Calculation of Combustion Products Using 6 Species Equilibrium Model

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ABSTRACT

An equilibrium model for hydrocarbon combustion calculation is developed. 6 major products in combustion gas are considered in this model. It gives more accurate result than that from low temperature combustion model and it is more simple than 10 species equilibrium model. In the development of the model, Elemental balance equations and equilibrium constant equations are combined to form only one equation requiring numerical solving. Newton-Raphson technique with Laguerre-Samuelson initialization method is applied to find the solution. The simulation result from the model shows that this model can be used to provide the initial values for other models, for example, 10 species model, without temperature and pressure limitations. If the mole fractions of major gas species are needed to know with high accuracy, the model can be employed with temperature and pressure conditions.

Keyword: Equilibrium constant, Combustion model, Laguerre-Samuelson initialization

1. Introduction

Combustion of fuel in automobiles and power generation systems are major sources of pollution emission. The knowledge of the exact gas composition in exhaust emission is an important data for estimation of an engine performance and pollution control in power generation system. For combustion analysis, the thermodynamic equilibrium model has been often used to find the gas composition [1,2]. However, for detailed analysis and high accurate result, it involves a large number of species. The calculation, therefore, highly consumes computational time and computer resources. In cylinder combustion, Heywood [3] and Ferguson [4] suggest that the analysis should be done with 10 gas species in exhaust gas for high temperature combustion. To find 10 constituents, a famous method developed by Olikara and Borman [5] is frequently employed. In this

method, mole fractions of some gas species are expressed as functions of mole fractions of CO, H_2, O_2, and N_2. Thus, only four equations are solved by numerical method. The initial values of these four gas species are required in numerical solving and a low temperature model is often used for this purpose [6].

In some studies, researchers usually applied an assumption of complete combustion of fuel in which the combustion gas consists of CO_2, H_2O and N_2 (for example [7]). This approach may not suitable for some applications, requiring fairly or high accurate result, because more than these 3 species can be detected in combustion gas with significant concentration. Even through the combustion takes place with 100 percent theoretical air, the dissociation can cause generation of other gas products. For example, CO_2 in combustion gas at high temperature can dissociate into CO and O_2. For H_2O, it can

generate H_2 and O_2 as well as other gas species which are formed by dissociation accompany with chemical reactions. In fuel lean combustion (also referred as lean mixture combustion in this paper), only N_2, H_2O, CO_2, and O_2 are considered to be found in combustion gas [8-11]. The number of moles of these species can be obtained by using elemental balance. For fuel rich combustion, the gas species presented in combustion gas are N_2, H_2O, CO_2, CO and H_2 [10,11]. The elemental balance method and an equation of equilibrium constant are introduced to find the number of moles of these products. This simplify method, discussed above, is also known as low temperature model [6, 12]. However, the simplify method may lack in precision, because at higher temperatures (greater than about 2,200 K), these major species dissociate and react to form additional species in significant amounts [3].
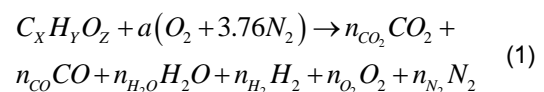
As found in the above discussions, 10 gas species model is required low temperature model or assumption of complete combustion as initial values for numerical solving. Moreover, it also needs to find 4×4 Jacobian matrix [4,6,13] in which the derivatives of reduced equations with respect to the number of moles of CO, H_2, O_2 and N_2 are found and these are quite complicated. In calculation, the Jacobian matrix also highly consumes computer resources. For the simplify method or low temperature model, it is simple and consumes less computer resources and computational time. However, the result has low accuracy as well.

To compromise between these two methods, 10 gas species model and low temperature model, a model predicting 6 compositions in combustion gas is developed in this study. CO_2, H_2O, N_2, CO, H_2, and O_2 are considered in the present model without neglecting in some conditions as treated in low temperature model. The model can be used to find the mole fractions of 6 gas species for hydrocarbon

combustion. 6 equations for calculation the number of moles of 6 gas species are reduced to one equation which is required a numerical method to find the solution. This final equation is simple to solve by Newton-Raphson method because of no Jacobian matrix and easily to find its derivative. The calculation result of this model is, then, verified with the result from CEA program, developed by NASA [14]. Moreover, the model is used to find the mole fractions of combustion products at high temperature and pressure. Its results are, then, compared with the results from CEA program calculating mole fractions of 10 gas species. The comparison is done only 6 major products in order to show the performance of the model for high temperature and pressure applications.

2. Method

The problem considered in this research is combustion of hydrocarbon fuel in air. The fuel is defined as $C_X H_Y O_Z$ and air is assumed that it contains 79% by mole of N_2 and 21% by mole of O_2. In this work, only 6 major gas species in combustion gas are focused. There are CO_2, H_2O, N_2, CO, H_2, and O_2. The combustion reaction for burning one mole of hydrocarbon fuel can be written as:

$$C_X H_Y O_Z + a\left(O_2 + 3.76 N_2\right) \rightarrow n_{CO_2} CO_2 + n_{CO} CO + n_{H_2O} H_2O + n_{H_2} H_2 + n_{O_2} O_2 + n_{N_2} N_2 \quad (1)$$

It can be observed that there are 6 unknown, needed to find the values, n_{CO_2}, n_{CO}, n_{H_2O}, n_{H_2}, n_{O_2}, and n_{N_2} Therefore, it requires 6 equations. The first 3 equations can be formed by elemental balances, as shown in the following.

Carbon balance:

$$X = n_{CO_2} + n_{CO} \quad (2)$$

Hydrogen balance:

$$Y = 2n_{H_2O} + 2n_{H_2} \qquad (3)$$
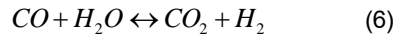
Oxygen balance:

$$Z = 2n_{CO_2} + n_{CO} + n_{H_2O} + 2n_{O_2} \qquad (4)$$
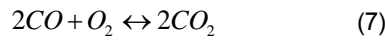
Nitrogen balance:

$$3.76a = n_{N_2} \qquad (5)$$

For 2 more equations, the equilibrium constant equations are used. Two chemical reactions involving the combustion reaction are utilized, there are:

Water gas shift reaction:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad (6)$$

Oxidation of carbon monoxide:

$$2CO + O_2 \leftrightarrow 2CO_2 \qquad (7)$$

The equilibrium constants corresponding to reactions (6) and (7), respectively, are:

$$K_1 = \frac{n_{CO_2} n_{H_2}}{n_{CO} n_{H_2O}} \qquad (8)$$

$$K_2 = \frac{n_{CO_2}^2 n_{tot}}{n_{CO}^2 n_{O_2} P} \qquad (9)$$

where n_{tot} is the total number of moles in combustion gas and P indicates the pressure of combustion reaction. To find the equilibrium constants, K_1 and K_2, Eq. (10) is recommended to used [15].

$$\ln K = -\frac{\Delta G_T^o}{RT} \qquad (10)$$

where R is the universal gas constant and ΔG_T^o is the standard Gibbs of reaction which can be calculated by [16]:

$$\Delta G_T^o = \sum_{P-R} v_i \left(\Delta h_{f,T}^o - T s_T^o \right) \qquad (11)$$

The standard enthalpy of formation, $\Delta h_{f,T}^o$, and The standard of entropy, s_T^o, at specific temperature T can be obtained from Ref [17]. However, finding the equilibrium constants following the above method, it is for general use, but it consists of at least 4 steps to be done. Ferguson [4] has shown the equilibrium constants as a function of temperature which were obtained from cure fitting by using JANAF table. The fitted equation for K_1 is:

$$\ln K_1 = 2.743 - \frac{1.761}{(T/1000)} - \frac{1.611}{(T/1000)^2} + \frac{0.2803}{(T/1000)^3} \qquad (12)$$

In order to find the equilibrium constant for reaction (9), the data from Ref. [4] is modified and it gives:

$$\log K_2 = 2\left(-0.415302 \times 10^{-2} \ln(T/1000) + (0.148627 \times 10^5)/T - 4.75746 + 0.124699 \times 10^{-3} T - 0.90027 \times 10^{-8} T^2 \right) \qquad (13)$$

To reduce the number of equations used to find the mole fractions of gas species in combustion gas, a new parameter is introduced. It is a ratio of mole of CO to mole of CO_2 in combustion gas, as:

$$CR = \frac{n_{CO}}{n_{CO_2}} \qquad (14)$$

In fact, there are many ways to reduce Eqs. (2-5) and (8-9). However, as observed from Eq. (1), the gas species that compose of carbon, C, are only CO and CO_2. Therefore, CR is defined as that it is expected to be able to represent the numbers of moles of CO and CO_2. In the next step, the numbers

of moles of other gas species are defined in terms of CR.

From Eq. (3), n_{H_2} can be written in terms of n_{H_2O} as:

$$n_{H_2} = \frac{Y - 2n_{H_2O}}{2} \qquad (15)$$

From Eqs. (8), (14), and (15), n_{H_2O} can be expressed in terms of CR as:

$$n_{H_2O} = \frac{Y}{(2K_1 CR + 2)} \qquad (16)$$

According to Eqs. (2) and (14), n_{CO} and n_{CO_2} can be written, respectively, as:

$$n_{CO} = \frac{CR(X)}{(CR+1)} \qquad (17)$$

$$n_{CO_2} = \frac{X}{(CR+1)} \qquad (18)$$

For n_{O_2}, Eq. (9) is employed and it is found that:

$$n_{O_2} = \frac{n_{tot}}{CR^2 (K_{2P})} \qquad (19)$$

where K_{2P} is $K_2 \times P$. For the last equation which has not been used, Eq. (4), Eqs. (16-19) are substituted into this equation and it gives:

$$Z = \frac{Y}{(2K_1 CR + 2)} + \frac{X(2+CR)}{(CR+1)} + \frac{2n_{tot}}{CR^2 (K_{2P})} \qquad (20)$$

Based on the definition of n_{tot}, it is finally found that:

$$n_{tot} = \left(X + \frac{[Y+(3.76a)]}{2} \right) \frac{CR^2 (K_{2P})}{[CR^2 (K_{2P}) - 1]} \qquad (21)$$

Substituting Eq. (21) into Eq. (20), it results:

$$2Z[K_1(CR)+1](CR+1)[CR^2(K_{2P})-1] =$$
$$(Y)(CR+1)[CR^2(K_{2P})-1] +$$
$$2X[K_1(CR)+1][CR^2(K_{2P})-1](2+CR) +$$
$$4[X+(Y+3.76a)/2][K_1(CR)+1](CR+1) \qquad (22)$$

Eq. (22) is rearranged and it, then, shows a fourth order polynomial equation or quartic equation in CR as:

$$A(CR)^4 + B(CR)^3 + C(CR)^2 + D(CR) + E = 0 \qquad (23)$$

where

$$A = 2K_1 K_{2P}(X-Z),$$
$$B = \begin{bmatrix} 2K_1 K_{2P}(2X-Z) + \\ 2K_{2P}(X-Z) + Y(K_{2P}) \end{bmatrix},$$
$$C = \begin{bmatrix} (-2Z+4X+Y)K_{2P} + \\ 2(Z+X+Y+3.76a)K_1 \end{bmatrix},$$
$$D = \begin{bmatrix} 2(Z+Y+3.76a)K_1 + \\ 2(Z+X+Y/2+3.76a) \end{bmatrix},$$
$$E = (2Z+Y+7.52a) \qquad (24)$$

To Find the numbers of moles of all gas species, the fuel and the amount of air per mole of fuel are firstly defined in order to know the chemical elements introduced to combustion system. The combustion pressure and temperature are chosen. The equilibrium constants can be estimated from Eqs. (12) and (13). CR in Eq. (23) is solved. The numbers of moles of gas species can be found by using Eqs. (14-19). For n_{N_2}, it can be calculated from Eq. (5).

3. Numerical Solving

As seen from Eq. (23), CR, which is needed to find the value, is presented in polynomial form. For quartic equation, the analytical method is available in some references [18, 19]. However, it is quite complicated. The numerical method is another way applied to find the roots. Newton-Raphson method is a numerical technique, often used to find the root in nonlinear equation. It is, then, selected to solve Eq. (23) in this study. Based on the Newton-Raphson method, if Eq. (23) is called f, roots of this equation can be found by:

$$n_j^{k+1} = n_j^k - \frac{f}{f'} \qquad (25)$$

where superscript k is the number of iterations and subscript j represents the number of roots. f' expresses the derivative of f with respect to CR. In this numerical method, the initial value adopted to find the solution to Eq. (25) can be simply obtained from many concepts. In this study, an initialization method, called Laguerre-Samuelson (LS) [20-22], is proposed. This method shows that for the polynomial equation $a_0 x^n + a_1 x^{n-1} + ... + a_{n-1} x + a_n = 0$, the roots of equation are bounded by

$$x_{low,high} = -\frac{a_{n-1}}{n} \pm \frac{n-1}{n} \sqrt{a_{n-1}^2 - \frac{2n}{n-1} a_{n-2}} \qquad (26)$$

However, it is possible that there are 4 roots for Eq. (23) and in some cases, the number of roots for quartic equation is less than 4, because there are repeated roots. In the next section, the root of Eq. (23), which relates to the physical meaning of combustion process considered, is investigated

and the Laguerre-Samuelson initialization is additionally discussed.

4. Results and Discussion

In the first part, the solution behavior of Eq. (23) and LS initialization method are investigated. Ethane (C_2H_6) is utilized as fuel in this section. The combustion is assumed to occur at pressure and temperature of 1 atm and 1800K, respectively. Both rich and lean mixture conditions are explored. Before investigation of characteristic of function f is conducted, a simple verify of the developed mole is done in order to make sure that the computer code is correctly written following the approach discussed in the previous section and it gives reasonable result. First, the equilibrium constants are computed and their values are validated with the data from Ref [23]. Next, the mole fractions of products in combustion gas are found at stoichiometric combustion at low temperature, 1600K, for various hydrocarbon fuels. Hand calculation using elemental balance is done with only 3 gas species, CO_2, H_2O, and N_2. The mole fractions of these gas species from the model and elemental balance method are compared. From the investigations, they show that the equilibrium constants from Eqs. (12) and (13) match with that from [20] at various temperatures. For mole fractions of CO_2, H_2O, and N_2, the model provides a slightly different value from elemental balance method. However, it is impossible to have the same mole fraction in each gas species from both approaches, because of different number of gas species considered in the calculation. Nevertheless, the slightly different results in all tests can be implied that the investigated model was correctly developed following the method previously discussed.

After simply checking the model, it is operated to study the behavior of function f. Fig. 1 depicts the variation of f at different CR for rich mixture with $a = 3.2$ (see Eq. (1)). For lean mixture, the behavior of f is quit the same as that found in rich mixture condition. From the figure, it expresses that the roots of Eq. (23) are both negative and positive values. However, the negative real root has no meaning in practice. Only positive real root is considered.
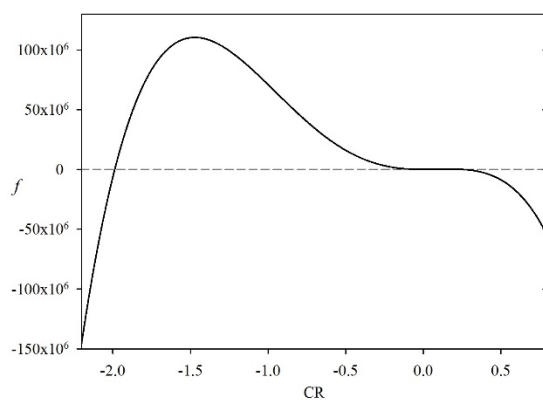

Fig. 1. The variation of f versus CR

Fig. 2 magnifies the value of f for $0.05 \leq CR \leq 0.26$ in which the root corresponding to
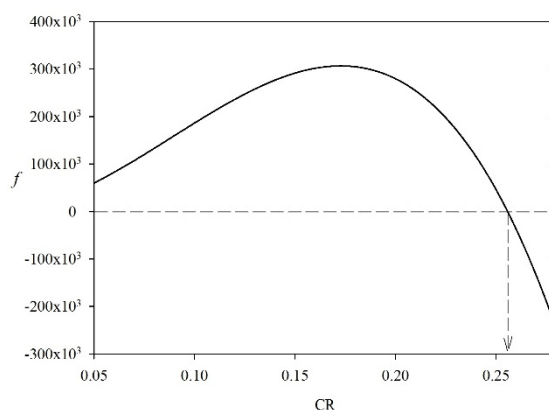

Fig. 2. The positive real root of f corresponding to the combustion condition

the combustion condition is found. As seen from Fig. 2, the root is 0.2558, associated with the rich combustion condition, and it is the maximum among all roots. This is also observed in lean mixture case. LS bounds the roots of considered case as -1.9974 and 1.1318. The lower bound, negative value, is useless for this study. From the investigation result, it leads to the summary that only the upper bound or higher value obtained from LS method is used as initial value to find the root of Eq. (23).

4.1 Validation

To show that the calculation result from the present model is correct, the CEA program developed by NASA is applied to validate the result. The comparison is done with the same condition and it focuses only 6 products in combustion gas. Methane (CH_4) is used as fuel and the combustion pressure is 1 atm. Figs. 3(a) and 3(b) show the validation result for rich mixture combustion with equivalence ratio, (ϕ), of 1.2. Both figures present the mole fraction of gas species at different temperatures. The symbols represent the results obtained from the present model while the results given by CEA program are expressed as lines. Figs. 3(a) and 3(b) illustrate that the mole fractions of gas species obtained from present model match with that from CEA program with very small different values. However, it is worth to point out here that the comparison has to be done with the same significant numbers of mole fraction for each gas species. A high value of relative percentage difference can be found in comparison of gas species having very low fraction in combustion gas if the comparison is done without fixing significant number. For example, CEA program was set to show the result only 5 decimals and it gives mole fraction of O_2 at 2000K as 0.00001 while the present model show that it is

0.0000143. The relative percentage difference is 43%. If it is truncated to show only 5 decimals, the comparison with the same significant number gives zero relative percentage difference. Moreover, the difference of both result, 4.3×10^{-6}, is very low and it does not have significant effect to other mole fractions of gas species if it is truncated.

each gas species, the symbols completely coincide with the line. As observed from rich and lean mixture cases, it can be finally concluded that the present model developed in this study can provide correct predicted result.
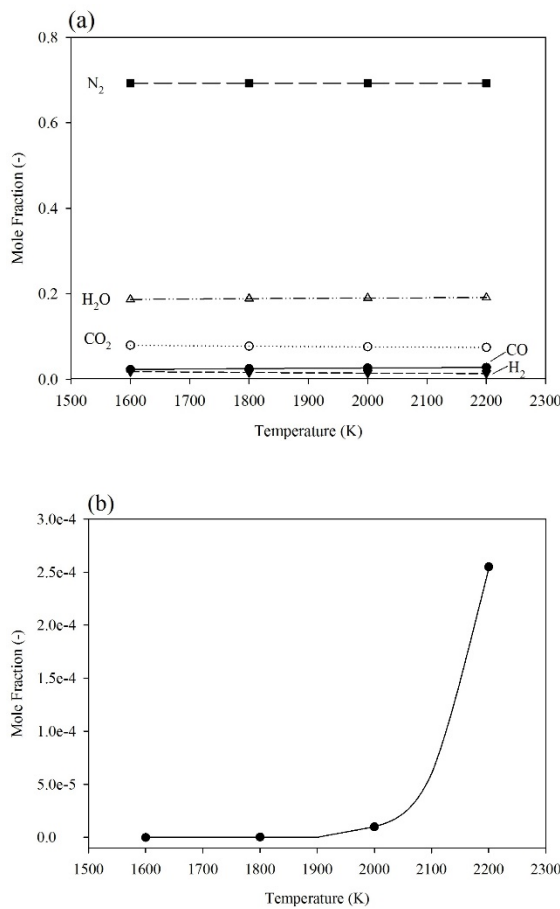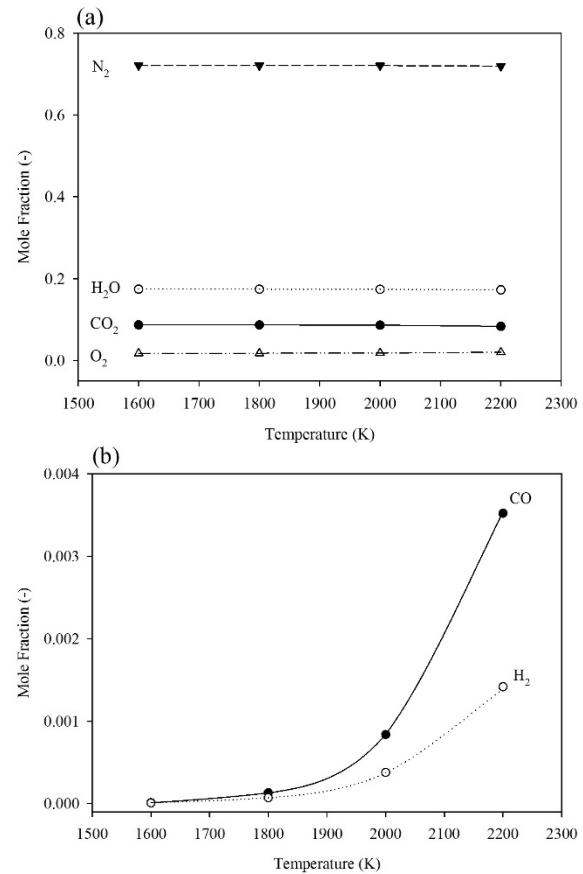

Fig. 3. Variation of gas species at different temperatures for CH_4 combustion with $\phi = 1.2$ at P=1 atm, symbols are results from present model and lines are results from CEA (a) N_2, H_2O, CO_2, CO, and H_2, (b) O_2

Fig. 4. Variation of gas species at different temperatures for CH_4 combustion with $\phi = 0.9$ at P=1 atm, symbols are results from present model and lines are results from CEA (a) N_2, H_2O, CO_2, and O_2, (b) CO and H_2

For lean mixture with $\phi = 0.9$ the mole fractions of combustion gas components at different temperatures are expressed in Figs. 4(a) and 4(b). From the figures, they are clearly seen that, for

It is worth to discuss here that, for rich mixture (Figs. 3(a) and 3(b)), O_2 cannot be found exhaust gas. However, when temperature increases, the dissociation causes rise of O_2 in combustion gas. Therefore, mole fraction of CO_2 reduces consequently mole fraction of CO increases. Due

to H_2 can react well with O_2, this results mole fraction of H_2O grows up, while mole fraction of H_2 decreases. For lean mixture (Figs. 4(a) and 4(b)), higher temperature makes O_2 dissociate, the mole fractions of CO_2 and H_2O, then, reduce. This dissociation also causes advent of H_2 and CO in combustion gas.

4.2 Comparison between 10 and 6 species models

As well known that at high temperature, the components in combustion gas are dissociated and the concentrations of some products, such as OH, O, H, and NO, increase. Prediction of combustion products with considering only 6 gas species may give less accurate result when combustion temperature grows up. In this section, CEA program is operated to find mole fraction of 10 gas species. Its results are compared with predicted mole fractions of 6 species obtained from the present model. The concentrations of only 6 major components are compared between both models. The limitation of the present model is finally discussed.
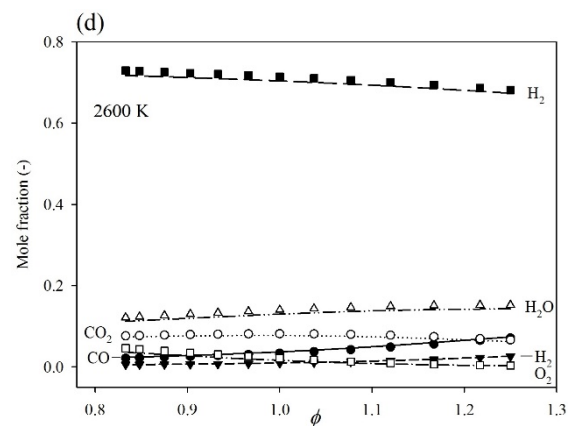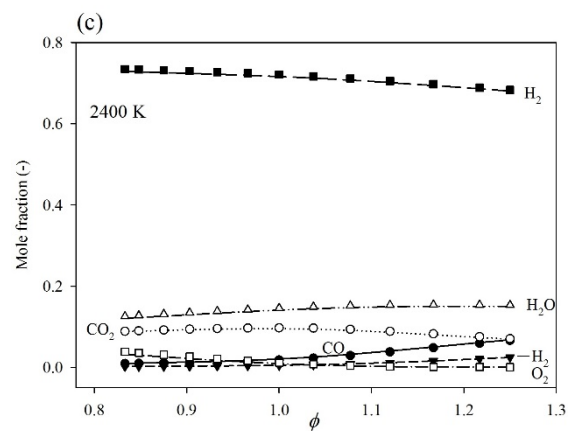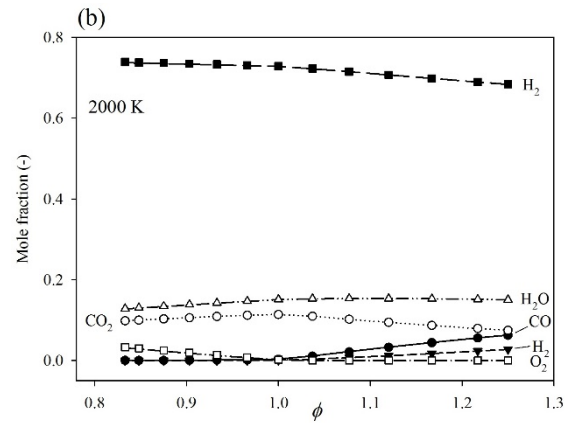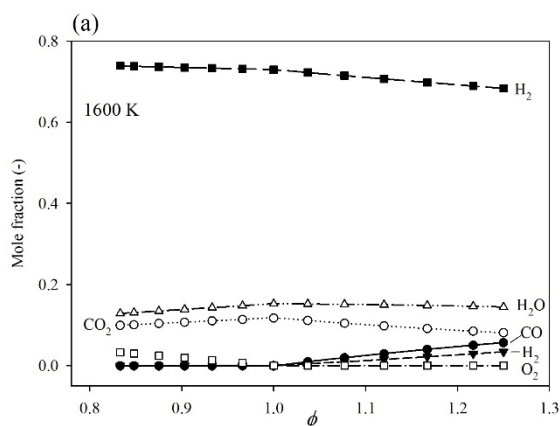

Fig. 5. The variation of 6 major gas species at different equivalence ratios for combustion of mixture of C_3H_8 and C_4H_{10} at P=1 atm (a) T=1600K, (b) T=2000K, (c) T=2400K, and (d) T=2600K

10 gas species focused in use of CEA program are CO_2, H_2O, N_2, CO, H_2, O_2, O, OH, H, and NO. The fuel used in this investigation is the mixture of propane (C_3H_8) and butane (C_4H_{10}) at the ratio of $0.6:0.4$. There are 4 combustion temperatures interested to observe the concentrations of compositions, 1600, 2000, 2400, and 2600K and the combustion is assumed to take place at 1 atm. The supply air is varied to generate lean to rich fuel combustion conditions. This is presented in terms of equivalence ratio, ϕ. The computational results from both programs are expressed in Figs. 5(a)-5(d). From the figures, only 6 major gas species (from totally 10) obtained from CEA program are used in this comparison. From the results, it can be mentioned that the mole fractions of 6 major gas species from the developed model are generally agree with that calculated from CEA program in all cases of combustion temperatures. However, in Fig. 5(a), the present model gives the mole fraction of O_2 at lean fuel combustion, $\phi < 1$, a little higher than that computed by CEA. It may be because of that O_2 can dissociate and react to generate other gas spices (O, OH, and NO). As expressed in [3], NO and OH can be found in lean mixture condition even low combustion temperature (1750K). Therefore, the mole fraction of O_2 should be lower than that predicted from the developed model in which O, OH, and NO are not considered. Another point, has to be discussed here, is that even mole fractions from the model match with that from CEA program, they continuously diverse from CEA results as combustion temperature increases. From Figs. 5(a)-5(d), the symbols, representing the data from developed model, are completely overlap to the lines at lower temperature. Then, they slightly

shift up to locate above the lines when combustion temperature raises. At T= 2600K, the relative percentage differences (RPD) are averagely higher than 5%, except N_2 case. Moreover, the higher RPD is found in the case of O_2. It varies from 21.5-34.2% through the studied range of ϕ. As it has been discussed, the developed model does not consider some gas species which compose of oxygen. This leads to over predicted O_2 in combustion gas. For T=2400K, the RPD of all gas species, except O_2 case, are usually lower that 5%. However, for CO in lean fuel combustion condition, the RPD is quite high. For example, at $\phi = 0.903$, CEA program give the mole fraction of CO as 0.01325 while the developed model shows it as 0.01215. The RPD, therefore, is 8.28%.

To show the effect of pressure on the predicted result, the combustion pressure is varied from 10 to 30 atm. The mole fractions of combustion products are calculated and compared with that from CEA program. The computational results from both programs for pressure of 20 atm are shown in Table 1. The RPD is also expressed in this table. For the case of 10 and 30 atm, only RPD is presented in Table 2. From Table 1, it can be found that the highest RPD occurs in the comparison of O_2 at stoichiometric combustion. Moreover, at $\phi = 1$, the RPD for the case of CO and H_2 are also high. These phenomena are also observed in combustion pressure of 10 and 30 atm. At specific ϕ, the RPD for CO increases as pressure increases. For CO_2, H_2O, and N_2, the RPD slightly reduces when pressure increases. As the pressure change from 10 to 30 atm, the RPDs for all gas species, however, marginally change.

Table 1 Comparison of mole fractions of gas species obtained from CEA program and the present model at 2400 K, 20 atm

ϕ		xCO	xCO_2	xH_2	xH_2O	xN_2	xO_2
	CEA	0.04767	0.08375	0.01489	0.15451	0.69743	0.00007
1.167	Model	0.04703	0.08450	0.01501	0.15520	0.69819	0.00007
	RPD	1.351	0.899	0.815	0.448	0.108	0.000
	CEA	0.00862	0.10849	0.00199	0.14829	0.72407	0.00351
1.000	Model	0.00753	0.10975	0.00179	0.14998	0.72629	0.00466
	RPD	12.669	1.161	10.151	1.142	0.307	32.705
	CEA	0.00281	0.09805	0.00062	0.12800	0.73280	0.02700
0.848	Model	0.00260	0.09838	0.00060	0.13008	0.73704	0.03130
	RPD	7.364	0.334	3.513	1.627	0.578	15.929

Table 2 The relative percentage differences for comparison of gas species at 10 and 30 atm

P (atm)	ϕ	RPD					
		xCO	xCO_2	xH_2	xH_2O	xN_2	xO_2
	1.167	1.672	1.151	0.493	0.699	0.153	8.174
10	1.000	11.759	1.3729	9.451	1.447	0.3630	30.822
	0.848	7.279	0.465	3.915	1.975	0.616	16.477
	1.167	1.209	0.783	0.991	0.337	0.088	0.000
30	1.000	13.149	1.055	10.784	0.999	0.278	34.087
	0.848	7.129	0.278	3.698	1.454	0.561	15.599

To show the prediction ability of model in widely range of ϕ, the developed model is performed to provide the mole fractions of 6 major gas species for $0.5 \le \phi \le 2$. The combustion temperature and pressure are 2400K and 10 atm, respectively, which are the upper accepted bound, previously discussed. The predicted results are compared with that from CEA program. There are, however, only 6 species considered in the comparison. Fig. 6 shows the mole fractions of 6 major gas species, derived from both models. It is clearly seen that mole fractions of all gas species presented by the developed model almost completely concur with these from CEA program.
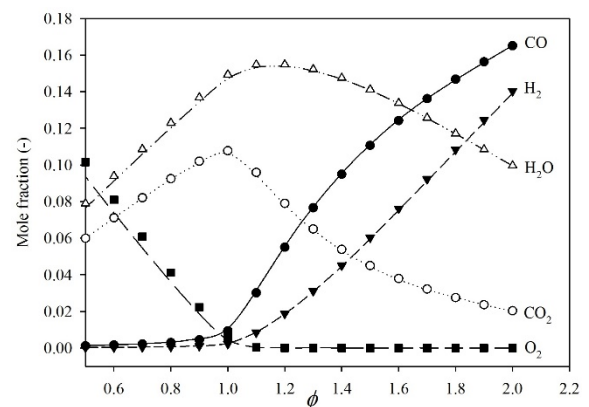

Fig. 6. Variation of mole fractions of 6 major gas species for combustion of mixture of C_3H_8 and C_4H_{10} at 2400 K, 10 atm for $0.5 \le \phi \le 2$

Only mole fractions of H_2O and O_2 in lean mixture range show slightly different values in comparison of data from both models.

5. Conclusion

A simple approach, used to find mole fractions of 6 major gas species in combustion gas, was developed in this study. The mole fractions obtained from this model can be employed as initial values for other models, for example, 10 species model. Moreover, it can also be used to find mole fractions of major products in combustion gas. As found that some combustion models are required initial values which are mole fraction of some gas species, the developed model in this study can serve for this propose. Due to the fact that the initial values, which approach to the solutions, can save computational time and protect the calculation from divergence, use of the developed model for initialization can achieve the convergence to the solution with less iteration in calculation. Moreover, the model developed in this study can be used to find mole fractions of 6 major combustion products with accurate result. However, if high accurate result is desired, the model should be performed with limitation of temperature and pressure not higher than 2400K and 10 atm, respectively.

6. References

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