed to be ideal and all reactions form at pressure 1 atm. Therefore, the equilibrium constants, which are functions of temperature, are as follows:

$$K_i = \prod_i (x_i)^{v_i} \left( \frac{p}{P^{\circ}} \right)^{\sum_i v_i} \quad (9)$$

Where  $x_i$  is the mole fraction of the species  $i$  in the ideal gas mixture  $x_i = \frac{n_i}{n_{\text{total}}}$ ,  $n_{\text{total}} = \sum_1^7 n_i$ ,

$v$  is stoichiometric number (positive value for products and negative value for reactants),  $P^{\circ}$  is

standard pressure, 1 atm, and  $n_{total}$  is total mole of producer gas.

-For the primary water gas shift reaction

$$K_1 = \frac{[CO_2][H_2]}{[H_2O]} \quad \text{or} \quad K_1 = \frac{x_1 \cdot x_2}{x_4} \quad (10 \text{ a})$$

-For the methane decomposition

$$K_2 = \frac{[CO][H_2]^2}{[CH_4][H_2O]} \quad \text{or} \quad K_2 = \frac{x_1 \cdot x_2^2}{x_4 \cdot x_5} \quad (10 \text{ b})$$

-For the water gas shift reaction

$$K_3 = \frac{[CO_2][H_2]}{[CO][H_2O]} \quad \text{or} \quad K_3 = \frac{x_1 \cdot x_3}{x_2 \cdot x_4} \quad (10 \text{ c})$$

The equilibrium constant is a function of temperature only as follow:

$$\ln K = -\frac{\Delta G^\circ}{RT} \quad (11)$$

$$\frac{d \ln K}{dT} = \frac{\Delta H^\circ}{RT^2} \quad (12)$$

$$\ln K = \int \frac{\Delta H^\circ}{RT^2} dT + I \quad (13)$$

Where  $I$  is the constant of integration,  $\Delta H^\circ$  is given in the following equation:

$$\frac{\Delta H^\circ}{R} = \frac{I}{R} + (\Delta A)T + \frac{\Delta B}{2}T^2 + \frac{\Delta C}{3}T^3 - \frac{\Delta D}{T} \quad (14)$$

$$\ln K = \frac{-I}{RT} + (\Delta A)\ln T + \frac{\Delta B}{2}T + \frac{\Delta C}{6}T^2 + \frac{\Delta D}{2T^2} + I \quad (15)$$

$$\Delta G^\circ = -I - RT \left[ (\Delta A)\ln T + \frac{\Delta B}{2}T + \frac{\Delta C}{6}T^2 + \frac{\Delta D}{2T^2} + I \right] \quad (16)$$

Where  $\Delta A, \Delta B, \Delta C$  and  $\Delta D$  are calculated for each equilibrium reaction as:

$$\Delta A = \sum_{j=prod} A_i - \sum_{j=react} A_j \quad (17a)$$

$$\Delta B = \sum_{j=prod} B_i - \sum_{j=react} B_j \quad (17b)$$

$$\Delta C = \sum_{j=prod} C_i - \sum_{j=react} C_j \quad (17c)$$

$$\Delta D = \sum_{j=prod} D_i - \sum_{j=react} D_j \quad (17d)$$

$$\ln K_1 = f(T) \quad (18a)$$

$$\ln K_2 = f(T) \quad (18b)$$

$$\ln K_3 = f(T) \quad (18c)$$

**Table.1** constants values for chemical species

<b>Chemical Species</b>	<b>Formula</b>	<b>T<sub>max</sub></b>	<b>A</b>	<b>10<sup>3</sup>B</b>	<b>10<sup>6</sup>C</b>	<b>10<sup>-5</sup>D</b>
<b>Methane</b>	<b>CH<sub>4</sub></b>	<b>1500</b>	<b>1.702</b>	<b>9.081</b>	<b>2.164-</b>	<b>0.000</b>
<b>Hydrogen</b>	<b>H<sub>2</sub></b>	<b>3000</b>	<b>3.249</b>	<b>0.422</b>	<b>0.000</b>	<b>0.083</b>
<b>Carbon monoxide</b>	<b>CO</b>	<b>2500</b>	<b>3.376</b>	<b>0.557</b>	<b>0.000</b>	<b>0.031-</b>
<b>Carbon monoxide</b>	<b>CO<sub>2</sub></b>	<b>2000</b>	<b>5.457</b>	<b>1.047</b>	<b>0.000</b>	<b>-1.157</b>
<b>Nitrogen</b>	<b>N<sub>2</sub></b>	<b>2000</b>	<b>3.280</b>	<b>0.593</b>	<b>0.000</b>	<b>0.040</b>
<b>Water</b>	<b>H<sub>2</sub>O</b>	<b>2000</b>	<b>3.470</b>	<b>1.450</b>	<b>0.000</b>	<b>0.121</b>
<b>Carbon</b>	<b>C</b>	<b>2000</b>	<b>1.771</b>	<b>0.771</b>	<b>0.000</b>	<b>0.867-</b>
<b>Oxygen</b>	<b>O<sub>2</sub></b>	<b>2000</b>	<b>3.639</b>	<b>0.506</b>	<b>0.000</b>	<b>0.227-</b>

### **Results and Discussions:**

Building-up an equation for each reaction, we calculate the constant factor of heat balance and ( $\Delta G$ ,  $\Delta H$ ,  $K$ ) for each reaction respectively, in order to find out the amount of energy that produces from gasification under heat degree (1500 °k - 273 °k). By using Matlab program (Newton-Raphson method), we find out ( $n_1, n_2, n_3, n_4, n_5, n_6, n_7, n_8$  and  $w$ ) for the main reaction and energy comes out of each reaction as follow:

1. The first reaction is non- impulsive reaction with ( $\Delta H+$ ) reached heat equilibrium degree (946 °k) and this is logical result because all the carbon turns into CO and CO<sub>2</sub> in temperature high to (600 °k) then it changed to ( $\Delta G-$ ) which means the reactions becomes impulsive at equilibrium degree as shown in figure (1) and we observe decreasing the free energy with increasing reaction temperature as shown in figure (2). Also equilibrium constant is increasing after the temperature (1200 °k).
2. The Second reaction is same as first reaction that is non- impulsive reaction with ( $\Delta H+$ ) reached heat equilibrium degree (763 °k), then it changed to ( $\Delta G-$ ) which means the reactions becomes impulsive after equilibrium degree shown in figure (4) and we observe decreasing the free energy with increasing reaction temperature as shown in figure (5). Also equilibrium constant is increasing after the temperature (1250 K) as shown in figure (6).
3. The third reaction is impulsive reaction with ( $\Delta H-$ ) and staying ( $\Delta H-$ ) and this clear for each imposed temperature degree shown in figure (7) where, we note the large gradient for enthalpy through temperature (250 K), and we observe decreasing the free energy with increasing reaction temperature and approximately similar behavior for free energy in first and second reaction and this shown in figure (8). The equilibrium constant is increasing after the temperature (1200 K) and also approximately similar in behavior for equilibrium constant in first and second reaction and this as shown in figure (9).

### **Conclusions**

Based on the results obtained in the present study, the following conclusions are drawn:

1. For the moisture clear effect on the wood combustion process, the more the amount of moisture high whenever moles numbers decreasing of burning wood because of the decreasing in carbonate compounds.
2. The molar fraction of water vapor in the gaseous phase is the highest in the pyrolysis zone and decreases as it travels through the oxidation and reduction zones of the gasifier.
3. In case of non- impulsive reactions when the reaction reaches to equilibrium state, the free energy ( $\Delta G$ ) becomes negative value.
4. The relation between free energy ( $\Delta G$ ) and temperature is linear and this clear in figures (2, 5 and 8) and this identify with theoretical relation for ( $\Delta G$ ) and temperature.

### **NOMENCLATURE**

$m$  is the amount of oxygen per mol of biomass

$n_1, n_2, n_3, n_4, n_5, n_6$  and  $n_7$  are the stoichiometric coefficients of the gaseous products

MC is moisture content per mole of biomass

$H_f^\circ$  is the heat of formation

$C_p$  the specific heats

$T_1$  is the ambient temperature

$T_2$  is the ambient temperature

$E$  is the electricity value

$\Delta H$  is the enthalpy change

LHV<sub>Biom</sub> is the lower heating value of the solid biomass in kJ/kmol.

$C_{p,mh}$  is the average specific heat over the temperature change

$T_{am}$  is the arithmetic mean temperature

A, B, C and D are the constants for the properties of the gases concerned

R is the universal gas constant (8.314 J/mol.K)

$H_{f,k}$  is the enthalpy of formation of product  $k$  under complete combustion of the solid biomass

$K_i$  is the equilibrium constant.

$x_i$  is the mole fraction

$\nu$  is stoichiometric number

$n_{total}$  is total mole of producer gas

I is the constant of integration

$\Delta G$  is the Gibbs Energy

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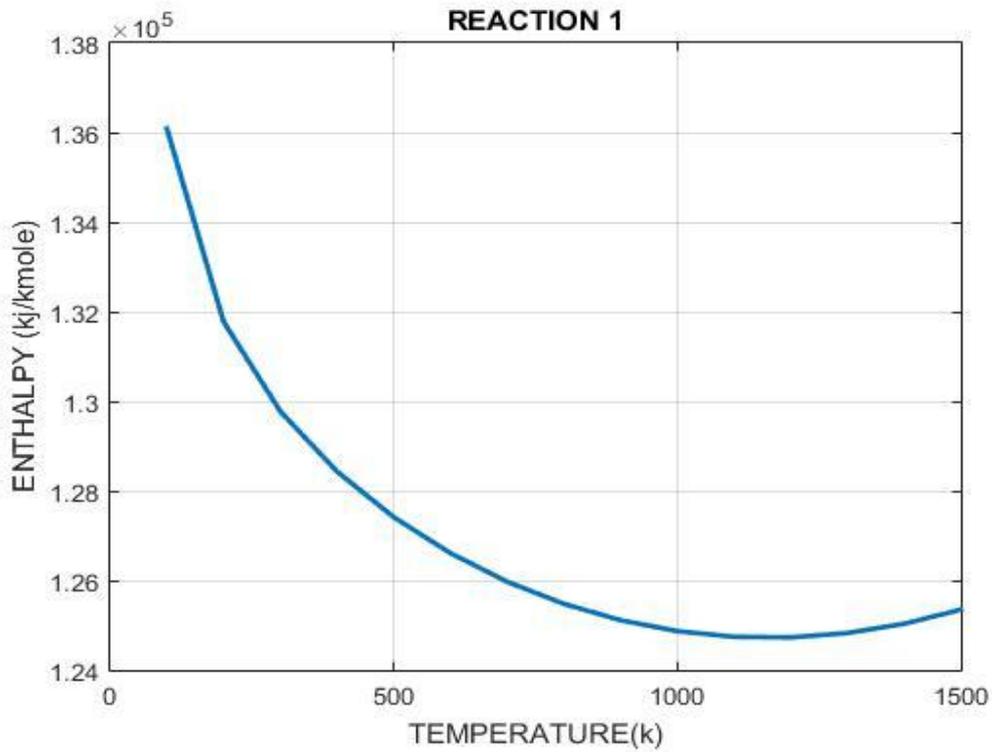
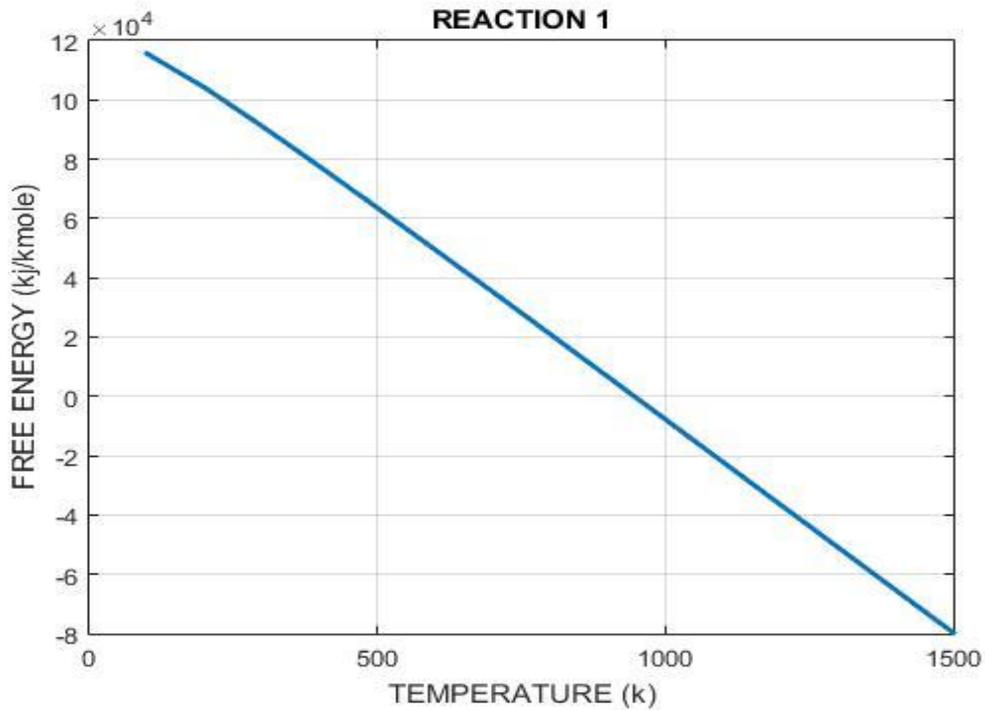
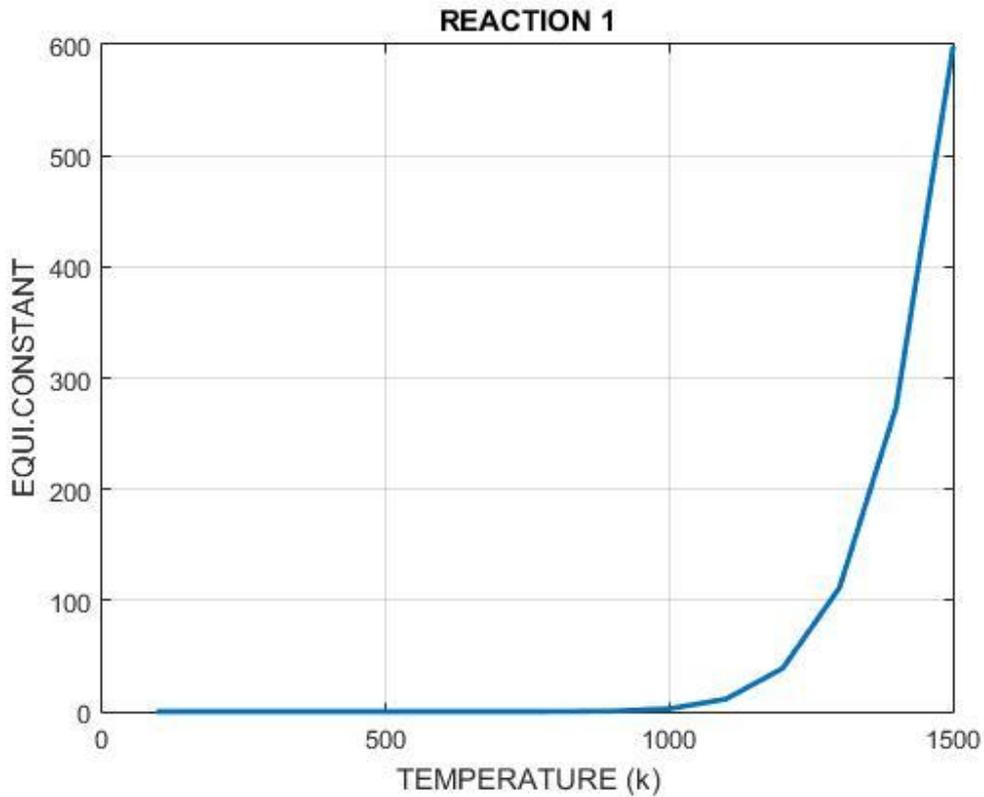


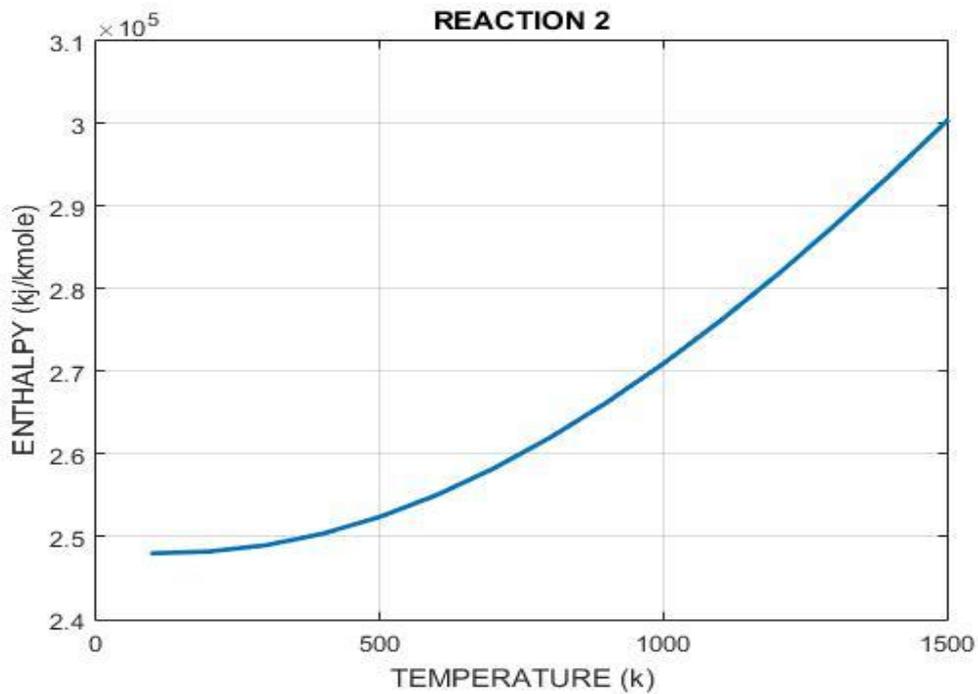
Fig.1 The relation between enthalpy versus temperature for reaction 1



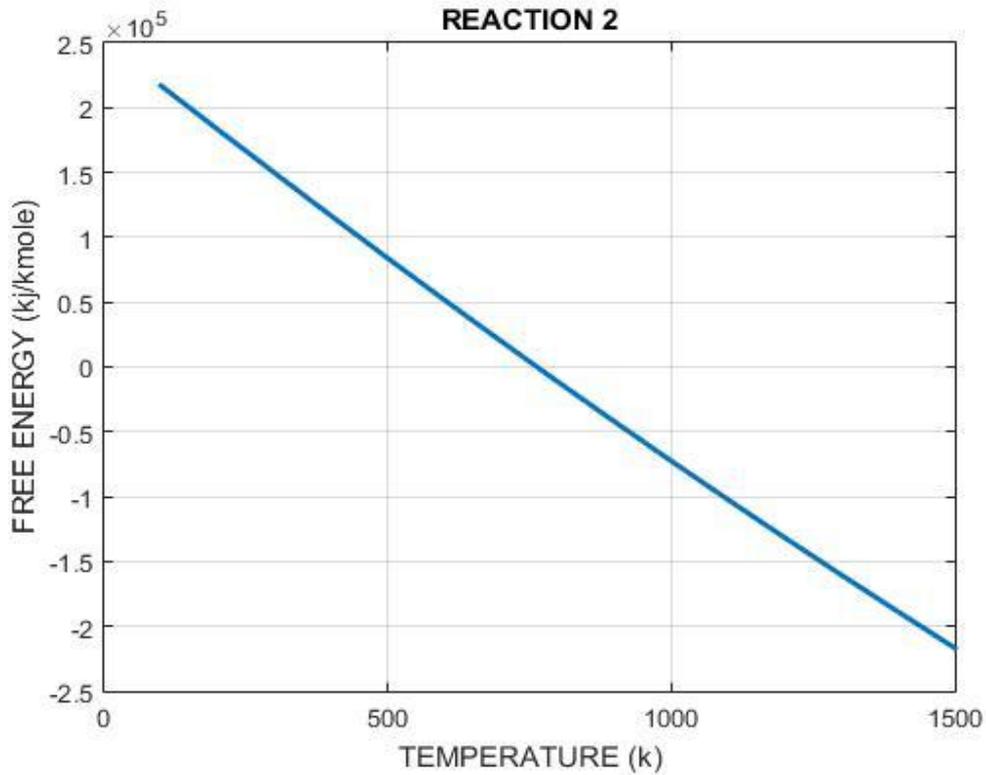
for reaction 1 temperature Fig.2 The relation between free energy versus



**Fig.3 The relation between equilibrium constant versus temperature for reaction 1**



**Fig.4 The relation between enthalpy versus temperature for reaction 2**



temperature for reaction 2 Fig.5 The relation between free energy versus

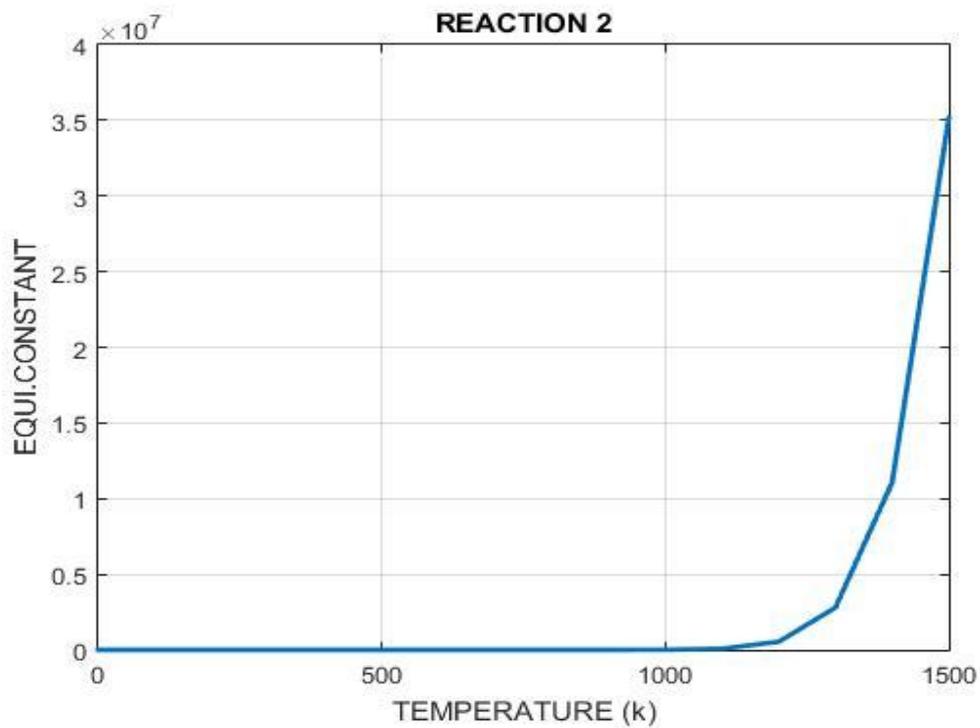


Fig.6 The relation between equilibrium constant versus temperature for reaction 2

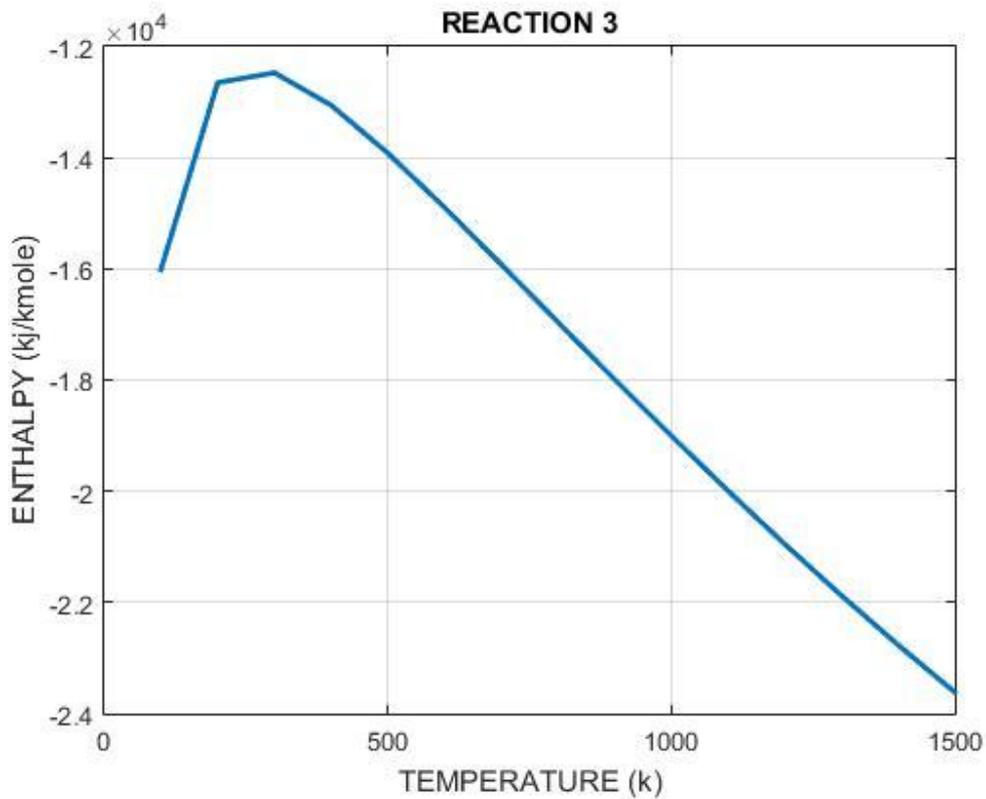
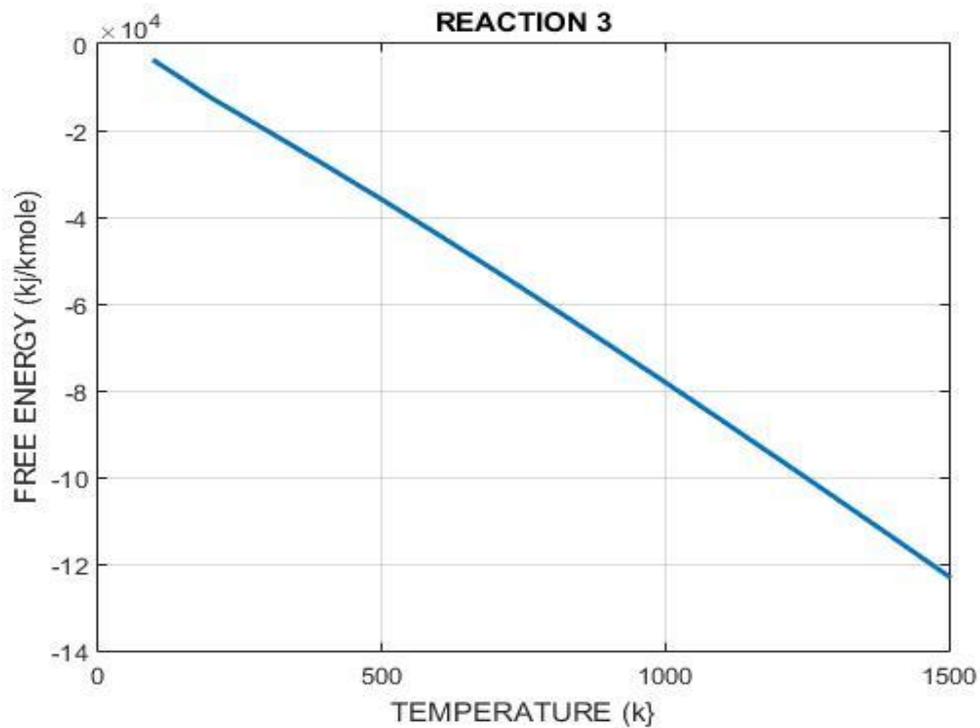
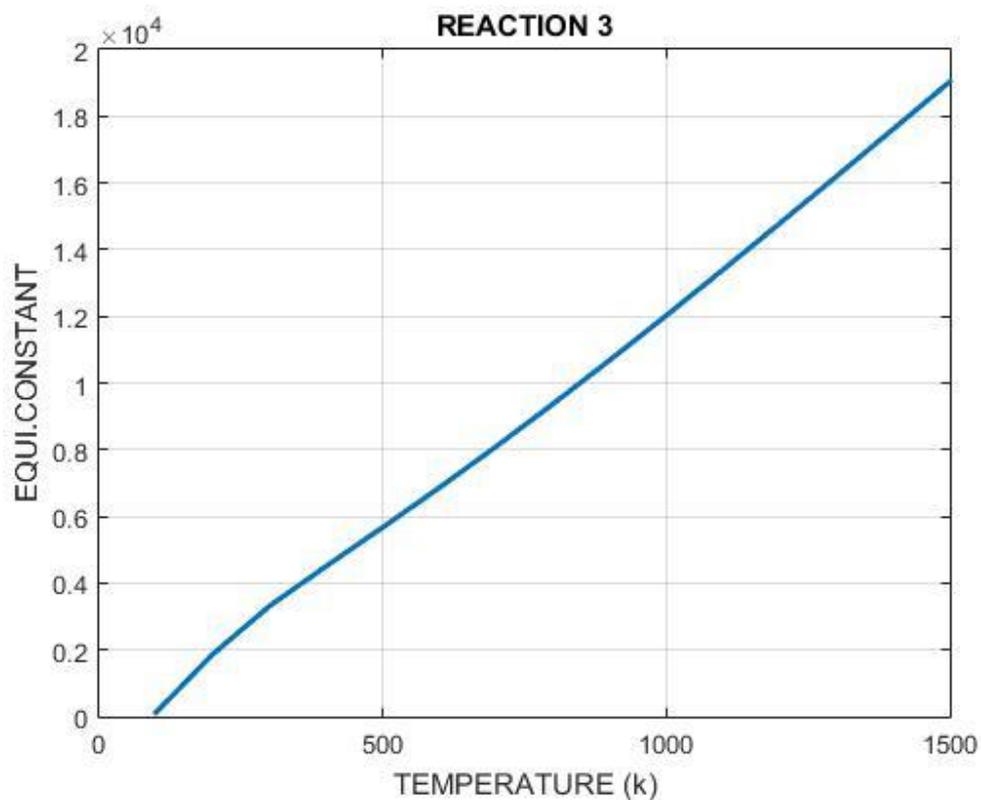


Fig.7 The relation between Enthalpy versus Temperature for reaction 3



temperature for reaction 3 Fig.8 The relation between free energy versus



**Fig.9** The relation between equilibrium constant versus temperature for reaction 3