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Study The Effect Of Water – Gas Shift Equilibrium on Adiabatic Flame Temperature for Alkanes Family Fuels at rich conditions

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Abstract

The effect of water – gas shift equilibrium on adiabatic flame temperature for Alkanes family fuels was studied. The calculations of adiabatic flame temperatures were carried out by developing a program by using visual basic 6 language, based on a general algorithm meant to compute the equilibrium composition of products for any fuel–oxidizer gaseous mixture. The algorithm is based on the thermodynamic principles. Ten compounds were considered as products: the fuel (C_nH_{2n+2}), CO_2, CO, H_2O, N_2, O_2, CH_4, C_2H_6, C_3H_8, C_4H_{10}, H_2, their heat were capacities expressed as function of temperature with the form: $C_p = a_o+a_1T+a_2T^2 +a_3T^3$. Two methods with and without water – gas shift equilibrium were used to analysis the products gases. The results showed, adiabatic flame temperature calculated with water – gas shift equilibrium greater than that calculated without water – gas shift equilibrium.

Keywords: Water – Gas shift Equilibrium, Adiabatic flame temperature, Flame & Combustion

Introduction

One of the most important features of a combustion process is the highest temperature of the combustion products that can be achieved. The temperature of the products will be greatest when there are no heat losses to the surrounding environment and all of the energy released from combustion is used to heat the products. If all the heat evolved in the reaction is employed solely to raise the product temperature, this temperature is called the adiabatic flame temperature. Because of the importance of the temperature and gas composition in combustion considerations, it is appropriate to review those aspects of the field of chemical thermodynamics that deal with these subjects.

Bhoia and Channiwala [1] are studied theoretical and experimental axial flame temperature distribution of producer gas fired premixed burner. Their experimental results showed that the maximum axial flame temperature distribution was achieved at A/F (air to fuel) ratio of 1 and the adiabatic flame temperature of 1653°C was calculated theoretically at A/F ratio of 1 Nurun Nabi [2] was carried out a theoretical investigation of engine thermal efficiency, adiabatic flame temperature, NO_x emission and combustion-related parameters for different oxygenated fuels. His results explained that with the increase in oxygen content in the fuels adiabatic flame temperature decreases linearly. Khalil and et al [3] were studied theoretically the effect of pressure and inlet velocity on the adiabatic flame temperature of a methane-air flame, the study was performed using Fluent software. The pressure was varied between 2 and 10 atmosphere, while the inlet velocity varied between 5 and 10 m/s. They were found in general the adiabatic flame temperature increase with pressure. Zhou and Donald [4] were studied a new method for adiabatic flame temperature estimations of hydrocarbon fuels. The investigation was conducted over a wide range of operating conditions in terms of fuel composition, pressure and temperature of reactants, fuel–air equivalence ratio and fuel vapor fraction and several neural network models for predicting the flame temperature for different applicable fuel ranges were built and examined. The neural network prediction results were compared with the calculated by a thermodynamic and chemical equilibrium-based computer code NASA program CET89. It was shown that trained neural network models can provide the adiabatic flame temperature prediction with a good level of accuracy over a wide range of operating conditions. Torii and et al [5] were studied theoretically study adiabatic flame temperature and specific heat of combustion gases for both hydrocarbon-air and alcohol-air mixtures by means of a method of chemical equilibrium calculation. It was found that the detailed properties of combustion gas compositions, to a certain degree, can be predicted by the approximated equations, which, based on the results of the chemical equilibrium calculations, which were produced with the aid of the method of least squares. Conroy and et al [6] were examined the effects of flame temperature and the effect of assuming Lewis Number (ratio of mass to heat transport to the surface), is one.

Theory

The combustion of an arbitrary hydrocarbon fuel(Alkanes fuels which has the form C_nH_{n+2}), for rich combustion, can be represented as [7]:

$$C_nH_{2n+2} + a(O_2 + 3.76N_2) \rightarrow bCO_2 + cCO + dH_2O + eH_2 + 3.76aN_2 \qquad \ldots\ldots\ldots\ldots 1$$

Since the coefficient *(a)* represent the ratio of the number of moles of O_2 in the reactants to the number of moles of fuel, then, the equivalence ratio can relate as:

$$\Phi = \frac{1.5n + 0.5}{a} \qquad \ldots\ldots\ldots\ldots 2$$

where n: number carbon atoms in fuel

The reaction in equation (1) which has four unknown variables (*b, c, d and e*), but from the material balance three equations can be written (carbon, hydrogen and oxygen balance). Then, two methods will be used in this paper to solve equation (1).

Method 1*(with water – gas shift equilibrium occurs)*

The water gas shift equilibrium occurs as the reversible reaction below:

$$cCO + dH_2O \Leftrightarrow bCO_2 + eH_2 \qquad \ldots\ldots\ldots\ldots 3$$

The water-gas shift equilibrium constant can be written as [7,8],

$$K_p = \frac{b.e}{c.d} \qquad \ldots\ldots\ldots\ldots 4$$

Solving the element balance in terms of the unknown coefficient *b* results,

$$c = n - b \qquad \ldots\ldots\ldots\ldots 5$$

$$d = 2a - b - n \qquad \ldots\ldots\ldots\ldots 6$$

$$e = -2a + b + 2n + 1 \qquad \ldots\ldots\ldots\ldots 7$$

Substituting equations *(5,6 and 7)* into equation *(4)* yields a quadratic equation in *b*, the solution of which is

$$b = \frac{2a(K_p - 1) + 2n + 1}{2(K_p - 1)} - \frac{1}{2(K_p - 1)} \left[\begin{array}{l} (2a(K_p - 1) + 2n + 1)^2 \\ -4K_p(K_p - 1)(2an - n^2) \end{array} \right]^{1/2} \qquad \ldots\ldots\ldots\ldots 8$$

The water – gas shaft is a function of temperature, Bustamante and Enick [7,10] were set the water – gas constant as :

$$K_p = \exp(-4.33 + \frac{4577.8}{T}) \qquad \ldots\ldots\ldots\ldots 9$$

Method2 *(without water – gas shift equilibrium occurs)*

If the water gas shift equilibrium not occurs, the hydrogen gas not created in products (i.e e=0). That leaves three unknowns (*b, c,* and *d*). To solve these, three element balances were employed (*C, H,* and *O*) as:

$$d = n + 1 \qquad \ldots\ldots\ldots\ldots 10$$

$$b = \frac{2(1.5n + 0.5)}{\Phi} - (2n + 1) \qquad \ldots\ldots\ldots\ldots 11$$

$$c = n - b \qquad \ldots\ldots\ldots\ldots 12$$

Adiabatic flame temperature

The adiabatic flame temperature can be determined by using the conservation of mass and conservation of energy principles. To illustrate the procedure, suppose that the combustion air and the combustion products for each form of ideal gas mixtures. Then, the energy rate balance on a per mole of fuel basis, is [7]:

$$\sum_{P} n_i\, h_i = \sum_{R} n_i\, h_i \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots13$$

where *i* denotes the incoming species.
The enthalpy to be formed from two parts : sensible and chemical parte as:

$$h_i = \int_{T_o}^{T} Cp_i\, dT + \Delta h^{o}_{f,i} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots14$$

Substituting equation (14) in to equation (13) yield,

$$\sum_{P}\left(\int_{T_o}^{T} Cp_i\, dT + \Delta h^{o}_{f,i}\right) = \sum_{R}\left(\int_{T_o}^{T} Cp_i\, dT + \Delta h^{o}_{f,i}\right) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots15$$

Rewrite equation (15), then

$$\sum_{P}\left(\int_{T_o}^{T} Cp_i\, dT\right) = \sum_{R}\left(\int_{T_o}^{T} Cp_i\, dT\right) + \left(\sum_{R}\Delta h^{o}_{f,i} - \sum_{P}\Delta h^{o}_{f,i}\right) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots16$$

The second term in the right hand of equation (16) represents heat of combustion and written as

$$Q = \left(\sum_{R}\Delta h^{o}_{f,i} - \sum_{P}\Delta h^{o}_{f,i}\right) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots17$$

Integrating the right hand of equation (16) from original temperature to initial temperature (Ti) (T_o=298K), Therefore the first term in right hand of equation (16) will be zero and the left hand integrated from original temperature to adiabatic flam temperature (T_a), then

$$\sum_{P}\left(\int_{T_o}^{Ta} Cp_i\, dT\right) = Q \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots18$$

The specific heat (C_p) can be calculation from the equation:

$$Cp_i(T) = a_0 + a_1 T + a_2 T^2 + a_3 T^3 \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots19$$

Where a_o, a_1, a_2 *and* a_3 are the specific heat coefficients, it values shown in appendix A
Substituting equation (19) in equation (18) and integrated, then

$$\left.\begin{aligned} &\sum_{P}\left(a_o T_a + \frac{a_1 T_a^{\,2}}{2} + \frac{a_2 T_a^{\,3}}{3} + \frac{a_3 T_a^{\,4}}{4}\right) = \\ &Q + \sum_{P}\left(a_o T_o + \frac{a_1 T_o^{\,2}}{2} + \frac{a_2 T_o^{\,3}}{3} + \frac{a_3 T_o^{\,4}}{4}\right) \end{aligned}\right\} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots20$$

This equation solved by Newton-Raphson Method.

Results

In combustion problems the adiabatic flame temperature depend on the heat of combustion. Also, both the heat of combustion and adiabatic flame temperature depends on the analysis of products gases. Therefore the analysis of products gases will be discussed first.

Figures (1 to 4) show the products analysis for methane, ethane, propane and butane fuel with change of equivalence ratio. The mole fraction of carbon monoxide and carbon dioxide were the same behavior for both methods, where mole fraction of carbon dioxide decreasing with increasing equivalence ratio as shown in figure (1) due to decreasing the number moles of air when the equivalence ratio increasing. This can be shown by equation (2), where reversible relationship between equivalence ratio and number moles of air (coefficient *a*). Also, in figure (1), can be noted, by usng method2, the mole fraction of (CO_2), *(coefficient b was given by equation 11)*,will be equal zero if the equivalence ratio takes the following values: for methane, ethane, propane and butane as $^{4}/_{3}, ^{7}/_{5}, ^{10}/_{7}$ *and* $^{13}/_{9}$ respectively, this is a limitation of method2.

The mole fraction of CO, in both methods, increased with the equivalence ratio increased as shown in figure (2), due to decreasing the number moles of oxidizer as above.

In figure (3) it can be shown that the mole fraction of water vapor by method1 decreasing with increasing equivalence ratio due to created hydrogen gas in products as a result of water gas shift equilibrium occurs, while using method2 it increased with increasing equivalence ratio due to decreasing total number moles of mixture for the products as a results of equivalence ratio increasing. In figure (4) the mole fraction of H_2 was increased with the equivalence ratio increasing because of the mole fraction of CO will increase too, as shown in figure (2). The reaction specified in equation (3) will be move to use the right hand to increase the moles of CO_2 and H_2.

Figure (5) shows the mole fraction of nitrogen decreasing with equivalence ratio increasing due to increasing moles of air according to eqation2. Also, in this figure it can be noted that the higher nitrogen mole fraction is for butane compared with propane, ethane and methane respectively because of number moles of air for butane is greater than for propane, ethane and methane respectively when equivalence ratio remain constant.

Figure (6) shows the heat of combustion varies with equivalence ratio. From this figure it can be noted that the heat combustion for butane is the greater than propane, ethane and methane because of the heat formation of butane is greater than heat formation for other fuels. Also, this figure shows with increasing equivalence ratio the heat of combustion decreasing. This phenomena can be explained as:

In figure (7) increasing mole fraction of CO_2 the heat of combustion will increase due to increasing enthalpy of products which is given by equation (17), but mole fraction of CO_2 decreasing with increasing equivalence ratio as shown in figures (1), since heat of combustion decreased with equivalence ratio increasing. In figure (8) heat of combustion decreased when increasing mole fraction of CO, but mole fraction of CO increased when equivalence ratio increased as shown in figures (2). Therefore heat of combustion will be decreased when equivalence ratio increasing. Figure (9) shows the heat of combustion increasing when the mole fraction of water vapor increased for method2, but mole fraction of H_2O was decreased if equivalence ratio was increased as shown in figure(3), therefore heat of combustion decreasing. For method1the same behave can be shown for water vapor with heat of combustion, where from figure(3) by method2 noted the water vapor at first slowly increasing then decreasing after the value of equivalence ratio reached greater than 1.15 for all fuels, since the behave of heat of combustion become as shown in this figure (9) for method2. Figure (10) show the heat of combustion decreased if the mole fraction of hydrogen was increasing for method1 only. But mole fraction of hydrogen was increased when the equivalence ratio increased as shown in figures (1 to 4). All results explained in figures (6, 7, 8 and 9) show that the heat of combustion will be decreased if the equivalence ratio increasing.

Figure (11) explained the relationship between adiabatic flame temperature with equivalence ratio. In this figure can be noted when increasing equivalence ratio the adiabatic flame temperature will be decreased due to decreasing heat of combustion. In this figure, the results show the adiabatic flame temperature for Propane and Butane are closed equally along the suing equivalence ratio although heat of combustion for Butane greater than Propane. This phenomena can be explanation due to increasing mole fraction of Nitrogen in products as a results of increasing the number of Carbone atom in form of fuel as shown in figure5, when equivalence ratio is constant. In adiabatic combustion, as in this research, the heat of combustion will be caused increasing of products temperature only. Mass of Nitrogen in products will be heated from initial temperature to products temperature, sine much of heat of combustion losses to heated Nitrogen. Therefor adiabatic flame temperature reduces if mass of Nitrogen increased. But Nitrogen mole fraction for Butane greater than for Propane (as in figure 5), therefor, adiabatic flame temperature for Butane reduced and closed equally adiabatic flame temperature for Propane although heat of combustion for Butane greater than heat of combustion for Propane. This phenomena can be shown if drawing the relationship between adiabatic flame temperature (T_a) and heat of combustion (Q) after dividing each of them by number moles of Nitrogen in products. This is will be shown in figure (16). Where in figure (16) the bigger of this relationship was for Methane, Ethane, Propane and Butane due to increasing mole fraction of Nitrogen respectively.

Figures (12 and 14) shows the adiabatic flame temperature increasing when the mole fraction of CO_2 and H_2O increasing too, but all results in figures (1and 3) shows decreasing mole fractions of CO_2 and H_2O if the equivalence ratio increasing therefore adiabatic flame temperature will be decreasing. In other hand, results in figures (13 and 15) show with increasing mole fraction of CO and H_2, the adiabatic flame temperature decreasing. The mole fraction of CO and H_2 were increasing when equivalence ratio increasing too, therefore the adiabatic flame temperature will be deceasing.

In figure (17) can be noted, the adiabatic flame temperature calculated, for all fuels, by method1 was greater than that calculated by method2 due to reducing, by method1, mole fraction of CO in products as a results of water gas shift equilibrium occurs as shown in figure 2.

Conclusions

The present theoretical investigation shows the significant effect the water – gas shift equilibrium on adiabatic flame temperature. From the obtained results and discussion the following conclusions can be drown:-

1. The water – gas shift equilibrium increased adiabatic flame temperature.
2. There are solving limitations without water – gas shift equilibrium represent by cutting analysis if the equivalence ratio riches the values $4/3, 7/5, 10/7$ *and* $13/9$ for Methane, Ethane, Propane and Butane fuel respectively.

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NOMENCLATURE

Symbol	Definition	SI Units
English Symbols		
a	Number moles of air	Mole
b	Number moles of CO_2	Mole
c	Number moles of CO	Mole
d	Number moles of H_2	Mole
c_p	Specific heat	KJ/mol. K
d	Number moles of H_2O	Mole
h_i	Total enthalpy of species i	KJ/mol. K
K_p	Water – gas shift equilibrium constant	-
n	Number of carbon atoms in fuel form	-
n_i	Number moles of species i	mole
Q	Heat of combustion	KJ/mole of fuel
T	Temperature	K
T_a	Adiabatic flame temperature	K
T_i	Initial temperature	K
T_o	Original Temperature	K
Δh_i	Heat formations of species i	KJ/mol.
Greek Symbols		
Φ	Equivalence ratio	-
Subscript		
i	Species i	
a	Adiabatic condition	

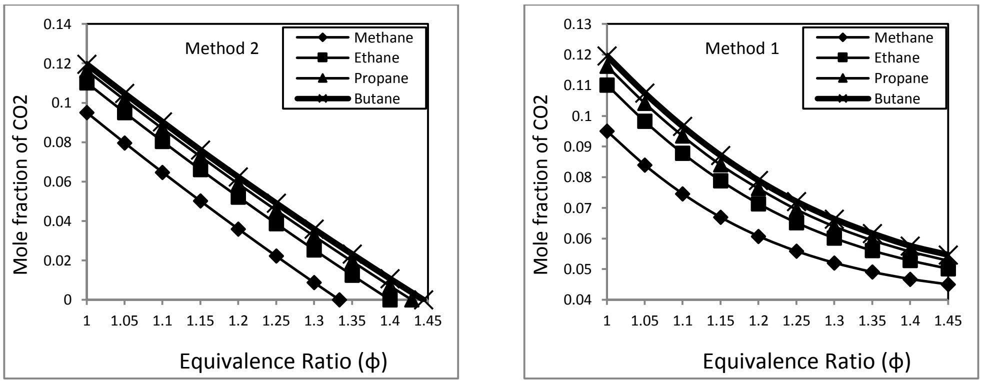


Figure (1) change mole fraction of CO_2 with equivalence ratio

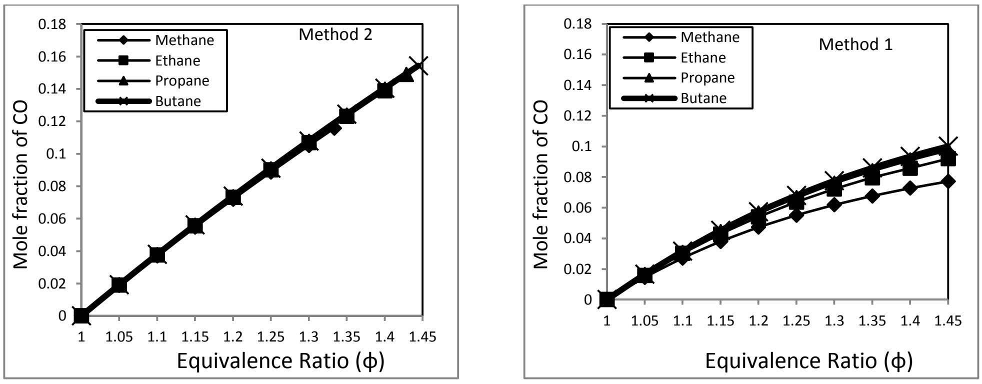


Figure (2) change mole fraction of CO with equivalence ratio

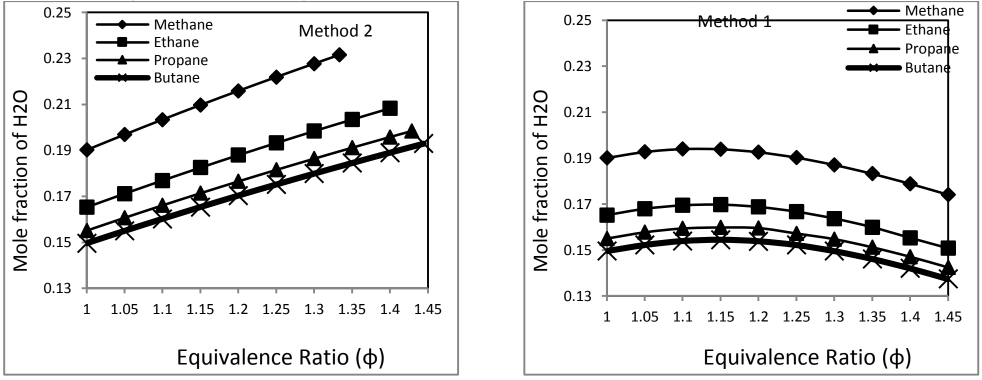


Figure (3) change mole fraction of H_2O with equivalence ratio

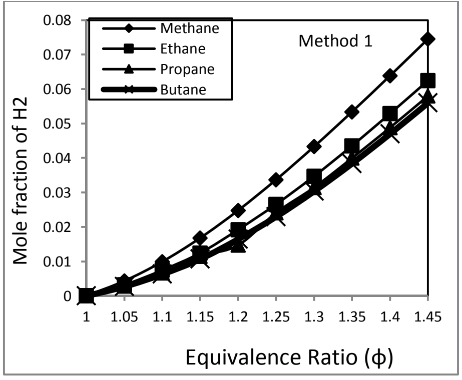


Figure (4) change mole fraction of H_2 with equivalence ratio

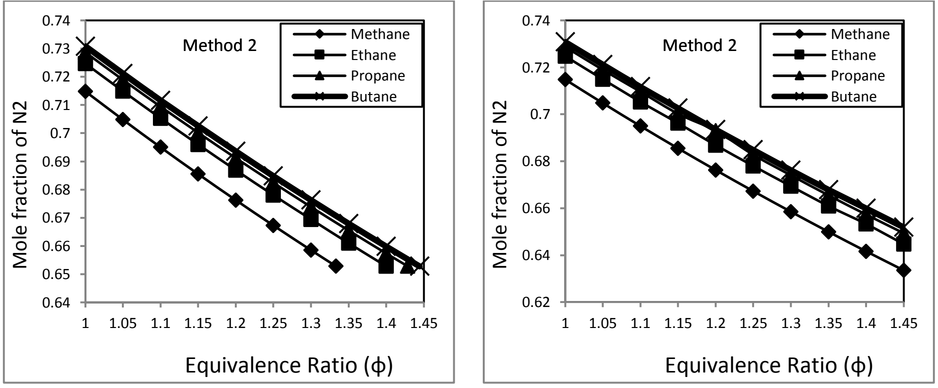


Figure (5) change mole fraction of N_2 with equivalence ratio

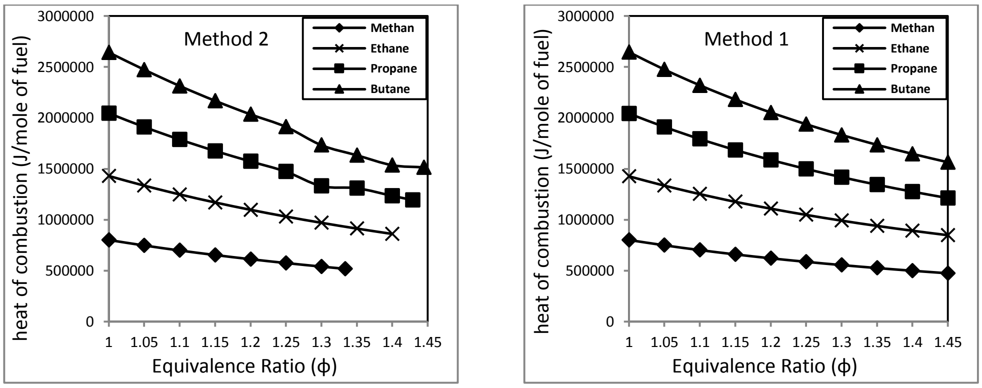


Figure (6) Heat of combustion (J/mole of fuel)

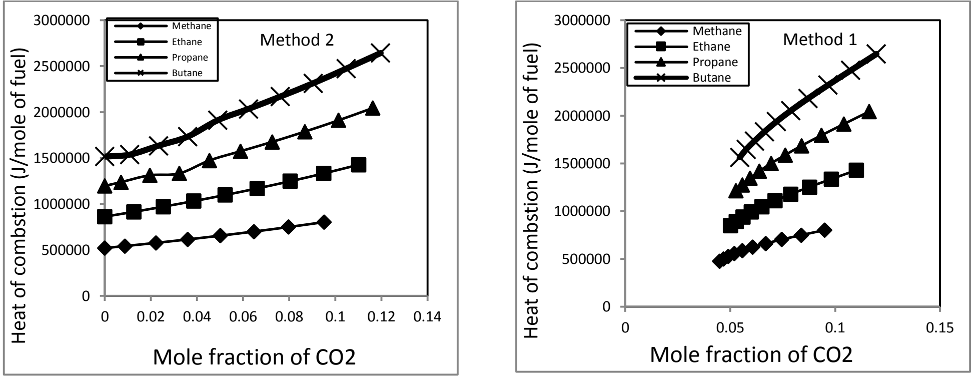


Figure (7) Heat of combustion vibration with mole FRACTION of CO_2

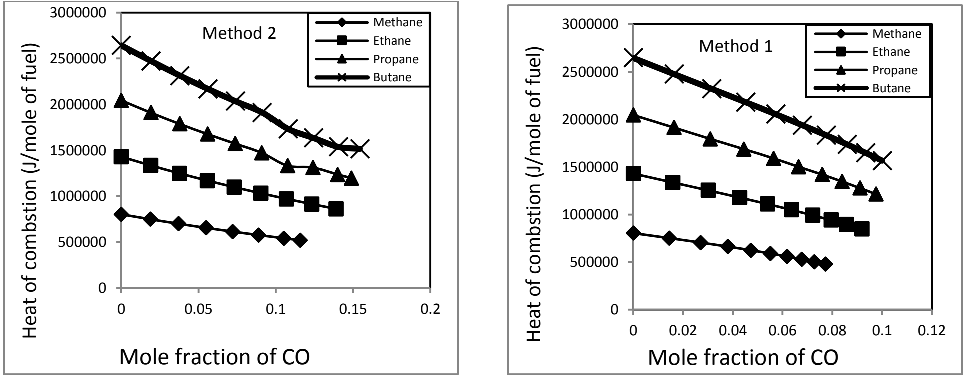


Figure (8) Heat of combustion vibration with mole fraction of CO

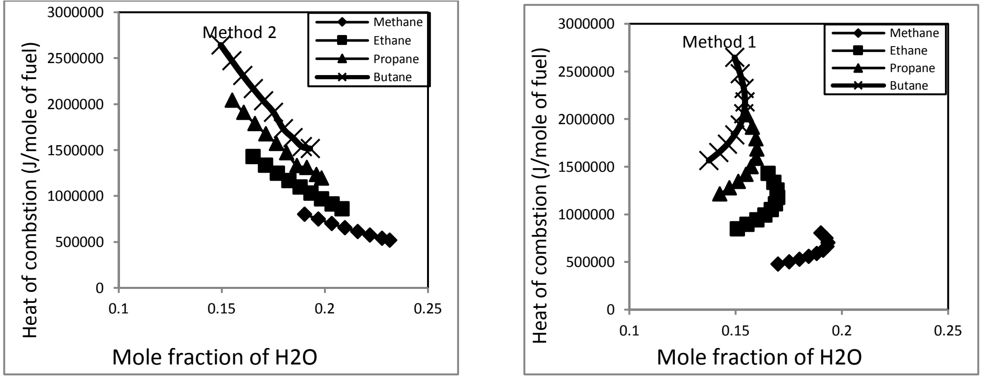


Figure (9) Heat of combustion variation with mole fraction of H_2O

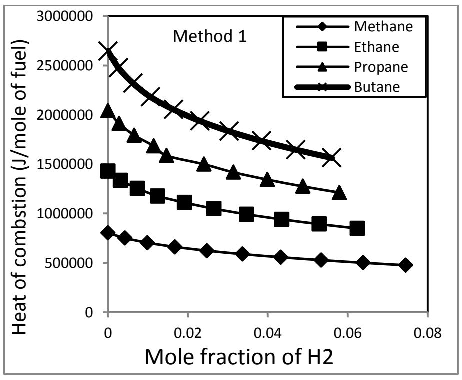


Figure (10) Heat of combustion vibration with mole fraction of H_2

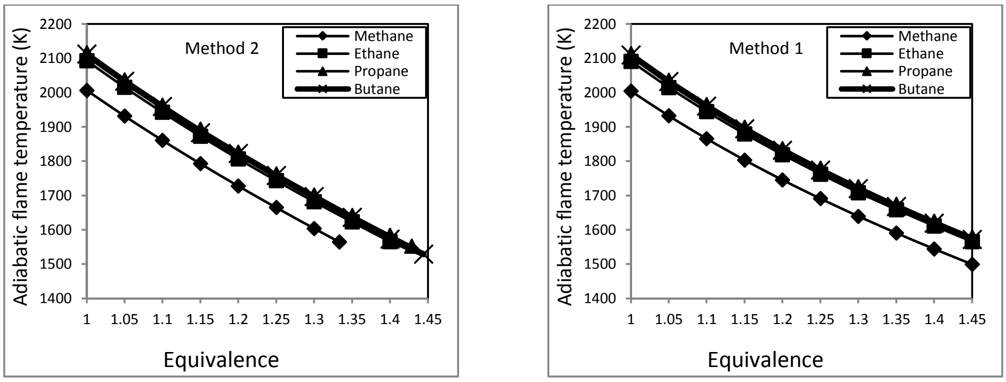


Figure (11) Adiabatic flame temperature (K)

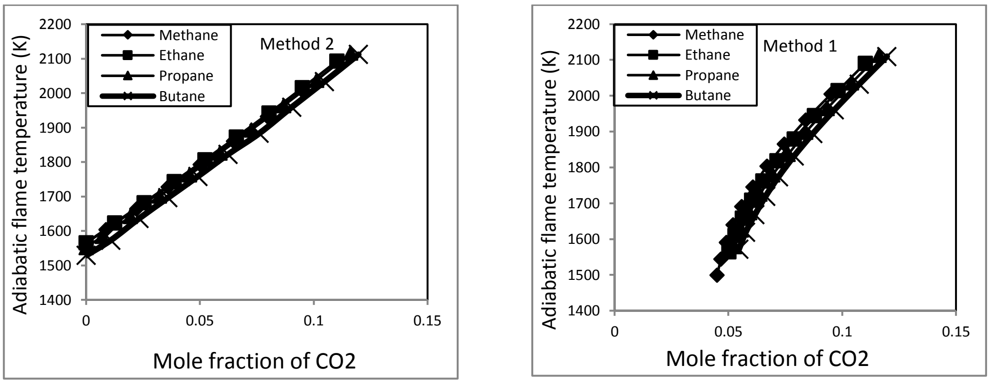


Figure (12) Adiabatic flame temperature (K)

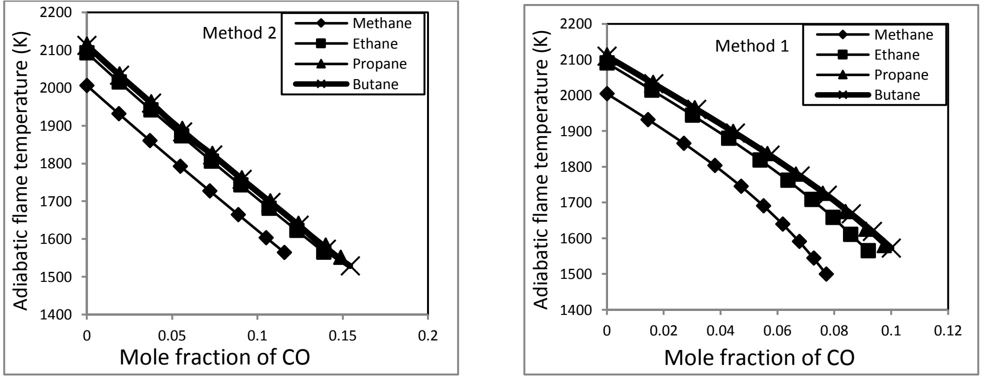


Figure (13) Adiabatic flame temperature (K)

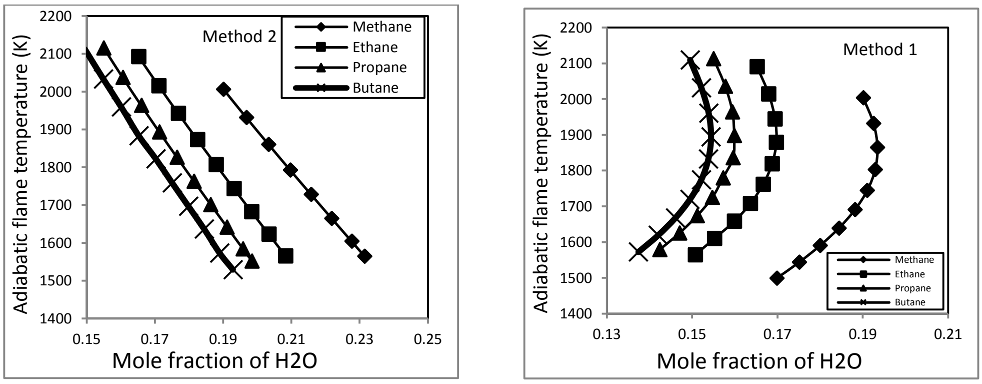


Figure (14) Adiabatic flame temperature (K)

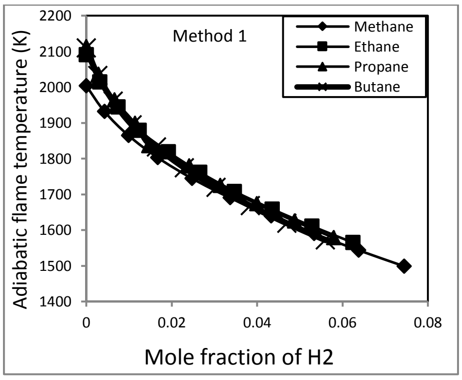


Figure (15) Adiabatic flame temperature (K)

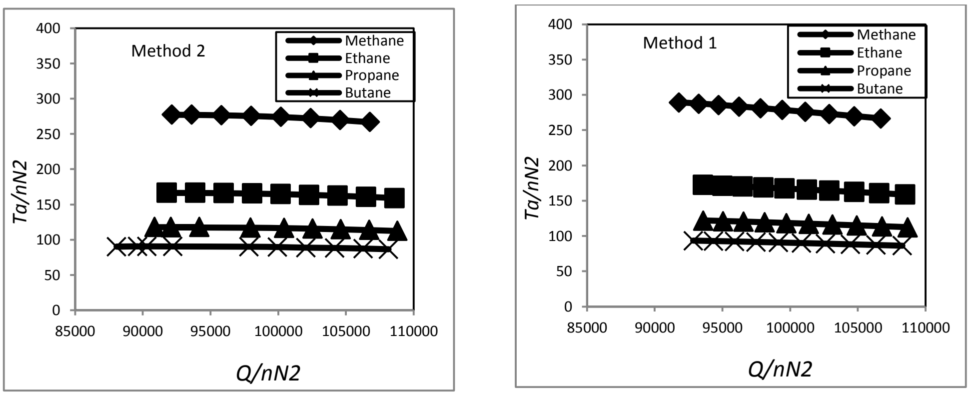
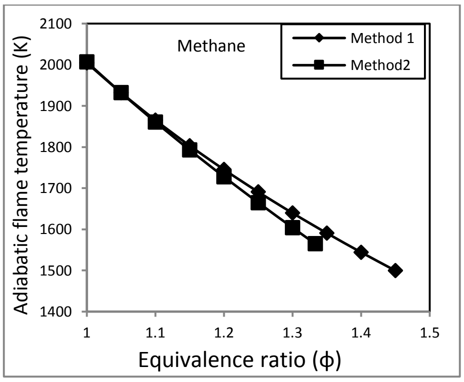
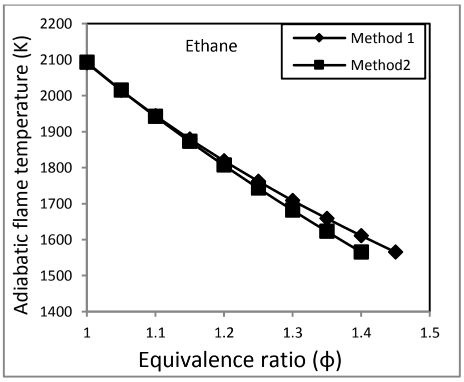


Figure (16)





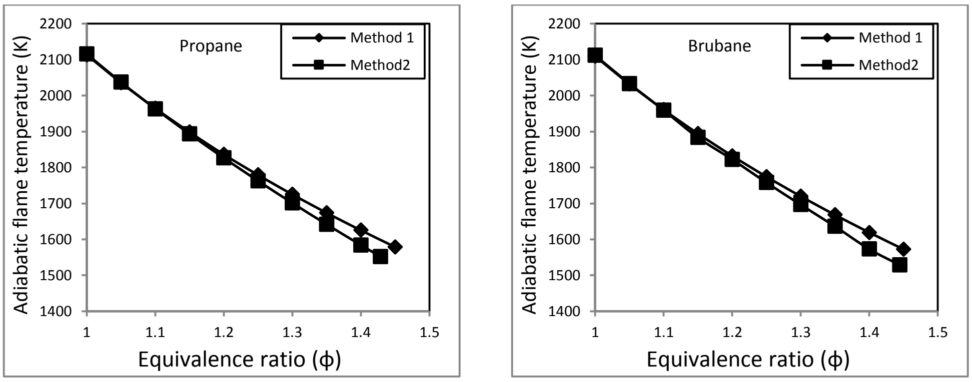


Figure (17) Various of Adiabatic flame temperature with equivalence ratio for all fuels

Appendix A : the specific heat coefficient and heat formations for species

Formula	*Name*	a_0 *J/mol K*	a_1 *J/mol K^2*	a_2 *J/mol K^3*	a_3 *J/mol K^4*
N_2	*Nitrogen*	*3.115E+01*	*–1.357E–02*	*2.608E–05*	*–1.168E–08*
O_2	*Oxygen*	*2.811E+01*	*–3.680E–06*	*1.746E–05*	*–1.065E–08*
H_2	*Hydrogen*	*2.714E+01*	*9.274E–03*	*–1.381E–05*	*7.645E–09*
CO	*Carbon monoxide*	*3.087E+01*	*–1.283E–02*	*2.789E–05*	*–1.272E–08*
CO_2	*Carbon dioxide*	*1.980E+01*	*7.344E–02*	*–5.602E–05*	*1.715E–08*
CH_4	*Methane*	*1.925E+01*	*5.213E–02*	*1.197E–05*	*–1.132E–08*
C_2H_6	*Ethane*	*5.409E+00*	*1.781E–01*	*–6.938E–05*	*8.713E–09*
C_3H_8	*Propane*	*–4.224E+00*	*3.063E–01*	*–1.586E–04*	*3.215E–08*
C4H10	*Isobutane*	*–1.390E+00*	*3.847E–01*	*–1.846E–04*	*2.895E–08*