MODULE - III

FUELS

- Fuel is a combustible substance containing C as main constituent which on proper burning gives large amount of heat that can be used for domestic & industrial purposes.
eg- wood, coal, charcoal, kerosene, petrol.

FOSSIL FUEL

The primary & the main sources of the fuel are coals & petrolium oils & these are stored fuel available in earth crust & are called fossil fuel.

Classification

(1) On the basis of occurance:

Fuel has classified as two types. ~~(a) natural~~

(a) natural → Primary fuel

(b) artificial → secondary fuel.

Natural fuel: Fuel which are found from nature. eg- wood, Petrolium, coal, natural gas.

Artificial fuel: Fuel which are derived artificially from ~~Primary~~ primary fuel, is known as artificial fuel.
eg- kerosene, coal gas, LPG.

(2) ~~On the~~ basis of physical state of aggregation

These are of 3 types.

solid - wood, coal, coke

liquid - kerosene, petrol, diesel

gas - LPG, coal gas, natural gas.

Unit of heat

CGS system - Calorie :- It is the amt. of heat required to raise the temp. of 1gm. of H_2O through 1°C.

MKS system - Killo calorie: It is the amt. of heat required to raise the temp. of 1 kg of H_2O through 1°c.

$$\boxed{1 \text{ kcal} = 1000 \text{ cal.}}$$

British thermal unit. (BTU / BTHU)

It is the amt. of heat required to raise temp. of 1 pound of H_2O through 1° F.

$$\boxed{1 \text{ BTHU} = 252 \text{ cal.} = 0.252 \text{ cal.}}$$

Centigrade heat unit. (CHU)

This ~~is~~ the amt. of heat required to raise the temp. of 1 pound of H_2O through 1°c.

$$\boxed{1 \text{ kcal} = 3.968 \text{ BTHU} = 2.2 \text{ CHU}}$$

Calorific value. (cv)

- It ~~is the~~ total amount of heat liberated when a unit mass or vol. of fuel is burnt completely.
- It is of 2 types. (I) Higher calorific value (HCV) Gross
  (II) Lower calorific value (LCV) Net. (NCV)

HCV - It is the total amt. of heat liberated when unit mass or vol. of the fuel has been burnt completely & the product of combustion are cooled to room temp.

LCV / NCV - It is defined as the net heat produced when a unit mass or vol. of fuel is burnt completely & the combustion products are allowed to escape.

$$\boxed{LCV = GCV / HCV - \text{Latent heat of vap}}$$
587.

= HCV - (mass of H_2 × latent heat of vapourisation)

(∵ 2 parts of H_2 produce 18 parts of H_2O)

= HCV − (mass of H_2 × 9 × latent heat of vap.)

(∵ 2 parts of H_2 produce 18 parts of H_2)

Unit of calorific value.

For solid & liquid fuel unit is Solid Calories/gm.

kcal/kgm, BTHU / Lb

heat fuel = cal / cm3

= kcal / m3

= BTHU / (ft)^3

→ High Caloreific Intensity
It is the maximum temp. attained when the fuel is burnt.
(2) → Should be high to melt certain.

Characteristic of good fuel.

(i) It should have high calorific value.

(ii) Moderate ignition temp:

- Low ignition temp. is dangerous for storage & transportation of fuel since it can cause fire hazard.

Ignition temp - The minm temp. required to preheat the fuel or to start combustion so that it starts burning smoothly

- High ignition temp. can cause difficulty in kindling or ignition. But the fuel is safe during storage, handling & transport. Hence the ideal fuel should have moderate temp.

(iii) Low moisture content - A good fuel should contain Low moisture bcz moisture will reduce the calorific value.

- Low non-combustible matter content it reduces the total heat by producing ash.

(iv) Moderate velocity of combustion

(v) Harmless combustion bi-product

(vi) Low cost.

(vii) Easy transportation - Solid & liq. fuels are easy for transportation. But the transportation of gasseous fuel is very costly.

viii) combustion may be controllable

ix) It should not undergo spontaneous combustion

x) It should burn in air with efficiency without much smoke.

Comparision betn solid, liquid, gasseous fuel

	Solid	liquid	gas
Calorific value →	least	higher	highest
Cost →	Cheap	more costly than solid	Costly
Storage & transportatn →	convinient	easy to transport through pipe lines but care must be taken to store them in close containers.	should be stored in voluminous storage tan[k] & can be distributed through pipe lines.
Risk of fire hazard →	least	greater risk than solid fuel	highly risk[y] as they are highly inflammable.
Rate of combustion →	slow process	quick process	very rapi[d] ~~efficient~~
Rate of control →	not easy	it can be controlled or stopped when needed	possible b[y] controlling air supply
handling cost →	high bcz need more labour & space.	low	low.

	Solid	liquid	gass
Ash contain →	Ash is always a problem or its disposal is also a problem	no ash	no ash.
smoke →	more smoke	less smoke	No.
Use in IC engine →	not possible	possible	possible
thermal efficiency →	least	higher	highest.

Imp. Theoritical calculation of calorific value by Dulong's formula :-

CV of the fuel is the sum of CV due to all components present in the given fuel.

Constituent	C	H	S
GCV in kcal/kg	8080	34500	2240

$$\boxed{GCV = \frac{1}{100}\left[8080C + 34500\left(H - O/8\right) + 2240S\right]}$$

$$\boxed{NCV = \left[GCV - 0.09\, H \times 587\right] \text{ kcal/kg.}}$$

where C is the % of C.
H is the % of H.
S is the % of S.

Calculate the gross & net CV of a sample having following composition. C = 80%, H = 7%, O = 3%, S = 3.5%, N = 2.5%, ash = 4.44%.

Soln

$$GCV = \frac{1}{100}\left[8080 \times 80 + 34500\left(7 - 3/8\right) + 2240 \times 3.5\right]$$

$$= 8828.025$$

$$NCV = GCV - 0.09H \times 587$$

$$= 8458.215$$

(2) Calculate the HCV & NCV of a sample of coal by wt. having the following composition $C = 75\%$, $H = 5.2\%$, $O = 12.1\%$, $N = 3.2\%$, ash $= 4.5\%$

Sol^n

$$HCV = \frac{1}{100}\left[8080C + 34500\left(H - O/8\right)\right]$$

$$= \frac{1}{100}\left[8080 \times 75 + 34500\left(5.2 - \frac{12.1}{8}\right)\right]$$

$$= 7332.1875 \text{ Kcal/kg}$$

$$NCV = \left[HCV - 0.09H \times 587\right] \text{ kcal/kg}$$

$$= 7332.1875 - 0.09 \times 5.2 \times 587$$

$$= 7057.4715 \text{ Kcal/kg.}$$

Imp.

Combustion calculation

The process of oxd^n of fuel producing heat & light at a rapid rate is called as combustion.

Calculation

Combustion calculation is based on balance chemical eq^n of oxd^n of constituents of fuel.

(1) Carbon

Combustion eq^n. $-$ $C + O_2 \longrightarrow CO_2$

12 gm.	32 gm.	44 gm.
1 vol.	1 vol.	1 vol.

Mass O_2 required $= \frac{32}{12} \times$ mass of C.

vol. of O_2 required $= \frac{1}{1} \times$ vol. of C.

(2) Hydrogen

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

2 gm.	16 gm.	18 gm.
1 vol.	½ vol.	1 vol.

mass of O_2 $= \frac{16}{2} \times$ mass of H.

vol. of O_2 $= \frac{1}{2} \times$ vol. of H.

CO

$CO + \frac{1}{2} O_2 \longrightarrow CO_2$

28gm   16 gm.   44 gm.

1 vol.   1/2 vol.   1 vol.

mass of O_2 $= \frac{16}{28} \times$ mass of CO.

vol^m of O_2 $= \frac{1}{2} \times$ vol. of CO.

S

$S + O_2 \longrightarrow SO_2$

32gm.   32gm.   64gm.

1 vol.   1 vol.   1 vol.

mass of O_2 $= 1 \times$ mass of S.

vol. of O_2 $= 1 \times$ vol. of S.

CH_4

$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

16gm.   64 gm.   44gm.   36 gm.

1 vol.   2 vol.   1 vol.   2 vol.

mass of O_2 $= \frac{64}{16} \times$ mass of CH_4.

vol. of O_2 $= 2 \times$ vol. of CH_4.

C_2H_6

$C_2H_6 + \frac{7}{2} O_2 \longrightarrow 2CO_2 + 3H_2O$

30gm   112 gm   88 gm.   54 gm.

1 vol.   7/2 vol.   2 vol.   3 vol.

mass of O_2 $= \frac{112}{30} \times$ mass of C_2H_6

vol. of O_2 $= \frac{7}{2} \times$ vol. of C_2H_6.

$C_2H_2 + \frac{5}{2} O_2 \longrightarrow 2CO_2 + H_2O$

26gm   80   88   18

So, total mass of theoretical O_2 required for combustion of fuel. = (sum of the O_2 required for each of individual component of the fuel − O_2 present in the fuel).

mass of air required = (mass of O_2 required $\times 100/23$) because 23% of O_2 by mass present in the air.

Vol. of air required = (vol. of O_2 required $\times 100/21$) As, 21% of O_2 by vol. present in air.

28.94 gm/mol. is taken as molar mass of

Note - 22.4 Lt of any gas at STP has mass equal to its 1mol.

(1) Cal. the wt. & vol. of air required for combustion of 3kg of carbon.

Soln

$$C + O_2 \longrightarrow CO_2.$$

12gm.	32gm.	44gm.
1vol.	1vol.	1vol.

mass of O_2 required $= \frac{32}{12} \times$ mass of

$= \frac{32}{12} \times 3000$

$= 8000$ gm.

mass of air required $= 8000 \times \frac{100}{23}$

$= 34.782160$ kg.

vol. of air required $= \frac{\text{mass of air req}}{\text{molar mass of air}}$

$1m^3 = 10^3$ Lt.

$= \frac{34.78}{28.94} \times 22.4$

$= 26.9$ L

~~vol. of O_2 req. = $\frac{1}{1}$ x vol. of C =~~

32 gm. of O_2 occupied = 22.4 lt.

1 " = $\frac{22.4}{32}$

8000 gm. of O_2 " = $\frac{22.4}{32} \times 8000$

= 5600 lt.

vol^n of O_2 req. = $\frac{1}{1} \times 5200$

vol^m of air req. = $5200 \times \frac{100}{21}$ = 26.66 m^3

The % composition of coal sample is C = 80%, H = 4%, O_2 = 3%, N = 3%, S = 2%, Ash = 5%, moisture = 3%. Cal. the ~~combu~~ quantity of O_2 & air required for complete combustion of 1 kg coal.

1 kg = 1000 gm. of coal.

mass of C = $\frac{80}{100} \times 1000$ = 800 gm

mass of H = $\frac{4}{100} \times 1000$ = 40 gm.

mass of O_2 = $\frac{3}{100} \times 1000$ = 30 gm.

mass of N_2 = 30 gm.

mass of S = 20 gm.

mass of ash = 50 gm.

mass of moisture = 30 gm.

mass of O_2 required $= \left[\left(\frac{32}{12} \times 800\right) + \left(\frac{16}{2} \times 40\right) + \left(\frac{32}{32} \times 20\right)\right] - 30$

$= (2133.34 + 320 + 20) - 30$

$= 2443.33$ gm.

mass of air req. $= 2443.33 \times \frac{100}{23}$

$= 10623.18\ gm.$

$= 10.623\ kg.$

(3) Cal. the quantity of air needed for complete combustion of 1kg of coal if 60% of excess air is supplied. Data same as above ques. (5

Sol^n If 60% of excess air is supplied then mass of air need is

$10623.18 \times \frac{160}{100}$

$= 16997.088\ gm$

$= 16.997\ kg.$

(4) Cal. the vol. of air required for complete combustion of 1 lt. of gaseous fuel having composition CO = 46%, CH_4 = 10%, C_2H_2 = 4%, H_2 = 4%, H_2 = 4%, N_2 = 1%

Sol^n 1 lt $= \cancel{1000}\ cm^3 = 1000\ ml$

Vol. of CO $= \frac{46}{100} \times 1000 = 460\ ml$

Vol. of CH_4 $= \frac{10}{100} \times 100 = 100\ ml$

Vol. of C_2H_2 $= 40\ ml$

Vol. of H_2 $= 40\ ml$

vol. of O_2 req. $= \left[\left(\frac{1}{2} \times 460\right) + \left(\frac{5}{2} \times 40\right) + (2 \times 100) + \left(\frac{1}{2} \times 40\right)\right]$

$= 230 + \cancel{200}\ 100 + 200 + 20$

$= 550\ ml$

vol. of air req. = $550 \times \frac{100}{21} = 2619.04$ ml.

$= 2.62$ lt.

(5) ~~LIQUID~~ Cal. wt. or vol. of air required for complete combustion of 1kg of coal having the composition of C = 80%, H = 7%, O = 3%, S = 3.5%, N = 2.5%, ash = 4.4%.

Soln Ans →

$1kg = 1000$ gm.

C = 80%. $\frac{80}{100} \times 1000 = 800$ gm.

H = 7%. $7/100 \times 1000 = 70$ gm.

O = 3%. $3/100 \times 1000 = 30$ gm.

S = 3.5%. $\frac{3.5}{100} \times 1000 = 35$ gm

N - 2.5%. N = 25 gm

ash = 4.4%. ash = 44 gm.

$$\text{mass of } O_2 \text{ reqd} = \left[\left\{\left(\frac{32}{12} \times 800\right) + \left(\frac{16}{2} \times 70\right) + 35\right\} - 30\right]$$

$= 2698.33$ gm.

$$\text{mass of Air reqd} = \frac{2698.33 \times 100}{23}$$

$= 11731.86$ gm

$= 11.731$ Kg

$$\text{Vol}^m \text{ of Air reqd} = \frac{\text{mass of air reqd}}{\text{molar mass of air}} \times 22.4$$

$$= \frac{11731}{28.94} \times 22.4$$

$= 9.0800$ m^3

LIQUID FUEL

The liquid fuel can be classified as in-to two categories. (I) Natural / Crude oil
(II) Artificial / manufactured oil.

Advantages. (follow comparision).

- They posses high cv per unit mass than solid fuel.
- They burn without smoke.

LIQUID FUEL

- These are used extensively in industrial & domestic field.
- The single largest source ~~to~~f liquid fuel is petrolium & crude oil.
- It is a dark, greenish, brown viscus oil - found ~~to~~ deep inside the earth crust.
- It is a mix of hydrocarbons such as straight chain parraffins, cyclo-parraffine, napthalenes, ~~polyphenes~~ polyphenes, aromatics along with small amt. of organic compound containing N_2, O_2 & S.

Composition - Carbon = 79.5 - 87.1 %
H_2 = 11.5 - 14.8 %
S = 0.1 - 3.5 %
N_2 = 0.4 - 0.9 %
O_2 = 0.1 - 0.9 %

Physical / Chemical Properties.

Petrolium are graded according to the following physico-chemical property.

(I) Specific gravity
(II) Calorific value.
(III) Flash pt. or ignition pt.
(IV) Viscosity

(v) S content

(vi) moisture & sediment content

(vii) specific heat & co-efficient of expansion

Classification of petroleum

The chemical nature of the crude petroleum varies with the part of the world in which it is found.

They appear in three varieties.

(I) Paraffinic base type crude :

- It is mainly composed of saturated hydrocarbons from CH_4 - $C_{35}H_{72}$ & a little of napthalene & aromatic compound.
- The hydrocarbons from $C_{18}H_{38}$ to $C_{35}H_{72}$ are semi-solid are called as wax (low grade)

(II) Asphaltic base type crude :

- It contains mainly cyclo-paraphenes or napthalenes with smaller amt. of paraffins & aromatic hydro-carbons. These are called Bitumens.

(III) Mixed base type crude :

- It contains both paraphenic & asphalytic hydrocarbons & is generally rich in semi-solid waxes.

∴ furnish medm grade straight run gasoline.

Imp.

Refining of Petroleum.

- The crude oil is separated into various fractn having diff. boiling ranges by fractional distillation & finally converted into desired specific product by removing undesirable impurities & the process is known as refining of crude oil. This process involves three steps.

(i) Separation of H_2O :

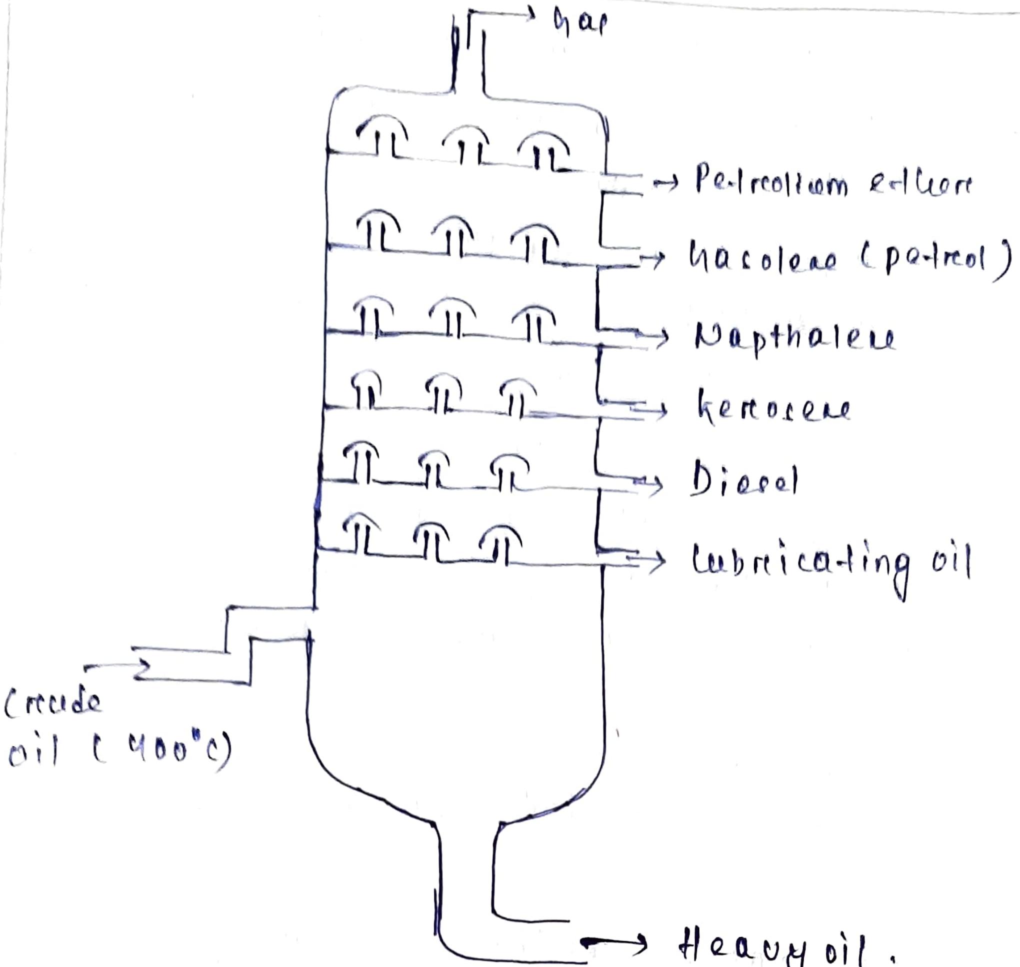
- The crude oil is separated from the H_2O by allowing the crude to flow betn highly charged electrodes.
- The colloidal water drooplets combine to form large drop & separated from the oil.

(ii) Removal of S. compound :

- S. compounds are removed by treating the crude oil with CuO & treatment results in the formation of CuS in solid form which can be easily removed by filteration.

(iii) Fractional distillation -

- The crude oil is heated to abt. 400°c in a pipe till all the volatile constituent are evaporated.
- The hot vapours then passed through a tall cylindrical tower known as fractionating column containing no. of horizontal stainless trays at short distance. Each tray is provided with a chiminy with loose caps.
- As the vapour goes up they become gradually cooler & fractional condensation takes place at diff. heights of the column.
- Higher boiling fractions are condensed first while lower boiling fractions are condensed afterwards.



Fraction	Composition	Boiling pt.
Gas	$C_1 - C_4$	less than 30°C (LPG)
Petrolium ether	$C_5 - C_7$.	30 - 70°C
Petrol	$C_5 - C_9$	70 - 90°C
Light petrolium	$C_6 - C_8$	90 - 120°C
Napthalene	$C_9 - C_{10}$	120°C - 180°C
Kerosene	$C_{10} - C_{16}$	180°C - 250°C
Dissel	$C_{15} - C_{18}$	250°C - 320°C
Heavy oil	$C_{18} - C_{30}$	320°C - 400°C

Dt. 17/08/19

PETROL / GASSOLINE / MOTOR SPIRIT

(i) The composition of petrol is mix. of hydrocarbon from $C_5H_{12} \rightarrow C_8H_{18}$

(ii) The straight run fractn is collected betn 40°-120°

(iii) It is highly volatile & inflammable in nature.

(iv) Its cv is 11250 Kcal/kg.

(v) It is used in IC engine.

(vi) The consumption per unit is more.

(vii) Its thermal efficiency is low.

(viii) Combustion process is simple & requires IC engine.

(ix) Costlier than diesel.

(x) No compression is needed during combustion of gassoline.

(xi) Its exhaust gasses contain higher amt. of pollutant gasses.

DIESEL

- The composition of diesel is $C_{15} - C_{18}$ ($C_{15}H_{32} - C_{18}H_{38}$)
- This fractn obtained betn 250°c - 320°c.
- Its density is 0.86 - 0.95.
- Its cv is about 11000 kcal/kg.
- It is used as fuel in diesel engine.
- Its consumption per unit is less.
- Its thermal efficiency is high.
- Combustion process is complex & requires a a more expensive fuel injection device.
- Its combustion requires heavy equipments to compress air.
- Its exhaust gasses contain lesser amount of pollutant (CO_2, oxides of N_2 & hydrocarbons)

	PETROL ENGINE	DIESEL ENGINE
Fuel used →	Petrol & air mix.	→ Diesel & air mix.
Ignition →	By sparking	→ By compression of air.
Cause of Knocking →	It is due to pre-ignition.	→ It is due to delayed ignition.
Knocking characteristic →	Knocking characterised by octane-rating.	→ It is characterised by Cetane (C_{16}) rating.
Additive to reduce knocking →	In this TEL, TML, BTX. (Tetra ethyl Pb) (Tetra methyl Pb) (Benzene + Toluene + xylene) are added to petrol to reduce knocking & to increase octane no.	→ In this alkali nitrites, acetone peroxides are used to reduce knocking & increase cetane no.

KEROSENE

- It is obtained betn 180°C - 250°C during fractional distillation of crude petroleum.
- Composition of kerosene is a mix. of hydrocarbon from $C_{10}H_{22}$ - $C_{16}H_{34}$ i.e. from decane to hexadecane.
- ~~Its~~ specific gravity 0.75 to 0.85.
- Its CV is 11100 Kcal/kg.
- Due to high boiling pt. range kerosene doesn't vapourise easily.
- It is used as domestic fuel in stove, as jet engine fuel & for making oil gas.

Cont. →

HEAVY OIL

- It is obtained b/w 320°c - 400°c during fractional distillation of crude petrolium.
- Lubricating oil is used as lubricants.
- Petrolium jelly (Vesseline) which is used as lubricants in medicine & cosmetics.
- Greases used as lubricants.
- Paraffin wax used as candle, boot polish, wax paper, tarpauline cloth for electrical insullation.

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CRACKING

- It is defined as decomposition of high molecular weight hydrocarbons of high B.P ranges into simpler & lower mol. weight hydro-carbons of low B.P. ranges.

eg - $C_{10}H_{22} \xrightarrow{(cracking)} C_5H_{12} + C_5H_{10}$

174°c (cracking) 36°c

decane Pentane Pentene.

It is of 2 types. (i) thermal cracking
(ii) catalytic cracking

Thermal Cracking-

- When heavy oil is cracked at high temp. & pressure in absence of catalyst i.e. called as thermal cracking.

In this process the bigger hydrocarbons molecules break down to form smaller molecules of alkenes along with H_2.

These are of 2 types. (a) Liq. phase thermal cracking.
(b) Vap. phase thermal.

Catalytic cracking :- (advantages over thermal cracking)
When cracking is done in presence of catalyst like aluminosilicate ($Al_2(SiO_3)_3$) or alumina i.e called as catalytic cracking.
In this case both quality & quantity of gasoline is better.
It requires much lower temp. & pressure compared to thermal cracking.
The yield of petrol is higher in this process.
The petrol produced by this process have better antiknock characteristics due to branched chain compound.
This product contains lower amt. of un-desirable substances like S.
Catalytic cracking are of two types.
(i) moving bed
(ii) fixed bed

KNOCKING

Due to premature instantaneous ignition of fuel, air mix. in IC engine leading to production of an explosive sharp metallic sound known as knocking.

Causes of Knocking

i) Chemical str. of the fuel hydrocarbon.
ii) Presence of some constituents having high ratio of combustion in fuel.
iii) Design of the engine i.e. shape of the head, Location of the plug.
iv) Running condn of the vehicle.
v) Compression ratio i.e. $C.R = \frac{V_1}{V_2}$.

where V_1 is the vol. of the fuel at the end of stoke.

V_2 – vol. of the fuel at the end of compression.

Note

With increase in compression ratio the efficiency of IC-engine also increases but after critical compression ratio the tendency to knock also increases.

Critical Compression ratio – The CR at which fuel tends to knock is called as critical compression ratio.

For Petrol fuel

The knocking tendency decreases in the order

n-alkane > mono-substituted alkane > alkene > Poly-substituted alkane > arometics (higher anti knock property)

- For st. chain hydrocarbon knocking increase with molecular wt. of & boiling pt.
i.e. n-hexane > n-pentane > n-butane.

Probable mechanism of chemical reaction that leads to knocking

- Free radical chain reactⁿ leading to cracking oxdⁿ of hydrocarbon is probably the mechanism of chemical reactⁿ that leads to knocking

Effect of knocking

- It increases the fuel consumption.
- It results in decreased power output.
- It causes mechanical damage by overheating the cylinder parts or piston.
- loss of energy.
- Increase in cost of maintainance.
- The driving being un-pleasant.

Prevention (Reduction / minimization of knocking)

- By suitable change in engine design.
- By using critical compression ratio.
- By using high rating fuel.
- By using anti-knock agents like TEL, TML, BTX for petrol fuel. as they form branched C-chain.

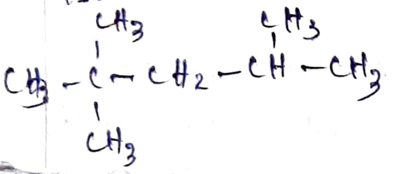
$(C_2H_5)_4Pb$ $(CH_3)_4Pb$

Octane number. (For petrol fuel)

- The resistance offered by gasoline to knocking can not be defined in absolute terms.
- In order to classify knocking characteristics of petrol fuel & a rating system is proposed by Graham Edjer in 1926 is known as octane number. or octane rating.

Defn :- Octane number of petrol fuel is defined as the % of iso-octane in a mix. of iso-octane & n-heptane that produce the same knocking characteristics as the fuel under same state of condn.

Fuel	Octane no.	Characteristics.
n-heptane $CH_3 + CH_2 +_5 CH_3$	0	Knocking 100%.
Iso-octane	100%.	Knocking = 0



eg- 91-octane petrol is a mix. of 91% iso-octane & 9% of n-heptane. i.e. since iso-octane has good anti-knock properties so, it has greater octane no. & greater resistance to knocking.

- Automobile gasoline have octane no. ranging from 75 - 95.
- Aveation gassoline have greater knock resistance & their octane no. are greater than 100.

- In such case the octane no. are compared using the relationship

$$\boxed{\text{Octane no.} = \frac{[\text{Power no.} - 100]}{3} + 100}$$

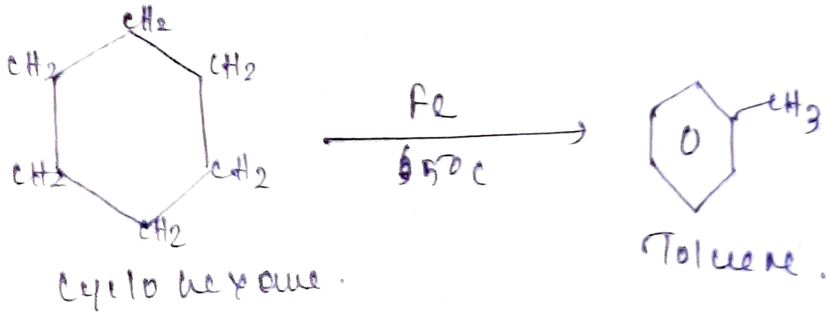
Where power no → is an arbitary no. proportional to the power being extracted by the engine.

- Incase of alkanes the octane no. increases with the no. of branches in the chain & decreases with increase in chain length.
- Alkenes have higher octane no. than alkane containing same no. of carbon-atoms.
- cyclo alkanes have higher octane rating than alkane with same no. of C-atom.
- The highest no. are associated with the aromatic hydrocarbon.

Q. How octane no. of fuel can be increased?

Ans (i) By isomerisation - st. chain hydrocarbons are converted to branched chain.

(ii) By aromatisation - aliphatic compound are converted aromatic compound.



(iii) By adding anti-knock agent - TML, BTX

(iv) The octane rating of gasoline sample can be increased by the addn of certain organometallic compounds called anti-knocking agent like TML, TEL

Dt. 23/03/17.

Que How TEL act as anti-knocking agent?

Ans TEL gives rise to Pb & PbO during combustion these particles act as free radical chain inhibitory as they arrest the propagation of the explosive chain reaction responsible for knocking.

Que Why a small quantity of ethyl-bromide is added to petrol along with anti-knocking agent like TEL?

Ans - If TEL alone is used the species Pb & PbO may get deposited on engine parts & causes mechanical damage & decrease the engine life. & also the vapours of Pb & PbO may pollute the air. So, inorder to minimize the air pollution & damaged to engine parts TEL is used along with ethylene bromide. ($C_2H_4Br_2$)

- The functn of these ethylene bromide is to convert the less volatile Pb & PbO into more volatile $PbBr_2$ which escapes into air along with the exhaust gases. But pollution problem still exist.

KNOCKING IN DIESEL ENGINE

- The basic difference betn petrol engine & diesel engine is that in case of diesel engine the fuel is ignited with the help of heat generated by the compression of air inside the combustion chamber & not by spark.

- The combustion of fuel is diesel engine is not instantaneous as that of petrol engine there is a time lag betn fuel injection & its ignition. & this is called as ignition delay or igniting lag

- Ignition delay is due to time taken for the vapourisation of the individual droplets & raising of the vapour to its ignition temp.

- It depends on ~~engi~~

(i) engine design.

(ii) efficiency of the mixing of the spray & air.

(iii) The injector design.

(iv) Chemical nature of the fuel.

- If the ignition delay is long it will lead to fuel accumulation in the engine even before the ignition.

- When ignited an explosion results as the combine effect of increased temp. & pressure & this is responsible for diesel knock.

- In order to grade the diesel fuel cetane rating is employed.

Imp.

CETANE NUMBER

- Cetane no. is a measure of ease at which fuel ignites under compression.

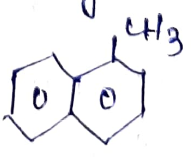
- Cetane no. is defined as the % of n-hexadecane (C_{16}) in a mix of hexadecane & (cetane) 2-methylnapthalene that has same knocking characteristic of fuel under consideration at the same set of condn.

n-hexadecane - $C_{16}H_{34}$

cetane no. - 100%.

very short ignition delay.

2-methylnapthalene -



Cetane no - 0

longer ignition delay.

St. chain hydrocarbons get ignited readily & have higher cetane rating. So, the order of cetane no. is as follows.

$\boxed{\text{n-alkane} > \text{napthalene} > \text{alkene} > \text{branched alkene} > \text{aromatics}}$

Ignition delay increases from left to right & ignition quality increases from right to left.

cetane no. increases from right to left.

ADDITIVES TO INCREASE CETANE NO.

~~Add~~ The cetane no. of fuel can be increased by addn of very small amount of compounds called as pre-ignition dopes such as alkali-nitrates ~~&~~ ethyl-nitrates, ethyl-nitrites, acetone peroxide etc.

Diesel fuel can be classified into 3 types.

(i) High speed diesel (cetane no. > 45)

(ii) Medm speed diesel (C.N > 35)

(iii) Low speed diesel (CN ≅ 25) (is about 25)

Que A sample of diesel fuel has same knocking characteristics as ~~a~~ 80ml of mix of cetane & 2-methylnapthalene mixed in a ratio of 3:1 by vol. Cal. the cetane no.

Soln

cetane = 80ml

ratio 3 : 1 3x & x

$4x = 80\text{ ml}$.

$x = 20\text{ ml}$

$3x = 60\text{ ml}$

cetane = 60ml.

2-M.N = 20ml.

Cetane no $= \frac{60}{80} \times 100$

$= 75$

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Cetane = 60 ml.

2-M.N = 20 ml.

$$\text{Cetane no} = \frac{60}{80} \times 100 = 75$$

Q. A sample of petrol fuel have same knocking characteristic as a 50 ml mix of iso-octane & n-heptane mixed in the ratio 3:2 by vol. Cal. the Octane no.

Sol^n

$5x \rightarrow 50$

$\Rightarrow x = 10$

$\Rightarrow 3x = 30$ (iso-octane)

$\Rightarrow 2x = 20$ (n-heptane)

Octane no. $= \frac{30}{50} \times 100 = 60$

Q. A sample of diesel has the same knocking chart. as 50 ml of cetane & 1-methyl-napthalene mixed in the ration 2:3 by vol. What is the cetane no.

Sol^n

$5x \rightarrow 50$

$\Rightarrow x = 10$

$\Rightarrow 2x = 20$ (cetane)

$\Rightarrow 3x = 30$

Cetane no. $\frac{20}{50} \times 100 = 40$

Dt 21/03/19.

UNLEADED PETROL.

- The petrol in which octane no. increased without the addition of Pb-compound is referred to as unleaded petrol.
- To improve the octane no. of the petrol conc. of high octane components like iso-pentane, iso-octane, ethyl benzene, isopropyl benzene are increased by the process molecular reforming.
- This process increases the contents of molecules having branched & aromatic str.
- Methyl tertiary butyl ether (MTBE) can also be added to petrol to improve the octane rating of the fuel.

MTBE has O_2 in the form of ether group & supplies O_2 for the combustion of the petrol in IC-engine reducing the formation of peroxy compound.

Advantages of unleaded petrol -

- It will reduces Pb-pollution.
- It permits ~~the~~ ~~cat~~ attachment of catalytic converter to the exhaust pipe in the automobile. Catalytic converters contain Rhodium (Rh) catalyst which converts toxic gases like CO, NO into harmless gases like CO_2 & N_2. It also oxidises unburnt hydrocarbon into CO_2 & H_2O

SYNTHETIC PETROL

- It is the mix. of alkanes with composition resembling that of petrol, obtained artificially from coal.
- The two important methods for the preparat[ion] of this petrols are

(i) Bergius Process

(ii) Fischer Tropsch Process

Bergius Process

- In this method coal is used as raw materials.
- Coal is a mix of high molecular complex organic compound with low content of H_2.
- The finely divided coal is made into a paste with heavy oil or coaltar & then a catalyst composed of organic compound of tin is added.
- The coal paste along with catalyst is prepared & then pumped into the converter where it is heated to 400 - 500°C under 200 - 250 atm. pressure in presence of H_2.

$$\underset{\text{(dust)}}{\text{Coal}} + H_2 \xrightarrow[450^\circ C,\ 200\,atm]{\text{Catalyst}} \text{Mix of hydrocarbon}$$

(ii) Cracking

Crude oil.

- Hydrogination takes place to form higher saturated compound which undergoes cracking and hydrogination process to yield mix. of alkanes.
- Thus the vapours leaving the converters upon condensation give crude oil or synthetic petrolium.
- Crude oil is fractionally distilled to give petrol, middle oil & heavy oil.
- The middle oil is again hydrogenated in the vapour phase in presence of a solid catalyst to give more gassoline.
- Actually the processing of middle oil gives 4 times the gassoline obtained by the primary hydrogination of the coal.

- Heavy oil is again used for making a paste with fresh coal dust.

Fischer - Tropsh process

- In this method hard coke is converted into a mix. of CO & H_2 by passing steam over a red hot ~~coal~~ coke.

$$C + H_2O \xrightarrow{1200^\circ C} \underset{\text{water gas.}}{CO + H_2O}$$

- From a part of water gas CO is removed by converting it into CO_2 which is obtained by passing the water gas with extra steam over a promotter iron oxide catalyst at 450°C.

$$CO + H_2O \xrightarrow[450^\circ C]{Fe} CO_2 + H_2O$$

- The residual CO_2 is again removed by absorption in Ammonia cuprous formate soln. H_2 so obtained is mixed with rest of water gas in the ~~mix of~~ ratio of synthetic gas i.e. H_2 & CO in the ratio of 2:1.

- The synthesized gas is passed at the atm. pressure (150 lb/m²) over a Cobalt throrium oxide catalyst at 200°C. The reaction production is mainly st. chain paraffine & olifffine.

- The formation may be presented by following eqn(s).

$$(2n+1) H_2 + nCO \longrightarrow C_nH_{2n+2} + nH_2O$$

$$2nH_2 + nCO \longrightarrow C_nH_{2n} + nH_2O$$

- The gas & vapour leaving the reactn vessel are passed through water cooled condensor to condense.

Dt. 28/03/19.

- From the residual gaseous mix. propane, butane are octane by absorbing activated carbon.
- The liquid on fractional distillation produces low grade motor diesel, high grade diesel oil, heavy oil & soft & hard waxes.
- A large amt. of the heavy oil after hydrogination is used for the production of sodium alkalisulphonate.
- The soft wax is mainly oxidised to a fatty acid by air at 100 - 120°c in the presence KMnO$_4$ as catalyst.
- Higher fatty acids are used for soap manufacturing & also for the production of synthetic fat. The hard wax is used for the conventional uses.
- Although Fisher process is required a cheap raw material it can not be comple. economically with petrolium as a source of gasoline. Hence this process is used for the production of. no. of hydrocarbon
- The gaseous mix. is & then passed under the pressure through a fluid bed of finely divided iron at 350 - 450°c
- The products obtained are gasoline, diesel fuel, an aqueous soln of oxiginated organic compounds namely alcohols, aldehydes, acids & ketones.

POWER ALCOHOL

- It is one of the most important non-petroleum fuel. The first four aliphatic alcohols are methanol, ethanol, propanol & butanol can be synthesized chemically & biologically

& used as fuel for IC-engine. These are not used as prime-fuel but used in blends as additives.
The chemical formula of power alcohol is.

$C_nH_{2n}+2OH$.

Manufacturing

Methanol can be prepared from bio-mass.

- Ethanol is commonly prepared from various biological organic substances through formentation process.
- However widely it is manufactured from molasses.

- It is a viscous semi-solid material left after crystalisation of sugar cane juice.
- It is a mix. of sucrose, glucose & fructose.
- The molasses are diluted with H_2O to reduce sugar conc. from about 50-60%. to 10-12%.

- Nutrients like $NH_4(SO_4)_2$ (amm. sulphate), Ammonium. Phosphate & some amount of H_2SO_4 is added to maintain the pH value to 4-5.
- Right proportion of yeast are added & maintain in the temp. is about 30°c.
- The invertase enzyme of yeast converts entire sucrose into glucose.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow[30^\circ]{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

Advantages

- These are prepared from waste, hence it reduces the pollution. Hence, it is a good non-petrolium alternate source of energy
- It can burn completely there by increasing combustion efficiency.

- It has an octane value of 90% but the petrol is having 60-70. When alcohol is mixed with petrol, it increases the octane rating & this blended petrol posses better anti-knock property & reduces the CO emission.

- Petrol is blended with alcohol & it can absorb traces of moisture.

Disadvantage

- Alcohol may cause corrosion due to easy oxdn with acids.
- Due to low calorific value of alcohol more fuel is required.
- Particularly at low temp. alcohol is difficult to get atomized due to its considerable surface tension.
- The zymase enzyme of yeast converts entire glucose & fructose into ethyl alcohol & release CO_2. During this process more CO_2 is produced. Hence this process is known as formaintation process.

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$$2(C_2H_5OH + 2CO_2(g)). \xleftarrow[H_2O]{\text{Zymase}}$$

→ The formaiutation process may be completed at about 36-38 hrs. depending on the con of alcohol, it is named as wash & rectifi spirit & absolute alcohol.

WASH.

- The formeated liquid containing 18-20%

of alcohol known as wash.

RECTIFIED SPIRIT

Fractionated distilled wash content 90-95% alcohol & is known as rectified spirit.

ABSOLUTE ALCOHOL

Rectified spirit is digested with lime for about 2-days & then distilled to get 100% alcohol is known as absolute alcohol.

Dt. 31/03/17

GASEOUS FUEL

Gaseous fuels can be obtained in many ways.

(a) from nature :- Example - Natural gas, methane from coal mines.

(b) from solid fuels :- Example - producer gas, water gas, coal gas, and blast furnace gas.

(c) from petroleum :- example Refinery gases, LPG, and gases from oil gasification

(d) By fermentation of organic wastes :- Examples include Biogas.

LPG → Composition n-butane + isobutane + butylene + propane.
C.V = 27800 Kcal/m³

Advantages of LPG over gaseous fuel

- high efficiency & heating rate. Its cv is 3 times that of natural gas & 7 times that of coal gas.
- Need little care for maintainance, cleanlyness in storage, handling & use.
- Flexibility & easy control.
- Portability in steel cylinder make its use possible in remoted places.
- less health hazard even incase of likange since it contains no CO but risk of fire hazard is more.
- Use of well designed & heavyly constructed burners ensures complete combustion with no smoke.

Advantages of LPG over motor fuel.

- It is cheaper than petrol.
- It can easily mix with air.
- Burning is smokeless, high knock resistan,
- Increase the engine life.

Disadvantages of LPG over motor fuel.

- Handling has to be done under pressure.
- Leakage can not be easily detected.
- LPG is advantages only in engine working under high compression ratio.
- Its response to blending is very poor.

~~CNG~~ NATURAL GAS

- It is generally found in associated with petroleum in nature & occurs near coal mines or oil field.
- It is used not only as fuels for domestic & industrial purposes but also as a raw material in various chemical synthesis.
- Natural gas i.e. derived from oil well may be dry or wet.
- When natural gas found to be associated with petroleum in oil well is known as wet gas. It is obtained from the oil producing well & is a mix of CH_4 & higher hydrocarbons such as n-propane, n-butane, isobutane, ~~iso~~ pentane etc.
- When natural gas is found to be associated wi crude oil it is termed as dry gas. It contains mainly CH_4 & ethane (C_2H_6) with small amount of CO, H_2, H_2S, N_2 & inert gases.
- Wet natural gas has a higher CV than dry gas because of higher % of heavier unsaturated molecule.

Composition.

$CH_4 \rightarrow$ 70 - 90%.
$C_2H_6 \rightarrow$ 5 - 10%.
$H_2 \rightarrow$ 3%.
CO & $CO_2 \rightarrow$ rest

CV = 12000 to 14000 Kcal / m^3.

Application of natural gas.

- Natural gas has wide range of application.
- It finds its use as a fuel in domestic & in industrial sectors as well as in motor vehicle.
- It is also used to prepare ethane, propane, butane, CH_3COOH etc.
- It serves as an important ingridient in the manufacture of various fertilizer, fabrics & antifreeze agents.

CNG (Compressed natural gas)

- It is obtained by compressing natural gas to a high pressure of about 1000 atm pressure.
- CNG is used as substitute for petrol & diesel.
- It is very economical & clean fuel.
- It is better than LPG. & is prefered over gasoline because

(i) Because its ignition temp. is higher than gasoline or diesel. So it is safer.
(ii) It is lighter than air & dispersed easily in air minimizing the risk of ignition but LPG being heavier, than air settles at the ground level & hence is risky.
(iii) As compared to gasoline CNG produces lesser CO on combustion.
(iv) CNG operated vehicle donot emit the forbidden pollutant such as CO_2, SO_3, C_6H_6 & HCHO

OIL GAS

- It is obtained by ~~brtee~~ cracking of kerosene.
- ~~It is obtai~~

Production

- The plant used for the purpose consist of a strong cast iron retort enclosed in a coal fired furnace.
- A burner is fitted at the mouth of retort through a water seal.
- A pipe from the hydrolic main leads to the gas holder. This pipe has a testing tap from where the sample of gas taken for testing.

Working

- The retort is heated to red hot & a stream of oil is continuously allowed to fall on the red hot bottom of the retort.
- The oil on coming in contact with red hot ~~bottle~~ retort ~~into~~ immediately get crack into the no. of lower gaseous hydro carbon.

$$C_{12}H_{26} \longrightarrow \underbrace{CH_4 + C_2H_6 + C_2H_4 + C_3H_8}_{\text{oil gas}} + \underset{\text{Tar}}{C}$$

- The gaseous mix. so obtained passes through the burner to a hydrolic tank, where tar get condensed. Then at the testing tap, proper colour of gas is ~~tested~~ ... A good oil gas has an golden colour.

By properly adjusting the supply of air golden colour is obtained. The gas is ~~firstly~~ properly stored in gas holder. Yield of gas is 40-50%.

WATER GAS

- It is essentialy a mix. of combustible gases like CO & H_2.
- It is also known as blue gas because it burns with a blue flame due to combustion of CO.
- The CV of water gas is 10,000 - 11000 kcal/m³
- The average composition of water gas is as follows

$CO \rightarrow 40-45\%$

$H_2 \rightarrow 45-50\%$

$CO_2 \rightarrow 4\%$

$N_2 \rightarrow 4\%$

Manufacture.

- It is produced by passing steam & little air alternatively through a bed of red hot coke maintained at 1000°C.

Principle

- When steam is blown through a bed of red hot coke at 1000°C water gas is formed.

$$C + H_2O \text{ (steam)} \longrightarrow CO + H_2 \quad \Delta H = 131.4 \text{ KJ}$$

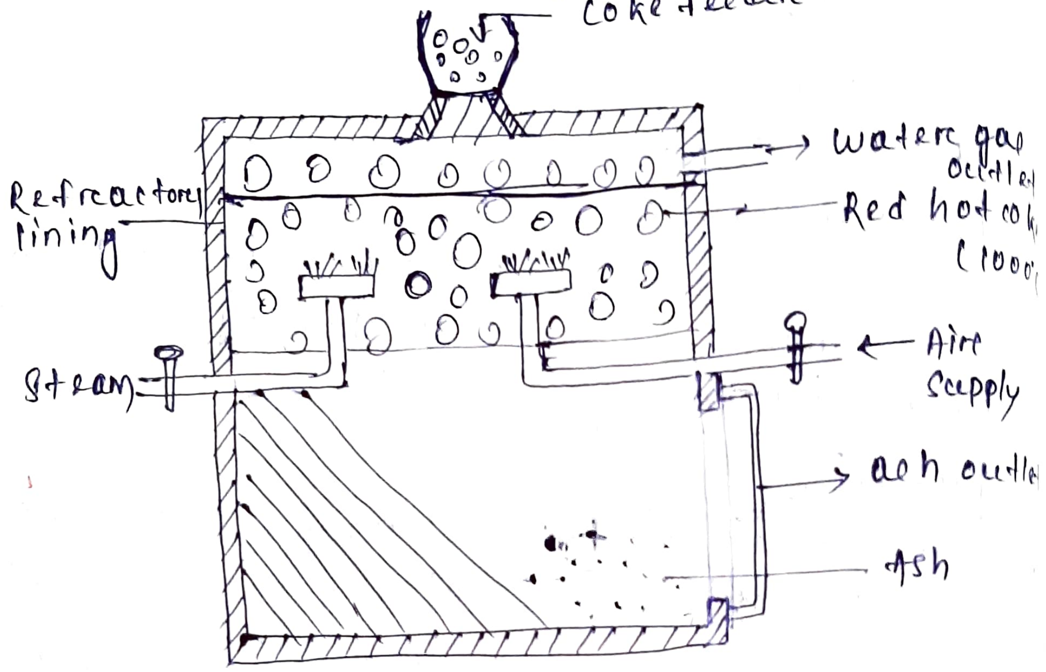
- The reaction being endothermic in nature. The temp. of coke bed gradually decreases with continuous passage of steam & the drop in temp. must be prevented.
- For this the steam supply is temporarily cut off. & air is blown in. The overall reaction during air blown is the formation of CO.

$$2C + O_2 \longrightarrow 2CO \quad \Delta H = -221.9 \text{ KJ}$$

- The reaction being exothermic increase the temp. of the coke bed to about 1000°C. Thus by blowing steam & air alternatively the temp. of coke bed can be maintained at 1000°C.

Uses

- It is used for the production of H_2.
- It is extensively used for the manufacture of CH_3-OH & synthetic petrol.
- It is used as a fuel in a glass & ceramic industry.
- Enriched water gas mixed with hydrocarbon which burns with luminous flame is used as illuminating agent.



PRODUCER GAS

- It is essentialy a mix. of CO & N_2.
- It is prepared by passing air mixed with little steam over a red hot coal-bed maintain at 1100°c.
- The avg. composition of producer gas is as follows.

CO - 25-30%.

N_2 - 50-55%.

H_2 = 10%.

CO_2 = 5%.

HC = 2-3%.

Its CV is 4000 - 5000 Kcal/m³.

Manufacture.

- The producer ~~gas~~ is charged with coal from the top & heated at about 1100°c. A mix of air & steam is passed over red hot coal through inlet at the bottom. The producer gas goes out through the outlet at the top.

- Reaction taking place in different zone of the fuel bed.

Oxdn zone

- This is the lowest part of the coal bed. Here the carbon burns in presence of excess air to give CO_2.

$$2C + 2O_2 \longrightarrow 2CO_2 \quad \Delta H = -393.5 \text{ KJ}.$$

Redn zone

CO_2 produced in the oxdn zone then rises through the hot bed & ~~is reduced by & is~~ reduced by the coal to CO

$$CO_2 + C \longrightarrow 2CO \quad \Delta H = -173.5 \text{ KJ}$$

The overall reaction in the formation of CO being exothermic the fuel bed gets heated up beyond 1100°c. At high temp. the ash form clinkers or slags which are difficult to remove so, the grade bar on the refractory line get ~~distored~~ distorted.

- In order to avoid these problems ~~th~~. in the producer a redn in temp. is achieved by passing air with steam instead of air alone.

- So, in the redn zone steam gets reduced to water gas

$$\underset{\text{steam}}{C + H_2O} \longrightarrow CO + H_2 \quad \Delta H = 131.4 \text{ KJ}$$

- This ~~exo~~ endothermic reactn brings down the temp.

to the optimum level.

Distilation zone.

- This is the upper most part of the fuel bed where the distilation of volatile matter of coal occurs.

Uses

- It is used as a fuel in manufacture of steel, glass, coal gas.
- It is used as reducing agent in metallurgical operation.