Comparison of combustion products by the iteration method and application of gasoline and biogas

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Abstract. For a specific combustion problem involving calculations of several species at the equilibrium state, it is simpler to write a general computer program and calculate the combustion concentration. Original work describes, an adaptation of Newton-Raphson method was used for solving the highly linear system of equations describing the formation of equilibrium products in reacting of fuel-additive-air mixtures. This study also shows what possible of the results. In this paper, it presents the efficient numerical algorithms for solving the combustion problem, to be used linear equations based on the iteration method and high order of the Taylor series. The modified the Adomian decomposition method was applied to construct the numerical algorithms. Some numerical illustrations are given to show the efficiency of algorithms. Comparisons of results by the new Matlab routines and previous routines, the result data indicate that the new Matlab routines are reliable and application with gasoline and biogas with the variance of equivalence ratios, typical deviations from previous results are less than 0.1%.

1. Introduction
Chemical equilibrium is a condition when the chemical reaction, by which individual species in the burned gases react together, produces and removes each species at equal rates; hence at this condition has no net change in species composition results. Chemical equilibrium is usually described by either of two equivalent formulations, namely the equilibrium constants method (ECM) and the minimization of free energy (\(\Delta g = 0\)). However, the two formulations reduce to the same number of iteration equations.

When considering a general chemical equilibrium, there are several disadvantages in the equilibrium constant method such as the system of chemical equilibrium which are linear equations, more data and recoding. Including are numerical difficulties with the use of components and more difficulties in solving. On the other hand, the equilibrium constant method is simpler to adopt and formulate for a simple situation, and it was found that for most combustion problems, it gives satisfactory results without elaborate and complicated computer programs.

Mohamed[1] and Caton [2] developed procedures that combines algebraically the equilibrium equations, eliminates some unknowns, and scales the simplified equations to obtain a set of simultaneous linear equations that are solved with linear algebra. Their procedures combine the Gauss-Seidel and Newton methods. They claim that the Gauss-Seidel is unreliable and the Newton-Raphson method is slow.
When considering a minimization of free energy, the application of approaches results in a system of non-linear equations which can be solved by different numerical methods Adnan[3]. The system uses the Newton-Raphson method for solving. The initial values of the independent variables and the Lagrangian multipliers used in the calculations are determined on the basis of a numerous calculations of the composition of gaseous, liquid, and solid fuel combustion products.

Butworth[4], an effort is made by developing a combustion mathematical model to simulate exhaust emissions in fuels. Based on Equilibrium Constants Method (ECM), a computer program using MATLAB has been developed for the fuels to calculate the mole fractions of the emission gases. ECM is based on thermodynamic measurements and empirical calculations. Thermodynamic data for elements, combustion products and many pollutants are available in a compilation published by the National Bureau of Standards, called the JANAF (Joint Army–Navy–Air Force) tables. The equilibrium constant data from this tables using polynomial curve fitted has been used in calculating the combustion products.

Ferguson[5], a solution for the properties of equilibrium combustion products based on an equilibrium constant method (ECM) with the gas phase products of combustion of hydrocarbon fuels. The use of equilibrium constants is based on minimization of the Gibb free energy of gas. The equilibrium constant method is simpler than the Lagrange multiplier approach when considering restricted species lists. However, the equilibrium constant method requires the equilibrium reactions, such the water-gas reaction.

Solving system of linear equations of combustion is one of the most important problems in numerical analysis. Much attention has given to develop several iterative methods for solving linear equations. Babolian[6] have proposed and studied several methods for linear equations with higher order convergence by using the decomposition technique. He has to use the higher order differential derivatives which are a serious drawback. To overcome this drawback, we suggest and analyze a method for solving linear equations, which does not been involved the higher order derivative of the function.

Scientists and engineers have adapted the application of iterative methods in linear algebraic equations such as Newton–Raphson method, Adomian decomposition method and Householder iteration method lately. It is because these methods simplify complex problems into simple solutions. Newton–Raphson method is the most popular and powerful method in solving non-linear combustion equations, for example, Rakopoulos[7] also used this method to solve equations of chemical equilibrium combustion model in 11 species diesel alone combustion products, Masood[8] used this method to solve equations of low-temperature combustion model with only 10 products species , and Rashidi [9] combined Newton–Raphson with successive substitution methods to solve combustion problem of hydrocarbon fuel with 18 products species and concluded that the combined method gives fast and reliable convergence during iteration process.

In the present study, it suggests and analyzes iterative methods for solving linear equations. And it used an effort made by developing a combustion mathematical model to simulate exhaust emissions in hydrocarbon fuel as Biogas and Gasoline. Based on Equilibrium Constants Method, a computer program using MATLAB has been developed for the fuels to calculate the mole fractions of the emission gases. ECM is based on thermodynamic measurements and empirical calculations. Thermodynamic data for elements, combustion products and many pollutants are available in a compilation published by Grill [10].

2. Methods

2.1 Problem formation

This paper involves the simulation for determining and comparing Newton–Raphson method [NRM], Householder’s iteration method [HoIM], Adomian Decomposition method [ADM] and High order iteration Method [HIM] for the mole fraction of each of the exhaust species when the hydrocarbon fuel is burnt along with air and the results are presented. The proportion of hydrocarbon in the hydrocarbon–air blend affecting the mole fraction of the exhaust species is also simulated. Numerical experiments investigations were carried out, in gasoline fuel mode, which showed a good agreement
between the predicted and experimental results. Here in this paper an effort is made to calculate the exhaust emissions in gasoline fuel mode. The optimal combination of fuels depending upon the exhaust can be found effectively and applied practically.

The fuel is to be specified in terms of the C, H, O and N atoms in the fuel. For the blend of fuel-air considered. The other parameters that need to be specified are equivalence ratio, pressure and temperature. For the calculation of equilibrium constant, the data for constants is considered from Grill [10] tables. The molar-air fuel ratio is calculated from the number of carbon, hydrogen, nitrogen and oxygen atoms present in the fuel.

2.2 Logic of the numerical simulation

The basis of the equilibrium combustion products with fuel-air mixture model is a solution to the atom balance equations from the chemical reaction equation of fuel and air forming. This mixture equation can be written as Eq-(1) and Eq-(4), the equation can be written as next equation.

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\[ H = \varepsilon \phi(a1 + a2) = 2y1 + 2y6 + y7 + y9 \]

\[ O = \varepsilon \phi(y1 + y2) + 0.42 = 2y1 + y2 + 2y4 + y5 + y8 + y9 + y10 \]

\[ N = \varepsilon \phi(01 + 02) + 1.5 = 2y3 + y10 + y11 \]

Also the constraint that the mole fractions add up to unity must be satisfied,

\[ y1 + y2 + y3 + y4 + y5 + y6 + y7 + y8 + y9 + y10 + y11 - 1 = 0 \]

The expression for atom balance of each equation can be eliminated by dividing Eq-(2) by Eq-(3). The equation can be written as next equation.

\[ 2y2 + 2y6 + y7 + y9 - d1(y1 + y3) = 0 \]

Likewise the Eq-(3) and Eq-(4), the equation can be written as

\[ 2y1 + y2 + 2y4 + y5 + y8 + y9 + y10 - d2(y1 + y5) = 0 \]

Likewise the Eq-(1) and Eq-(4), the equation can be written as

\[ 2y2 + y10 + y11 - d1(y1 + y3) = 0 \]

Equations of constant value for a simple studied can be defined as, \[ d1 = \frac{b1 + b2}{a1 + a2}, d2 = \frac{y1 + y2}{a1 + a2}, d3 = \frac{0.42}{\varepsilon \phi(a1 + a2)}, d4 = \frac{1.58}{\varepsilon \phi(a1 + a2)} \]

The above 4 equations (Eq-(6) through Eq-(9)) have 11 unknowns, therefore in order to solve for these 11 unknowns other 7 more equations are needed which may be derived from the
consideration of equilibrium among products. The equilibrium constant can be related to the partial pressure of the reactants and products as show Table 1.

Table 1. The partial pressure of the reactants and products and the equilibrium constant equations

| Reaction                  | Equilibrium Constant |
|---------------------------|-----------------------|
| $CO_2 \leftrightarrow CO + (1/2)O_2$ | $K_1 = y_5^{1/2} y_4^{1/2} p^{1/2} / y_1$ |
| $H_2 + (1/2)O_2 \leftrightarrow H_2O$ | $K_2 = y_2 / y_4^{1/2} y_6^{1/2} p^{1/2}$ |
| $(1/2)H_2 + (1/2)O_2 \leftrightarrow OH$ | $K_3 = y_9 / y_4^{1/2} y_6^{1/2}$ |
| $(1/2)H_2 \leftrightarrow H$ | $K_4 = y_2 p^{1/2} / y_4^{1/2}$ |
| $(1/2)O_2 \leftrightarrow O$ | $K_5 = y_8 p^{1/2} / y_4^{1/2}$ |
| $(1/2)N_2 \leftrightarrow N$ | $K_6 = y_1 p^{1/2} / y_3^{1/2}$ |
| $(1/2)O_2 + (1/2)N_2 \leftrightarrow NO$ | $K_7 = y_{10} / y_4^{1/2} y_3^{1/2}$ |

And the partial pressure of a component is defined relative to the total pressure and the mole fraction, thus the equilibrium constant can be rewritten as,

Table 2. The equilibrium constant of constant term

| Reaction                  | Equilibrium Constant |
|---------------------------|-----------------------|
| $y_1 = C_1 y_5 y_4^{1/2}$ | $C_1 = P^{1/2} / K_1$ |
| $y_2 = C_2 y_4^{1/2} y_6^{1/2}$ | $C_2 = K_2 p^{1/2}$ |
| $y_9 = C_3 y_4^{1/2} y_6^{1/2}$ | $C_3 = K_3$ |
| $y_7 = C_4 y_6^{1/2}$ | $C_4 = K_4 / P^{1/2}$ |
| $y_8 = C_5 y_4^{1/2}$ | $C_5 = K_5 / P^{1/2}$ |
| $y_{11} = C_6 y_3^{1/2}$ | $C_6 = K_6 / P^{1/2}$ |
| $y_{10} = C_7 y_4^{1/2} y_3^{1/2}$ | $C_7 = K_7$ |

The equilibrium constants are treated as a function of gas temperature $T$ (K). It is the highest possible temperature that can be achieved during combustion. For computation of temperature, it is assumed that no heat will be transferred through combustion chamber walls, that is heat must be zero and all energy transferred to engine work and exhaust product. Values for $K$ have been tabulated for several reactions at various temperatures. These values come from the above relations, which are determined by statistically thermodynamics. Equilibrium constant in Table 2 are curve fitted to the Thermo chemical Grill[10] and their expressions are,

$$K_i = \exp \left( (a_i)(\ln T) + \frac{a_2 T^2}{2} + \frac{a_3 T^3}{6} + \frac{a_4 T^4}{12} + \frac{a_5 T^5}{20} + a_6 + a \right)$$

(10)

Where $T$ is temperature (Kelvin). For the range of $3500 \leq T \leq 5000$K, coefficients for calculating the equilibrium constant $K_i$. Substitution of the equilibrium constants from Eq-(10) and the curve-fit coefficient constants into Table 1 and rearranging to express mole factions of all species in terms of $y_5,y_4,y_2$ and $y_6$, the mole factions of CO,H$_2$,O$_2$ and N$_2$ respectively. The expressions resulted are four linear equations in four unknowns are as follows,

$$f_i(y_5,y_4,y_2,y_6) = 0$$

(11)
Where,

\[ C_1 y_5 y_5^{1/2} + C_2 y_4^{1/2} y_6^{1/2} + y_3 + y_4 + y_5 + y_6 + C_4 y_6^{1/2} + C_5 y_4^{1/2} y_6^{1/2} + C_3 y_4^{1/2} y_3^{1/2} + C_6 y_3^{1/2} -1 = 0 \]  \quad (12)

\[ 2C_2 y_4^{1/2} y_6^{1/2} + 2y_6 + C_4 y_6^{1/2} + C_3 y_4^{1/2} y_6^{1/2} - d_1 (C_4 y_6^{1/2} + y_5) = 0 \]  \quad (13)

\[ 2C_1 y_5 y_4^{1/2} + C_2 y_4^{1/2} y_6^{1/2} + 2y_4 + y_5 + C_5 y_4^{1/2} + C_3 y_4^{1/2} y_6^{1/2} + C_7 y_4^{1/2} y_3^{1/2} - d_1 (C_1 y_5 y_4^{1/2} + y_5) = 0 \]  \quad (14)

\[ 2C_2 y_4^{1/2} y_6^{1/2} + C_7 y_4^{1/2} y_3^{1/2} + C_6 y_3^{1/2} - d_3 (C_1 y_5 y_4^{1/2} + y_5) = 0 \]  \quad (15)

2.3 Numerical solution using modified iteration method for Combustion equation

In this study, Newton–Raphson method, Householder’s iteration method, Adomian Decomposition method and High order iteration Method were selected to solve equilibrium constants combustion equations of 11 combustion products of gasoline-air blend, which were summarized in Eqs. (12)–(15). This system can be written in more compact vector form as

\[ F(y) = \begin{bmatrix} f_1(y_1, y_4, y_5, y_6) \\ f_2(y_1, y_4, y_5, y_6) \\ f_3(y_1, y_4, y_5, y_6) \\ f_4(y_1, y_4, y_5, y_6) \end{bmatrix} \]  \quad (16)

The iteration method requires the evaluation of a matrix, known as the Jacobian (J) of the system. The that system is the elements of the Jacobian matrix, J for the previously derived combustion reaction equations are shown in Eq-(12) until Eq-(15). The stated values were obtained from mole fractions of these species in atmospheric air at room temperature.

The solution was unique as long as mole fractions of all 11 products species showed positive values. By using the stated initial guess, most of the results indicated almost constant values after tenth iterations, which shows that there were no convergence problems. Multiple solutions will be detected if the result showed negative value of mole fraction for one or more products that was due to wrong selection of initial guess. Furthermore, there was no result shown after 1000 iterations if divergence occurred.

2.3.1 Newton–Raphson method. The given equations can be solved by using the Newton Raphson method. The general form of Newton Raphson method for linear systems is

\[ Y_{k+1} = Y_k - \frac{f(x_k)}{f'(x_k)} \quad k=Iteration \]  \quad (18)

Each of these may be expanded in Taylor expansion of \( f(x) \) to a second order for Newton Raphson method,

\[ f_j + \frac{\partial f}{\partial y_3} \Delta y_3 + \frac{\partial f}{\partial y_4} \Delta y_4 + \frac{\partial f}{\partial y_5} \Delta y_5 + \frac{\partial f}{\partial y_6} \Delta y_6 \approx 0, \quad j = 1, 2, 3, 4 \]  \quad (19)

Functions \( f_j \) are evaluated from the solution of interested functions (Eq-(12) through Eq-(15). \( f_j = f_{(1,2,3,4)} \). The independent set of derivatives is obtained by solution of matrix equation that results
from differentiating with respect to mole faction. The above can be arranged as set of linear equations in the matrix form, \([A][Z] - [B] = 0\), where \([A] = \left[ \frac{\partial f}{\partial y} \right], [B] = [f_y], [Z] = [\Delta y] \)

2.3.2 Householder’s iteration method. The given equations can be solved by using Householder’s iteration method. The general form of Householder’s iteration method for linear systems

\[
\begin{align*}
(f(x_k) + f^2(x_k) f^r(x_k) f^{-2}(x_k)) + f^r(x_k)(Y_{K+1} - Y_k) &= 0 \\
(20)
\end{align*}
\]

Each of these may be expanded in Taylor expansion of \(f(x)\) to a higher order for Householder’s iteration method. That is,

\[
f_j = f(x_k) + f^2(x_k) f^r(x_k) f^{-2}(x_k)
\]

2.3.3 The Adomian Decomposition method. The given equations can be solved by using Adomian Decomposition method. The general form of Adomian Decomposition method for linear systems is

\[
f(x_k) + f^2(x_k) f^r(x_k) f^{-2}(x_k) + \frac{f^3(x_k) f^{-2}(x_k) f^{-4}(x_k)}{2} + f^r(x_k)(Y_{K+1} - Y_k) = 0 \\
(21)
\]

Each of these may be expanded in Taylor expansion of \(f(x)\) to a higher order for Adomian Decomposition method, that is

\[
f_j = f(x_k) + f^2(x_k) f^r(x_k) f^{-2}(x_k) + \frac{f^3(x_k) f^{-2}(x_k) f^{-4}(x_k)}{2}
\]

(22)

2.3.4 High order iteration method. The given equations can be solved by using High order iteration method. The general form of High order iteration method for linear systems is

\[
f(x_k) + f^2(x_k) f^r(x_k) f^{-2}(x_k) + \frac{f^3(x_k) f^{-2}(x_k) f^{-3}(x_k)}{6} + f^r(x_k)(Y_{K+1} - Y_k) = 0 \\
(23)
\]

Each of these may be expanded in Taylor expansion of \(f(x)\) to a higher order for High order iteration method.

\[
f_j = f(x_k) + f^2(x_k) f^r(x_k) f^{-2}(x_k) + \frac{f^3(x_k) f^{-2}(x_k) f^{-3}(x_k)}{6}
\]

(24)

2.4 Matlab inputs
In this study, Matlab program code for the combustion simulation has been developed. The input parameters such as Biogas+Air (C\(_5\)H\(_7\)O\(_2\)N+0.21O\(_2\)+0.79N\(_2\)), Gasoline+Air (C\(_7\)H\(_{17}\)+0.21O\(_2\)+0.79N\(_2\)) and Gasoline 50%+Biogas 50% by mole with air (0.5C\(_7\)H\(_{17}\)+0.5C\(_5\)H\(_7\)O\(_2\)N+0.21O\(_2\)+0.79N\(_2\)), respectively, after that substitution in term of equivalence ratio such as 0.5 to 2.0. Assuming the invariant adiabatic temperatures were 2,000-3,000 K with constant pressure was 50 atm and the difference of convergence was 1.0x10\(^{-10}\).

3. Results and discussion
This section presents summarized Eq-(12) through Eq-15 to illustrate the efficiency of the iterative method proposed in this paper. We compare the method [denoted by Iteration method] with Newton-
Raphson method (NRM), Householder’s iteration method (HoIM), Adomian Decomposition method (ADM), and High order iteration Method (HIM). The results were compared the number of iteration in each method obtained solution or mole fraction of combusions and difference value from Newton-Raphson method (NRM-HoIM, NRM-ADM and NRM-HIM).

Numerical computations have been carried out by using the software Matlab 2010. The results are presented in Table 3 for comparing with Newton-Raphson method of the mole fractions of H₂O, CO₂ and equivalence ratio 0.8-1.2, temperature 2000 K and 3000 K.

At low adiabatic temperature, 2000 K, the number of iterations of High order are less than the old method of Newton Raphson method in Table below, but the solutions computed by the new method are more exact and similar values. At high adiabatic temperature, 3000 K, the number of iterations of High order are more than the old method of Newton Raphson method in Table below but the solutions computed by the new method are more exact and similar values.

### Table 3. The obtained solution of the mole fractions of H₂O, CO₂

| Equivalence ratio 0.8 | Method   | Obtained Solution | Iteration |
|----------------------|----------|-------------------|-----------|
|                      | Mole fraction of H₂O, 2000 K |                  |
| NRM                  | 0.088661111630029 | 145              |
| HoIM                 | 0.088661134281620 | 145              |
| ADM                  | 0.088661134474148 | 145              |
| HIM                  | 0.106774699970414 | 146              |
| NRM-HoIM             | -0.000000026251591 |                 |
| NRM-ADM              | -0.00000002641429  |                 |
| NRM-HIM              | -0.000000026843268 |                 |

|                      | Mole fraction of CO₂, 2000 K |                  |
| NRM                  | 0.078560867873312 | 145              |
| HoIM                 | 0.078560894228601 | 145              |
| ADM                  | 0.07856094481443  | 145              |
| NRM-HoIM             | -0.000000026355289 |                 |
| NRM-ADM              | -0.000000026605991 |                 |
| NRM-HIM              | -0.000000026608131 |                 |

|                      | Mole fraction of H₂O, 3000 K |                  |
| NRM                  | 0.088690819062502 | 144              |
| HoIM                 | 0.088690844446441 | 188              |
| ADM                  | 0.088690844609297 | 231              |
| NRM-HoIM             | -0.000000025383938 |                 |
| NRM-ADM              | -0.000000025630471 |                 |
| NRM-HIM              | -0.000000025633157 |                 |

|                      | Mole fraction of CO₂, 3000 K |                  |
| NRM                  | 0.039869692159035 | 144              |
| HoIM                 | 0.039869706649732 | 188              |
| ADM                  | 0.039869706808635 | 231              |
| NRM-HoIM             | -0.000000014490697 |                 |
| NRM-ADM              | -0.000000014647799 |                 |
| NRM-HIM              | -0.000000014649570 |                 |

The results illustrating composition with temperature and equivalence ratio are given in figure 1 to 3 for the combustion of C₃H₆O₂N (Biogas), C₆H₁₇ (Gasoline) and gasoline-biogas blend as 50% by mole.
at $P=50$ bar. The largest mole fractions are $N_2$, $H_2O$ and $CO_2$. At this pressure, the composition predicted by using Newton Raphson method is a good approximation for all temperature 2000 K. At low pressure, dissociation is even greater. So that, at atmospheric pressure, Newton-Raphson method is low order iteration method which are valid for all temperature. The clean illustrating results was an experiential rise in product species such as $CO$, $NO$, $OH$, $O_2$, $O$, $H_2$ and $H$. For lean $\phi<1$ condition, the $O_2$ fraction is relatively insensitive to temperature. For rich condition, the $H_2$ mole fraction first decreases, then increases with increasing temperature.

4. Conclusions
The accuracy of the MATLAB program equilibrium combustion products routine was established through comparison with a comparable MATLAB program routine (Buttsworth[5]). Maximum differences in molar concentrations of less than 0.01% were typically apparent over the range of conditions calculated by the four routines (NRM, HoIM, ADM and HIM). Adiabatic flame temperature calculations (1500-3000 K) also confirmed that differences between the new Matlab routines and established results are typically less than the round-off errors in the established results around 0.1%.

**Figure 1.** Mole fraction of Biogas combustion products at Temperature 2000 K, Pressure 50 Bars

**Figure 2.** Mole fraction of Gasoline combustion products at Temperature 2000 K, Pressure 50 Bars
Figure 3. Mole fraction of Gasoline (50%) and Biogas (50%) combustion products at Temperature 2000 K, Pressure 50 Bars

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