

Volumetric Analysis of a Gaseous Fuel Containing Methane, Ethane and Propane

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ABSTRACT

Most gaseous fuels and liquid fuels are mixtures of multiple chemical compounds. In recent years, these mixtures became more complicated when the suppliers started to admix bio-fuels into the petrochemical basic fuels. In the volumetric analysis of methane, ethane and propane in the process of combustion, one takes into cognizance the effects of the presence or absence of each constituent in determining the efficiency of industrial machines. As the properties of such mixtures can vary with composition, there is a need for reliable analytical techniques in order to ensure stable operation of devices such as internal combustion engines and gas turbines. The focus of the paper lies on gaseous and liquid fuels, which are dominant in the transportation sector and in the distributed generation of power. Besides introduction to the physical principles and review of the literature, various techniques are critically discussed and compared with each other. Also, equation can only be solved by iterative trials and error procedure using sensible enthalpy vs temperature components. The knock resistance for a given gaseous fuel mixture is expressed as an equivalent fraction of propane in methane, under identical engine conditions.

1. Introduction

In this paper, we introduce the chemistry and thermodynamics of combustion of methane, ethane and propane as hydrocarbon fuels - (C_xH_y), in which the oxydizer is the oxygen contained in atmospheric air. Note that we will not cover the combustion of solid fuels or the complex blends and mixtures of the hydrocarbons which make up gasoline, kerosene, or diesel fuels. Modern energy conversion technology relies on primary sources based on fossil as well as renewable fuels. Gas analysis is so paramount; and must be made rapidly and accurately to ascertain its pureness. Methane and ethane have low heating capacity compare to propane on a volumetric basis. Propane, on the other hand, has lower anti-knocking property than methane, thus reduces methane number [1-5]. Gaseous and liquid fuels represent the major part of the energy mix. This is illustrated in Figure 1 based on data from the recent EU Energy in Figures Pocketbook 2014 [6-7]. These latest figures from 2011 suggest that ~53% of the overall global fuel consumption is related to fossil oil and gas resources. The third large slice with ~29% represents solid fuels like coal. Coal and other solid fuels are commonly used in large scale power plants for base load coverage. On the other hand, mobile and flexible energy conversion technology, including automotive propulsion and gas turbines for balancing peak electricity demands, are predominantly based on gaseous and liquid fuels. In the following, the term fuel refers to gases and liquids, and solids will not be covered [8-12].

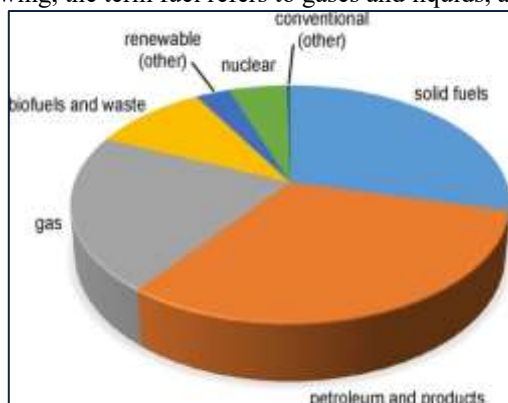
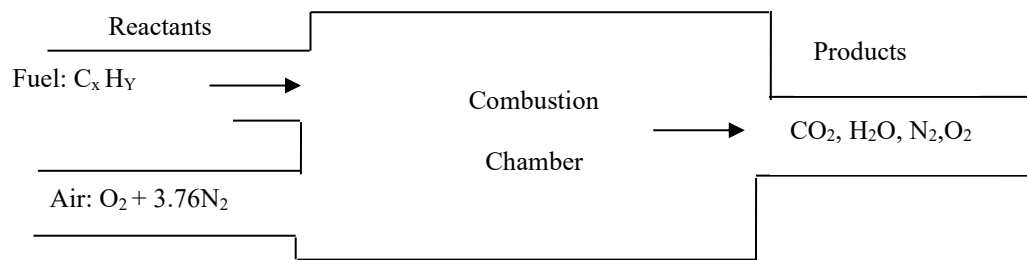


Figure 1: World gross inland consumption by fuel. The “renewable (other)” slice comprises hydro, geothermal, solar, and wind power. The data are taken from the EU Energy in Figures Pocketbook 2014 [6].

Many commercial fuels are, nowadays, blends of a fraction from the petrochemical industry (like natural gas, gasoline, and diesel) and a bio-fuel (like biogas, bio-ethanol or biodiesel). When fuels are blended, the physicochemical properties and hence the performance in an engine may vary substantially [11]. Atmospheric air contains approximately 21% oxygen (O_2) by volume. The other 79% of “other gases” is mostly nitrogen (N_2), so we will assume air to be composed of 21% oxygen and 79% nitrogen by volume. Thus each mole of oxygen needed to oxidize the hydrocarbon is accompanied by $79/21 = 3.76$ moles of nitrogen. Using this combination the molecular mass of air becomes 29 [kg/kmol].

The First Law Analysis of Combustion - The main purpose of combustion is to produce heat through a change of enthalpy from the reactants to the products. From the First Law equation in a control volume, ignoring kinetic and potential energy changes and assuming no work is done, we have:



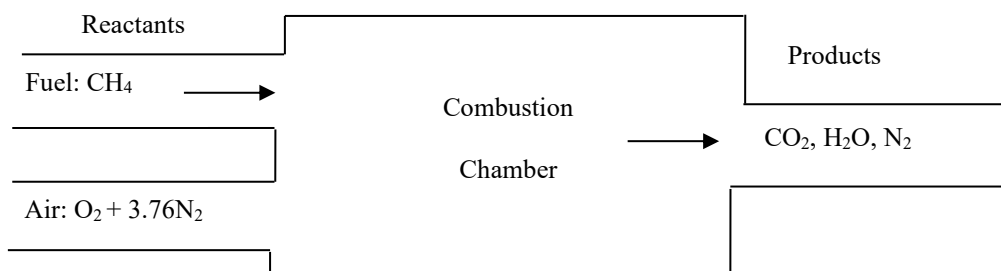
Where z is known as the stoichiometric coefficient for the oxidizer (air)

Note that this reaction yields five unknowns: z, a, b, c, d , thus we need five equations to solve. Stoichiometric combustion assumes that no excess oxygen exists in the products, thus $d = 0$. We obtain the other four equations from balancing the number of atoms of each element in the reactants (carbon, hydrogen, oxygen and nitrogen) with the number of atoms of those elements in the products. This means that no atoms are destroyed or lost in a combustion reaction [13-19].

Atoms of those elements in the products, means that no atoms are destroyed or lost in a combustion reaction, see Table 1 below;

Element	Amount in reactants	=	Amount in Products	Reduced equation
Carbon (C)	X		A	$a = x$
Hydrogen (H)	Y		$2b$	$b = y/2$
Oxygen (O)	$2z$		$2a+b$	$z = a + b/2$
Nitrogen (N)	$2(3.76)z$		$2c$	$c = 3.76z$

Note that the water formed could be in the vapor or liquid phase, depending on the temperature and pressure of the combustion products. As an example consider the stoichiometric combustion of methane (CH_4) in atmospheric air. Equating the molar coefficients of the reactants and the products we obtain:



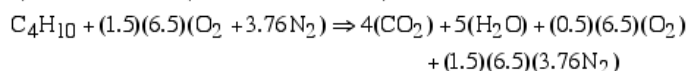
Theoretical Air and Air-Fuel Ratio -The minimum amount of air which will allow the complete combustion of the fuel is called the Theoretical Air (also referred to as Stoichiometric Air). In this case the products do not contain any oxygen. If we supply less than theoretical air then the products could include carbon monoxide (CO), thus it is normal practice to supply more than theoretical air to prevent this occurrence [20]. This Excess Air will result in oxygen appearing in the products.

The standard measure of the amount of air used in a combustion process is the Air-Fuel Ratio (AF), defined as follows:

$$AF = \frac{m_{\text{air}}}{m_{\text{fuel}}}$$

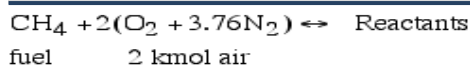
Thus considering only the reactants of the methane combustion with theoretical air presented above, we obtain:

b) 50% Excess air (150% Theoretical air):



$$50\% \text{ Excess } AF = \frac{m_{\text{air}}}{m_{\text{fuel}}} = \frac{9.75(4.76) \left[\frac{\text{kg}}{\text{kmol}} \right] 29}{1 \left[\frac{\text{kg}}{\text{kmol}} \right] (4(12) + 10) \left[\frac{\text{kg}}{\text{kmol}} \right]}$$

$$AF = 23.2 \frac{\text{kg-air}}{\text{kg-fuel}}$$



$$AF = \frac{m_{\text{air}}}{m_{\text{fuel}}} = \frac{2(4.76) [\text{kmol}] \cdot 29 \left[\frac{\text{kg}}{\text{kmol}} \right]}{1 [\text{kmol}] (12 + 4) \left[\frac{\text{kg}}{\text{kmol}} \right]}$$

$$AF = 17.3 \frac{\text{kg-air}}{\text{kg-fuel}}$$

2. Materials and Method

Combustion always occurs at elevated temperatures and we assume that all the products of combustion (including the water vapor) behave as ideal gases. Since they have different gas constants, it is convenient to use the ideal gas equation of state in terms of the universal gas constant, as follows:

$$P \cdot V = m \cdot R \cdot T = \frac{m}{M} R \cdot M \cdot T$$

where: m is mass [kg], V is volume [m^3], P is pressure [kPa] and T is temperature [K]

$$R \left[\frac{\text{kJ}}{\text{kg} \cdot \text{K}} \right] \text{ is the gas constant}$$

$$M \left[\frac{\text{kg}}{\text{kmol}} \right] \text{ is the molar mass of the substance}$$

$$\text{thus: } P \cdot V = N \cdot R_u \cdot T$$

where: $R_u = R \cdot M = 8.314 \left[\frac{\text{kJ}}{\text{kmol} \cdot \text{K}} \right]$ is the Universal Gas Constant

$$N = \frac{m}{M} \text{ is the number of kmols}$$

The mechanism used to compute the auto-ignition delay time is optimized based on RCM measurements performed at engine conditions. After optimization, the knock resistance is measured by the knock-limited spark timing (KLST) and calculated using PKI. These were found to agree within the uncertainty of the measurement (0.75Oca) for all fuels. In the analysis of the products of combustion there are a number of items of interest [21]:

- What is the percentage volume of specific products, in particular carbon dioxide (CO_2) and carbon monoxide (CO)?
- What is the dew point of the water vapor in the combustion products? This requires evaluation of the partial pressure of the water vapor component of the products.
- There are experimental methods of volumetric analysis of the products of combustion, normally done on a **Dry Basis**, yielding the volume percentage of all the components except the water vapor. This allows a simple method of determining the actual air-fuel ratio and excess air used in a combustion process.

For ideal gases we find that the mole fraction y_i of the i 'th component in a mixture of gases at a specific pressure P and temperature T is equal to the volume fraction of that component.

Since from the molar ideal gas relation: $P \cdot V = N \cdot R_u \cdot T$, we have [22-30]:

$$y_i = \frac{N_i}{N} = \frac{P \cdot V_i / R_u \cdot T}{P \cdot V / R_u \cdot T} = \frac{V_i}{V}$$

Furthermore, since the sum of the component volumes V_i must equal the total volume V , we have:

$$\sum_{i=1}^n y_i = 1$$

Using a similar approach we determine the partial pressure of a component using Dalton's Law of Partial Pressures:

$$P = P_1 + P_2 + P_3 + \dots$$

where: $P_i = \frac{N_i \cdot R_u \cdot T}{V}$ is the partial pressure of the i 'th component assuming that it occupies the entire volume V

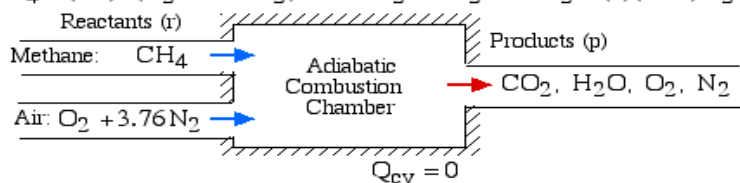
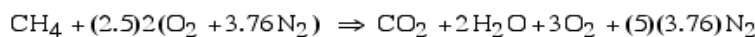
$$\text{thus: } \frac{P_i}{P} = \frac{N_i \cdot R_u \cdot T / V}{N \cdot R_u \cdot T / V} = \frac{N_i}{N} = y_i$$

3. Results and Discussion

3.1 Analysis of combustion of Methane

Determine the adiabatic flame temperature for the complete combustion of Methane (CH_4) with 250% theoretical air in an adiabatic control volume.

250% Theoretical air:



$$Q_{cv} = 0 = \sum_p N_p h_p - \sum_r N_r h_r$$

$$0 = \sum_p N_p [h_f^\circ + h(T)]_p - \sum_r N_r [h_f^\circ + h(T)]_r$$

where: $h(T)$ is the sensible enthalpy as a function of temperature T

thus since the reactants are assumed to be at 25°C :

$$1[-393,520 + h(T)] + 2[-241,820 + h(T)] + 3[h(T)] + 18.8[h(T)] = 1(-74,850)$$

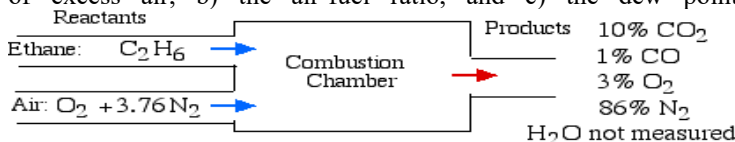
$$\begin{array}{ccccc} \uparrow & \uparrow & \uparrow & \uparrow & \uparrow \\ \text{CO}_2 & \text{H}_2\text{O} & \text{O}_2 & \text{N}_2 & \text{CH}_4 \end{array}$$

Simplifying:

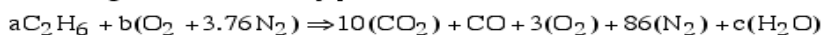
$$h(T)\text{CO}_2 + 2[h(T)\text{H}_2\text{O}] + 3[h(T)\text{O}_2] + 18.8[h(T)\text{N}_2] = 802,310 \left[\frac{\text{kJ}}{\text{kmol fuel}} \right]$$

3.2 Analysis of Combustion of Ethane

In this analysis, Ethane (C_2H_6) is burned with atmospheric air, and the volumetric analysis of the dry products of combustion is determined the following: 10% CO_2 , 1% CO , 3% O_2 , and 86% N_2 . Also, the combustion equation, and determine a) the percentage of excess air, b) the air-fuel ratio, and c) the dew point of the combustion products are separately calculated.



Assuming 100 kmols of dry products:



equating coefficients for each component:

$$\text{nitrogen N}_2: b = \frac{86}{3.76} = 22.87$$

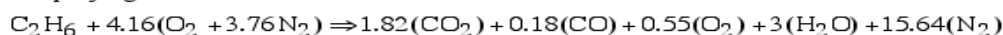
$$\text{carbon C: } 2a = 10 + 1 \Rightarrow a = 5.5$$

$$\text{hydrogen H: } 6a = 2c \Rightarrow c = 3a = 16.5$$

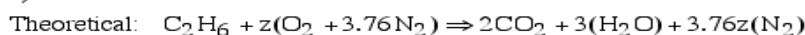
thus:



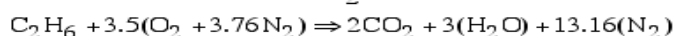
Simplifying for 1 kmol fuel:



a) determine % excess air:



equating coefficients, $z = 2 + \frac{3}{2} = 3.5$ (oxygen component balance), thus:



$$\% \text{ Theoretical air} = \frac{4.16}{3.5} = 1.19 \Rightarrow 119\%$$

thus % Excess air = 19%

$$\text{b) Air - fuel ratio: } AF = \frac{m_{\text{air}}}{m_{\text{fuel}}} = \frac{4.16(4.76) \left[\frac{\text{kg}}{\text{kmol}} \right]}{1 \left[\frac{\text{kg}}{\text{kmol}} \right] (2(12) + 6) \left[\frac{\text{kg}}{\text{kmol}} \right]}$$

$$AF = 19.1 \frac{\text{kg - air}}{\text{kg - fuel}}$$

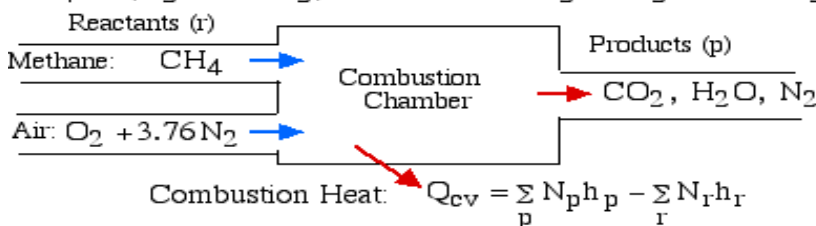
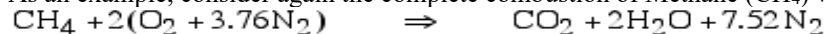
$$\text{c) Dew - point: } N_{\text{H}_2\text{O}} = 3, N_{\text{total}} = 1.82 + 0.18 + 0.55 + 3 + 15.64 = 21.19$$

$$\frac{P_{\text{H}_2\text{O}}}{P} = \frac{N_{\text{H}_2\text{O}}}{N_{\text{total}}} = \frac{3}{21.19} \Rightarrow P_{\text{H}_2\text{O}} = (101.32 \text{ kPa}) \left[\frac{3}{21.19} \right] = 14 \text{ kPa}$$

$$T_{\text{dew-point}} = T_{\text{sat}@14\text{kPa}} \approx 53^\circ\text{C}$$

3.2.1 Combustion Molar Enthalpy Tables

As an example, consider again the complete combustion of Methane (CH_4) with theoretical air:



Notice that in the reactants and the products of the above example we have basic elements O_2 and N_2 as well as compounds CH_4 , CO_2 , and H_2O . When the compound is formed then the enthalpy change is called the Enthalpy of Formation, denoted h_f° , and for our example:

Substance	Formula	h_f° [kJ/kmol]
Carbon dioxide	$\text{CO}_2(\text{g})$	-393,520
Water Vapor	$\text{H}_2\text{O}(\text{g})$	-241,820
Water	$\text{H}_2\text{O}(\text{l})$	-285,820
Methane	$\text{CH}_4(\text{g})$	-74,850

Where (g) refers to gas and (l) refers to liquid.

The negative sign means that the process is Exothermic, i.e. heat is given off when the compound is formed. Note that the enthalpy of formation of basic elements O_2 and N_2 is zero. Consider first the case in which there is sufficient heat transfer such that both the reactants and the products are at 25°C and 1 atm pressure, and that the water product is liquid. Since there is no sensible enthalpy change the energy equation becomes:

$$Q_{cv} = \sum_p N_p (h_f^\circ)_p - \sum_r N_r (h_f^\circ)_r$$

$$= 1(-393,520) + 2(-285,820) - 1(-74,850)$$

$$Q_{cv} = -890,310 \left[\frac{\text{kJ}}{\text{kmol fuel}} \right] \rightarrow$$

on a unit mass basis:

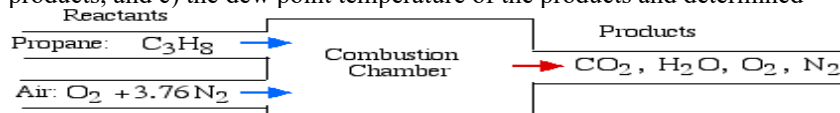
$$q_{cv} = \left[\frac{Q_{cv}}{M_{\text{CH}_4}} \right] = \frac{-890,310}{(12 + 4)} = -55,644 \left[\frac{\text{kJ}}{\text{kg fuel}} \right] \rightarrow$$

This heat (Q_{cv}) is called the Enthalpy of Combustion or the Heating Value of the fuel. If the products contain liquid water then it is the Higher Heating Value (as in our example), however if the product contains water vapor then it is the Lower Heating Value of the fuel. The enthalpy of combustion is the largest amount of heat that can be released by a given fuel.

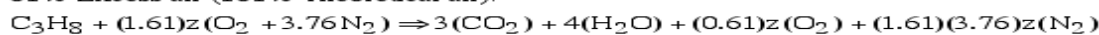
Adiabatic Flame Temperature - The opposite extreme of the above example in which we evaluated the enthalpy of combustion is the case of an adiabatic process in which no heat is released. This results in a significant temperature increase in the products of combustion (denoted by the Adiabatic Flame Temperature) which can only be reduced by an increase in the air-fuel ratio.

3.3 Analysis of Combustion of Propane

Here, Propane (C_3H_8) is burned with 61% excess air, which enters a combustion chamber at 25°C . Assuming complete combustion and a total pressure of 1 atm (101.32 kPa), the air-fuel ratio [kg-air/kg-fuel], the percentage of carbon dioxide by volume in the products, and c) the dew point temperature of the products and determined



61% Excess air (161% Theoretical air):



equating coefficients, $z = 3 + 2 = 5$ (oxygen component balance), thus:



$$\text{a) } AF = \frac{m_{\text{air}}}{m_{\text{fuel}}} = \frac{8.05(4.76) [\text{kmol}] 29 \left[\frac{\text{kg}}{\text{kmol}} \right]}{1 [\text{kmol}] (3(12) + 8) \left[\frac{\text{kg}}{\text{kmol}} \right]}$$

$$AF = 25.3 \frac{\text{kg-air}}{\text{kg-fuel}} \rightarrow$$

$$\text{b) } N_{\text{CO}_2} = 3, \quad N_{\text{total}} = 3 + 4 + 3.05 + 30.27 = 40.32$$

$$\frac{V_{\text{CO}_2}}{V_{\text{total}}} = \frac{N_{\text{CO}_2}}{N_{\text{total}}} = \frac{3}{40.32} = 0.074 \Rightarrow \% \text{CO}_2 = 7.4\% \rightarrow$$

$$\text{c) } N_{\text{H}_2\text{O}} = 4, \quad \frac{P_{\text{H}_2\text{O}}}{P} = \frac{N_{\text{H}_2\text{O}}}{N_{\text{total}}} = \frac{4}{40.32} \Rightarrow P_{\text{H}_2\text{O}} = (101.32 \text{ kPa}) \left[\frac{4}{40.32} \right] = 10.05 \text{ kPa}$$

$$T_{\text{dew-point}} = T_{\text{sat}@10\text{kPa}} = 45.8^\circ\text{C} \rightarrow$$

This equation can only be solved by an iterative trial and error procedure using the tables of Sensible Enthalpy vs Temperature for all four components of the products - CO₂, H₂O, O₂, and N₂. A quick approximation to the adiabatic flame temperature can be obtained by assuming that the products consist entirely of air. This approach was introduced to us by Potter and Somerton in their Schaum's Outline of Thermodynamics for Engineers, in which they assumed all the products to be N₂. We find it more convenient to use air assuming a representative value of the Specific Heat Capacity of Air: C_{p,1000K} = 1.142 [kJ/kg.K].

Thus summing all the moles of the products we have:

$$N_{\text{total}} = 1 + 2 + 3 + 18.8 = 24.8 \text{ kmols products.}$$

$$24.8[h(T) - h^{\circ}]_{\text{air}} = 24.8(M_{\text{air}})(C_{p,1000K})(T_{\text{adiabatic}} - 298K) = 802,310 \left[\frac{\text{kJ}}{\text{kmol fuel}} \right]$$

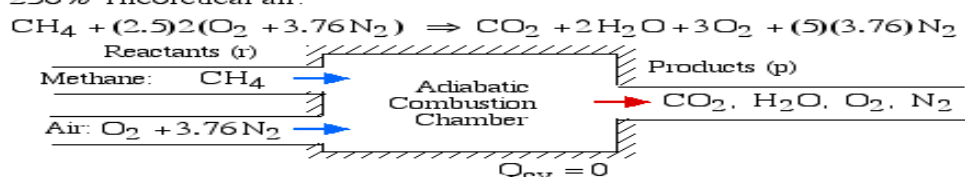
where: $M_{\text{air}} = 29 \left[\frac{\text{kg}}{\text{kmol}} \right]$ is the molecular mass of air

$C_{p,1000K} = 1.142 \left[\frac{\text{kJ}}{\text{kg.K}} \right]$ is the specific heat capacity of air

thus solving: $T_{\text{adiabatic}} = 1275K$ (assuming that all the products are air)

Using the tables of Sensible Enthalpy vs Temperature we evaluated the enthalpy of all four products at a temperature of 1280K. This resulted in a total enthalpy of 802,410 [kJ/kmol fuel], which is extremely close to the required value, thus justifying this approach.

250% Theoretical air:



$$Q_{cv} = 0 = \sum_p N_p h_p - \sum_r N_r h_r$$

$$0 = \sum_p N_p [h_f^{\circ} + h(T)]_p - \sum_r N_r [h_f^{\circ} + h(T)]_r$$

where: $h(T)$ is the sensible enthalpy as a function of temperature T

thus since the reactants are assumed to be at 25°C:

$$1[-393,520 + h(T)] + 2[-241,820 + h(T)] + 3[h(T)] + 18.8[h(T)] = 1(-74,850)$$



Simplifying:

$$h(T)\text{CO}_2 + 2[h(T)\text{H}_2\text{O}] + 3[h(T)\text{O}_2] + 18.8[h(T)\text{N}_2] = 802,310 \left[\frac{\text{kJ}}{\text{kmol fuel}} \right]$$

In determination on the adiabatic flame temperature for the complete combustion of Propane (C₃H₈) with 250% theoretical air in an adiabatic control volume [$T = 1300K$]. This equation can only be solved by an iterative trial and error procedure using the tables of Sensible Enthalpy vs Temperature for all four components of the products - CO₂, H₂O, O₂, and N₂. A quick approximation to the adiabatic flame temperature can be obtained by assuming that the products consist entirely of air. This approach was introduced to us by Potter and Somerton in their Schaum's Outline of Thermodynamics for Engineers, in which they assumed all the products to be N₂. We find it more convenient to use air assuming a representative value of the Specific Heat Capacity of Air: C_{p,1000K} = 1.142 [kJ/kg.K].

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$$24.8[h(T) - h^{\circ}]_{\text{air}} = 24.8(M_{\text{air}})(C_{p,1000K})(T_{\text{adiabatic}} - 298K) = 802,310 \left[\frac{\text{kJ}}{\text{kmol fuel}} \right]$$

where: $M_{\text{air}} = 29 \left[\frac{\text{kg}}{\text{kmol}} \right]$ is the molecular mass of air

$C_{p,1000K} = 1.142 \left[\frac{\text{kJ}}{\text{kg.K}} \right]$ is the specific heat capacity of air

thus solving: $T_{\text{adiabatic}} = 1275K$ (assuming that all the products are air)

Using the tables of Sensible Enthalpy vs Temperature we evaluated the enthalpy of all four products at a temperature of 1280K. This resulted in a total enthalpy of 802,410 [kJ/kmol fuel], which is extremely close to the required value, thus justifying this approach.

The above presentation gives an overview of the analysis of gaseous fuels – specifically the analysis of natural gas, biogas and other alternatives (such as syngas). The definition of the Wobbe index establishes a comparability and exchangeability of gaseous fuels. In other words, for a given burner system, one fuel can be replaced by another when they exhibit the same Wobbe index, without the need for modifying the burner settings and configuration.

4. Conclusion

Most gaseous fuels are not in the purest forms. There is often, a blend of two or more hydrocarbons in any designated fuel mixture. That is why it becomes expedient to undertake a volumetric analysis of fuel, just as we have done. From the foregoing, it could be adduced that given the conditions in the above analysis, a fuel mixture of Methane, Ethane and Propane does not produce a homogenous combustion. The whole gamut of the characteristics and/or behaviors of the component fuel that make up the mixture must be factored in, in order to arrive at a plausible and intelligible conclusion. Hence, the need for volumetric analysis of this kind, to ascertain the behaviors of fuel-mixtures; and make possible projections. Also, Volumetric analysis of gaseous fuel helps to

promote knock resistance of gaseous fuels and undertake knock measurements in the engine. It also described the characteristics to the effects of changes in the composition of gaseous fuels on engine knock by computing auto-ignition process during the compression and burn periods of the engine cycle.

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