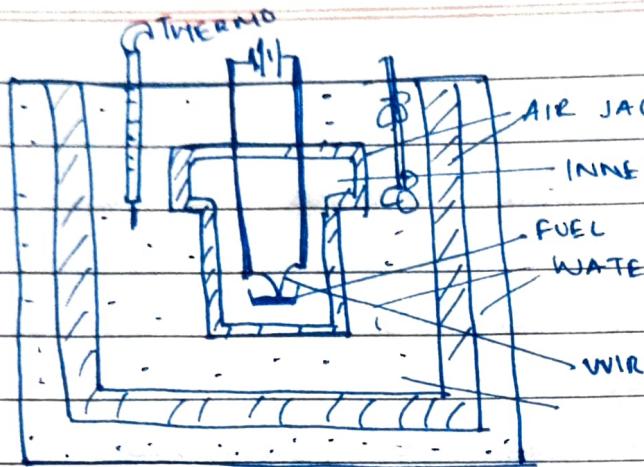


## FUELS



AIR JACKET (0.5-lg) full is burnt in inner bomb and heat temperature raised in the intermediate bath with water of known mass is noted.

## # BOMB CALORIMETER

$m$  = mass of fuel (g)

$W$  = Mass of water

$w$  = water equivalent

$t_1$  = initial temp.

$t_2$  = final temp.

$H$  = Higher Calorific value

$L$  = Lower " "

Heat liberated =  $m \times H$

Heat absorbed =  $(W+w)(t_2 - t_1)$

$$\therefore mH = (W+w)(t_2 - t_1)$$

$$H = (W+w)(t_2 - t_1) / m \text{ cal/g}$$

$L = H - \text{Heat of vaporization}$

$$= (W+w)(t_2 - t_1) - 0.09 \times a \times 587 \quad (\text{where, } a \text{ is} \\ \text{ % Hydrogen})$$

## # Corre

### \* Corrections :

1) Wire corrections: Heat due to burning of wire subtracted

2) Acid correction: Sulphur & nitrogen burnt liberate produce respective acids with an exothermic  $\nu^{\circ}$ . This needs to be separated after calculating their amounts through titration (with  $N/10 \text{ Ba(OH)}_2$ )

15) Explain process of ultimate analysis of coal.

3) Cooling correction: Time taken to cool the water down in case of HCV is noted and added to  $t_2 - t_1$ .

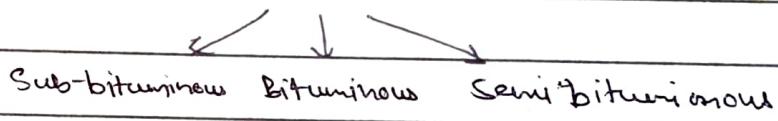
$$\therefore L = \frac{(W+w)}{m} (t_2 - t_1 + \text{cooling corr.}) - (\text{Acid corr.} + \text{Fus. corr.})$$

# OAL:

$\Rightarrow$  Composed of C (preferable), H, N, and O.

$\Rightarrow$  Ranking (based on %):

Wood  $\rightarrow$  Peat  $\rightarrow$  Lignite  $\rightarrow$  Bituminous  $\rightarrow$  Anthracite.



$\Rightarrow$  Criteria of Selection:

(i) Calorific Value: (preferably High)

(ii) Moisture content: ( $t_{ref.}$  low)

(iii) Ash content: (pref. low) : 1% ash causes 1.5% heat loss

~~•~~  $\rightarrow$  Composition of heat: Affects metal & slag composition

$\rightarrow$  Fusion temperature of ash: If used below this temp. ash forms clinkers and restricts air flow, it also sticks to boiler and cause heat transfer issues.

(iv) Calorific intensity: ( $t_{ref. low}$ ): maximum temperature at which coal burns completely. \* Flaming fuels have low C while flameless fuels have high C.

(v) Size of coal: (pref. uniform). Non uniformity interferes in flow of air ~~and~~, inconsistent combustion ~~and~~ difficult handling.

(vi) Sulphur/Phosphorus content (pref. low); produce corrosive/polluting gas

Proximate analysis: Determination of proportion of combustible & non-combustible constituents of coal to have an idea of its buying, selling and using. Date: Page No:

### (vii) Coking quality:

Coals which on heating without air become soft, plastic and fusible are called coking coals while those which become porous, hard and strong are called coking coals.

## → Analysis of Coal:

### \*1 PROXIMATE ANALYSES

(i) Moisture: Though it evaporates during combustion & reduces calorific value, 10% moisture is essential to make uniform fuel-bed & less fly-ash. ( $105^{\circ}-110^{\circ}\text{C}$  test temp.)

1. Weigh 1g powdered air-dried coal
2. Place in oven with  $105^{\circ}-110^{\circ}\text{C}$  for 1 hr.
3. Take out, cool, and measure weight:  
 $\% \text{ moisture} = \frac{\text{loss in wt.}}{\text{wt. of coal}} \times 100$

(ii) Volatile matter: Burn with long flame, high smoke and lower the CV.

1. Take 1g dried sample.
2. Place it in a furnace with  $925^{\circ}\pm 20^{\circ}\text{C}$  for 7 min.
3. Take the crucible out, cool, place in desiccator, weigh again:  
 $\% \text{ volatile matter} = \frac{\text{loss in wt.}}{\text{wt. of coal}} \times 100$

(iii) Ash: Useless, non-combustible matter that hinders air flow, reduces CV, forms clinkers, increases costs of transport, handling, disposal.

, wear and tear

1. Heat the residual coal without Ud at  $700 \pm 5^\circ\text{C}$  for 30 min.
  2. Take crucible out, cool, place in desiccator, weigh till constant.
  3. Repeat till constant wt. is achieved.
- $\% \text{ ash content} = \frac{\text{Wt. of remaining ash}}{\text{Wt. of coal}} \times 100$

(iv) Fixed Carbon: Higher the better.

$$\% \text{ fixed C} = 100 - \% (\text{moisture} + \text{volatile} + \text{ash})$$

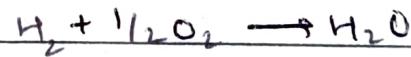
## \*2 ULTIMATE ANALYSIS:

(i) Carbon & Hydrogen: Greater the better as both increase CV. However, H is volatile.

1. Weigh 1-2g and burn it in  $O_2$ .

\* C converts to  $CO_2 \rightarrow$  absorbed in KOH tube

\* H converts to  $H_2O \rightarrow$  absorbed in  $CaCl_2$  tube

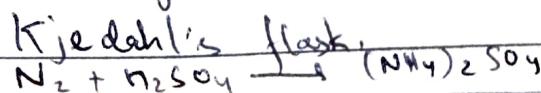


$$\% C = \frac{\text{Increase in wt. of KOH tube} \times 12 \times 100}{\text{Wt. of coal sample} \times 44}$$

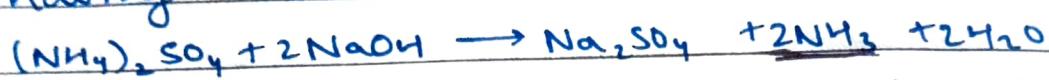
$$\% H = \frac{\text{Increase in wt. of } CaCl_2 \text{ tube} \times 2 \times 100}{\text{Wt. of coal sample} \times 18}$$

(ii) Nitrogen: No calorific value, generates pollutants, lesser the better.

1. Heat 1g coal with conc.  $H_2SO_4$  &  $K_2SO_4/CuSO_4$  in



2. After clearance transfer contents to another flask having excess KOH/NaOH.



3. Absorb this  $NH_3$  in known vol. of acid after distillation.

4. Perform back titration to find unused acid amount (with NaOH)

$$\%N = \frac{\text{Volume of acid used} \times \text{Normality} \times 1.9}{\text{Wt. of coal sample}}$$

(iii) Sulphur: Adds CV but makes corrosive acids, enters in metals during metallurgy, and causes pollution.

1. Treat calorimeter washings with BaCl<sub>2</sub>

2. Filter BaSO<sub>4</sub> ppt., wash, heat and weigh.

$$\%S = \frac{\text{Wt. of BaSO}_4 \times 32 \times 100}{\text{Wt. of coal in boats} \times 233}$$

(iv) Ash: Same as proximate analysis

(v) Oxygen: Decreases CV, indicates high moisture, lesser coking power, 1% increase in O<sub>2</sub> decreases CV by 1.7%.

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

⇒ Pulverized Coal: Coal broken into fine particles.

Slow combustion of normal solid coal can be increased by

(i) Increasing O<sub>2</sub> supply. or,

\* (ii) Increasing surface area (done in pulverized coal)  
to increase air contact.

Adv:

1. Easy transport

2. Controlled rate of combustion

3. Ease of starting/stopping combustion.
4. Uniform flame
5. less air required for complete combustion.
6. High thermal efficiency.
7. High temp.
8. No clinkers.

Disadvantages:

1. Cost of pulverization
2. Extremely fine ash, greater pollutant.

## # PETROLEUM:

Composed of hydrocarbons (straight chain paraffins, cycloparaffins, naphthalenes, olefins, aromatics). Also contains small amounts of organic compounds of O, N & S.  
\* Oil is found floating on brine (seawater) with gas layer on it.

$$C = 80 - 87\% ; H = 12 - 15\% ; S = 0.1 - 3.5\% , N + O = 0.1 - 0.5\%$$

$\Rightarrow$  classifications:

1. Paraffin-based - composed of saturated hydrocarbons ( $C_4 - C_{35}H_{72}$ ) and some aromatics & naphthalenes.  
\*  $C_{18}H_{38} - C_{35}H_{72}$  are semi-solid called waxes
2. Asphaltic-based - composed of cycloparaffins and some aromatics, naphthalenes & paraffins.
3. Mixed-based - composed of both, especially rich in waxes.

## ⇒ Refining:

1. Separate Water (Cottrell's Process):  
split water and oil from stable emulsion.

2. Remove sulphur compounds:

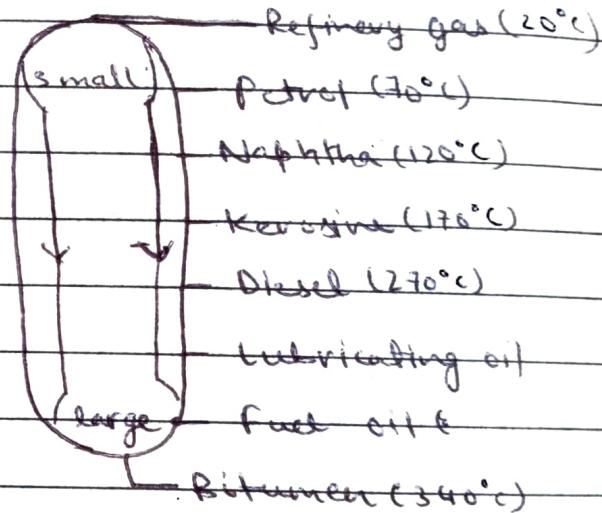
Treatment with CuO (remove S by filtration)

3. Fractional Distillation:

Heating @  $400^{\circ}\text{C}$ , condensing through difference in boiling point of volatile compound.

Height of tower = 60m

Diameter at top/bottom = 1.2 - 2m



### \* Major Refined fuels ←

(i) Petrol (Gasoline)

(ii) Kerosene

(iii) Diesel

	Petrol	Kerosene	Diesel
Boiling	$40-120^{\circ}\text{C}$	$180-250^{\circ}\text{C}$	$250-320^{\circ}\text{C}$
Hydrocarb composition	$\text{C}_{5}\text{H}_{12} - \text{C}_{8}\text{H}_{18}$ $\text{C}=84\%, \text{H}=15\%$	$\text{C}_{10}\text{H}_{22} - \text{C}_{16}\text{H}_{34}$ $\text{C}=84\%, \text{H}=16\%$	$\text{C}_{18}\text{H}_{32} - \text{C}_{18}\text{H}_{38}$ $\text{C}=86\%, \text{H}=14\%$
$\text{N} + \text{S} + \text{O} = 1\%$		$\text{S} = 0.1\%$	$\text{S} \leq 0.1\%$
C%	11.250	>	11.100
specific gravity	$0.68-0.74$	<	$0.75-0.85$
Volatility	High	Low	Low

+ Octane Rating = Ability to resist knock (described later)

Date:

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## # IMPORTANT COMPARISON B/w PETROL & DIESEL

### Diesel Fuel

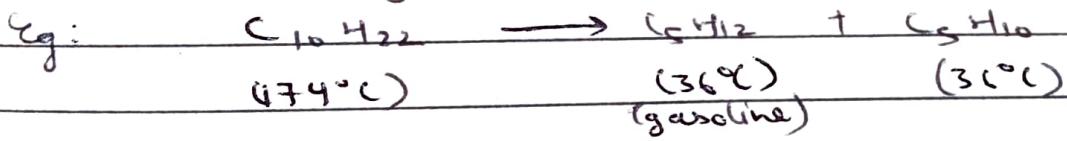
- 1. Cheap
- 2. less consumption per unit power  
(Thermal efficiency 30-35%)
- 3. Less pollutants ( $\text{CO}_2$ , oxides of N, hydrocarbons etc.)
- 4. Requires a complex and expensive fuel injection device
- 5. Requires heavy air compressors
- 6. Eject more particulate pollutants

### Gasoline Fuel

- 1. Costly
- 2. More consumption per unit power  
(Thermal efficiency 25%)
- 3. More pollutants
- 4. Simple combustion engine
- 5. No compressor required
- 6. Eject less particulate matter.

## ⇒ Cracking:

Decomposition of bigger hydrocarbons to simpler, low BP, high usability hydrocarbons.



Highly demanded gasoline is achieved only at 20% from direct refining that too in poor quality. To resolve this middle/heavy fuels are cracked to fetch gasoline.

### I THERMAL CRACKING (Heavy fuels @ high temp. & press)

(a) Liquid-phase thermal cracking: ( $T = 475-530^\circ\text{C}$ ;  $P = 100\text{ kg/cm}^2$ )

Yield = 50-60%      Octane Rating  $\dagger = 65-70$

(b) Extracted from fractionating column.

(b) Vapour-phase thermal cracking: ( $T = 600-650^\circ\text{C}$ ;  $P = 10-20\text{ kg/cm}^2$ )

Yield = 50-60%      Octane Rating  $> 70\%$

Quicker but less stable.

## \* 2 CATALYTIC CRACKING: (Usage of $\text{Al}_2\text{O}_3$ (alumina) / $\text{Al}_2(\text{SiO}_4)_3$ , (alumina silicate))

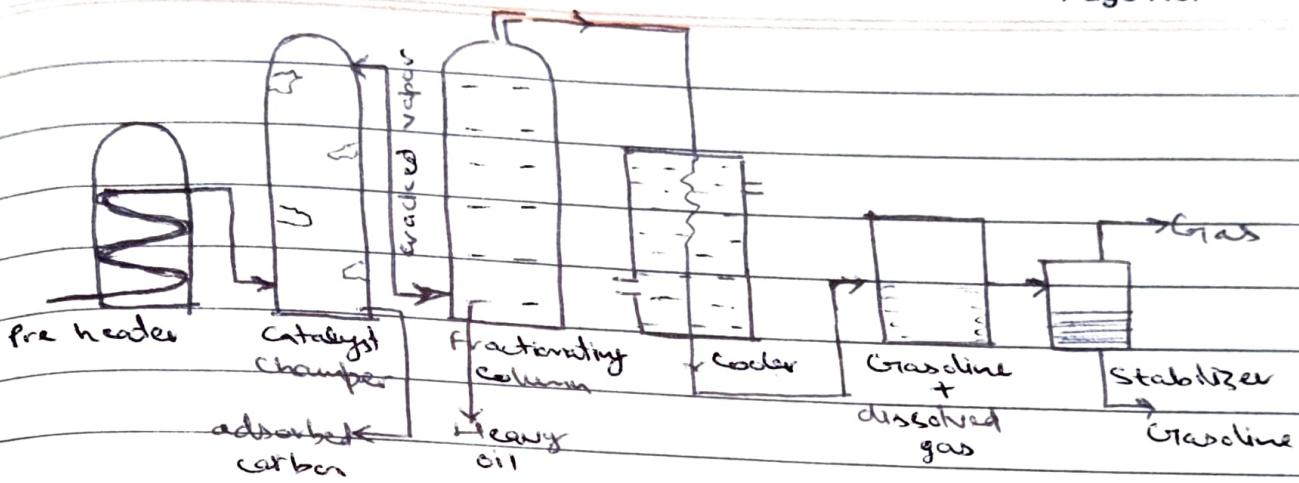
Adv. :

- (i) High yield
- (ii) High quality
- (iii) No external fuel required
- (iv) Low pressure suitable
- (v) Controllable process
- (vi) Negligible by-products
- (vii) More aromatics (better at anti-knocking  $\therefore >$  octane rating)
- (viii) More branched hydrocarbon (desirable)
- (ix) Low sulphur production
- (x) Aromatic decomposition doesn't break the ring }

(a) Fixed-bed catalytic cracking : ( $T = 425 - 450^\circ\text{C}$ )  $P = 1.5 \text{ kg/a}$

Procedure :

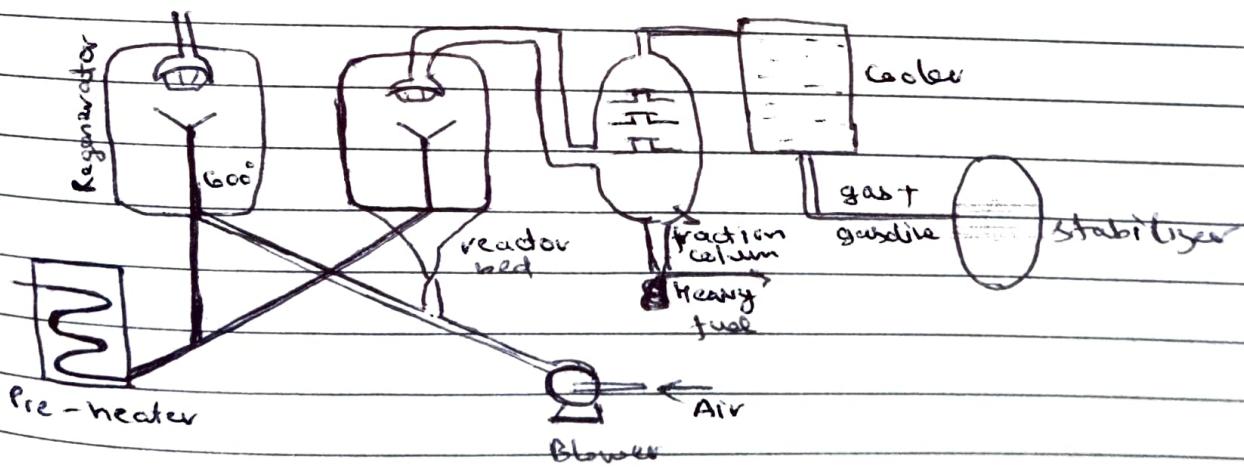
1. Oil vapours @  $425 - 450^\circ\text{C}$  are put in a catalytic chamber with bauxite/zeolite/alumina silicate/bentonite at cont temp & press.
2. Gasoline vapours are produced alongwith solid C. This C gets adsorbed in catalyst bed.
3. The vapours pass through fractionating column, then through cooler (for condensation) (a part of these vapours get condensed and extracted while the rest move further)
4. These gases go to stabilizer where other dissolved gases are removed and pure gasoline is achieved.
5. Once the catalyst gets saturated after every 8-10 hours, it can be reactivated by the adsorbed carbon in step 2.



### (b) Moving - bed catalytic cracking:

Procedure:

1. Finely powdered solid catalyst gets mixed with the vapour stream and the fluidized mixture is forced into reactor bed.
2. A centrifugal separator (cyclone) separates the cracked product with catalyst.
3. The catalyst settles at bottom after carbon coating from where the blower throws it in the regenerator ( $600^{\circ}\text{C}$ )
4. While the cracked vapours are passed through the fractionating column followed by coker followed by stabilizer (same as fixed-bed).



## ⇒ Knocking

When a mixture of air-fuel is ignited by spark in an internal combustion engine, the flame is expected to spread rapidly though smoothly. However due to certain fuel components, this mixture can ignite instantaneously. This is called knocking and is undesirable.

### \* Some key points:

1. Gasoline engines: air : fuel  $\approx 14.6 : 1$  (Stoichiometric)

2. Diesel engines: air : fuel  $= 25 - 30 : 1$

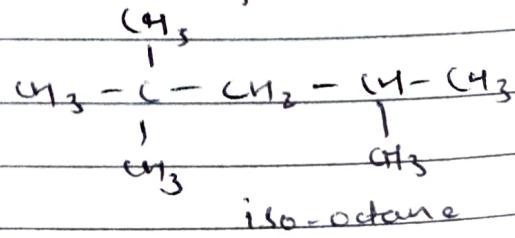
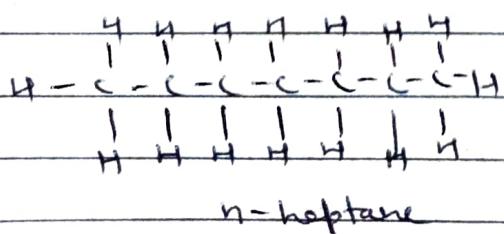
2. Compression Ratio: The ratio of volume of gas in cylinder at the end of suction stroke of the piston to the volume of gas in cylinder at the end of compression stroke of piston. (Higher the better).

3. Tendency to knock: straight chain paraffins  $>$  branched-chain paraffins  $>$  olefins  $>$  cycloparaffins  $>$  aromatics.

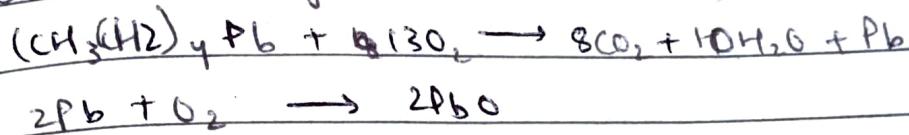
## # Octane rating / Octane number (O.N.)

It was observed that n-heptane knocks badly while isooctane knocks negligibly. Thus an octane rating scale was made with n-heptane given an O.N. of 0 and iso-octane an O.N. of 100.

Thus, if a fuel has 70 as O.N. it knocks equivalent to a 70:30 mixture of isooctane & n-heptane.



\* Anti-knocking: Tetraethyl lead (TEL) burns to produce a cloud of finely divide PbO which prevents knocking ( $V/V = 0.5 \text{ ml/l}$ )



However, this PbO is harmful for engine life.

Thus, 1,2-dibromoethane is used to eradicate the unusable.  $Pb + C_2H_2Br - (C_2H_2Br)_{(v\text{olatile})} \rightarrow PbBr_2 + H_2$

\* Another additive is diethyl telluride ( $V/V = 1-1.5 \text{ ml/l}$ )

### => Diesel Engines:

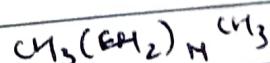
- > Diesel has longer hydrocarbon chain than petrol
- > Diesel can ignite below compression temperature
- > In diesel engines, air is compressed to reach very high temp. Diesel is thereafter injected to it. This fuel ignites by the heat of compression. Thus, diesel engines are called compression-ignition engine.

### # Cetane Number (C.N)

Similar scale as octane rating but in case of diesel. The 0 CN is assigned to 2-methyl naphthalene (knocks badly) while 100 CN is given to n-hexadecane.



2-methyl naphthalene



n-hexadecane

\* Additives to decrease knocking: Ethyl nitrite, isoamyl nitrite, acetone peroxide.

⇒ Liquefied Petroleum Gas (LPG) / Refinery Gas

Properties:

- > Comprises of gases under atm which easily liquify on pressure
- > Composed of: n-butane, iso-butane, butylene, propane, small amounts of propylene & ethane.
- > Generally extracted as a by-product of cracking of natural gas.
- > Added with odorous organic sulphides (mercaptanes) for gas leak warning.
- > Calorific value = 27800 kcal/m<sup>3</sup>
- > Used as domestic, industrial and motor fuel.

#### # Adv. over gaseous fuels

1. High efficiency (3 times of Natural gas, 7 times of coal gas)
2. Complete combustion (without smoke)
3. Less maintenance
4. Portable in cylinders
5. Clean & easy to handle, store, use.
6. Controllable (less hazardous)
7. No  $\text{CO}_2$  produced.

#### # Adv. over gasoline (motor fuel)

1. Cheap
2. Miscible with air
3. Knock resistance
4. No residue
5. Increased engine life

- # Disadv. over gasoline (motor fuel)
  1. Less odor thus tough leakage detection
  2. Pressurized handling required
  3. Engine must have high compression ratio
  4. Low octane no.

⇒ Natural Gas