* Fuel Chemistry *

* What is fuel ?

Ans:- A fuel can be defined as any combustible, substance, containing carbon as main constituent, which on proper burning gives large amount of heat which can be used economically for domestic & industrial purpose.

During the process of combustion of fuel the atoms of carbon, hydrogen etc. combined with O_2 with simultaneously liberation of heat resulting in the formation of new compounds like CO_2, H_2O --- etc.

Fuel + O_2 ⟶ Product + Heat
(more heat content) (lesser heat content)

The primary (or) main sources of fuels are coals or petroleum oils.

Classification of fuels :-

Fuels can be classified based on their occurance -

1) Natural (or) Primary fuels :-

This fuels are found in nature.

Ex:- wood, peat, petroleum, Natural gas etc.

2) Artifical (or) Secondary fuels :-

These fuels are prepared artifically from primary fuels are called A.F.

Ex:- Coal, Kerosene oil, Coal gas -- etc.

On the basis physical state :-

1) solid fuel 2) Liquid fuel 3) Gases fuel.

types of fuel	Natural (or) primary	Artificial (or) secondary
1) Solid	wood, peat, lightning, coals anthracite coal.	charcol, coke, etc
2) Liquid	Crude oil	Petrol, desiel & various function of petroleum
3) Gases	Natural gases	coal gas, oil gas, bio-gas water gas etc.

Characteristics of Good fuel :-

1) High calorific value
2) Moderate ignation temperature
3) Low moisture content.
4) Low non-combustible matter contain
5) Moderate rate of compression.
6) Haumless combustion product
7) Low cost
8) A fuel should burn in air with efficiency without smo

Calorific Value :-

The total amount of heat liberate from combustion of a unit mass (or) volume of a fuel in air (or) oxygen

⇒ There are two types of calorific value

Lower calorific value (LCV) :-

It is also termed as Net calorific value (NCV) and is defined as the heat produced when a unit quantity (mass or volume) of a fuel is burned completely and hot combustion products are allowed to escape. Then it is called LCV (or) NCV

Relation between LCV & HCV :-

LCV = HCV - latent heat of H_2O vapours formed

LCV = HCV - wt of hydrogen in fuel x 9 x latent heat of steam.

$$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$$

2 $\longrightarrow$ 18

1 $\longrightarrow$ (9)

* The Gross calorific value of a fuel containing 8% hydrogen was formed) found to be 9225.9 Kcal/kg. Find out the Net calorific value. If the latent of steam is 587 Kcal/kg

Sol:- NCV (or) LCV = GCV (or) HCV - wt of hydrogen x 9 x latent heat

$$= 9225.9 - 9 \times \frac{8}{100} \times 587$$

$$= 8803 \text{ Kcal/kg}$$

Solid fuel :-

Solid fuel is refer to various type of solid material that are used as fuel to produce energy.

The primary fuel of solid commonly used are

(i) Wood :- freshly cut wood contains 25-50% moisture which reduced to 15% after drying in air

The average composition of wood is

C = 55%
H = 6%
O = 38%
ash = 1%

} Its calorific value is about 3500 - 4500 kcal/kg

(ii) Coal :-

Analysis of coal → Ultimate analysis

Proximate analysis

1) % of moisture.
2) % of volatile matter.
3) % of fixed carbon
4) % of ash.

1) % of C
2) % of H
3) % of N.

* 1) % of moisture :- [100 - 110°C]

% of moisture = $\frac{\text{Loss in weight of the sample}}{\text{weight of coal sample taken}} \times 100$

2) % of volatile matter

= $\frac{\text{Loss in weight due to removal of volatile}}{\text{weight of coal sample taken}} \times 100$

3) % of ash.

= $\frac{\text{weight of ash formed}}{\text{weight of coal sample taken}} \times 100$

v) High calorific value:

Hydrogen is found to be present in almost all fuel and when the calorific value of hydrogen containing fuel is determined experimentally, the hydrogen is converted to steam If the product of combustion are cooled to the room temperature

The latent heat of condensation also get include in the result heat which is called HCV

Definition of HCV:-

The total amount of heat is liberated when unit mass (or) volume of fuel has been burned completly and the product of combustion pulled to room temperature.

* H.C.V is also known as 'Gross Calorific Value'

vi) % fixed Carbon

= 100 - % of (moisture + volatile + ash)

Problem:

A sample of coal is analysed as follow exactly 1.5gm of coal was weighted into a silica crucible. After heating for 1 hour at 105°C, the residue weighed 1.415g. The crucible was then covered with a lid & strongly heated for exactly 7 min at 950 ± 20°C. The residue weighed 0.528g. The crucible was then heated without the cover until a constant weight was obtained the last residue was found to weight 0.254gm

Ans :-

% of moisture = $\frac{1.5 - 1.4158}{1.5} \times 100$ = 5.62

% of volatile = $\frac{1.45 - 0.528}{1.5} \times 100$ = 59.1

% of ash = $\frac{0.0254}{1.5} \times 100$ = 16.93

% fixed carbon = 18.4 %

Ultimate Analysis :-

$C + O_2 \rightarrow CO_2$

12

$H_2 + O_2 \rightarrow H_2O$

2 → 18

% of carbon = $\frac{\text{Increase wt of KOH tube}}{\text{wt of coal sample taken}} \times \frac{12}{44} \times 100$

% of Hydrogen = $\frac{\text{Increase wt of } CaCl_2 \text{ tube}}{\text{wt of coal sample taken}} \times \frac{2}{18} \times 100$

$CO_2, H_2O \rightarrow$ KOH 000000 | $CaCl_2$ 0000

$CO_2 + KOH \rightarrow K_2CO_3 + H_2O$

$CaCl_2 + 1H_2O \rightarrow CaCl_2 \cdot 1H_2O$

Analysis of Nitrogen

$N_2 + H_2SO_4 \xrightarrow[\text{catalyst}]{K_2SO_4} (NH_4)_2SO_4 \xrightarrow[KOH]{NaOH} NH_3\uparrow + Na_2SO_4 + H_2$ ← side produ

About @1gm of equivalent weight powder coal is heated with Gerdu
con. H_2SO_4 along with K_2SO_4 (In long neck flask). After the solutio
become clear it is treated with excess of KOH or NaOH & liberated NH_3
is distilled over & absorb in known volume of standard acid solutio
the unused acid is then determ
by back

* 3.12gm of coal was taken & heated in a long-necked flask and NH_3 gas then evolved was absorbed in 50ml of 0.1(N) H_2SO_4. After absorbeition, the excess acid required 12.5 ml of 0.1(N) NaOH for exactly neutralization. Determine the % N in the sample of coal

Ans:-

$$\%N = \frac{\text{Volume of acid used} \times \text{Normality}}{\text{wt of sample coal}} \times 1.4$$

$$= \frac{(50-12.5) \times 0.1}{3.12} \times 1.4$$

$$= \underline{1.68\%}$$

* 1gm of accurately weighed coal sample was burnt in a current of O_2 in a combustion apparatus C & H of coal were converted CO_2 & H_2O respectedly, which were then absorbed repetedly in KOH & $CaCl_2$ tube of known weight. Increase weight in KOH tube was 2.75gm & the increase in weight of $CaCl_2$ is 0.45gm. Calculate %C & H%.

Sol:-

$$\%C = \frac{12}{44} \times \frac{\text{Increase of KOH wt}}{\text{wt of sample coal}} \times 100$$

$$= \frac{12}{44} \times \frac{2.75}{1} \times 100 = 75\%$$

$$\%H = \frac{2}{18} \times \frac{\text{Incr of } CaCl_2 \text{ wt}}{\text{wt of sample coal}} \times 100$$

$$= \frac{1}{9} \times \frac{0.45}{1} \times 100 = \underline{5\%}$$

Liquid fuel :-

Liquid fuels are fuel which is

** Table [1.5]

Cracking :-

** Percentage of composition fuels / solids

Fuel	C (%)	H %	O %	Moisture (90°C) %	Calorific value kcal/kg
Wood	50	6.0	43.5 %	25	4000 – 4500
Peat	57.0	5.7	35.3	25	4125 – 5400
Lignite	67.0	5.0	26.5	20	6500 – 7100
Sub-bituminous coal	77.0	5.0	16.2	11	7000 – 7500
Bituminous coal	83.0	5.0	10.0	4	8000 – 8500
Semi-Bituminous	90.0	4.5	4.0	1	8350 – 8500
Anthracite	93.3	3.0	3.0	1.5	8650 – 8700

Caborization of coal :-

The process of converting of coal into coke is called as

	Fraction's name	Hydrocarbon atom	Use
1)	Uncondensed gas	$C_1 - C_4$	Used as domestic fuel (LPG)
2)	Petroleum ether	$C_5 - C_7$	Solvents for fats, dry cleaning
3)	Gasoline (i) petrol (ii) motor spirit	$C_5 - C_9$	Motor fuel, dry cleaning
4	Naptha (i) solvent spirit	$C_9 - C_{10}$	Paints, Varnishes dry cleaning,
5)	Kerosene oil	$C_{10} - C_{16}$	Fuel, Stoves, Jet engine fuel
6	Diesel oil	$C_{15} - C_{18}$	Diesel engine fuel
7	Heavy oil	$C_{19} - C_{30}$	Fuel ship, metallurgical furnace
8	Residue	C_{30} above	As fuel moulding clothes

Liquid fuels :-

→ The largest source of liquid fuels is petroleum.

→ The Calorific Value of petroleum is 40000 KJ/kg.

The ultimate analysis shows that average composition of petrole

Element	C	H	S	O	N
Percentage	80-87	11-15	0.1-3.5	0.1-0.9	0.1-0.9

Cracking of petroleum :-

Cracking is a process in which complex high molecule weight of organic compound [petroleum] is are broken into smaller molecules by application of with (or) without catalyst.

$$C_{10}H_{22} \xrightarrow{\text{Cracking}} C_5H_{12} + C_5H_{10}$$

(Decane) (n-pentane) (pentene)

* 50% of today gasoline is obtained by Cracking.

Thermal cracking :-

When a heavy oils are subjected to high temperature & pressure in the absence of ~~oxy~~ catalyst is called T.C

(i) liquid phase thermal cracking.

(ii) Vapour phase thermal cracking

Catalytic cracking :

When heavy oils are subjected to low temperature & pressure in the presence of catalyst. The catalyst is used in these mixtures is Zeolite [silica & alumina hydrated]

Synthetic petrol :-

The petrol which can be made by synthetic process.

1) Polymerization :-

In these process small molecules combine to form a heavier molecules (colorless) resembling gasoline.

a) Thermal polymerization :

The polymerization process in which occurs at high temperature (500-600°C) and pressure. The product is gasoline and gas oil which are separated by fractional distillation.

b) Catalytic polymerization :

The polymerization process which occurs in presence of catalyst like H_2PO_3, H_2SO_4 etc. but low temperature is low. (150-200°C)

2) Alkylation :

This method is used to convert olefins to gasoline.

Conversion of coal into liquid fuel :

(a) Fischer Tropsch method :-

In this method coke is converted into water gas by passing steam over red hot coke.

$$C + H_2O \xrightarrow{1200°C} (CO + H_2)$$ water gas

(coke)

1) A mixture of water gas and hydrogen is purified by passing through Fe_2O_3 [to remove H_2S] and then again mixture through $Fe_2O_3 + Na_2CO_3$ [to remove organic sulphur compn]

2) The purified gas is compressed 5-25 atm and then passed through catalytic converter mainted about (200-300)°

3) The catalyst consists of mixture of cobalt, MgO, Th.. etc.

4) finally mixture of saturated and unsaturated hydrocarbon is formed. The reaction is exothermic reaction.

$$n CO + 2n H_2 \longrightarrow C_n H_{2n} + n H_2O$$

$$n CO + (2n+1) H_2 \longrightarrow C_n H_{2n+2} + n H_2O$$

5) These hydrocarbons is subjected to fractional distillation to yeild gasoline, diseal oil and heavy oil.

6) The gasoline formed by Fischer Tropch method is rich in straight chain hydrocarbons.

(b) Bergius process :-

In this process bituminous coals converted into liquid and gaseous fuels by hydrogenating them in presence of catalyst

1) The coal is powdered and mixed with heavy oil and catalyst (Ni and Co oleate) to make a paste.

2) This paste is heated with hydrogen at 450°C and 200-250atm pressure

3) The coal undergoes hydrogenation to form saturated hydrocarbons that decomposes at high temperature and pressure to give low-boiling liquid hydrocarbons.

4) This is subjected to fractional distillation to give.
(i) gasoline (ii) middle oil (iii) heavy oil

5) The gasoline obtained contained 74% paraffins, 22% aromatics and 4% olefins.

Refining of gasoline :-

=> Refing of gasoline we have to Refine following.

(a) Removal of Sulphur compound :

The procus of removal of sulphur is called sweetning. It occurs due to by treating gasoline with Sodium plumbite & also add Sulphur The sulphur compound converted into PbS. These procus is termed Doctors procus.

$$Na_2PbO_2 + 2RSH \longrightarrow Pb(SR)_2 + 2NaOH$$

$$Pb(SR)_2 + S \longrightarrow PbS + RSSR$$

(b) Removal of olefins :

Olefins are removed by percolating gasoline through the fuller's earth which preferentially absorb colouring & olefins

c) Stabilization of gasoline :

Impure gasoline may contain dissolved gases like CH_4, ethane propane & butane. The procus of removal of these impurities is called Stabilization.

(d) Blending :-

purified gasoline is blended with high octane number fractions

Knocking :-

The metallic sound similar to produced in internal combustion engine due to immature ignition of fuel air mixture.

Chemical structure and knocking:

1) Knocking tendency decreases with increase in complexities of the molecule.
2) Knocking decreases with the increase in the no. of double bonds and rings.
3) Knocking increases with increase in length of hydrocarbon chain.

n-butane < n-pentane < n-hexane] order of knocking.

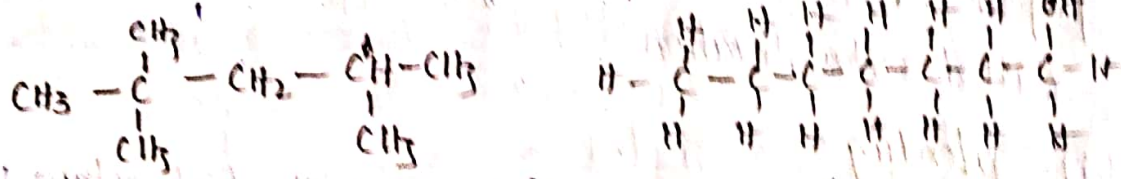
4) Knocking decreases with increase of branched in carbon

n-heptane > 2-methylhexane > 2,3-dimethyl pentane

5) Aromatics such as benzene & toulene have very high anti-knock properties.

Octane rating (or) octane number

The percentage of isooctane in a mixture of isooctane & n-heptane which at the same knocking characteristics as that of the fuel under ex same set of conditions.



Isooctane; (2,2,4-trimethyl pentane)
octane no - 100

(n-heptane)
octane no - 0

Anti knocking agents:

The substance which is used to control knocking. It called

TML (tetra methyl lead) & TEL (tetra ethyl lead) is used as antiknock.

* Prevention of knocking :-

1) High octane number fuel may used.
2) Anti-knocking agents may be used.

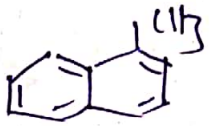
Adverse effect of knocking :

1) It results in decrease in efficiency.
2) It increase fuel consumption.
3) Driving and hauling become unpleasant.

Cetane rating / cetane number :-

The percentage of cetane [n-hexadecane] in a mixture of cetane and α-methylnaphthalene which will have the same ignition characteristics as the fuel under same conditions.

$CH_3-(CH_2)_4-CH_3$
(cetane)
(cetane no = 100)



α-methyl naphthalene.
(cetane no = 0)

Order of cetane :

n-alkanes > naphthalene > alkenes > branched alkene > aromatic

Re forming :-

Re forming is the process of improving the anti knocking characteristics of gasoline by bringing about certain (mod) structural modification in it.

* Paraffins converted to isoparaffins
* Paraffins are converted to naphthenes.