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CHEMICAL FUEL

→ fuel → defined as any subst. used to produce heat by combustion.

Combustion: any chemical process accompanied by evolution of light.

#

Classification of fuel

Physical State			Occurrence	
Solid fuel e.g wood, coal	Liquid fuel e.g: crude petrol.	Gaseous fuel e.g natural gas.	primary on natural	secondary or prepared e.g charcoal
			primary on wood	

#

Unit of heat

→

$$1 \text{ K cal} = 1000 \text{ cal} = 3.968 \text{ BTU} = 2.2 \text{ CHU}$$

$$1 \text{ BTU} = 252 \text{ cal} = 0.252 \text{ K cal}$$

⇒

$$1 \text{ cal/g} = 1 \text{ K cal/kg} = 1.077 \text{ BTU/lb}$$

$$1 \text{ K cal/m}^3 = 0.1077 \text{ BTU/ft}^3$$

$$1 \text{ BTU/ft}^3 = 9.3 \text{ K cal/m}^3$$

#

Gross & net calorific Value :-

i)

Gross Calorific value: (higher calorific value).

Total amount of heat generated when a unit quantity of fuel is completely burnt in oxygen & the products of combustion are cooled down to room temperature.

⇒ Latent heat is also involved.

⇒ HCV is determined by bomb calorimeter.

ii)

Net calorific value: (lower calorific value)

net heat produced when a unit quantity of fuel is completely burnt & the product of combustion are allowed to escape.

$$LCV = HCV - \text{Latent heat of Combustion}$$

$$= HCV - (\text{weight of H} \times 9 \times \text{latent heat of steam})$$

$$LCV = GCV - (H \times 0.09 \times 587)$$

$n = \text{wt. of H in fuel.}$

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Bomb Calorimeter

Determination of calorific value of solid & non-volatile liquid fuels.

⇒

Principle: The heat liberated by the fuel is equal to the heat absorbed by calorimeter & water.

weight of fuel taken = x

weight of water taken in calorimeter = w

initial temp = t_1 °C

final temp of water = t_2 °C

water equivalent of calorimeter, stirrer, bomb etc = w_{gm}

$$GCV = C \text{ cal/gm}$$

heat gained by water = $w \times \Delta t \times \text{specific heat of water}$

$$= w \times \Delta t \times 1$$

heat gained by calorimeter = $w(t_2 - t_1)$

heat liberated by fuel = $x C$

heat liberated by fuel = heat gained by water & calorimeter

$$x C = (w + w) \Delta t$$

$$x C = \frac{(w + w)(t_2 - t_1)}{x} \text{ cal/g}$$

\Rightarrow heat liberated during condensatⁿ of steam
 $= 0.09 \times 587 \text{ cal.}$

$$LCV = GCV - 0.09 \times 587$$

\Rightarrow 1) (a) The amount of H_2SO_4 & HNO_3 is analysed by washing of bomb by dilution while H_2SO_4 is determined by precipitation as $BaSO_4$.

for each 0.1 N H_2SO_4 , 3.6 cal. should be (-)
 " " 0.1 N HNO_3 , 1.43 " "

→ Correct GCV

$$GCV = \frac{(W+w)(t_2 - t_1 + tc) - (t_A + t_f + t_l)}{\text{mass of fuel}} \text{ c/g}$$

t_A = acid correction

t_f = fuse wire correction

t_l = cotton thread correction

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Boy's Calorimeter

Determination of calorific value of gases & volatile liquid fuels

W = wt. of cooling water passed in time t

V = volume of gas burnt at S.T.P in t

t_1 = incoming water temp

t_2 = outgoing water temp.

m = weight of steam condensed in t in a graduated cylinder.

θ = HCV of fuel.

Heat absorbed by circulating water = heat produced by combustion of fuel.

$$W(t_2 - t_1) = V\theta$$

$$\theta = \frac{W(t_2 - t_1)}{V} \text{ kcal/m}^3$$

Weight of H_2O condensed per m^3 of gas = $\frac{m}{V}$ kg.

Latent heat of steam per m^3 of gas = $\frac{m}{V} \times 587$ kcal.

$$NCV = \left[GCV - \frac{m \times 587}{V} \right] \text{ kcal/m}^3$$

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Coal:

fossil fuel produced from vegetable debris.

This transformation takes place in two stages:-

a) Biochemical or peat stage:

plant material were attacked by various microorganism.

b) Chemical stage or metamorphism:

the peat deposit buried under sedimentary deposits
lose moisture & volatile components.

Classification of Coal

On the basis of their degree of coalification from
parent material (wood.)

1. peat

lignite

Sub-bituminous bituminous

Anthracite

#

Analysis of Coal:

1. Proximate Analysis

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

$$\% \text{ of volatile matter} = \frac{\text{Loss of weight due to volatile matter} \times 100}{\text{Weight of coal taken}}$$

% of ash = $\frac{\text{weight of residue left}}{\text{height of coal}} \times 100$

% of fixed carbon = $100 - \% \text{ of (moisture + V.M + ash)}$

Significance of proximate analysis:

(i) Moisture:

- Excess of moisture is undesirable in coal. Increases transport costs.
- presence of excessive moisture quenches fire in the furnace.

(ii) Volatile matter:

- A high percent of volatile matter indicates that a large proportion of fuel is burnt as gas.
- high volatile content gives long flames, high smoke & relatively low heat heating values.

(iii) Ash:

- The high percentage of ash is undesirable.
- In furnace grates, the ash may restrict the passage of air & lower the rate of combustion.

(iv) ↑ the % of fixed carbon, ↑ its C.V.

2. Ultimate analysis:

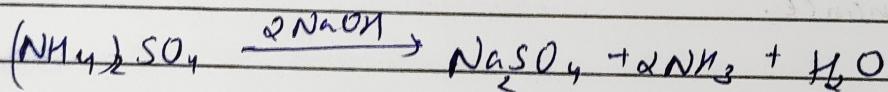
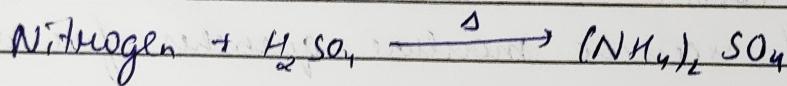
$$\% \text{ of Carbon} = \frac{12}{44} \times \frac{y \times 100}{\text{weight of coal taken}}$$

$$\% \text{ of H} = \frac{2}{18} \times \frac{z \times 100}{\text{weight of coal taken}}$$

$y =$ increase in weight of KOH tube
 $z =$ increase in weight of CaCl_2 tube.



(2) Kjeldahl's method : (for Nitrogen).



$$\% \text{ of N} = \frac{\text{Vol. of acid used} \times \text{normality of acid} \times 1.4}{\text{wt. of coal taken}}$$

(3) Sulphur:

$$\% \text{ of sulphur} = \frac{\text{wt. of } \text{BaSO}_4 \times 32 \times 100}{\text{wt. of coal} \times 233}$$

(4) Ash as above

$$\% \text{ of O} = 100 - \% (\text{C} + \text{H} + \text{S} + \text{N} + \text{ash})$$

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Dulong's Formula:

Substrate	C.V
C	8080
H	34500
S	2240

$$HCV = \frac{1}{100} [8080C + 34500(H - \frac{O}{8}) + 2240S] \text{ kJ/kg}$$

$$LCV = [HCV - \frac{9H}{100} \times 587]$$

$$= [HCV - 0.09H \times 587] \text{ kJ/kg}$$

⇒ If O is also present, it combines with H to form H_2O . Thus H in the combined form is not available for combustion & is called fixed Hydrogen.

mass of H for combustion = Total mass of H - $\frac{1}{8}$ mass of O in fuel

$$= H - \frac{O}{8}$$

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Liquid fuels:-

① Refining of petroleum :-

Demulsification: The crude oil coming out from the well, is in the form of stable emulsion of oil & salt water, which is yellow to dark in colour.

Demulsification is achieved by Cottrell's process, in which the water is removed from the oil by electrical process. The crude oil is subjected to an electrical field, when droplets of colloidal water coalesce to form large drops which separate out from the oil.

Removal of harmful impurities:

$\text{NaCl} \& \text{MgCl}_2$ → by washing with water

Sulphur → Copper oxide.

Then copper sulphide so formed is separated by filtration.

(iii) fractional Distillation: (done in tall fractionating tower)

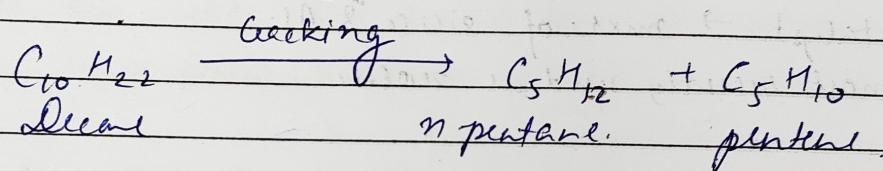
- Crude oil is preheated to 400°C in specially designed tubular furnace known pipe still.
- The hot vapours from the crude are passed through a tall fractionating column, called bubble tower.
- Bubble tower consists of horizontal trays provided with a no of small chimneys, these chimneys are covered with loose caps called bubble caps.
- Bubble caps helps to provide an intimate contact b/w the escaping vapours & down coming liquid.
- The temp. in the fractionating fractionating tower decreases gradually on moving upwards.
- As the vapours of the crude oil go up, they become gradually cooler & fractional condensation take place at different heights of column.

→ The residue from the bottom of fractionating tower is vacuum distilled to recover various fractions.

CRACKING :-

→ Gasoline is most imp. fraction of crude petroleum.
The yield = 20% of crude oil.

The decomposition of high boiling bigger hydrocarbon molecules into simple low boiling hydrocarbons of lower molecular weight



Cracking is usually done by two methods

Thermal cracking Catalytic Cracking

1) Thermal Cracking:

takes place simply by application of heat & pressure

a) Liquid Phase thermal cracking

The charge is kept in the liq. form by applying high pres. at suitable temp. The cracked products are separated in a fractionating column.

important fractions: cracked gasoline (30-35%)

Cracking gases (10-45-1)

cracked fuel oil (50-55%)

Octane Rating of petrol \Rightarrow 65 - 70

cycle → 50-60%.

b) Moving bed catalytic cracking
also called fluid bed catalytic cracking.

→ Catalyst is in the form of fine powder which flows down to the cracking chamber via gas stream.

→ Advantages of catalytic cracking over thermal cracking :-

- no high temp & press. req.
- yield of gasoline is higher & quality is better
- no extra fuel is required.
- yield less coke, less gas & more liq. product.
- process can be better controlled so desired products can be obtained.
- not only accelerates the cracking reaction but also introduces new rxns.

Reforming : Change the st. of molecule:-

process of bringing st. modification in components of straight run gasoline with primary obj. of improving its anti-knock.

→ Obtained by ↑ volatility &
conversion of "pentaffins" to iso pentaffins, olefins to aromatics.

→ Cracking converts → heavier oils $\xrightarrow{\text{into}}$ gasoline $\xrightarrow{\text{into}}$ higher octane number.

① Thermal Reforming:-

- carried out in 500-600°C & @ 85 atm.
- To avoid formation of gas, we have rapid cooling of product.
- During this, some cracking also occurs to yield alkanes & alkenes & these might undergo dehydrogenation followed by

b) Vapor phase thermal cracking:-

- Only those oil which vaporize at low temp. can be cracked.
- The oil is first vaporized & then cracked at about high temp. & under a low press.
- Petrol obtained from vapor phase cracking has better anti-knock properties.

2) Catalytic Cracking:-

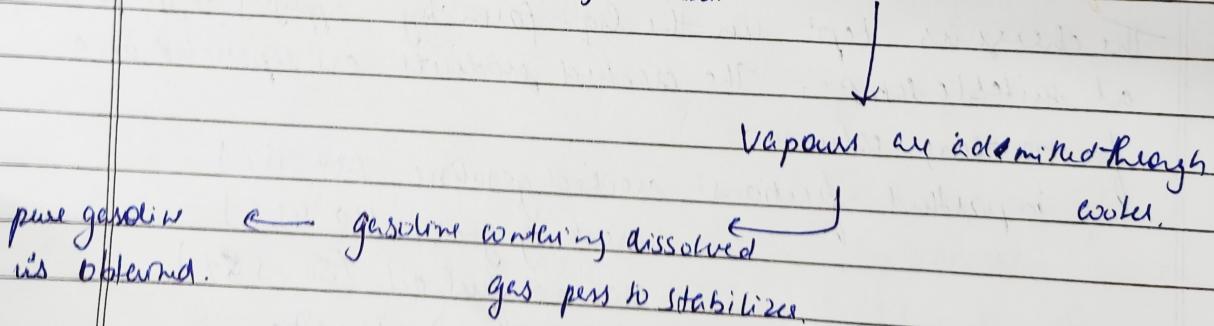
~~#~~ Catalytic Cracking:-

- It is done in the presence of catalyst at much low temp. & press.
- Catalyst → mixt. of silica & Al.
most recently used is zeolites.
- The quantity & yield of gasoline is greatly improved.

Types of catalytic cracking:

a) fixed bed catalytic cracking:

- Catalyst is in the form of granules or pellets.
 - These granules are used in form of fixed beds on catalyst towers.
- Heavy oil $\xrightarrow{\text{converted}} \text{vapor}$ $\xrightarrow[\text{by passing through packed tower.}]{\text{H}_2\text{O, chey} \rightarrow \text{gasoline}}$ now enters fractionating column



dehydrocyclization to yield π naphthalene (aromatization).

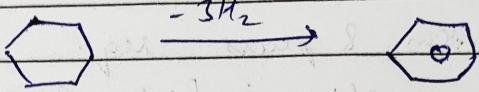
n -alkanes $\xrightarrow[\text{refining}]{\text{heated}}$ branched chain alkanes

(2)

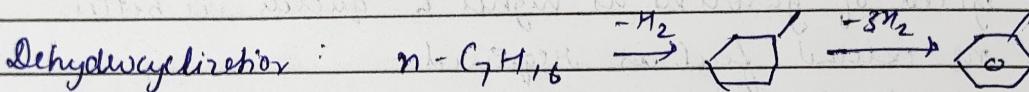
Catalytic reforming :-

main rxns during catalytic reforming process are \rightarrow

i) Dehydrogenation :



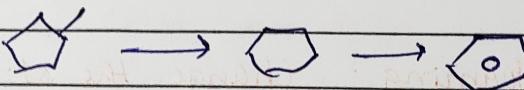
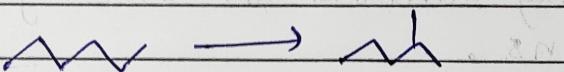
ii) Dehydrocyclization :



iii) Hydrocracking



iv) Isomerization



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Knocking

In an internal combustion engine, a phenomenon that occurs when unburned fuel-air mixt. explodes in the combustion chamber before being ignited by the spark. The resulting shock waves produce a metallic knocking sound.

→ straight chain Hydrocarbon \uparrow Knocking \uparrow

Aromatics < cycloalkanes < olefins < branched chain alkanes
< straight chain alkanes

Antiknocking:

⇒ That's Anti-knocking agent is gasoline additive to reduce engine knocking & fuel octane rating.

e.g. of antiknocking \rightarrow

diethyl ethyl lead (toxic)

methyl tertiary butyl ether
toluenes

①

Octane number: % of iso-octane present in a mix of iso-octane & n-heptane, which has same knocking characteristics under same set of conditions.

Thus gasoline with 80 octane no., gives same knocking as mixt. of iso-octane & n-heptane containing 80% of iso-octane by volume.

\uparrow Octane no., \uparrow antiknock

②

Cetane number:

A separate scale is used to grade the diesel oils as they cannot be graded on octane no. scale.

\rightarrow It is defined as % of cetane in a mixture of cetane & a methyl naphthalene which will have the same ignition characteristics as fuel under same set of condⁿ.

#

Producer Gas:-

mixt. of combustible gas (O₂ & H₂ with large) of non-combustible gas N₂, CO₂ etc.

typical producer gas from coke contains 27% CO, 12% H₂, 0.5% CH₄, 5% CO₂ & 55% N₂ by volume.

heating value \rightarrow 5000 kJ/m³.

\rightarrow It is cheap, clean & easily preparable gas.

Applications

- (1) industrial fuel for iron & steel manufac.
- (2) cement & ceramic kilns
- (3) as reducing agent
- (4) for mechanical power

Water Gas :-

→ poisonous flammable gas mixt. of CO & H_2 , with small amount of CH_4 , CO_2 , N_2

Applications

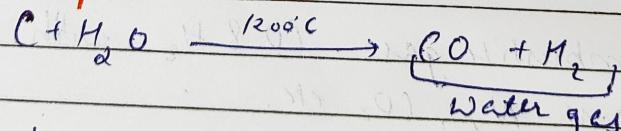
- as source of H_2 gas.
- fuel gas
- an illuminating gas

Synthetic Petrol :

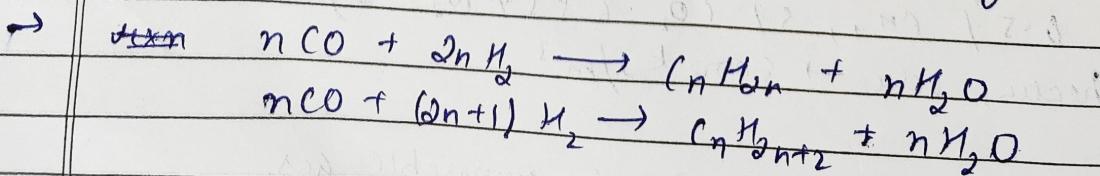
direct ~~solid~~ coal $\xrightarrow{\text{conversion}}$ synthetic fuel (Bergius process).

indirect coal \rightarrow synthetic (where coal is gasified & then converts to synthetic fuel)
Fischer Tropsch process

(1) Fischer Tropsch method :-



→ purified by passing through Fe_2O_3 (removes H_2S) & then through $\text{Fe}_2\text{O}_3 \cdot \text{Na}_2\text{CO}_3$ (removes organic S compound).

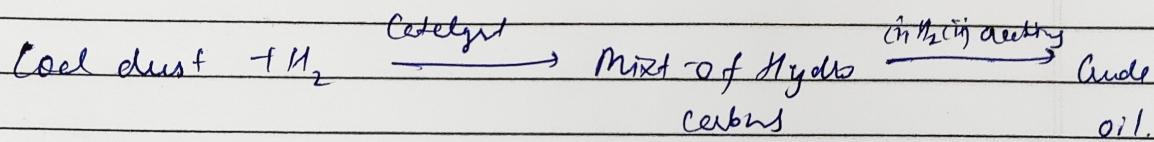


Mixt. of saturated & unsaturated hydrocarbons result.

- Rxn is exothermic.
- crude oil thus obtained is then fractioned to yield
(i) gasoline (ii) high boiling heavy oil.

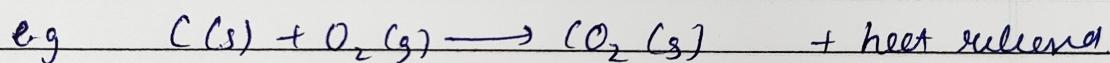
② Bergius process :-

- Indirectly coal is converted to synthetic fuel.
- first coal is gasified & then converts to synthetic fuel.



Combustion :

- exothermic chemical fuel.
- accompanied by evolution of heat & light & temp rises.



Ignition temp: minⁿ temp at which the sub. ignites & burns without further additⁿ of heat from outside.
e.g. H = 6 to 71 (ignitⁿ range).



Numerical Part