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THERMODYNAMIC PROPERTIES AND HEAT GENERATION POTENTIAL OF OCTANE FUEL, UNDER STOICHIOMETRIC CONDITION

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ABSTRACT

A chemical reaction during which a fuel is oxidized and a large quantity of energy is released is called combustion. The oxidizer most often used in combustion process is air; since it is free and readily available. Any material that can be burned to release thermal energy is called a fuel. Most familiar fuels consist primarily of hydrogen and carbon. They are called hydrocarbon fuels and are denoted by the general formula, C_nH_m. In this paper, the thermodynamic properties and heat generation potential of octane fuel, under stoichiometric condition, was studied. The colorless and flammable fuel, when oxidized stoichiometrically, yielded a heat output, Q_{out}, of 5,470,720 kJ/kmol; and an air-fuel ratio, AFR, of 15.14 Kg_{air}/Kg_{fuel}. A combustion between octane and air (in excess of theoretical air), gives an air-fuel ratio, AFR, of 24.22 Kg_{air}/Kg_{fuel}. AFR is the ratio of the mass of air to the mass of fuel for a combustion process. This ratio helps the engineer to predict how economical and feasible the combustion of fuel will be.

Keywords: Octane Fuel, Heat Generation Potential, Stoichiometric Condition, Thermodynamic Properties.

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INTRODUCTION

Octane (C_8H_{18}) is a colorless liquid that is insoluble in water. It is obtained by fractional distillation of petroleum. Octane is flammable, and moderately toxic. It is used for octane number calibration of antiknock properties of fuels. It is, also, used as a solvent and in organic synthesis (Thermopedia, 2018). Any material that can be burned to release thermal energy is called fuel. Most familiar fuels consist primarily of hydrogen and carbon. They are called hydrocarbon fuel and are denoted by the general formula C_nH_m. Hydrocarbon fuels exists in all phases; some examples being coal, gasoline and natural gas. The main constituent of coal is carbon. Coal, also, contains varying amount of oxygen, hydrogen, nitrogen, sulphur, moisture and ash (Yunus and Michael, 2011). It is difficult to give an exact mass analysis for coal since its composition varies considerably from one geographical area to the next; even within the same geographical location. Most liquid hydrocarbon fuels are a mixture of numerous hydrocarbons, and are obtained from crude oil by distillation. The most volatile hydrocarbon vaporize first, forming what we know as gasoline. The less volatile fuels obtained during distillation are kerosene, diesel fuel, and fuel oil. The composition of particular fuel depends on the source of the crude oil as well as on the refinery. Although, liquid hydrocarbon fuels are mixtures of different hydrocarbons, they are usually considered to be a single hydrocarbon, for convenience (Silberberg, 2004). For example, gasoline is treated as *octane*, C_8H_{18}, and the diesel fuel as *dodecane*, $C_{12}H_{26}$. Another common liquid hydrocarbon fuel is methyl alcohol CH_3OH, which is also called *methanol*, and is used in some gasoline blends. The gaseous hydrocarbon fuel natural gas, which is a mixture of methane and smaller amounts of other gases, is often treated as methane, CH_4, for simplicity.

Natural gas is produced from gas wells or oil wells rich in natural gas. It is composed mainly of methane, but also contains small amount of ethane, propane, hydrogen, helium, carbon dioxide, nitrogen, hydrogen sulphate, and water vapour. On vehicles, it is stored either in the gas phase at pressures of 150 to 250 atm. as CNG (Compressed Natural Gas), or in the liquid phase at -162 ^oC as LNG (Liquefied Natural Gas). Over a million vehicles in the world, mostly buses, run on natural gas (Natural Gas, 2018). Liquefied petroleum gas (LPG) is a byproduct of natural gas processing or crude oil refining. It consists mainly of propane, and thus LPG is usually referred to propane. However, it contains varying amount of butane, propylene, and butylenes. Propane is commonly used in fleet vehicles, taxis, school buses, and private cars. Ethanol is obtained from corn, grains, and organic waste. Methanol is produced mostly from natural gas, but it can also be obtained from coal and biomass. Both alcohols are commonly used as additives in oxygenated gasoline and reformulated fuels to reduce air pollution.

A chemical reaction during which a fuel is oxidized and a large quantity of energy is released is called *combustion.* The oxidizer most often used in combustion processes is air, for obvious reasons – it is free and readily available. Pure oxygen, O_2 is used as an oxidizer only in some specialized applications, such as cutting and welding, where air cannot be used. On a mole or a volume basis, dry air is composed of 20.9 % oxygen, 78.9 % nitrogen, 0.9 % argon, and small amount of carbon dioxide, helium, neon, and hydrogen (Rajput, 2009). In the analysis of combustion process, the argon in the air is treated as nitrogen, and the gases that exit in trace amounts are disregarded. Then, the dry air can be approximated as 21 % oxygen, and 79 % nitrogen by mole numbers. Therefore, each mole of oxygen entering a combustion chamber is accompanied by 0.79/0.21 = 3.76 mol. Of nitrogen, thus;

$$1 \text{ kmol } O_2 + 3.76 \text{ kmol } N_2 = 4.76 \text{ kmol air} \quad (1)$$

During combustion, nitrogen behaves as an inert gas and does not react with other elements, other than forming a very small amount of nitric oxides. However, even then, the presence of nitrogen greatly affects the outcome of the combustion process wince nitrogen enters the combustion chamber in large quantities at low temperature and exits at considerably high temperature, absorbing a large proportion of the chemical energy releases during combustion.

Air that enters a combustion chamber normally contains some water vapour (or moisture), which also deserves consideration. For most combustion processes, the moisture in the air, and the H_2O that forms during combustion, can also be treated as inert gas, like nitrogen. At very high temperatures, however, some water vapour dissociates into H_2 and O_2 as well as into H, O, and OH. When the combustion gases are cooled below the dew-point temperature of the water vapour, some moisture condenses. Bringing a fuel into close and intimate contact with oxygen is not sufficient to start a combustion process; otherwise, the whole world would be on fire now. The fuel must be brought above its *ignition temperature*, to start the combustion. The minimum ignition temperatures of various substances in atmospheric air are shown in Table 1.

Table 1: Ignition Temperature of Some Common Fuels

Some Common Fuels	Ignition Temperature
Gasoline	260 ^oC
Carbon	400 ^oC
Hydrogen	580 ^oC
Carbon monoxide	610 ^oC
Methane	630 ^oC

Moreover, the proportion of the fuel and air must be in proper range for combustion to begin. For example, the natural gas does not burn in air in concentration less than 5 % or greater than about 15 %. A frequently used quantity in the analysis of combustion processes to quantify the amounts of fuel and air, is the *air-fuel ratio*, AF. It is usually expressed on a mass basis and is define as *the ratio of the mass of air to the mass of fuel*, for a combustion process, thus:

$$AF = \frac{m_{air}}{m_{fuel}} \qquad (2)$$

The mass, *m*, of a substance is related to the number of moles, *N*, through the relation;

$$m = NM \qquad (3)$$

where M is the molar mass

The air-fuel ratio can also be expressed on a mole basis as *the ratio of the mole numbers of air to the mole numbers of fuel*. The reciprocal of air-fuel ratio is called *the fuel-air ratio.*

Insufficient oxygen is an obvious reason for incomplete combustion, but it is not the only one. Incomplete combustion occurs even when more oxygen is present in the combustion chamber than is needed for complete combustion. This may be attributed to insufficient mixing in the combustion chamber, during the limited time that the fuel and oxygen are in contact. Another cause of incomplete combustion is dissociation, which becomes important at high temperatures. Oxygen has a much greater tendency to combine with hydrogen than it does with carbon. Therefore, the hydrogen in the fuel normally burns to completion, forming H_2O, even when there is less oxygen than needed for complete combustion. Some of the carbon, however, ends up as CO or just as plain C particles (soot), in the products. The minimum amount of air needed for the complete combustion of a fuel is called the *stoichiometric* or *theoretical air*. When the fuel is completely burned with theoretical air, no uncombined oxygen is present in the product gases. The theoretical air is, also, referred to as *the chemically correct amount of air*, or *100 percent theoretical air*. A combustion process with less than the theoretical air is bound to be incomplete. The ideal combustion process during which a fuel is burned completely, with theoretical air is called the stoichiometric or theoretical combustion of that fuel. For example, the theoretical combustion of methane is;

$$CH_4 + 2(O_2 + 3.76N_2) ===> CO_2 + 2H_2O + 7.52N_2 \qquad (4)$$

Notice that the products of the theoretical combustion, in the above equation for instance, contain no unburned methane and no C, H_2, CO, OH, or free O_2. The complete combustion process with no free oxygen in the product is called theoretical combustion.

MATERIALS AND METHOD

One mole of octane (C_8H_{18}) is burned with air that contains 20 kmol. of oxygen, O_2. Assuming the products contain only carbon (IV) oxide, CO_2; water, H_2O; oxygen, O_2; and nitrogen, N_2; determine the mole number of each gas in the products, and the air-fuel ratio for this combustion process. If the fuel is burned stoichiometrically, calculate the power output of the combustion process.

RESULTS AND DISCUSSION

The molar mass of air, M_{air} equals 28.97 Kg/kmol. This approximates to 29.0 Kg/kmol.

The chemical equation for the combustion can be written as:

$$C_8H_{18} + 20[O_2 + 3.76N_2] \rightarrow x\, CO_2 + y\, H_2O + z\, O_2 + w\, N_2 \qquad (5)$$

Note that (O_2 + 3.76N_2) represent the composition of dry air that contains 1 kmol of O_2, and x, y, z, and w represent the unknown mole numbers of the gases in the product. The values of x, y, z, and w are determined by applying a mass balance to each of the elements. That is:

C: $8 = x$
or $x = 8$

H $18 = 2y$
or $y = 9$

O_2 $20 \times 2 = 2x + y + 2z$
$40 = 16 + 9 + 2z$
$2z = 15$
or $z = 7.5$

N_2 $20 \times 3.76 \times 2 = 2w$
$150.4 = 2w$
or $w = 75.2$

Substituting in the eqn. (5), we obtain;

$$C_8H_{18} + 20[O_2 + 3.76N_2] \rightarrow 8CO_2 + 9H_2O + 7.5O_2 + 75.2N_2 \qquad (6)$$

It is worth noting that the coefficient *20* in the balanced equation (eqn.6) represents the number of moles of oxygen and not the number of moles of air. The number of moles of air is got by adding (20 x 3.76) 75.2 moles of nitrogen to the 20 moles of oxygen which gives a total of 95.2 moles of air.

The air-fuel ratio for the combustion process, $\frac{A}{F}$, can be determined thus;

$$\frac{A}{F} = \frac{m_a}{m_f} = \frac{(nM)_{air}}{(nM)_C + (nM)_H}$$

$$\frac{A}{F} = \frac{(20x4.76)(29)}{(8x12)+(18x1)}$$

$$= \frac{2760.8}{114}$$

$$= 24.22\ Kg_{air}/Kg_{fuel}$$

For the stoichiometric combustion of octane fuel, the following equation holds sway;

$$C_8H_{18} + a[O_2 + 3.76N_2] \rightarrow bCO_2 + cH_2O + dN_2 \qquad (7)$$

Similarly, a, b, c, and d represent the unknown mole numbers of the gases in the reactants and products. The values of a, b, c, and d are determined, as earlier done, by applying a mass balance to each of the elements. Hence, we have:

C: $8 = b$
or $b = 8$

H: $18 = 2c$
or $c = 9$

O_2: $16 + 9 = 2a$

$25 = 2a$

or $a = 12.5$

N_2: $12.5 \times 3.76 \times 2 = 2d$

$94 = 2d$

or $d = 47$

Hence, the stoichiometric equation corresponds to;

$$C_8H_{18} + 12.5[O_2 + 3.76N_2] \rightarrow 8CO_2 + 9H_2O + 47N_2 \quad (8)$$

Power = Heat Output x Mass Flow Rate

Heat Output, $Q_{out} = \Sigma H_{Reactant} - \Sigma H_{Product}$

$= \Sigma(h_f + \check{h} + h_o)_{Reactant} - \Sigma(h_f + \check{h} + h_o)_{Product}$

$= [-249{,}910 + 12.5(0 + 8682 - 8682) + 3.76(0 + 8669 - 8669)]$

$+[8(-393{,}520 + 9364 - 9364) + 9(-285{,}830 + 9904 - 9904) + 47(0 + 0]$

$= -249910 - (-3148160) + (-2572470)$

$= -249910 - (-5720630)$

$= 5{,}470{,}720$ kJ/kmol

$Q_{out} = 5{,}470{,}720$ kJ/kmol

For the stoichiometric reaction of octane, the air-fuel ratio, AFR, can also be calculated as we have below;

$$\frac{A}{F} = \frac{m_a}{m_f} = \frac{(nM)_{air}}{(nM)_C + (nM)_H}$$

$$= \frac{12.5x4.76x29}{(8x12) + (18x1)}$$

$= 15.14\ Kg_{air}/Kg_{fuel}$

In actual combustion processes, it is common practice to use more air than the stoichiometric amount to increase the chances of complete combustion or to control the temperature of the combustion chamber. The amount of air in excess of the stoichiometric amount is called *excess air*. The amount of excess air is usually expressed in terms of stoichiometric air as *percent excess air* or *percent theoretical air*. The stoichiometric air can be expressed as 0 % excess air or 100 % theoretical air. Amounts of air less than the stoichiometric amount are called *deficiency of air*, and are often expressed as *percent deficiency of air*. For instance, 90 % theoretical air is equivalent to 10 % deficiency of air. The amount of air used in combustion processes is, also, expressed in terms of the *equivalence ratio*, which is the ratio of the actual fuel-air ratio to the stoichiometric fuel-air ratio.

CONCLUSION

The combustion of fuels is construed as a chemical combination of oxygen, in the atmospheric air, and hydro-carbon. It is, usually, expressed both qualitatively and quantitatively by equations known as chemical equations. A chemical equation shows in a concise form, the complete nature of the chemical action or reaction taking place. It is germane to point out that stoichiometric condition is not only unattainable in nature, but almost impossible to have. It is not possible, in real life, to achieve a state of equal proportion of fuel and oxygen passing through the combustion process. More air must be allowed to go into the reaction for the combustion to be complete. To ensure complete and rapid combustion of fuel, some quantity of air, in excess of the theoretical or minimum air, is supplied. If just minimum amount of air is supplied, a part of the fuel may not burn properly. This is a condition referred to as incomplete combustion; and it leads to wastage of fuel. Therefore, determining the theoretical and actual mass of oxygen required for the combustion of gasoline, had been our primary concern in this paper.

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