Chemical fuels
Contents

- Introduction & Classification

- Gross Calorific value and Net Calorific value.

- Solid fuel (coal) – proximate & ultimate analysis.

- Liquid fuels: Petroleum-Refining, Cracking and reforming. Synthetic Petrol: Methods of production.

- Gaseous fuels: bio-gas production and uses.

Learning objectives

- Define calorific value and describe the classification of fuels

- Understand the terms NCV and GCV

- To know about the petroleum refining, cracking and reforming techniques

- Understand about Synthetic fuels, production process

- To know about the production of bio-gas and their uses

Introduction

Chemical fuel: A combustible carbonaceous material which on proper burning in the presence of oxygen liberates large amount of heat that can be used for domestic & industrial purposes.

Eg. coal, petrol, water gas

Fuel+ oxygen → Oxidation products + heat

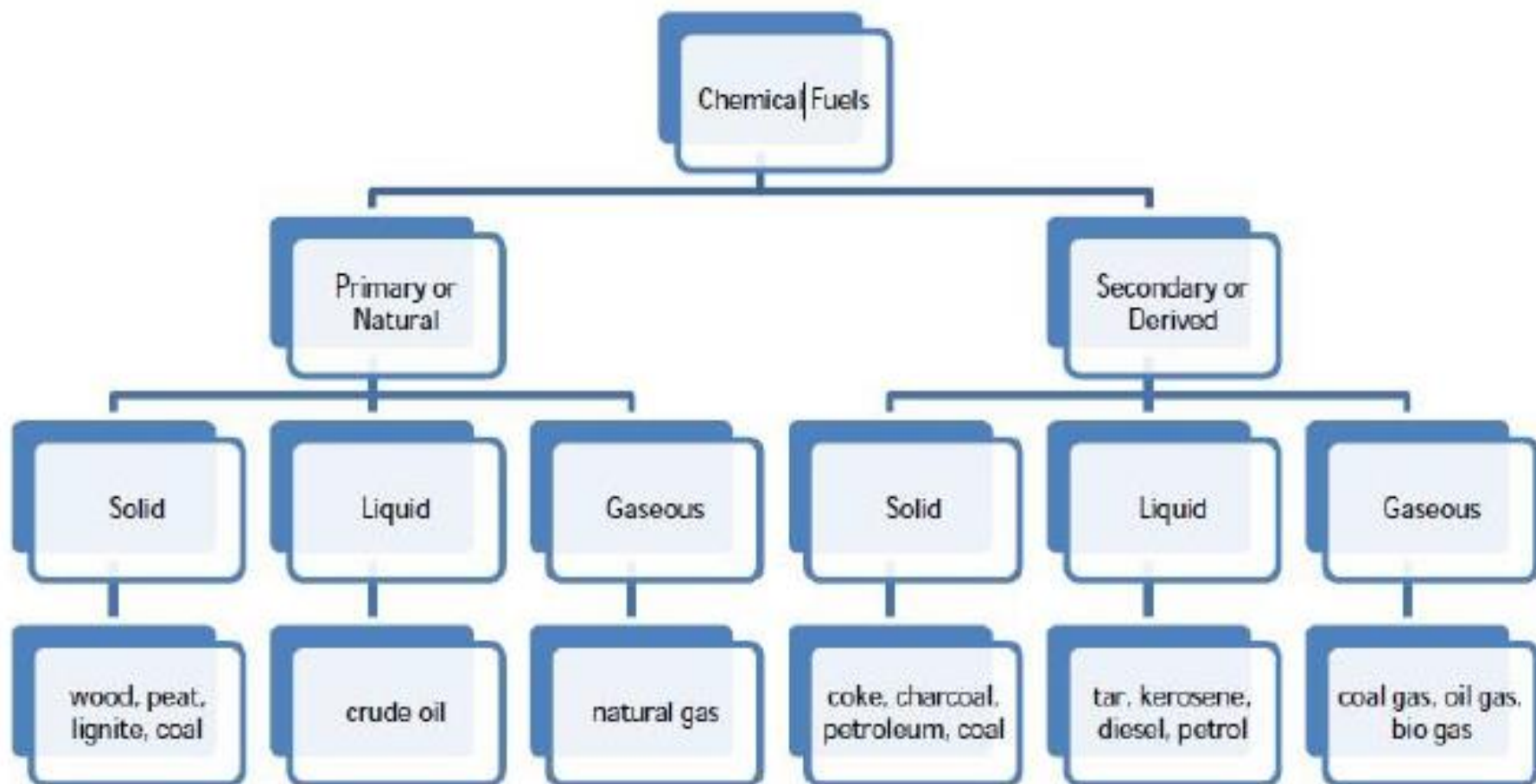**Organic matter + Oxygen ➔ CO_2 + H_2O + heat**

Combustion components

❖Temperature – high enough to ignite the fuel and the gases released during the process

❖Time- must be sufficient to complete the combustion process.

❖Turbulence -to allow complete mixing of combustible elements, fuel, and oxygen.

HEAT

OXYGEN

FUEL

CHAIN REACTION
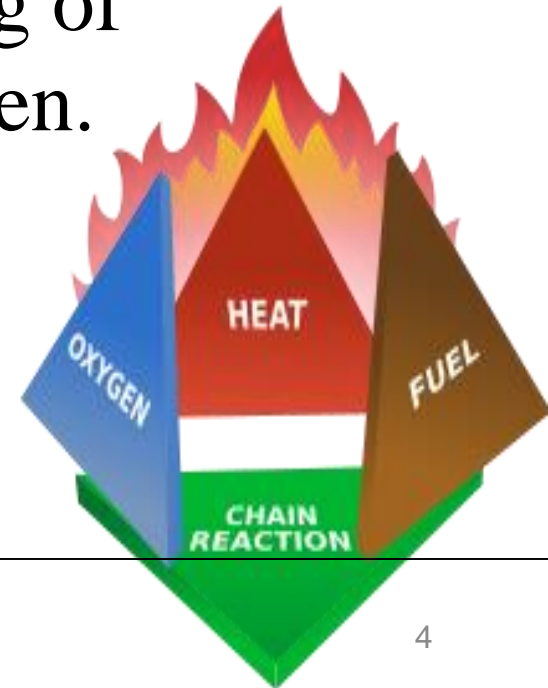
Classification of fuels

Calorific value

The amount of heat liberated when unit mass/volume of fuel is completely burnt in pure oxygen.

Units :   *S or L fuels* : cal/g or kcal/kg or J/kg

   G fuels : $kcal/m^3$ or J/m^3

Types : * **Gross Calorific Value (GCV)**

   * **Net Calorific Value (NCV)**

GCV- the amount of heat liberated when unit mass/volume of the fuel is burnt completely in oxygen, and the products of combustion are cooled to room temperature

NCV-the amount of heat produced when unit mass/volume of fuel is completely burnt in air, and the products of combustion are allowed to escape into the atmosphere

GCV = NCV + Latent heat of condensation of steam

NCV = GCV - Latent heat of condensation of steam

= GCV – Mass of hydrogen $\times$ 9 $\times$ latent heat of steam

= GCV – $\dfrac{9 \times \% \text{ of hydrogen}}{100}$ $\times$ latent heat of steam

NCV = GCV – $0.09 \times \%$ H $\times 587$

Calculate net calorific value of a coal sample having 2.5 %percentage of hydrogen and gross calorific value of 25969.3 × 10^3 J/kg.

$$NCV = GCV - 0.09 \times \% \ H \times 587 \times 4.184 \times 10^3$$

$$= \ 25969.3 \times 10^3 - 0.09 \times 2.5 \times 587 \times 4.184 \times 10^3$$

$$= \ 25416.7 \ J/Kg$$

Note: 1 calories = 4.18 J
1 kcal =J

Solid fuels

Natural fuels- wood & coal

Manufactured fuels- charcoal & coke.

Advantages

(a) Easily transportable.

(b) Conveniently stored without risk of any spontaneous explosion.

(c) Low production cost.

(d) Possess moderate ignition temperature.

Disadvantages

(a) High ash content.

(b) Wastage of large proportion of heat.

(c) Clinker formation when they burn.

(d) Combustion process cannot be easily controlled.

(e) High handling cost.

Solid fuels

Coal - a fuel source

Charcoal is prepared by the dry distillation of wood. It is the best fuel since it has no sulfur content. But it is costly.

Coke has increased C content is obtained by destructive distillation of soft coals in closed retorts.

Peat (< 60% C Content) and coal – Currently used in the generation of electricity

Coal

Peat

Charcoal

Coke

Analysis of coal- Proximate Analysis
Significance

- determination of moisture, volatile matter, ash, and fixed carbon.

- Establish the rank of coals

- Show the ratio of combustible to incombustible constituents

- Provide the basis for buying/selling

- Identify appropriate coal for different purposes

1. Moisture: Weigh coal sample into dry silica crucible. Heat for 1h at 110 ^{0}C. Cool & weigh. Calculate the loss in wt. as percentage.

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

moisture evaporates by taking some liberated heat in the form of latent heat of evaporation, lowering the effective calorific value of coal.

- *Less moisture content → better quality coal*

2. Volatile matter: Cover coal left in step **1.** Place in a muffle furnace at 950 ^{0}C for 7 minutes. Cool & weigh. Calculate the loss in wt. as %age.

$$\% \text{ Volatile matter} = \frac{\text{Loss in weight}}{\text{Wt. of coal taken}} \times 100$$

- Higher % volatile matter: high proportion of fuel will distill over as vapor and a large portion of which escapes unburnt.

  burns with a long flame, high smoke

Less volatile matter → *better the rank of coal*

3. Ash: Heat coal left in step **2** without lid in a muffle furnace at 750 ^{0}C to complete the combustion & constant weight of residue is obtained.

$$\% \text{ Ash} = \frac{\text{Wt. of ash left}}{\text{Wt. of coal taken}} \times 100$$

- Intrinsic ash: Mineral matter originally present in the vegetable material from which the coal was formed, consists of oxides of K, Mg and Ca. Low %

- Extrinsic ash: Non-essential mineral matters such as clay, gypsum or other inorganic matters. More %

- *Ash-forming constituents → undesirable*

(i)   The calorific value of the coal is decreased

(ii)   Removal and disposal of ash poses problems

(iii)   The ash deposited in the fire bars interferes with the circulation of air

(iv)   If the ash fuses to form a clinker on the fire bars, it hinders air circulation and promotes corrosion of the fire bars.

 However, some ash is desirable since it serves to protect the grates from direct contact with incandescent coal, which might lead to oxidation of the grate bars.

Fixed carbon: Sum total of the % ages of volatile matter, moisture & ash subtracted from 100.

i.e. 100 − (% moisture + % volatile matter + % ash)

• *High percentage of fixed carbon → greater CV & better the quality*

- A coal sample of 2.5 g was weighed into a silica crucible. After heating for one hour at 110 °C the residue weighed 2.415 g. The crucible was covered with a vented lid, strongly heated for seven minutes at 950 °C and the residue weighed is 1.528 g. Calculate the percentage of moisture and volatile matter.

- Mass of moisture = 2.5 − 2.415 = 0.085 g
- Mass of volatile matter = 2.415 − 1.528 = 0.887 g

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

- %age of moisture = 0.085 × 100 / 2.5 = 3.4 %

$$\% \text{ Volatile matter} = \frac{\text{Loss in weight}}{\text{Wt. of coal taken}} \times 100$$

- % age of volatile matter = 0.887 × 100 / 2.5 = 35.48 %

Analysis of coal - Ultimate analysis

- Significance

- To find the chemical composition of coal with respect to the elements like C, H, O, N, S and ash
- To predict the suitability of coal for purpose of heating
- For combustion calculations
- To determine the composition of flue gases

Analysis of coal - Ultimate analysis

1. C & H: Weigh coal & burn in pure O_2. C & H convert into CO_2 & H_2O on combustion. Absorb in weighed KOH & $CaCl_2$ tubes. Increase in the weights of tubes → amount of CO_2 & H_2O formed

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

$$\% \text{ Hydrogen} = \frac{\text{Increase in wt. of } CaCl_2 \text{ tube} \times 2 \times 100}{\text{Wt. of coal taken} \times 18}$$
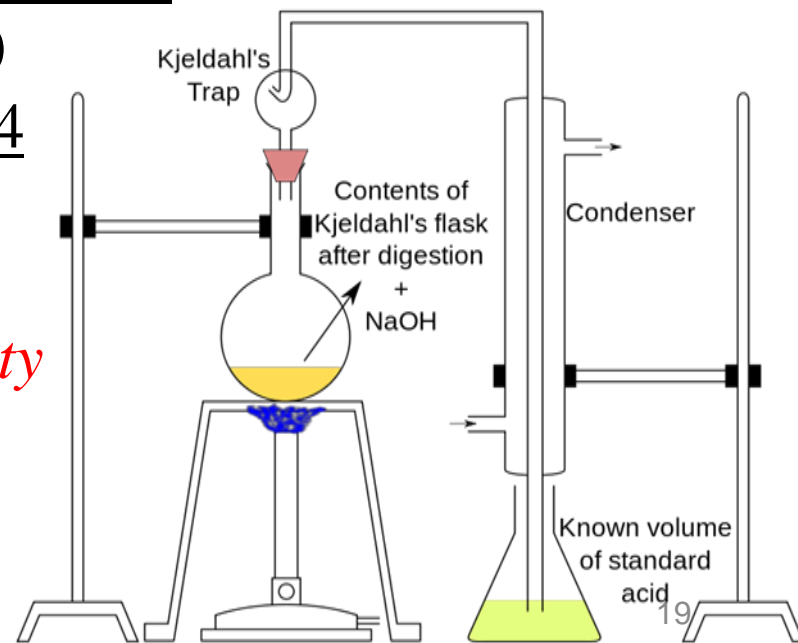
•*High percentage of C & H → better coal quality*
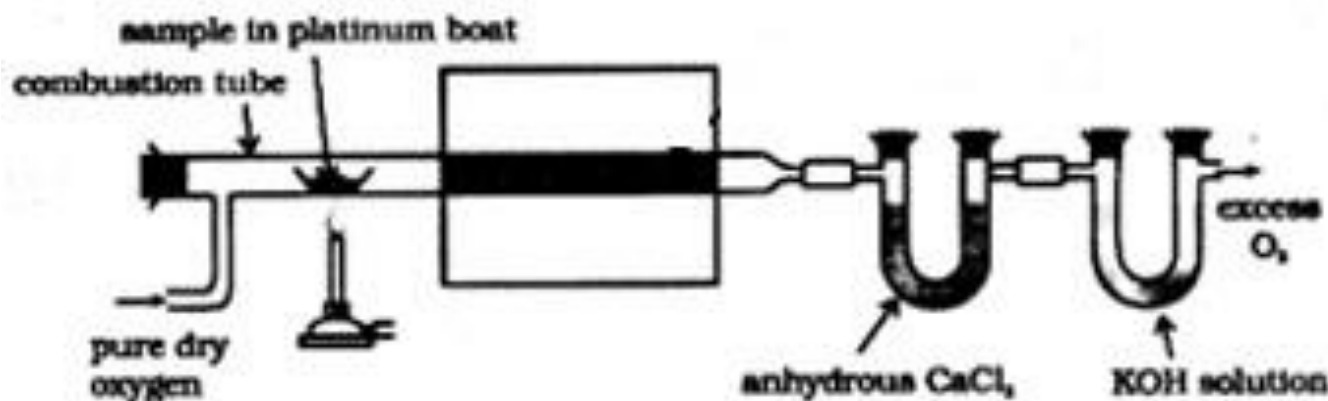
2. Nitrogen: Digest known quantity of coal in a Kjeldhal flask with conc. H_2SO_4 & $HgSO_4$ with K_2SO_4 catalyst. Treat clear soln. with excess NaOH. Distill liberated NH_3 into known volume of std. acid solution. Determine volume of residual acid by back titration with std. NaOH soln.

- % of nitrogen = $\dfrac{\text{Weight of nitrogen}}{\text{Wt. of coal taken}} \times 100$

- 1000 ml, 1Normal acid = 14 g of N

  V ml, N Normal = $14 \times N \times V/1000$

% Nitrogen = $\dfrac{\text{Vol. of acid used} \times N_{acid} \times 14 \times 100}{\text{Wt. of coal taken} \times 1000}$

% Nitrogen = $\dfrac{\text{Vol. of acid used} \times N_{acid} \times 1.4}{\text{Wt. of coal taken}}$

* *Less nitrogen content → Good coal quality*

Kjeldahl's Trap

Contents of Kjeldahl's flask after digestion + NaOH

Condenser

Known volume of standard acid

3. Sulfur: Weigh coal sample & burn in bomb calorimeter. Sulfur converts to sulfates. Treat washings with $BaCl_2$ soln. to obtain $BaSO_4$ ppt (at. wt. = 233). Filter, wash, ignite & weigh. Calculate S present in coal.

$$\textbf{\% Sulfur} = \frac{\text{Wt. of } BaSO_4 \text{ obtained} \times 32 \times 100}{\text{Wt. of coal taken} \times 233}$$

Corrosive combustion products
* *Low sulfur-coal is useful*

4. Ash: Determine as described under proximate analysis.

5. Oxygen: Determine by difference as follows:

$$\textbf{\% Oxygen} = \textbf{100} - \% \ (C + H + N + S + Ash)$$

Lower oxygen content → greater CV

1. About 0.6 g of a coal sample was allowed to undergo combustion in a bomb calorimeter. The calorific value of the sample was found to be 8600 cal/g. The ash formed was extracted with acid, and this was heated with BaCl2 solution. The weight of dried barium sulfate obtained was found to be 0.05 g. Calculate the % of S in the coal sample.

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

$$= \frac{0.05 \times 32 \times 100}{0.6 \times 233}$$

$$= 1.14 \%$$

1. About 1.6 g of coal sample was kjeldahlised and NH3 gas thus evolved was absorbed in 50 mL of 0.1 N sulphuric acid. After absorption, the excess of acid required 6.5 mL of 0.1 N NaOH for neutralization. Calculate the % of nitrogen in the sample.

$$\% \text{ Nitrogen} = \frac{\text{Vol. of acid used} \times N_{acid} \times 1.4}{\text{Wt. of coal taken}}$$

$$\% \text{ Nitrogen} = \frac{43.5 \times 0.1 \times 1.4}{1.6}$$

$$= 3.8 \%$$

About 0.5g of a coal sample was used for nitrogen estimation by Kjelldahl method. The evolved ammonia was collected in 30 ml of 0.2 N HCl acid. To neutralize excess acid 20 ml 0.1 N sodium hydroxide was required. Calculate the percentage of nitrogen in the sample.

V_{acid} = 30 − 10 = 20 mL   20 x 0.1 = ? X 0.2

Strength of acid = 0.2   %

Nitrogen = $\dfrac{\text{Vol. of acid used} \times N_{acid} \times 1.4 \times 100}{\text{Wt. of coal taken} \times 1000}$

= 1.12

Numerical Problems

- 1. *About 1.5 g of coal was used for nitrogen estimation by Kjeldahl method. The evolved ammonia was collected in 25 mL of 0.1 N H_2SO_4. the excess acid was neutralized by 15 mL of 0.1 N NaOH. Calculate the % nitrogen in the sample.*

- 2. *The residue obtained when 2.5 g of coal was heated in a silica crucible for 1 h at 110 ^{o}C weighed 2.42 g. This was heated strongly for 7 minutes at 950 ^{o}C covered with a vented lid. The residue weighed 1.55 g & it was further heated until a const. wt. of 0.25 g was obtained. Calculate % moisture, volatile matter, ash & fixed carbon.*
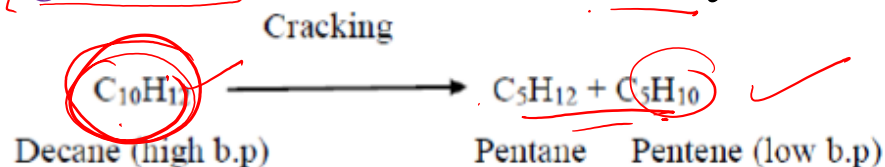
Liquid fuels

❑ They are combustible molecules that can be harnessed to create energy

❑ Formed by anaerobic decay of marine plant & animal life under the influence of high T & P

❑ Complex mixture of hydrocarbons

❑ Refining- separation of crude oil into different useful fractions on the basis of their boiling points

❑ Petroleum- An important primary liquid fuel

Petroleum cracking

Decomposition of *higher* **mw** into *lower* **mw** hydrocarbons.

$$\text{C}_{10}\text{H}_{1?} \xrightarrow{\text{Cracking}} \text{C}_5\text{H}_{12} + \text{C}_5\text{H}_{10}$$

Decane (high b.p)   Pentane   Pentene (low b.p)

quality
octane number
with knocking

Cracking

Thermal Cracking

[*high T & P, Absence of catalyst*]

gives mixtures of products containing high proportions of hydrocarbons with double bonds- alkenes.

free radicals are formed

Catalytic Cracking

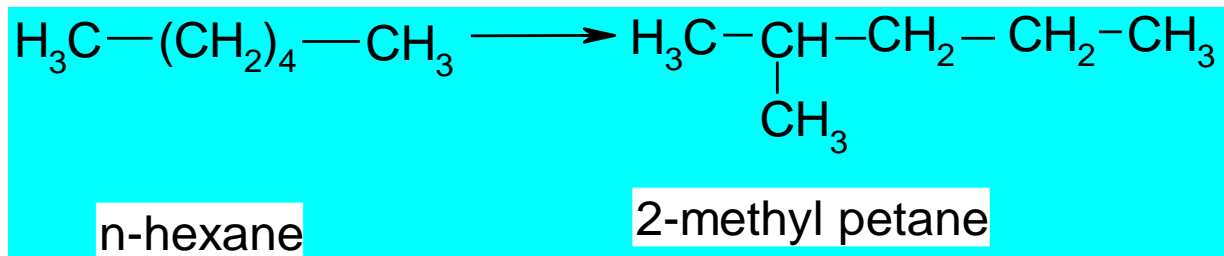Low T & P, Presence of catalyst e.g. $(\text{Al}_2\text{O}_3 + \text{SiO}_2)$

Catalytic cracking

- Zeolites as the catalyst.

- Alkane is brought into contact with the catalyst at a temperature of about 500 oC and moderately low pressures.

- The zeolites as catalysts give high percentages of hydrocarbons with between 5 and 10 carbon atoms- particularly useful for petrol. It also produces high proportions of branched alkanes and aromatic hydrocarbons like benzene.

- The zeolite catalyst has sites which can remove hydrogen from an alkane together with the two electrons which bound it to the carbon. That leaves the carbon atom with a positive charge. Ions like this are called carbonium ions. The reorganization of these leads to various products of the reaction.
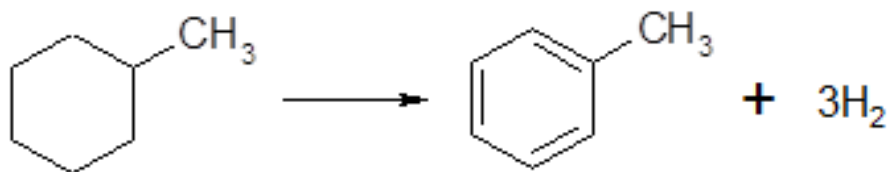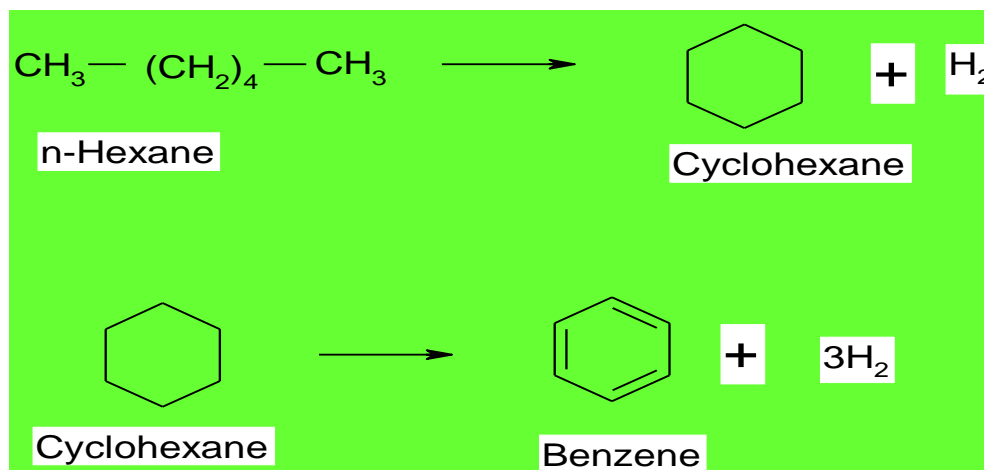
- Upgrading gasoline by increasing its octane number in presence of a catalyst.

- **Isomerization**

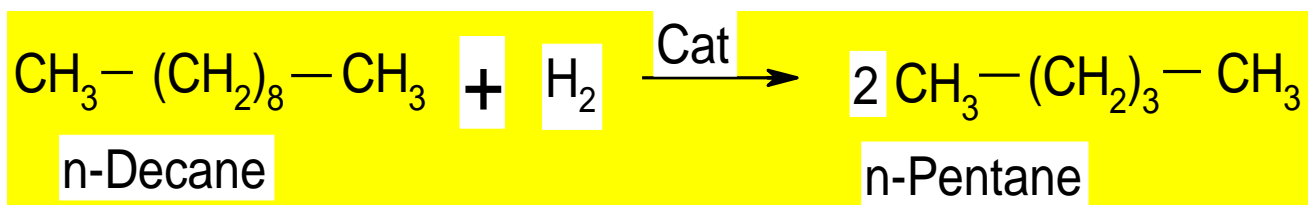$$H_3C-(CH_2)_4-CH_3 \longrightarrow H_3C-CH-CH_2-CH_2-CH_3$$
$$| $$
$$CH_3$$

n-hexane   2-methyl petane

- **Dehydrogenation:**

- **Cyclisation & dehydrogenation:**

$$CH_3-(CH_2)_4-CH_3 \longrightarrow \text{Cyclohexane} + H_2$$

n-Hexane → Cyclohexane + H_2

$$\text{Cyclohexane} \longrightarrow \text{Benzene} + 3H_2$$

- **Hydro cracking:**

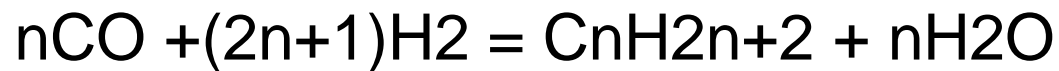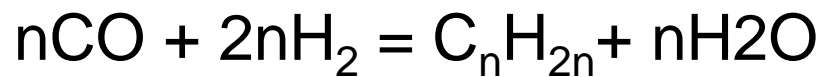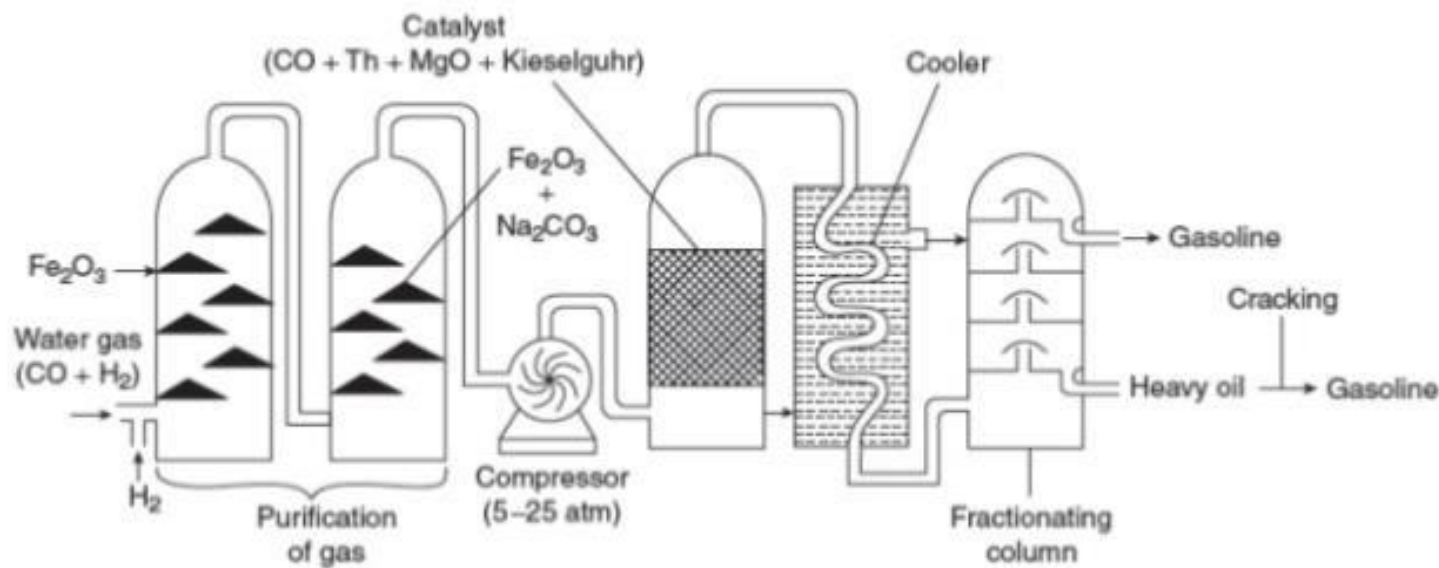$$CH_3-(CH_2)_8-CH_3 + H_2 \xrightarrow{Cat} 2\ CH_3-(CH_2)_3-CH_3$$

n-Decane → n-Pentane

Synthetic Petrol

- **Method of producing Synthetic Petrol:**
- 1. Polymerisation
- 2. Fischer-Tropsch method
- 3. Bergius process

$$nCO + 2nH_2 = C_nH_{2n} + nH_2O$$

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

Fischer–Tropsch Process

Gaseous fuel

- Fixed composition gases - acetylene, methane, ethylene, and ethane.

- Composite industrial gases - blast furnace gas, coke oven gas, producer gas, illuminating gas, blue water gas, carbureted water gas, etc.

Biogas

- Biogas is a type of biofuel that is naturally produced by the decomposition of organic waste

- Process of producing biogas is also known as anaerobic digestion

- The digestion chamber is fully submerged in water, making it an anaerobic (oxygen-free) environment

- **Bio-gas composition:**

Compound	Formula	%
Methane	CH_4	50–75
Carbon dioxide	CO_2	25–50
Nitrogen	N_2	0–10
Hydrogen	H_2	0–1
Hydrogen sulfide	H_2S	0.1 –0.5
Oxygen	O_2	0–0.5

Applications

- Biogas can be used for electricity production, cooking, space heating, water heating and process heating. If compressed, it can replace compressed natural gas for use in vehicles, where it can fuel an internal combustion engine or fuel cells.

Summary

✓ Types of fuels based on their origin & physical state

✓ Methods to determine GCV & NCV of fuels using bomb & boys calorimeters

✓ Procedure of proximate & ultimate analysis of **solid fuels** like coal

✓ Liquid fuels- Refining, Cracking, Reforming, Knocking

✓ Gaseous fuels – Biogas