

## Thermodynamic Properties models for unburned mixtures and combustion gases in internal combustion engines

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**Abstract:**

*This paper describes a simple model for calculating the thermodynamic properties by mathematical models for unburned mixtures and combustion gases in internal combustion engines. The fuels used in this paper are methane, propane, hexane, Iso-octane, gasoline, and natural gas. Functions that estimate the thermodynamic curve fit coefficients for a variety of fuel, air, and combustion product species are described, the coefficients for these polynomial functions are obtained by least square method with property data from the JANAF tables [1]. The model of Olikara and Borman is also presented to calculate the equilibrium state of combustion products at high temperatures and pressure is set at 1 bar. This model was written in MATLAB. Also a model was developed to calculate the amount of theoretical and actual air and lower heating value for any composition for natural gas. The model was validated by mathematical calculations. The model was validated by experimental data found in the literature for various fuels.*

**Keywords:** models fraction, unburned mixtures, combustion gases, equilibrium.

Date of Submission: 22-11-2020

Date of Acceptance: 07-12-2020

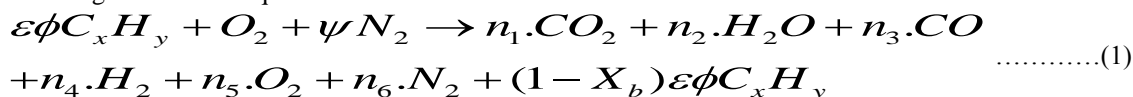
### I. Introduction:

During the last years numerous researchers have made effort for calculate thermodynamics properties for various fuels in internal combustion engine cylinder. Most internal combustion engine depend on the combustion of hydrocarbon fuels, as gasoline, methane and natural gas, etc. The combustion chamber is divided into two zones consisting of unburned gas (mixture of fuel, air and residuals) and burned gas (combustion products), Both zones are assumed to have the same uniform in-cylinder pressure, the burned zone are assumed in chemical equilibrium during combustion and for main expansion stroke, while near the end of the expansion process the mixture is assumed frozen [1][2]. The thermodynamic properties for the unburned and the burned mixture are needed for the description of the gases. These are related to the mixture composition given by the mass fraction or the mole fraction. From the composition and the thermodynamic state properties (P,T) we can find all the other properties. The methods employed are most accurate to the lean side of stoichiometry, since the rich mixture is chemically more complex.

#### 1- Calculations of methane, propane, hexane, Iso-octane, gasoline:

**Combustion reaction:**

The calculations are based on the moles fractions of components of mixtures and products according to the following combustion equation:



Where:

$$x = MWF / (12 + HCR.1) \quad \dots\dots\dots(2)$$

$$y = HCR.x$$

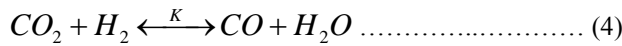
$$\varepsilon = \frac{4}{4x + y} \quad \dots\dots\dots(3)$$

Consider the burned and unburned gases separately  $n_i$  determined by using following assumption:

- For lean mixtures CO, H<sub>2</sub> can be neglected.
- For rich mixtures O<sub>2</sub> can be neglected. And  $n_3$  will be determined from the water gas reaction.

For the rich case, there are not enough equations to solve the problem. Equilibrium consideration between the product species CO<sub>2</sub>, H<sub>2</sub>O, CO and H<sub>2</sub> is assumed to determine the product composition.

The water gas reaction:



The equilibrium constant K(T) equation is a curve fit of the JANAF Table as :

$$K(T) = \exp(2.743 - 1.761 * 10^3 * \left(\frac{1}{T}\right) - 1.611 * 10^6 * \left(\frac{1}{T^2}\right) + 0.2803 * 10^9 * \left(\frac{1}{T^3}\right) \dots\dots\dots (5)$$

The relation between the equilibrium constant and partial pressure of species:

$$K(T) = \frac{P_{CO}P_{H_2O}}{P_{CO_2}P_{H_2}} \dots\dots\dots (6)$$

Gives a quadratic equation for  $n_3$  :

$$(1 - K)n_3^2 + \left\{ \frac{1}{2} \varepsilon \phi y - 2(\phi - 1) + [2(\phi - 1) + \varepsilon \phi x]K \right\} n_3 \dots\dots\dots (7)$$

$$-2\varepsilon \phi x(\phi - 1)K = 0$$

$n_3$  is given by solution of quadratic equation:

$$n_3 = \frac{-b + \sqrt{b^2 - 4.a.c}}{2.a} \dots\dots\dots (8)$$

$$a = (1 - K)$$

$$b = \frac{1}{2} \varepsilon \phi y - 2(\phi - 1) + [2(\phi - 1) + \varepsilon \phi x]K$$

$$c = -2\varepsilon \phi x(\phi - 1)K$$

$$d = [2 * (\phi - 1) + \varepsilon \phi x] * K$$

The number of moles of each species in burned mixture and unburned mixture summarized in Tables (1) and (2) [1].

**Table 1: Burned gas composition species:**

Species	$n_i$ , moles/mole $O_2$ reactant	
	$\phi \leq 1$	$\phi > 1$
$CO_2$	$\varepsilon \phi$	$\varepsilon \phi - n_3$
$H_2O$	$2(1 - \varepsilon)\phi$	$2(1 - \varepsilon \phi) + n_3$
$CO$	0	$n_3$
$H_2$	0	$2(\phi - 1) - n_3$
$O_2$	$1 - \phi$	0
$N_2$	$\psi$	$\psi$

**Table 2: Unburned mixture composition**

Species	$n_i$ , moles/mole $O_2$ reactant	
	$\phi \leq 1$	$\phi > 1$
Fuel	$4(1 - X_b)(1 + 2\varepsilon)\phi / M_f$	$4(1 - X_b)(1 + 2\varepsilon)\phi / M_f$
$O_2$	$1 - X_b\phi$	$1 - X_b$
$N_2$	$\psi$	$\psi$
$CO_2$	$X_b\varepsilon\phi$	$X_b(\varepsilon\phi - n_3)$
$H_2O$	$2X_b(1 - \varepsilon)\phi$	$X_b[2(1 - \varepsilon\phi) + n_3]$
$CO$	0	$X_b n_3$
$H_2$	0	$X_b[2(\phi - 1) - n_3]$

Where mole fraction are given by :

$$x_i = \frac{n_i}{n_{b,u}} \dots\dots\dots (9)$$

Mole fraction of residual gas:

$$X_{res} = \frac{1}{1 + \frac{M_b}{M_{fa}} \left( \frac{1}{f} - 1 \right)} \dots\dots\dots (10)$$

Where

$$n_{b,u} = \sum_i n_i \dots\dots\dots (11)$$

The partial derivative of  $n_3$  with respect to T we can get it from equations (5) and (8) :

$$\frac{\partial n_3}{\partial T} = \frac{\partial n_3}{\partial K} \frac{\partial K}{\partial T} \dots\dots\dots (12)$$

Where the first part on the right hand side is:

$$\frac{\partial n_3}{\partial K} = \frac{n_3^2 - d * n_3 + c}{a * n_3 + b} \dots\dots\dots(13)$$

And the second part is:

$$\frac{dK}{dT} = K(-1.761 - 3.222 * 10^3 * \frac{1}{T} + 0.8409 * 10^6 * \frac{1}{T^2}) \dots\dots\dots (14)$$

**II. Natural gas calculations**

Natural gas is a naturally occurring hydrocarbon gas mixture consisting largely of methane ( $CH_4$ ) and ethane ( $C_2H_6$ ), with also propane ( $C_3H_8$ ), butane ( $C_4H_{10}$ ), pentane ( $C_5H_{12}$ ), hexane ( $C_6H_{14}$ ), nitrogen ( $N_2$ ), carbon dioxide ( $CO_2$ ), and hydrogen sulfide ( $H_2S$ ).

- **Natural gas theoretical amount air:**

$$(V_a)_{th} = 4.75 \left[ \begin{array}{l} 0.5CO + 0.5H_2 + 2CH_4 + \\ (x + \frac{y}{4})C_xH_y + 1.5H_2S - O_2 \end{array} \right] .0.01 \dots\dots\dots (15)$$

- **Actual amount of the air:**

$$(V_a)_{act} = \phi \cdot (V_a)_{th} \dots\dots\dots (16)$$

**Moles numbers of natural gas combustion products:**

$$n_{CO_2} = (CO_2 + CO + CH_4 + \sum n.C_nH_m)0.01 \dots\dots\dots (17)$$

$$n_{H_2O} = \left[ \begin{array}{l} H_2 + H_2S + 2CH_4 + \frac{y}{2} C_xH_y \\ + H_2O + 0.124.g_a.(V_a)_{act} \end{array} \right] 0.01 \dots\dots\dots (18)$$

$$n_{SO_2} = 0.01H_2S \dots\dots\dots (19)$$

$$n_{O_2} = 0.21(n-1)(V_a)_{th} \dots\dots\dots (20)$$

$$n_{N_2} = [N_2 + 79(V_a)_{act}]0.01 \dots\dots\dots (21)$$

**Lower heating value of natural gas:**

The lower heating value of natural gas is the total heat liberated by the combustion of all the combustible components. Thus the lower heating value  $Q_L$  of natural gas fuel with the given composition is calculated as follows:

$$\begin{aligned} Q_L = & 126CO + 107.6H_2 + 358CH_4 + 590.37C_2H_4 \\ & + 635C_2H_6 + 915C_3H_8 + 1180C_4H_{10} \dots\dots\dots (22) \\ & + 1460C_5H_{12} + 147.3H_2S \end{aligned}$$

**III. The thermodynamic relations:**

**For burned zone:**

Gordon and McBride [3], proposed the following expressions that were curve-fitted to the tabulated JANAF Thermochemical tables

For each species  $i$  in its standard state at temperature  $T(K)$ , the specific heat is approximated by:

$$\frac{c_{p,i}}{R} = a_{i1} + a_{i2}T + a_{i3}T^2 + a_{i4}T^3 + a_{i5}T^4 \dots\dots\dots (23)$$

The standard state enthalpy of species  $i$  is then given by:

$$\frac{h_i}{RT} = a_{i1} + \frac{a_{i2}}{2}T + \frac{a_{i3}}{3}T^2 + \frac{a_{i4}}{4}T^3 + \frac{a_{i5}}{5}T^4 + \frac{a_{i6}}{T} \dots\dots\dots (24)$$

The standard state entropy of species  $i$  at temperature  $T(K)$ :

$$\frac{s_i}{R} = a_{i1} \ln T + a_{i2}T + \frac{a_{i3}}{2}T^2 + \frac{a_{i4}}{3}T^3 + \frac{a_{i5}}{4}T^4 + a_{i7} \dots\dots\dots (25)$$

Where  $c_p$  is the specific heat at constant pressure,  $h$  is the specific enthalpy and  $s$  is the specific entropy. The coefficients  $a_1$  to  $a_7$  are given in table and calculated over two different temperature ranges: (1)  $300 < T < 1000$  K; and (2)  $1000 < T < 5000$  K [1].

**For unburned zone:**

Heywood [1] has represented the thermodynamic properties of fuels (in vapor phase) using curves that slightly differ from (23) (24). Polynomial functions for various fuels:

$$c_{p,f} = A_{f1} + A_{f2}t + A_{f3}t^2 + A_{f4}t^3 + \frac{A_{f5}}{t^2} \dots\dots\dots (26)$$

$$h_f = A_{f1}t + A_{f2} \frac{t^2}{2} + A_{f3} \frac{t^3}{3} + A_{f4} \frac{t^4}{4} - \frac{A_{f5}}{t} + A_{f6} + A_{f8} \dots\dots\dots (27)$$

Where:  $t = T(K)/1000$

**For mixture (burned and unburned zones and residual gas):**

The specific heat, enthalpy and entropy of the mixture inside the combustion chamber can be calculated as following:

$$c_p = \sum X_i \cdot c_{pi}$$

$$h = \sum X_i \cdot h_i$$

$$s = \sum X_i \cdot s_i$$

#### IV. Simulation Results:

Having formulated the mathematical framework, we simulate specific heat, enthalpy, entropy and specific heat ratio for IC cylinder mixture for both stoichiometric and lean mixture. The model running on methane, propane, gasoline, hexane and Iso-octane. It can be seen from the below figures (1-8) that the specific heat, enthalpy and entropy increases as the temperature increases. The figure (9) show the methane specific heat ratio based on the results of the equilibrium combustion model for burned and unburned mixtures at various equivalence ratios, where It can be seen that the specific heat ratio decreases as the temperature increases, while it increases as the equivalence ratio increases.

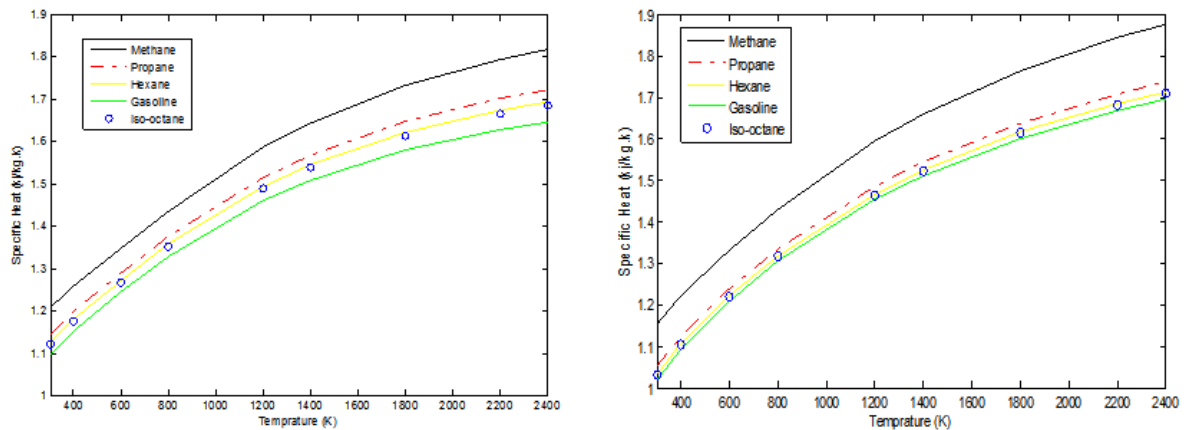
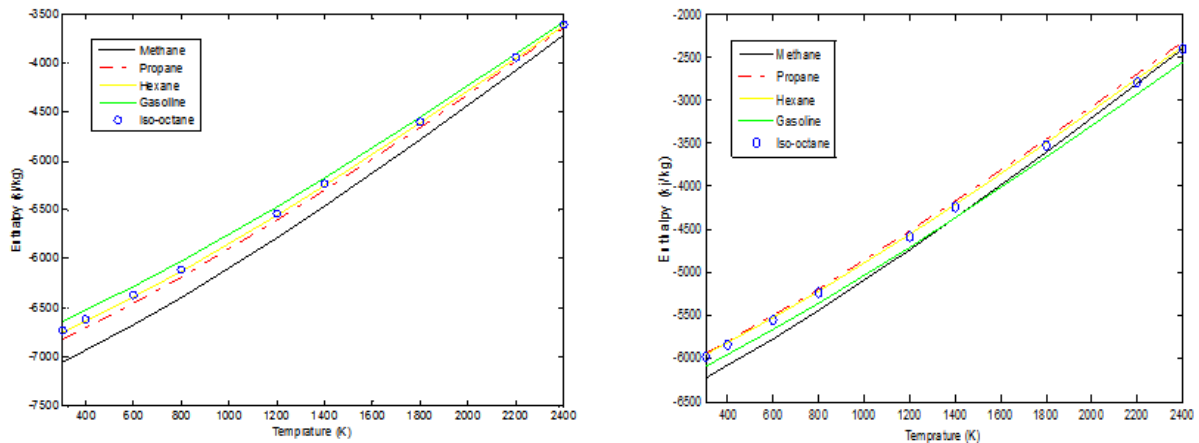
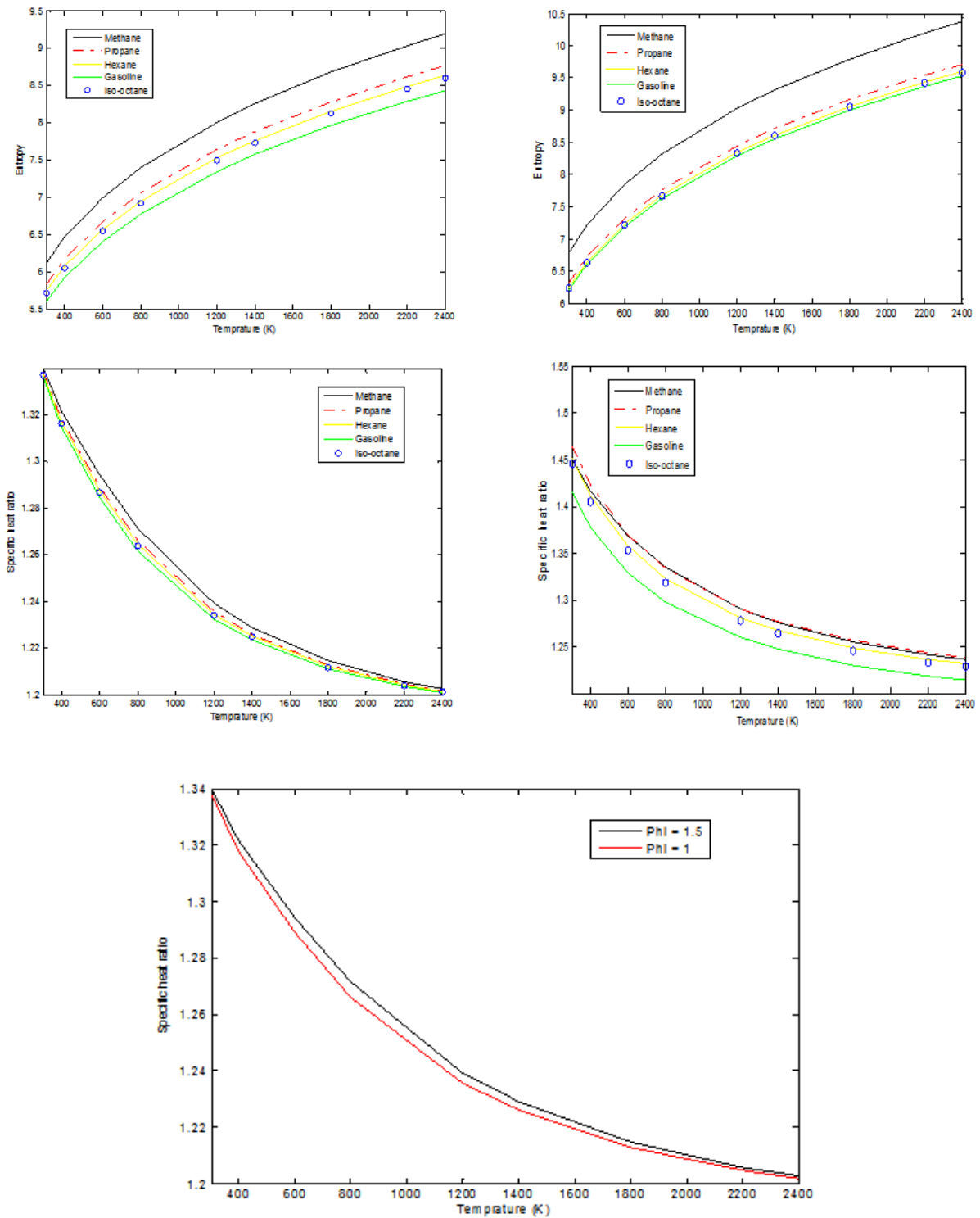


Fig. 1 : Variations of specific heat with T(K) at (Phi = 1)





**V. Conclusion:**

The present paper achieves its goal by being a simple, fast and accurate thermodynamic properties simulation model. The simulation results have shown that the model can be used as a first-degree approximation and is useful in numerous IC engine applications including general design predictions. The model can predict an array of thermodynamic properties and combustion process and easily adapt to any alternate hydrocarbon fuels. Also the model can predict the natural gas combustion products, lower heating value and actual amount of the air for any natural gas chemical composition.

### **FUTURE WORK:**

The future work it will be calculating specific heat, enthalpy, entropy and specific heat ratio for natural gas and hydrogen fuels and compared the model results with experimental results.

### **NOMENCLATURE**

$\varepsilon$	stoichiometric mole fuel oxygen ration.
$\Phi$	equivalence ratio.
$x$	number of carbon atoms in fuel molecules.
$y$	number of hydrogen atoms in fuel molecules.
$X_b$	burned mass fraction of the fuel.
$\Psi$	molar N:O ratio of the air.
$n_i$	moles of species $i$ per of $O_2$ reactant.
HCR	ration of hydrogen to carbon in fuel.
MWF	molecular weight of fuel.
$K(T)$	equilibrium constant.
$P_i$	partial pressure of species.
$(V_a)_{th}$	theoretical air amount of natural gas.
$(V_a)_{act}$	actual air amount of natural gas.
$Q_L$	lower heating value of natural gas.
$X_{res}$	mole fraction of residual gas.
$M_b$	molecular weight of burned zone.
$M_{fa}$	molecular weight of unburned zone.
$f$	residual mass fraction.
$c_{pi}$	specific heat of the species.
$h_i$	specific enthalpy of the species.
$S_i$	specific entropy of the species.

### **Acknowledgments**

The author are thankful to the Libyan government for financial support and Tobruk University for providing the necessary facilities.

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Hassan A. Khairallah. "Thermodynamic Properties models for unburned mixtures and combustion gases in internal combustion engines." *IOSR Journal of Mechanical and Civil Engineering (IOSR-JMCE)*, 17(6), 2020, pp. 38-44.