

CHAPTER FOUR

Fuels

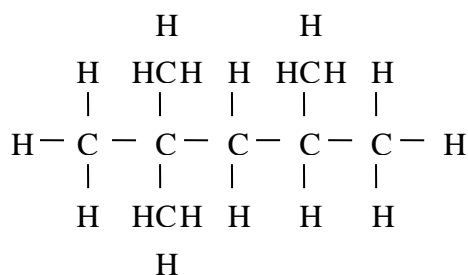
Over 99% of the worlds, internal combustion engines use liquid fuel derived from petroleum. In some countries where natural petroleum is scarce, fuel having very similar composition and characteristics are being produced. There are four significant sources of crude oil: (1) petroleum; (2) coal liquefaction; (3) shale oil and (4) tar sands. Most of the crude oil used to date has been petroleum derived since what is found in the ground requires processing before delivering to a refinery. Coal, on the other hand must be treated to increase its hydrogen content and removes undesirable elements such nitrogen, sulfur, arsenic, mercury, cadmium or phosphorous. Shale oil is difficult to get out ground since it is soaked up in rocks. Tar sands contain hydrocarbons mixed with sand and are more difficult to remove from the ground than petroleum.

Crude oil contains a large number of different hydrocarbons. For example, 2500 different compounds have been found in one sample of petroleum-derived crude oil subjected to an extraordinarily thorough analysis. The compounds range from gases to viscous liquids and waxes.

Crude petroleum is a mixture of hydrocarbons compounds, small quantities of sulfur, small quantities of oxygen and nitrogen, small quantities of metallic compound such as iron, radium, nickel, ...etc. The exact composition of crude oil differs widely according to its source.

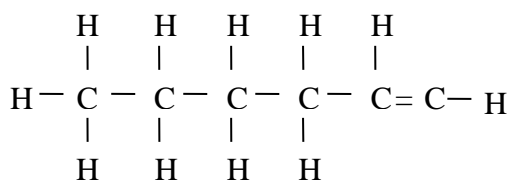
Refining of crude oil usually starts with distillation at atmospheric pressure during which process of the distillate separated into various fractions according to volatility. The resulting distillates are called straight run products. Distillates may then be subjected to heat treatments and chemical treatments at various pressures and temperatures, such treatments are define as cracking, when they chiefly tend to reduce the average molecular size and as polymerization when the reverse predominates. The products resulting from the retirement are classified by their usage and according to their specific gravity and their volatility. The important products of refining process are:

2) **Branched Chain or Isoparaffins**: the general formula is $[C_n H_{2n+2}]$. In these compounds, the chain of carbon atoms is branched, for example isooctane (C_8H_{18})

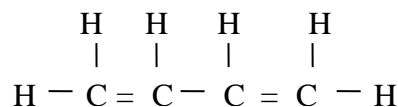


3) **Olefins**: are compounds with one or more double bonded carbon atoms in a straight chain. The general formulas are: **(1)** for the mono-olefins (one double bond) is $[C_n H_{2n}]$ for example; Hexane (C_6H_{12}) and **(2)** for the diolefins (two double bonds), for example; Butadiene (C_4H_6) is $[C_n H_{2n-2}]$.

Hexane

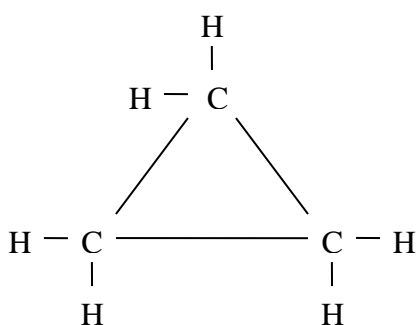


Butadiene

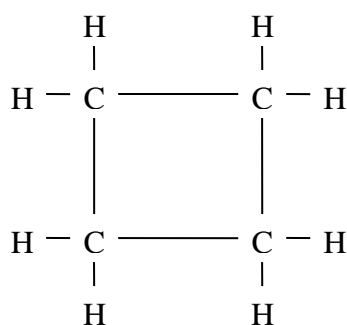


4) **Naphthenes**: are characterized by a ring structure, examples:

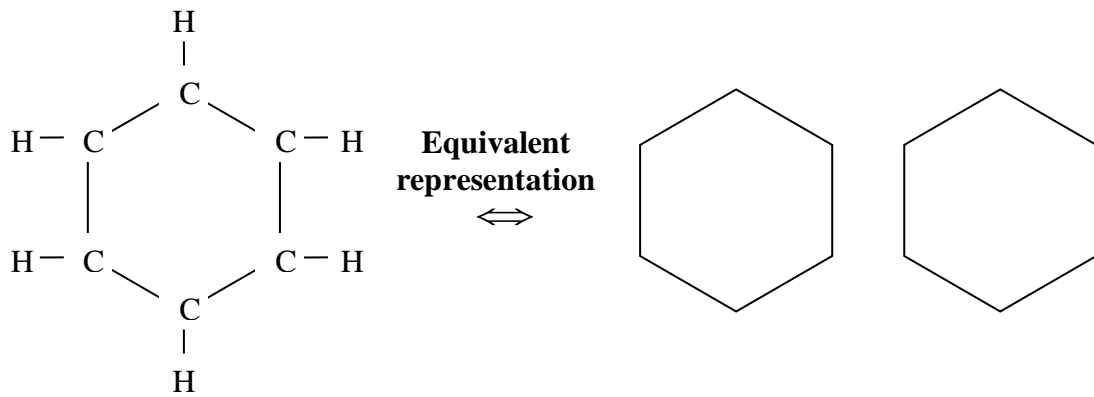
Cyclopropane



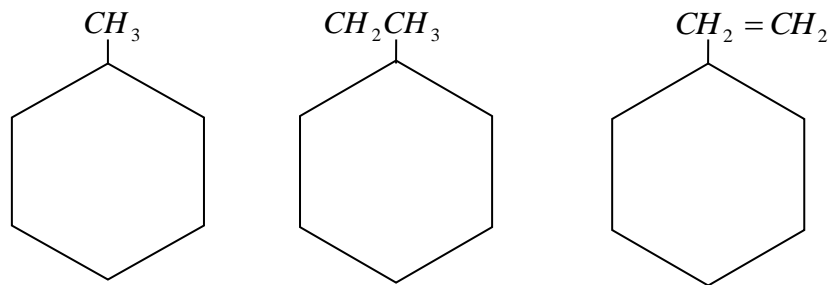
Cyclobutane



5) **Aromatics**: are hydrocarbons with carbon-carbon double bonds internal to a ring structure. The most common aromatic is benzene (C_6H_6):



Some common aromatics have groups substituted for hydrogen atoms:



4.2 Fuel for S. I. E:

The following characteristics are important for fuel used in S.I.E.

1. Volatility:

It defines as the tendency of fuel to evaporate under a given set of conditions (i.e. tendency of fuel to go from a liquid to a gaseous state). Volatility is an important characteristic of gasoline that affects the engine performance and fuel economy. It is expressed in term of the volume percentage that is distilled at or below fixed temperature.

Volatility can be divided into three regions called front end (0%-20% evaporated), the mid range (20%-80% evaporated) and tail end (80%-100% evaporated). The above affect could be distributed as follows:

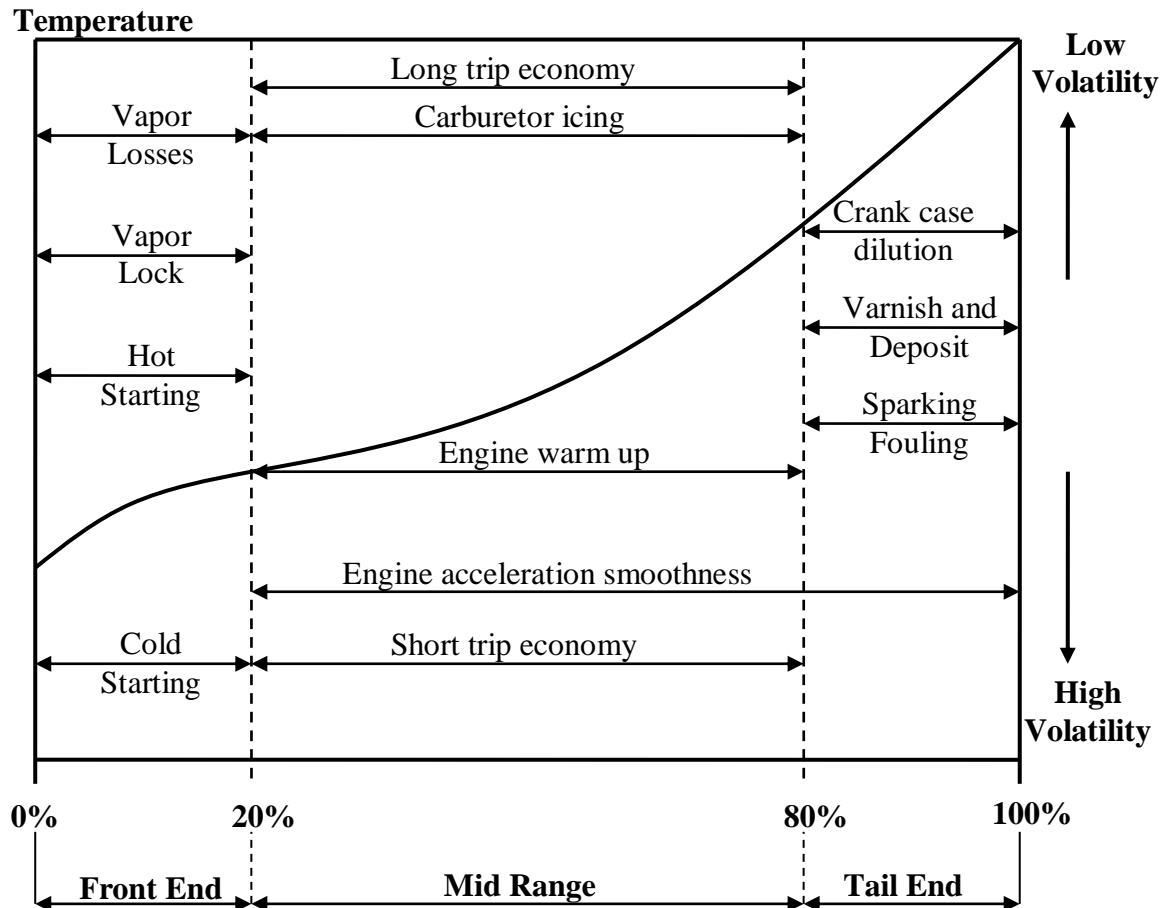
A) Front End Volatility:

a) Cold Starting:

The problem of cold starting is to have sufficient fuel vapor, thus a more volatile fuel is desirable. The approximate limits of inflammability of air-gasoline mixture are; **8:1**(for rich mixture), **20:1** (for lean mixture), and **12:1** (the best for starting from cold).

b) Hot Starting:

Good cold starting fuel causing hot starting problems, because the amount of fuel evaporating and so going into the inlet manifold under hot shutdown condition is high and the mixture formed is too rich to ignite. This could be avoided by proper placement and design of the fuel system.



c) Vapor Lock:

The vapor lock is situation where too lean mixture is supplied to the engine which cause uneven running of an engine, stalling while irregular acceleration, difficult starting when hot. The vapor lock can be reduced by:

- i) Keeping the fuel system element away from heat
- ii) Improving the vapor handling capacity of fuel system
- iii) Limiting the fuel from propane and butane

Mid Range Volatility:

a) Engine Warm up:

When an engine is first starting, it does not respond as rapidly to change in operating conditions as it does after having been run for sometime. The interval between starting-up and the time at which flexible operation is possible, referred to as the warm-up period. The mid range portion should be volatile enough to give satisfactory A/F ratios under various operation conditions.

b) Engine acceleration, Smoothness and Fuel economy:

A part from the size, design and its mechanical condition the acceleration of an engine depends upon its ability to deliver suddenly to the intake an extra supply of fuel-air mixture in a sufficiently vaporized form to burn quickly (good acceleration occurs when an A/F vapor ratio is about 12:1).

For power and smoothness of operation correct fuel-air ratio should be delivered to all cylinders. As low as mid-range and tail end volatility as practical will help in good mixture distribution and hence good fuel economy.

c) Short and Long trip economy:

Short trip economy is related to warm-up characteristics. Keeping the warm-up period to a minimum by having a fuel, which is relatively volatile in mid-range permits more efficient operation and great economy.

In long trip, a gasoline that has more weight per liter will give more (kms/liter) in a warmed-up engine, since the higher boiling hydrocarbons are generally heavier than the more volatile ones, the mid-range and tail-end parts of the fuel should be as involatile as practical for good long trip economy.

d) Carburetor Icing:

When the gasoline is vaporized in the carburetor there will be drop in temperature of carburetor body and if the humidity is high (greater than 75%) and the air temperature lower than $10^{\circ}C$, water condenses out of air and freezes on carburetor. The presence of ice-up-sets carburetion resulting

in poorer economy, because ice formation restricts the air path and thus engine stalls due to richness of mixture and even can stop completely due to air starvation. Two types of gasoline additives are used to overcome this problem. One is a freezing point depressant type, such as dipropylene glycol (DPG) to reduce the temperature at which ice forms. The other is a surfactant type, which coats the carburetor surface to prevent the ice sticking to it.

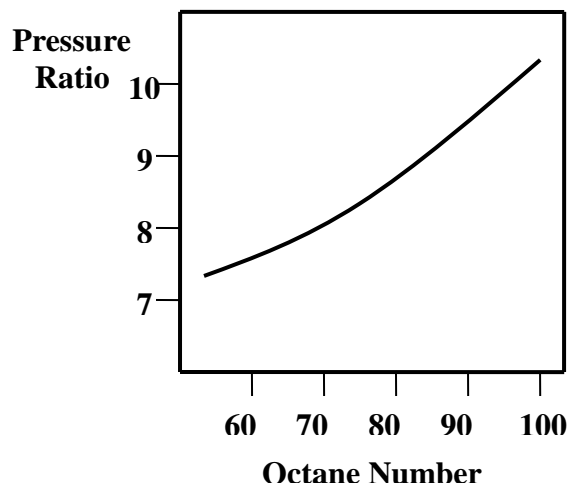
D) Tail End Volatility:

- a) Crankcase Dilution:** If part of fuel has too high evaporation temperature, this part will not be completely vaporized and will be carried as fuel droplets into the combustion chamber. This liquid fuel gets past the piston rings into the crankcase where it dilutes the oil and decrease viscosity. It also washes away the lubricating oil film on cylinder walls. Crankcase dilution is more at low engine operating temperature, also engines using heavy fuels, such as kerosene and distillate.
- b) Varnish and Sludge Deposit:** Certain types of high boiling hydrocarbons contribute to varnish and sludge deposition inside an engine. These deposits can cause piston ring plugging, sticking, and valve sticking resulting in poor operation and poor fuel economy.
- c) Spark Plug Fouling:** Some high boiling hydrocarbons form deposits leading to spark plug fouling. Lower the tail end volatility less are the chances of spark plug fouling.
- d) Evaporation Loss:** Evaporation loss from storage tanks and carburetor depends on vapor pressure, which is a function of fraction components, and initial temperature, vapor pressure of the gasoline is also responsible for evaporation losses due to venting from the tanks. This loss decrease the fuel economy also decreases its anti-knock (the fuel anti-knock) quality as the lighter fraction has higher anti-knock properties.

2. Knock Characteristics:

Octane rating is a measure of its anti-knock performance of fuel. A scale of (0-100) is devised by assigning a value of (0 to n-heptanes) and a value of 100 to isooctane [a fuel resistant to knock]. For example, a 95-octane fuel has the performance equivalent to that of a mixture of 95% isooctane and 5% normal heptane by volume. The octane requirement of an engine depends:

- a) Engine pressure ratio
- b) Operation conditions
- c) Geometrical and mechanical considerations



The octane number of a fuel is determined by using special standard single cylinder engine "CFR" (Cooperating Fuel Research) in which the fuel being tested is compared with a reference mixture of two chemically pure hydrocarbons; isooctane (C_8H_{18}) and normal heptane (C_7H_{16}). The test must be done under standard condition and setting compression ratio to give standard knock intensity as measured by the knock indicator. While holding compression ratio and other test conditions constant, various mixtures of the two reference fuels (called Primary Reference Fuels "PRF") are tried until a mixture, which gives the same knock intensity as the fuel under, is discovered. The percentage of isooctane in the matching mixture is called the octane number of the fuel. The octane number of gasoline engine fuel is improved by adding additives. These additives or antiknock must have the following properties:

- a) Low cost per unit increase in octane rating
- b) No deposits left in the engine or exhaust system
- c) Relatively low boiling temperature to ensure good distribution in multi cylinder engines
- d) Complete solubility
- e) Nontoxic, and nontoxic exhaust emissions
- f) Stable

The primary commercial antiknock is: **(1) Lead additives** taking the form of lead alkyls, either tetramethyl lead $[(CH_3)_4Pb]$, or tetraethyl lead $[(C_2H_5)_4Pb]$. Most countries now have restrictions on use of lead in fuels for environmental reasons (the danger of lead pollution). **(2) Iron carbonyl** has been tried in Europe, but the product of combustion (iron oxide), which tends to short the spark plug and to cause extreme wear of the cylinder and rings. Also, ethyl alcohol is used as antiknock additives. For example;

Name	Grams to match gallon gasoline
Tetraethyl lead	1
Methyl triethyl lead	1.05
Dimethyl diethyl lead	1.1
Tetramethyl lead	1.3
Ethyl alcohol	158

Sensitivity: is the difference between research octane number (RON) and motor octane number (MON).

$$\text{Sensitivity} = \text{RON} - \text{MON}$$

The higher the sensitivity the poorer its performance under service condition.

3. Gum Deposits:

All petroleum motor fuels oxidize slowly in presence of air. The oxidation of unsaturated hydrocarbons (also unstable sulfur and nitrogen compounds) results in formation of resinous materials called gum. High gum content fuels may clog carburetor jet, promote sticking of automatic chokes, sticking of the intake valve, piston rings and promote formation of manifold deposit reducing volumetric efficiency (η_v), thus the gum content as well as the tendency to form gum is limited in gasoline specifications.

4. Sulfur:

Hydrocarbon fuel (motor fuels) may contain free sulfur, hydrogen sulfide and other sulfur compounds, which are objectionable for several reasons:

- a) They are corrosive elements and corrode fuel lines, carburetor and injection pump
- b) The sulfur will unite with oxygen to form sulfur dioxide that in the presence of water at low temperature may form sulfurous acid or the sulfur dioxide to unit with other substance to form products that could cause engine wear at low or even high temperatures.
- c) Sulfur has a low ignition temperature, the presence of sulfur can reduce the self-ignition temperature, and thus promoting knock in the S.I.E. and tending to decrease knock in the C.I.E.
- d) It is found that the response of S.I. fuel to tetraethyl lead reduces by the presence of sulfur.

4.3 Non Petroleum Fuels:

- 1) Methyl alcohol, or methanol (CH_3OH) and ethyl alcohol or ethanol (C_2H_5OH), methanol is used in racing engines on account of the cooling effect produced by its very large (negative) heat of vaporization. Ethanol blended with gasoline has been used in locations where it is plentiful as a byproduct of sugar refining.
- 2) Benzol: it is a mixture of about 70% benzene (C_6H_6), 20% toluene (C_7H_8) and 10% xylene (C_8H_{10}) and some sulfur components. It has a very high knock resistively, but its freezing point is $5.5^\circ C$ so it cannot be used in cold climate. Also, the heating value is lower than gasoline. It is used as a blending agent with gasoline.
- 3) Gaseous: the main gaseous fuel are used in internal combustion engines are natural gas, liquid petroleum gas (LPG), producer gas, blast-furnace gas, coke oven gas.

4.4 Fuel for Diesel Engines:

The requirement for good C.I. fuel cannot be as were these for gasoline. This situation arises because of the added complexity of the C.I. engine from its heterogeneous combustion process, which is strongly affected by injection characteristics. However, the following general observation can be made:

1) Knock characteristics:

Cetane rating (octane number) is the measure of knock characteristics. The best fuel in general will have a cetane rating sufficiently high to avoid objectionable knock.

$$CN = \frac{104 - ON}{2.75}$$

Cetane number: the cetane rating of a Diesel fuel is a measure of its ability to auto ignites quickly (ignitability) when it injected into the compressed and heated air in the engine. Through ignition is affected by:

- i) Engine design parameters such as compression ratio, injection rate, injection time, inlet air temperature, ...etc
- ii) Hydrocarbon composition of the fuel
- iii) Volatility of fuel

2) Starting Characteristics:

The fuel should start the engine easily. The requirement demands high volatility to form readily a combustible mixture and a high cetane rating in order that the self-ignition temperature will be low.

3) Smocking and Odor:

The fuel should not promote either smoke or odor from the exhaust pipe. In general, good volatility is demanded as the first prerequisite to ensure good mixing and therefore complete combustion.

4) Corrosion and Wear:

The fuel should not cause corrosion before combustion, or corrosion and wear after combustion. These requirements appear to be directly related to the sulfur ash and residue contents of the fuel.

H. W.

1) C_4H_8 is burned in an engine with a rich fuel-air ratio. Dry analysis of the exhaust gives the following volume percentages: $CO_2 = 14.95\%$, $C_4H_8 = 0.75\%$, $CO = 0\%$, $O_2 = 0\%$, with the rest being N_2 . Calculate:

a) Air-fuel ratio

b) Equivalence ratio

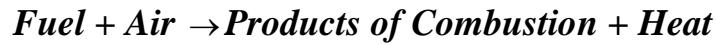
2) Methanol (CH_3OH) is burned in an engine with air at equivalence ratio of 0.75.

Write the balanced chemical equation for this reaction and air-fuel ratio.

3) Isooctane (C_8H_{18}) is burned with air in an engine at an equivalence ratio of 0.833, find air-fuel ratio and write the balanced chemical reaction equation.

Combustion of Fuels:

Combustion of fuel is accomplished by mixing fuel with air at elevated temperature:



The oxygen contained in the air unites chemically with carbon, hydrogen and other elements in fuel to produce heat. The amount of heat liberated during the combustion process depends on the amount of oxidation of the constituent of fuel and the nature of fuel.

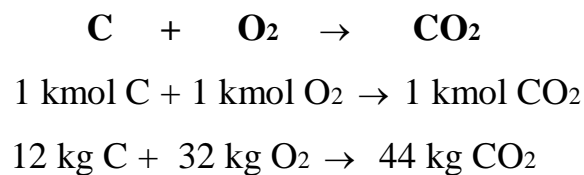
In order that the combustion of fuel may take place with high efficiency, the following conditions must be fulfilled:

1. The amount of air supplied should be sufficient.
2. The air and fuel should be thoroughly mixed.
3. The temperature of the reactants should be high enough to ignite the mixture.
4. Sufficient time should be available to burn fuel completely.

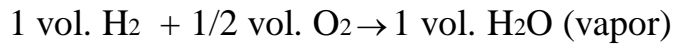
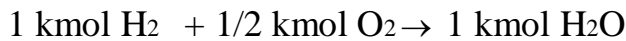
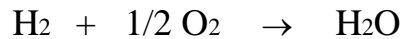
Chemical Equation:

The chemical equation shows how the atoms of the reactants are arranged to form products. Before the chemical equation can be written, it is necessary to know the number of atoms of elements in the molecules of the reactants and products. During combustion process, the atoms are rearranged to form new molecules, and the total number of atoms of each element is unchanged. A chemical equation expresses the principle of the conservation of mass in terms of the conservation of atoms

i- Combustion of Carbon



ii- *Combustion of Hydrogen*



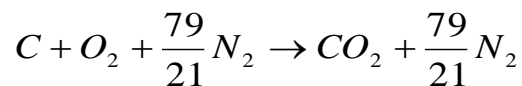
In most engineering combustion systems the necessary oxygen is obtained by mixing the fuel with air (except rockets) and it is necessary to use accurate and consistent analysis of air by mass and by volume. It is usual in combustion calculations to take air as 23.3% O₂, 76.7% N₂ by mass, and 21% O₂, 79% N₂ by volume. The small traces of other gases in dry air are included in the nitrogen, which is sometimes called "*atmospheric nitrogen*".

The moisture or humidity in atmospheric air varies over wide limits, depending on meteorological conditions. Its presence in most cases simply implies an additional amount of inert material.

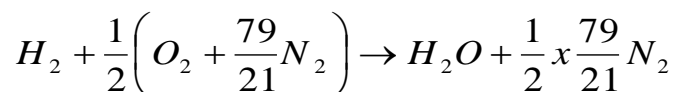
The molar mass of O₂ can be taken as 32 kg/kmol, and that of N₂ as 28 kg/kmol and air 29 kg/kmol.

Since oxygen is accompanied by nitrogen when air is supplied for combustion, then this nitrogen should be included in the combustion equation, it will appear on both sides of the equation. With one mole of O₂, there are $\frac{79}{21} = 3.762$ moles of N₂,

Hence,



Also,



A frequently used quantity in the analysis of combustion process is the *air fuel ratio* A/F. it is defined as the ratio of the mass of air to the mass of fuel for a combustion process.

$$A / F = \frac{m_a}{m_f} = \frac{\text{mass of air}}{\text{mass of fuel}}$$

The mass m of a substance is related to the number of moles n through the relation: $m = n \cdot M$, where M is the *molar mass*. The reciprocal of A/F ratio is called the *fuel-air ratio*.

The minimum amount of air needed for the complete combustion of a fuel is called the stoichiometric or theoretical air. In actual combustion processes, it is common practice to use more air than the stoichiometric amount. The amount of extra air than the stoichiometric is called (*excess air*). Amount of air less than stoichiometric amount is called (*deficiency of air*). *Equivalence ratio* is the ratio of the actual fuel- air ratio to the stoichiometric fuel-air ratio. Sometimes this ratio is given in term of A/F ratio and called *mixture strength*.

$$\text{Equivalence ratio} = \phi = \frac{(A/F)_{\text{stoich}}}{(A/F)_{\text{actual}}} = \frac{(F/A)_{\text{actual}}}{(F/A)_{\text{stoich}}}$$

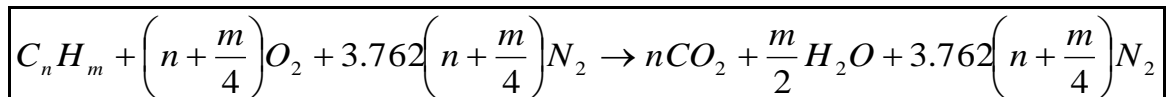
Where:

$\phi = 1$: stoichiometric

$\phi < 1$: lean (weak) mixture- excess of air.

$\phi > 1$: rich mixture- deficiency of air.

A general reaction equation of a hydrocarbon fuel for stoichiometric condition with air is given by:

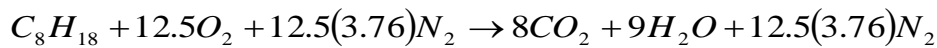


Example (1): Isooctane is burned with 120% theoretical air in small three cylinder turbocharged automobile engine. Calculate:

- 1) air fuel ratio
- 2) fuel air ratio
- 3) equivalence ratio

Solution:

Stoichiometric reaction:



With 20% excess air:



$$1) \quad A / F = \frac{m_a}{m_f} = \frac{N_a M_a}{N_f M_f} = \frac{(15)(4.76)(29)}{(1)(114)} = 18.16$$

$$2) \quad F / A = \frac{m_f}{m_a} = \frac{N_f M_f}{N_a M_a} = \frac{1}{A / F} = \frac{1}{18.16} = 0.055$$

3) Fuel-air ratio of stoichiometric combustion:

$$(F / A)_{stoich} = \frac{m_f}{m_a} = \frac{N_f M_f}{N_a M_a} = \frac{(1)[(12 * 8) + (2 * 9)]}{(12.5)(4.76)(29)} = 0.066$$

Equivalence ratio is obtained from:

$$\text{Equivalence ratio} = \phi = \frac{(A/F)_{stoich}}{(A/F)_{actual}} = \frac{(F/A)_{actual}}{(F/A)_{stoich}} = \frac{0.055}{0.066} = 0.833$$

Example (2): The four-cylinder engine of a light truck owned by a utility company has been converted to run on propane fuel (C_3H_8). A dry analysis of the engine exhaust gives the following volumetric percentages:

$$CO_2 = 4.90\%$$

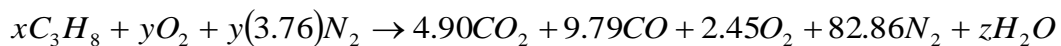
$$CO = 9.79\%$$

$$O_2 = 2.45\%$$

Calculate the equivalence ratio at which the engine is operating.

Solution:

The three components identified sum up to $(4.90+9.79+2.45=17.14\%)$ of the total, which means that the remaining gas (nitrogen) accounts for (82.86%) of the total.



Conservation of nitrogen (N_2) during reaction gives:

$$y(3.76) = 82.86 \Rightarrow y = 22.037$$

Conservation of carbon (C):

$$3x = 4.90 + 9.79 \Rightarrow x = 4.897$$

Conservation of hydrogen (H_2):

$$8x = 2z$$

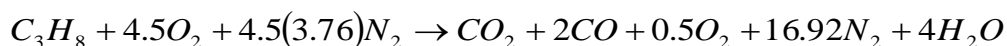
$$8 * 4.897 = 2z$$

$$\therefore z = 19.588$$

The reaction is:



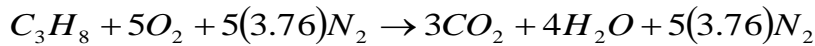
Dividing by 4.9:



Actual air-fuel ratio:

$$(A/F)_{actual} = \frac{m_a}{m_f} = \frac{(4.5)(4.76)(29)}{(1)[(3*12) + (2*4)]} = 14.12$$

Stoichiometric combustion:



Stoichiometric air-fuel ratio:

$$(A/F)_{stoich} = \frac{m_a}{m_f} = \frac{(5)(4.76)(29)}{(1)[(3*12) + (2*4)]} = 15.69$$

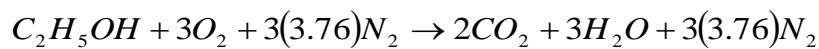
Equivalence ratio can be calculated as following:

$$\phi = \frac{(A/F)_{stoich}}{(A/F)_{actual}} = \frac{15.69}{14.12} = 1.11$$

Example (3): Find the stoichiometric A/F ratio for the combustion of ethyl alcohol (C₂H₅OH) in a petrol engine. Calculate the A/F ratios for 0.9 & 1.2 equivalence ratios (ϕ). Determine the wet and dry analyses by volume of the exhaust gas for each equivalence ratio.

Solution:

Combustion equation of ethyl alcohol is:



One mole of fuel has a mass of ((2×12) + 16+6) =46 kg

Mass of air required for complete burning of one mole of fuel is:

$$(3*4.76*29) = 414.12$$

$$\therefore \text{Stoichiometric (A/F) ratio} = \frac{414.12}{46} = 9.002 \cong 9$$

$$\phi = \frac{(A/F)_{stoich}}{(A/F)_{actual}}$$

$$0.9 = \frac{9}{(A/F)_{actual}}$$

$$\therefore (A/F)_{actual} = \frac{9}{0.9} = 10$$

Volumetric (A/F) ratio = 3 × (1+3.762) =14.3

\Rightarrow For $\phi = 0.9$; air supplied is $\frac{1}{0.9} = 1.11$ times as much air supplied for complete combustion, then: combustion equation becomes:



The total number of moles of products = $2+3+0.33+12.52 = 17.85$.

Total dry moles = $2+0.33+12.52 = 14.85$

Hence dry analysis is:

$$CO_2 = \frac{2}{17.85} * 100 = 11.204\%$$

$$O_2 = \frac{0.33}{17.85} * 100 = 1.848\%$$

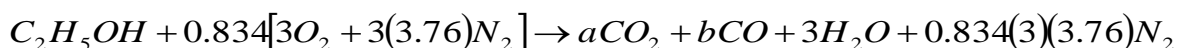
$$H_2O = \frac{3}{17.85} * 100 = 16.806\%$$

$$N_2 = \frac{12.52}{17.85} * 100 = 70.144\%$$

\Rightarrow For $\phi = 1.2$:

$$(A/F)_{actual} = \frac{9}{1.2} = 7.5$$

This means that $\frac{1}{1.2} = 0.834$ of the stoichiometric air is supplied. The combustion cannot be complete & is usual to assume that all the hydrogen is burned to H_2O , since H_2 atoms have a greater affinity for oxygen than C atoms. The carbon in the fuel will burn to CO and CO_2 :



C balance: $2 = a + b$

O balance: $1 + 2 \times 0.834 \times 3 = 2a + b + 3$

Subtracting the equations gives: $a = 1.004$

Then: $b = 2 - 1.004 = 0.996$

The rest of question is homework