

Module I

ENERGY SOURCES

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Introduction



Definition of Fuel: Any carbon containing material, which on combustion gives large amount of heat that can be utilised domestically or industrially.

Or

Fuel is a material used to produce energy or heat that can be used domestically or industrially.

Chemically carbon containing fuel can be represented as carbon bonded to hydrogen by covalent bond (C-H). There may be presence of nitrogen, sulphur, oxygen along with hydrogen in a fuel.

Classification



Fuels can be classified based on occurrence, state of fuel and based on chemical reaction.

Classification based on occurrence:

- o Natural (Primary fuel): Wood, Coal, Crude oil
- Artificial or Synthetic fuel (Secondary fuel): Charcoal,
 Petrol, Diesel

Classification based on state of fuel:

- o Solid: Coal, Wood, coke
- o Liquid: Crude oil or petroleum, Petrol, Diesel
- o Gaseous: Natural gas, CNG, LPG

Classification



Classification of fuel based on chemical reaction

- 1. Based on combustion reaction
 - a) In presence of excess of oxygen: Fossile fuel, wood
 - b) In presence of sufficient oxygen: IC engine fuel like diesel, petrol
 - c) In absence of oxygen: rocket fuel
- 2. Based on spontaneous oxidation reduction reaction: Fuel cell e.g. Hydrogen, ethanol, hydrocarbon
- 3. Based on nuclear reaction
 - a) Nuclear Fusion: deuterium, tritium, hydrogen
 - b) Nuclear Fission: U²³⁵, P²³⁹

Sr. No.	Criteria	Solid Fuel	Liquid Fuel	Gaseous Fuel
1	Calorific Value (C.V.)	Low	Higher	Highest
2	Ignition Point (I.P.)	Very high	Moderate	Very low
3	Cost	Very cheap	costly	Costly
4	Noncombustible matter (ash)	High	Negligible	Ni1
5	Rate of Combustion	Not controllable	Controllabl e	Controllable
6	Transportation	Laborious but hazard free	Easy (piping)	Easy but risk of hazard
7	Air requirement fro complete combustion	Large excess	Small excess	Just sufficient
8	Use in I.C. engine	Cannot be used	Convenien t	Can be used
9	Volatile matter	Large	Negligible	Ni1
10	Space for storage	Small	Smaller	Very large
11	Moisture	High	Ni1	Ni1
12	Smoke (pollution)	Considerable	Lower	Ni1
1316-10-2	Thermal efficiency	© Bhavna M. Vyas Low	High	High 5

Solid Fuels: Coal

Coal: highly carbonaceous material, regarded as a fossil fuel produced from the vegetable debris under conditions of high temperature and pressure over million of years.

The process of conversion of **wood into coal** is known as **coalification**.

Coalification is a very slow process and takes millions of years for formation.

- Main constitute of coal is C atom mostly sp² hybridized
- Atoms like H,O,N,S are covalently bonded to C atom
- Coal molecules are huge with **indefinite number of carbon** atom.
- Coal contains water and minerals particles entrapped

Solid Fuels: Coal



- Complex mixture of organic and inorganic materials, primarily composed
 of carbon along with various other elements like hydrogen nitrogen,
 sulphur etc.
- Coal is formed when the plant and animal debris under the earth crust are subjected to conditions of high temperature and pressure over millions of years. Hence, regarded as a fossil fuel.
- Process of formation of coal is called as Coalification.
- Mainly comprises of carbon, hydrogen, nitrogen and oxygen along with non-combustible matter. **Composition** of coal varies according to the coalification, based on its carbon content, energy content & other content.
- Different types of coal in increasing order of alteration are **Peat, Lignite** (brown coal immature), **Bituminous and Anthracite** (mature).

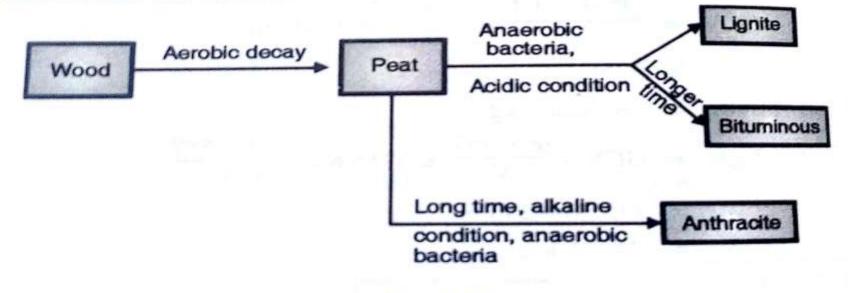


Fig. 4.6.1

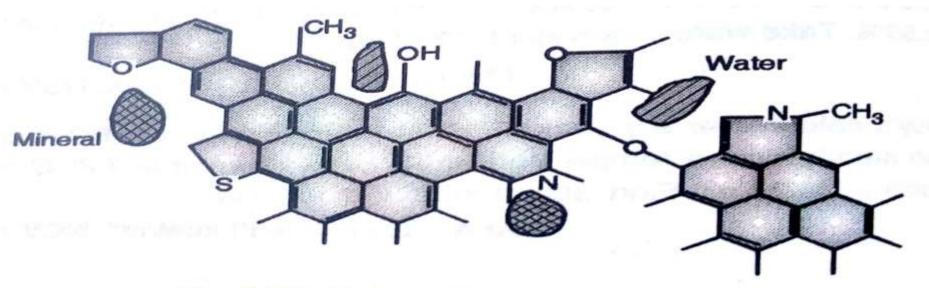


Fig. 4.6.2 : Schematic coal structure

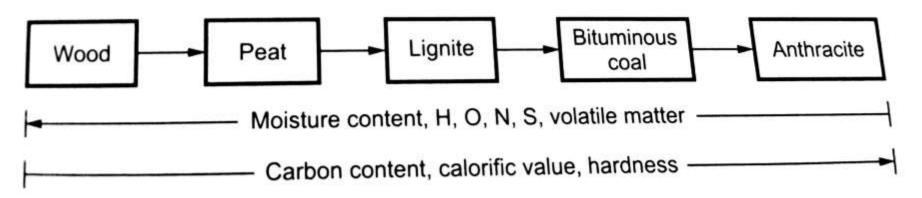
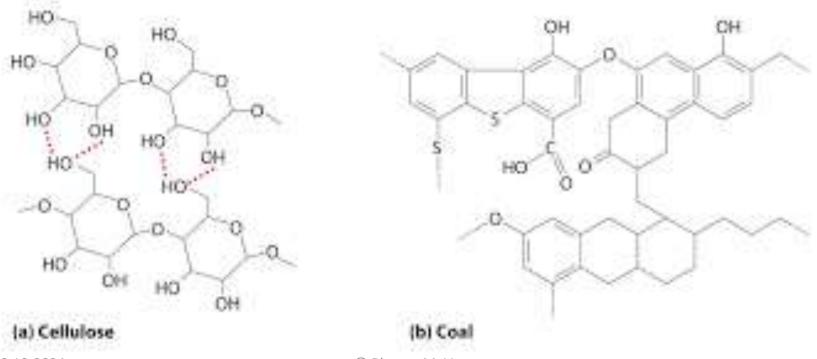


Fig. 4.6.1 Stages of coalification



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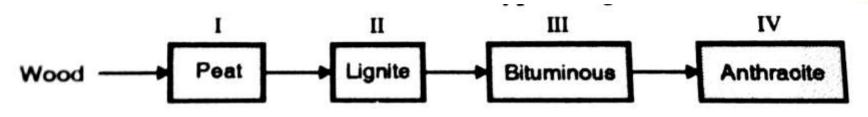


Fig. 4.7.1: Schematic coal structure

Table 4.7.1

Type of coal	Moisture	C	H	N	o	Ash	Volatile matter	Calorific value
Peat	25	57	6	2	35	10	50	~ 5400 cal/gm
Lignite	20	65	5	2	25	15	45	~ 6700 cal/gm
Sub-bituminous	11	75	5	1.8	16	20	35	~ 7000 cal/gm
Bituminous	4	80	5	2.0	10	15	20 – 30	~ 8000 cal/gm
Semibituminous	2.5	85	4	1.0	5	10	15	~ 8400 cal/gm
Anthracite	1.5	95	3	0.7	3	3	2	~ 8700 cal/gm

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Analysis of Coal



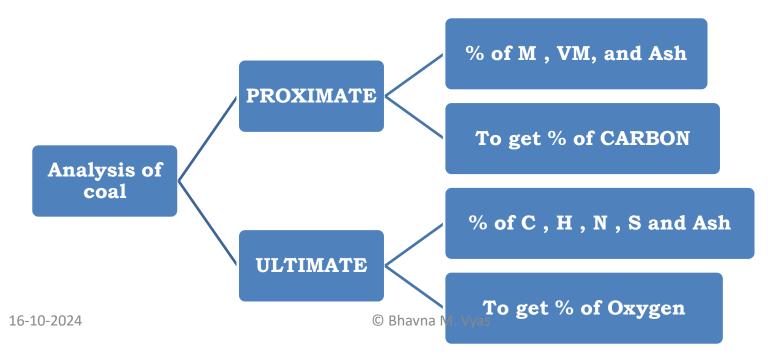
To fix price and use of coal

To calculate CV of coal

To calculate air and oxygen requirement for complete combustion of coal

Analysis of coal: 1) Proximate analysis

2) Ultimate analysis



Analysis of Coal



Analysis of Coal

The results of analysis are generally reported in the following ways:

- As received basis
- Air dried basis
- Moisture free basis (oven dried)
- Moisture and ash free basis

Proximate Analysis:

Determination of % Moisture, % Volatile Matter, % Ash and % Fixed Carbon.



1) % Moisture

Air-dried coal sample

Porcelain crucible,

110°C Electric oven

Time: 1 hr

Initial weight of coal = w g,

Final weight is w₁ gm (Moisture free coal)

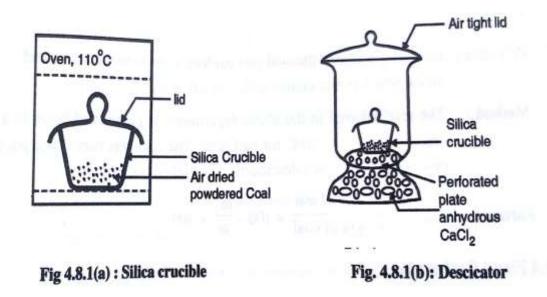
Loss in weight of the coal sample = $w-w_1$

% Moisture
$$=$$
 $\frac{\text{Loss in weight of the sample or weight of moisture}}{\text{Weight of coal sample taken}} * 100$

% Moisture
$$=\frac{(W - W1)}{W} * 100$$



1) % Moisture



 A coal sample weighing 1 gm, looses 0.09 gm weight on heating at 110 °C for 1 hour calculate % moisture.



1) % Moisture

Significance

- Excess of moisture is **undesirable** in coal
- Moisture lowers the heating value of coal and takes away appreciable amount of the liberated heat in the form of latent heat of vaporisation. For every percent of moisture present 1% of heat is lost.
- Moisture increases ignition temperature.
- Moisture also **increases** the transport costs.
- Excessive surface moisture may cause difficulty in handling the coal.
- Prescence of excessive moisture **quenches fire** in the furnace.
- Hence lesser the moisture content better is the quality of coal as a fuel. However, presence of about 5-10% moisture is desirable as it produces a uniform fuel bed and less of "fly ash".

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2) % Volatile Matter (VM)

The volatile matter in coal consists of a complex mixture of gaseous and liquid products resulting from the thermal decomposition of the coal. Volatile matter does not include moisture of coal. It consists mainly of combustible gases such as H₂, CO, CH₄ and other hydrocarbons.

Porcelain crucible with lid having vent, Muffle furnace, 925° C for 7 min.

Initial weight of coal = w_1 g,

Final weight is w₂ gm (Moisture free coal)

Loss in weight of the coal sample = $w_1 - w_2$

% Volatile Matter = $\frac{\text{Loss in weight of the sample or weight of volatile matter}}{\text{Weight of coal sample taken}} * 100$

% Volatile Matter =
$$\frac{(W1 - W2)}{W} * 100$$



2) % Volatile Matter (VM)

- a) 1.0 gm of a coal sample is heated to remove all moisutre. Then the residual coal looses 0.21 gm weight when heated in muffles furnace at 950 °C. Calculate % volatile matter.
- b) A coal contains 10 % moisture and 1 gm of coal looses 0.3 gm weight on heating at 925 0 C in the absence of air. Calculate % volatile matter.

For fresh coal sample

$$V.M \% = \frac{\text{loss in weight due to}}{\text{moisture, V.M.}}$$

$$V.M. \% = \frac{(W - W_1) \times 100}{W}$$



2) %Volatile Matter (VM)

Significance

- A high percent volatile matter indicates that a large proportion of fuel is burnt as a gas or vapor or may escape unburnt.
- For efficient use of fuel, the outgoing combustible gases (volatile matter) have to be burned by supplying secondary air. This requires a large combustion space.
- The high volatile matter content coal produce long flames, high smoke and relatively low heating values.
- The high volatile coals **do not cake well** whereas medium-volatile coals containing 20-30% of volatile matter are capable of forming hard and strong coke on carbonization.
- Coals containing less than 14% of volatile matter do not cake at all and are thus not suitable for manufacturing coke.
- Hence, lesser the volatile matter content, better is the quality of coal. However, high volatile matter content is desirable in coal gas manufacture because volatile matter in coal denotes the proportion of the coal which will be converted into gas and star products by heat.



3) % Ash

Ash is the non-combustible, useless matter that is left behind when all the combustible substances have burnt off from coal. Ash usually consist of silica, alumina, iron oxide and small quantities of lime, magnesia etc.

Open silica crucible, 750° C for half hour in muffle furnace Heating, Cooling and Weighing is continued till constant weight of ash

% Ash =
$$\frac{\text{weight of ash formed}}{\text{Weight of coal sample taken}} * 100$$

% Ash
$$=\frac{W3}{W} * 100$$

1 gm of coal sample is ignited at 750 °C in a muffle furnace the residue weighed is 0.15 gm. Calculate the % ash



3) % Ash

Significance

- High percentage of ash is **undesirable** as it **reduces the calorific value** of the fuel.
- Presence of ash **increases** the transporting, handling and storage cost. It also involves **additional cost** of ash disposal.
- Fused ash lumps (clinkers) block the interspaces of the grate on which coal is being burnt. This **causes obstruction in air supply**. Hence, burning of coal becomes irregular.
- Hence, lower the ash content better the quality of the coal.



4) % Fixed Carbon

Fixed carbon content increases from low ranking coals such as lignite to high ranking coals such as anthracite.

% Fixed Carbon = 100 - (% Moisture + % Volatile Matter + % Ash)

Significance

Higher the percentage of fixed carbon greater is its calorific value and better is the quality of coal.



Numericals:

Exactly 2.2 gm of the sample on heating in a silica crucible for about an hour at $110 \,^{\circ}\text{C}$ gave a residue of 1.98 gm. The crucible was then covered with a vented lid and strongly heated for exactly 7 minutes at $950 \pm 20 \,^{\circ}\text{C}$. 1.2 gm of residue was left behind. The crucible was then heated without the lid until constant weight was reached. The final residue weighed 0.240 gm. Calculate the percentage results of the above data. [Ans.: % moisture = 10 %

% VM = 35.45 %

% ash = 10.91 %

% Fixed carbon = 43.64 %]

A sample of coal (2.7 gm) was weighed in a silica crucible. After heating for one hour at 110 °C, the residue weighed 2.625 gm. The crucible is next covered with vented lid and strongly heated at 950 °C. After cooling, the residue weighed 2.5 gm. The crucible is then heated without lid to get a constant weight of 0.240 gm. Calculate percentage results of the above analysis.

[Ans.: % moisture = 2.78 %

% VM = 4.63 %

% ash = 8.89 %

% Fixed carbon = 83.7 %]

Significance of Proximate Analysis



Moisture

- decreases calorific value, increases ignition temperature
- Lower the % moisture, better the quality of coal.

Volatile matter

- Decreases calorific value, increases pollution, elongates flame
- Lesser the % V.M., better the quality of coal.
- 25-30 % volatile matter content is desirable or suitable for making hard and strong coke.

Ash

- Reduces calorific value, disposal is a problem, fuses to from clinker that blocks air supply
- Lesser the % ash, better the quality of coal .

Combustion



- Fuel can be represented as C-H i.e. hydrocarbons
- Combustion is a chemical process in which the carbon and hydrogen from fuel reacts with oxygen to produce CO₂ and H₂O along with liberation of heat.

$$C-H + O_2 \longrightarrow CO_2 + H_2O \Delta H = -97 \text{ kcal.}$$

- As in case of combustion there is a production of water molecule along with heat, some part of heat produced is taken away by water molecule.
- This amount of heat taken away by water molecule is called as latent heat (587 cal/g).



- To ensure complete combustion of a fuel, it is essential that appropriate amount of oxygen and air is supplied. If the amount of oxygen and air supplied is insufficient, complete combustion will not take place and too much excess should also not be supplied.
- Hence in any industrial and metallurgical processes it is essential to calculate the minimum amount of oxygen and air required for the complete combustion of the fuel used.



Calculation of air required for the combustion

• Weight of each constituent present per kilogram of the fuel is calculated from the percentage composition of the fuel.

Let the weight of carbon, hydrogen, oxygen, and sulphur in one kg of the fuel be C kg, H kg, O kg and S kg, respectively.

• The quantity of oxygen required for the combustion of C kg of carbon, H kg of hydrogen, S kg of sulphur can be calculated with the help of the reactions.



Combustion of carbon

$$C + O_2 \rightarrow CO_2$$

12 kg 32 kg (12 kg of carbon requires 32 kg of oxygen) C kg of carbon requires (32/12) C kg or 2.67 C kg of oxygen

Combustion of hydrogen

$$H_2 + (1/2)O_2 \rightarrow H_2O$$

2 kg 16 kg (2 kg of hydrogen requires 16 kg of oxygen) H kg of hydrogen requires (16/2)×H kg or 8 H kg of oxygen

Combustion of sulphur

 $S + O_2 \rightarrow SO_2$

32 kg of sulphur requires 32 kg of oxygen.

S kg of sulphur requires (32/32)× S kg or 1 S kg of oxygen.

The other constituents present in fuel do not require oxygen.

Total quantity of oxygen required for the complete combustion of 1 kg of fuel = ((32/12) C + 8 H + S) kg.



If oxygen is already present in the fuel, then, the quantity of oxygen to be supplied from air = (Total oxygen required - O $_2$ present in fuel)

or =
$$((32/12) C + 8 H + S - O) kg$$

So, minimum quantity of O_2 or the theoretical amount of O_2 required for the complete combustion of 1 kg of a fuel

$$= ((32/12) C + 8 H + S - O) kg$$

As air contains 23% oxygen by weight,

Minimum weight of air theoretical amount of air required for complete combustion = $(100/23) \times (2.67 \text{ C} + 8 \text{ H} + \text{ S} - \text{ O})$ kg.



Calculation of volume of oxygen or air required

22.4 liters of any gas at NTP has a mass equal to its gram molecular weight and air contains 21% oxygen by volume. Hence, the volume of air required can also be calculated.

Calculation of quantity of flue gases

The gases coming out after combustion CO_2 , SO_2 , CO, O_2 , N_2 are called flue gases. The water vapours formed condense as the gases cool down while the ash is excluded as it does not take part in combustion. Therefore, water vapours and ash are not included while calculating the percentage of dry combustion products.



Calculation of the flue gases when minimum amount of air is supplied

All the O_2 of air will be used in combustion of carbon and sulphur while N_2 in air remains unreacted.

Let 1 kg of fuel contain C kg of carbon and S kg of sulphur. The weight of CO₂ and SO₂ thus formed by the combustion of fuel is calculated as follows:

$$C + O_2 \rightarrow CO_2$$

12 kg 44 kg 12 kg of carbon on combustion gives 44 kg of CO_2 . Therefore, C kg of carbon gives $(44/12)\times C$ kg of CO_2 .



Calculation of the flue gases when minimum amount of air is required

32 kg of sulphur on combustion gives 64 kg of sulphur dioxide.

S kg of sulphur gives $(64/32)\times$ S kg or 2 S kg of SO₂.

Weight of $N_2 = (77/100) \times$ weight of air supplied + weight of N_2 per kg of fuel.

Total weight of dry flue gases formed by the combustion of 1 kg of fuel

= Weight of CO₂ + weight of SO₂ + weight of N₂

The % composition by weight of each constituent can then be calculated.



Calculation of the flue gases when excess of air is supplied

- (i) CO₂ and SO₂ are calculated as mentioned above.
- (ii) N_2 in flue gas = N_2 of total air supplied + N_2 present in the fuel.
- (iii) When excess air is supplied, the flue gas will contain O_2 of excess air.

Hence, the total weight of flue gas per kg of the fuel (when excess air is supplied) = weight of CO_2 + weight of SO_2 + weight of N_2 (from actual air supplied & from fuel if present) + weight of O_2 (from excess air)



Important facts for combustion calculation

(i) Substances always combine in definite proportion.

C +
$$O_2 \rightarrow CO_2 + 97 \text{ kcal}$$

12 kg 32 kg 44 kg

- (ii) Composition of air: Air contains 79% nitrogen and 21%oxygen by volume and 77% nitrogen and 23%oxygen by weight.
- (iii) The average molecular weight of air is taken as 28.94 g mol-1

1 g mol of any gas at STP (0 °C and 760 mm pressure) occupies 22.4 L, that is weight of 22400 mL of a gas at STP is its molecular mass.

- (iv) The mass of any gas can be converted into its volume by the gas law PV = nRT where n is the number of moles of the gas.
- (v) Minimum oxygen required for combustion

= Theoretical oxygen required – O_2 present in fuel.



Important facts for combustion calculation

(vi) Combustion seldom takes place efficiently with minimum weight of oxygen or air. An excess of air has to be supplied for proper combustion.

$$\% Excess Air = \frac{Actual \ air \ used - Minimum \ weight \ of \ air \ required}{Minimum \ weight \ of \ air \ required} \times 100$$

- (vii) Actual amount of air supplied is found out by taking excess air into consideration.
- (ix) To convert weight into volume and vice versa the Avogadro's law is used.
- (xi) If excess air is used is used for combustion, then the dry flue gases will contain $CO_2 + SO_2 + N_2$ of the total air supplied $+ O_2$ from excess air.



Combustion of gaseous fuel

CO, H_2 and hydrocarbons such as CH_4 , C_2H_6 , etc. are the main constituents of common gaseous fuels. The quantity of O_2 or air required in such cases is measured by the volume according to the combustion reactions of the constituents.

Combustion of carbon monoxide

$$2 \text{ CO} + \text{O}_2 \rightarrow 2\text{CO}_2$$

2 volume of CO combine with 1 volume of O₂ to give 2 volume of CO₂

Combustion of H₂

2H₂ + O₂ → 2H₂O
 Here 2 volumes of H₂ combines with 1 volume of O₂

Combustion of CH₄

CH₄+ 2O₂ → CO₂ + H₂O
 1 volume of methane reacts with 2 volumes of O₂



Combustion of gaseous fuel

$$C_2H_2 + 5/2 O_2 \rightarrow 2CO_2 + H_2O$$

1 vol 2.5 vol 2 vol

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$$

1 vol 5 vol 3 vol

The other constituents such as CO_2 and N_2 do not require any oxygen. If the percentage composition of a gaseous fuel is known, then the amount of O_2 required for combustion can be calculated with the help of the combustion equations. If the fuel already contains oxygen, then that amount is subtracted from the total O_2 required. As air contains $21\% O_2$ by volume, the volume of air required can be calculated by multiplying



Combustion of gaseous fuel

- To determine the percentage composition of dry flue gases the volume of CO_2 is also calculated as above. N_2 of the fuel comes out along with the flue gases; hence, the total N_2 in flue gases is (N_2 in fuel + N_2 in air supplied) for combustion. If excess air is supplied, then the volume of O_2 present in the excess air is also taken into account.
- Percentage composition of dry flue gases is then calculated. Dry flue gases do not contain water vapour as they condense on cooling, hence,
 H₂O is not included in the calculation of the % composition of dry flue

gases.



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	Dry Products in flue gas: Flue gases contain CO2, SO2, O2 from excess and & N2 fro actual air supplied
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Power Alcohol: When ethanol is blended with petrol (about 20-25%) and is used as fuel for IC engines, it is known as Power Alcohol.

Preparation of Ethanol:

➤ It can be obtained from Molasses which contains sucrose. Sucrose is converted into Glucose and Fructose by means of enzyme invertase from yeast at 30°C

$$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

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Preparation of Ethanol:

The enzyme Zymase (from yeast) converts glucose and fructose into ethyl alcohol and CO₂ by fermentation

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + CO_2$$

- Fermented liquid (containing 18-20% of alcohol) is then subjected to fractional distillation to give 90-95% alcohol (also called as rectified spirit)
- For getting 100% alcohol (absolute alcohol) rectified spirit is treated with lime and distilled

Advantages:

- 1) High Octane number (ON) about 90 as compared to conventional petrol with ON:60-70 (provide better antiknocking properties)
- 2) Ethanol renewable source of energy; reduces foreign dependency
- 3) Reduced emission of harmful gases as alcohol blended with petrol burns clean
- 4) Reduces the overheating of engine; extending engine life
- 5) Reduces deposition of Carbon and the gummy products on internal parts of engine when alcohol is blended
- 6) Removes all traces of moisture in the petrol as Alcohol capable to absorb



Disadvantages:

- 1) Ethanol lowers the calorific value of petrol
- 2) Alcohol may get oxidized to acetic acid which may cause corrosion of engine parts
- 3) Air required for complete combustion is less as as ethanol contains Oxygen atoms; hence needed modification of air inlet or operation of choke
- 4) Alcohol has high surface tension, hence difficult to atomize, particularly at low temperatures, causes starting trouble; hence carburetor needs special



Biodiesel: Also called as Biofuel obtained from

renewable sources of energy such as vegetable oils or

animal oils by transesterification

- Mainly used as a fuel for diesel engines (compression Ignition engine)
- > Vegetable oils like sunflower oil, peanut oil, palm oil,
- Soyabean oil, rapeseed oil etc. used for biodiesel.

 (Normally non edible vegetable oils are preferred)



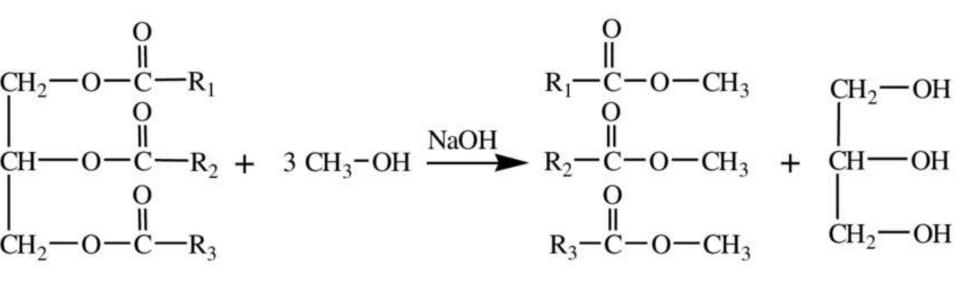
Chemical Nature of Biodiesel:

- ➤ Vegetable oils are mainly triglycerides of fatty acids _____ (ester of glycerol and 3 fatty acids) with High Viscosity,
- [≠]High Flash point and Low calorific value CV √
- ➤ Vegetable oils can be converted into Biodiesel by the process called **Transesterification**.
- Transesterification: Conversion of one type of ester to other. In this process, animal/vegetable oils are heated with excess of methanol in presence of catalysts like sodium methoxide, potassium methoxide, NaOH/KOH. Catalysts should be free from moisture (otherwise it promotes the saponification and not transesterification)

PICT SO

Alternative Fuels: Biodiesel

Chemical Nature of Biodiesel:



Triglycerol (Oil)

Methanol

Fatty Acid Methyl Esters (FAME)

Glycerol

- R_1 , R_2 , R_3 fatty acid alkyl groups (same or different)
- Biodiesel (FAME) may contain compound like:
- Methyl Stearate ($C_{17}H_{35}COOH CH_3$),
- Methyl2Palmitate (C₁₅H₃₁COOH CH₃)



Chemical Nature of Biodiesel:

- ➤ Biodiesel (also called as **B100**) used as an alternative fuel for diesel engine or it can be blended with petroleum diesel
- ➤ Most commonly used blends are **B5** (**5% of Biodiesel** mixed with **95% of petroleum diesel**) and **B20**
- ➤ Blended Biodiesel can be used directly into diesel engine (designed for conventional diesel) while B100 needs modification in engine
- Jatropa and Karanja oil seeds are used in India for Biodiesel

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Preparation of Biodiesel:

- Filtered non edible vegetable/animal oil(free from moisture) taken in Reaction vessel and heated to about 110°C. About 2% sodium methoxide (Na metal + Methanol) and 20% methanol added to reaction vessel
- ➤ Mixture is refluxed at 60-70°C for about 1 to 7 hours depending on the type of oil used
- Mixture is cooled and mixed with water to dissolve glycerine formed in the reaction
- ➤ Water insoluble Biodiesel phase is then separated from water phase through a separating funnel
- Suitable antioxidants are added to avoid oxidation & increase stability

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Advantages:

- 1) Non conventional and renewable source of energy obtained from domestic sources.
- 2) High Cetane Numbers 46 to 54 and high Calorific Value of about 40 kJ/gm than that of conventional diesels
- 3) Clean fuel as Oxygen present in fuel helps for complete combustion and thus no particulates/CO pollutants
- 4) Reduces dependency on foreign countries for diesel
- 5) Non toxic, free from Sulphur
- 6) Better Lubricity
- 7) Higher Flash point and thus safer for storage



Limitations:

- 1) Higher Cloud Point and Pour point than conventional diesel (cause problem in fuel flow line, hence cannot be used in cold countries)
- 2) Strongly adheres on some metals and can become gummy
- 3) Not compatible with some rubber hoses and gaskets as it's dissolving action
- 4) Costly in the regions where there is shortage of vegetable oils (costly starting material)

HYDROGEN AS A FUTURE FUEL



- Its availability from fully renewable resources (water and sunlight)
- o It is nontoxic
- o It's a clean fuel
- It has high calorific value
- It is used as a rocket fuel
- Can be used as a fuel for vehicles
- In a fuel cell, directly Hydrogen gas or by using
 CH₃OH as H₂ carrier which avoids the need to store

H₂ under pressure, constant source of energy

PROPERTIES OF HYDROGEN



- Colorless, odorless and insoluble in water
- Diatomic molecule in which two H atoms are joined by strong covalent bond with bond energy 435.9 KJ/mole
- Density is 0.08987 gm/cc at 0° C and 1 atm. Pressure, it is 14 times lighter than air
- It burns in air forming water and liberates a large amount of energy. This reaction is often explosive
- It reacts with halogen, many metals, with N₂
- Clean source of energy hence it can replace coal and oil as major source of energy in future
- Liquid hydrogen is used as a fuel in space rockets



- 1) Industrial Method:
 - a) Steam reforming of Methane
 /Natural gas
 - b) Steam reforming of coal/coke
- 2) Electrolysis of water
- 3) Lab scale: by acids or alkalies.
- 4) Solar Energy Method:

Water Splitting (Thermal Processes)

Photolysis of water using coordination

catalyst i.e. Photosensitizer, e.g. [Ru(bPy)₃]⁺²



1) Steam Reforming of Methane:

3 Steps process

i) Steam reforming reaction: Methane with steam at 800° C in presence of Ni catalyst to produce water gas (CO+H₂)

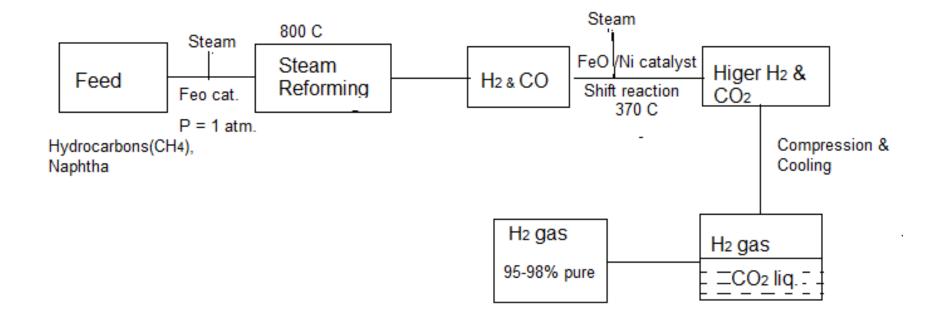
$$CH_4 + H_2O \rightarrow CO + 3H_2$$

ii) Water Gas Shift reaction: At 370° C in presence of FeO catalyst to produce $CO_2 \& H_2$ with steam

$$CO + H_2 \xrightarrow[H_2O]{FeO,370^0} CO_2 + H_2$$



iii) Removal of CO₂: Compression & liquefaction of mixture (obtained from Water Gas Shift reaction) to separate Hydrogen gas





1) Steam Reforming of coal/coke

3 Steps process

i) Steam reforming reaction: Coal/Coke with steam at 1000° C in presence of Ni/FeO catalyst to produce water gas (CO+H₂)

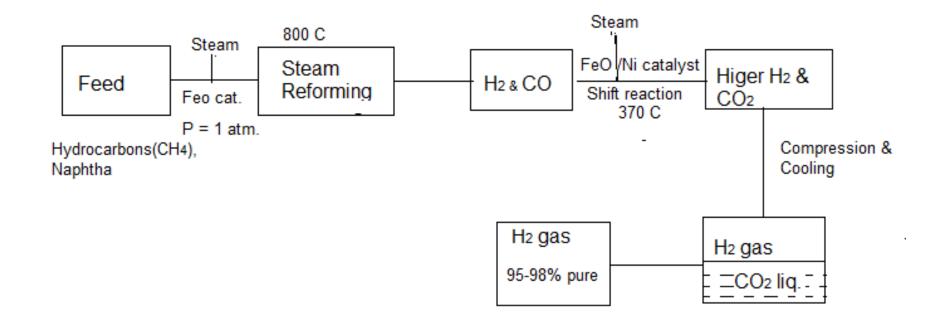
$$C + H_2O \rightarrow CO + H_2$$

ii) Water Gas Shift reaction: At 370° C in presence of FeO catalyst to produce $CO_2 \& H_2$ with steam

$$CO + H_2 \xrightarrow{FeO,370^0 C} CO_2 + H_2$$



iii) Removal of CO₂: Compression & liquefaction of mixture (obtained from Water Gas Shift reaction) to separate Hydrogen gas



 H_2 obtained from coal is less & with impurities like H_2S , SO_2 hence less preferred although cheap

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Storage of Hydrogen



Difficulties:

- Decarburization
- Lightest gas (MW:2); Quantity stored less
- High cost of compression & energy
- Very low Boiling Point -252.6°C, difficult to liquefy;
 high cost of cooling &insulation
- Very low Ignition Temp., highly inflammable
- Mixture of 2:1H₂-O₂ highly explosive
- Storage in hydrides requires longer duration & Decomposition requires high Temp

Storage of Hydrogen



Physical Storage:

- **Compression** Storage involves tanks and cylinders filled at high pressure to increase the density of the gas and optimize storage space.
- **Liqueraction** Gaseous substances are cooled to cryogenic temperatures to condense them into liquid form for efficient storage and transport.
- **Adsorption on Carbon Nanomaterials** Utilizes the small size, perous structure, low density, and high surface area of carbon nanomaterials to adsorb gases at molecular dimensions, enhancing storage capacity.
- **Metal-Organic Framework (MOF)** A highly crystalline and porous material made from inorganic metal ions linked with organic ligands, offering a hybrid structure ideal for gas storage due to its large surface area and tunable properties.

Applications of hydrogen



- 1) As a fuel in Internal combustion engine of vehicles
- 2) For preparation of ammonia (Haber's process)
- 3) As a Rocket propellant
- 4) As a fuel for fuel cells
- 5) Used in industries:

 annealing of metal,

 cutting metals,

 oxy-hydrogen flame for fabrication

Batteries



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- Batteries are called as the store house of energy
- It is a simple device which stores chemical energy and converts it into electrical energy through electrochemical reactions.
- A battery is a collection of one or more cells connected together to provide a desired voltage or current.
- Commonly, a battery can refer to either a single cell or a combination of cells that either generate electricity spontaneously like a Voltaic or Galvanic cell or electrolytic cells that require an external source of electricity to drive non spontaneous reactions. Similar to Voltaic or Galvanic cell, a battery also consists of an anode, a cathode and an electrolyte.

Components of Batteries



- **Electrodes:** The **negative electrode** where oxidation (loss of electrons) occurs called as **anode** and the **positive electrode** where reduction (gain of electrons) occurs called as **cathode**.
- Electrolyte: The medium usually an ionic solution or the substance that allows the movement of ions between the anode and cathode to facilitate the chemical reaction to produce electrical energy.
- Separator: A barrier which prevent the contact between the anode and cathode and still allow the flow of ions.
- External Circuit: It is a pathway through which electrons flow from anode to cathode which generates the electric current that can power devices.

Working of Batteries



Explained as follows with two types of cycles.

- Discharge Cycle: During the discharge, battery supplies electric power. The anode undergoes oxidation releasing electrons, while the cathode undergoes reduction, accepting those electrons. The electrolyte facilitates the flow of ions, balancing the charge within the cell.
- Recharge Cycle (for rechargeable batteries): During the recharge, an external power source reverses the chemical reactions. The electrons are forced back to the anode and ions move in the opposite direction resulting in the restoring of charge of the battery.

Types of Batteries



Primary batteries: These are non-rechargeable batteries. In these batteries, the cell reaction is irreversible, i.e., the reaction taking place in the forward direction cannot be reversed by the application of external potential. Once the cell reaction has taken place and the reactants have been converted into products, the cell gets discharged and cannot be used again like Dry cells or Leclanche cell. Common examples of primary batteries are alkaline batteries and zinc-carbon batteries.

Types of Batteries

- Secondary batteries: These are rechargeable batteries. In these batteries, the cell reaction is reversible. Once the forward reaction occurs and the cell is discharged, it can be charged again by applying external power source. Hence can be used multiple times. Common examples include lithium-ion batteries, nickel-cadmium (Ni-Cd) batteries, and lead-acid batteries.
- Alkaline Batteries: Widely used in household devices. They are primary batteries that use zinc and manganese dioxide as electrodes.
- **Lead-Acid Batteries:** Used in automobiles for starting engines and in backup power supplies. They are large, heavy, and

Types of Batteries





- **Lithium-ion Batteries:** Popular in portable electronics and electric vehicles. They have a high energy density and are rechargeable.
- Nickel-Metal Hydride (NiMH) Batteries: Common in rechargeable household batteries and hybrid vehicles. They have a lower energy density compared to Li-ion but are safer.

• Flow Battery: H_2 - O_2 Fuel Cells

Lithium Ion Battery



Stanley Whittingham, John B. Goodenough and Akira Yoshino shared the Nobel prize in Chemistry in 2019, for the development of Lithium-ion battery

Type of rechargeable LiCoO₂ and Graphite battery having high energy density.

Lithium-ion battery uses the **reversible intercalation of Li⁺ ions** into electronically conducting solids to store energy.



Construction:

Lithium ion battery consists of the key components as anode, cathode, electrolyte and separator.

• **Anode (Negative Electrode)**: It is typically made of graphite (a form of carbon). It functions as a kind of stable storage space for lithium atoms and one lithium atom per six carbon atoms is the most thermodynamically stable (LiC₆). The anode stores lithium ions when the battery is fully charged. During discharge, lithium ions move from the anode to the cathode.



Construction:

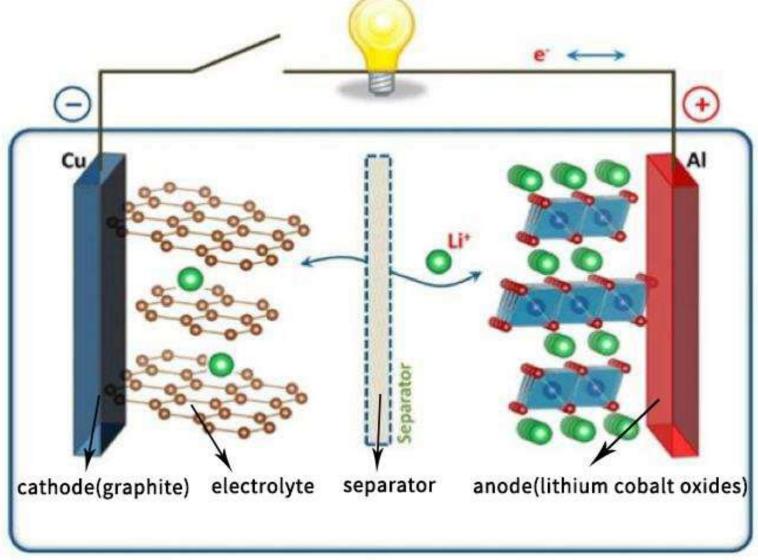
- Cathode (Positive Electrode): It is made from a lithium metal oxide, such as lithium cobalt oxide (LiCoO₂), lithium iron phosphate (LiFePO₄), or lithium manganese oxide (LiMn₂O₄). The specific material determines the battery's characteristics, such as energy density, safety, and lifespan. The most commonly used is lithium cobalt oxide (LiCoO₂).
- Both the electrodes (anode and cathode) allow lithium ions to move in and out of their structures with a process called intercalation (insertion) or deintercalation (extraction), respectively.



Construction:

- **Separator**: It is a thin, porous membrane generally made up of polyethylene (PE) and polypropylene (PP) that prevents physical contact between the anode and cathode while allowing lithium ions to pass through it. The separator is critical for the safety of the battery, as it prevents short circuits.
- **Current Collectors**: The electrodes are separated from external electronics with a piece of metal called a current collector. Graphite and Cobalt oxides are not good at collecting or distributing the electrons, hence a conductive copper layer is added next to the graphite and a conductive aluminium layer next to the cobalt oxide.







Working of Lithium-ion Batteries:

Discharge Cycle or Discharging: During the discharge, the negative electrode is the anode (Graphite) and the positive electrode is the cathode (lithium cobalt oxide) and the electrons flow from the anode to the cathode through the external circuit. Lithium is oxidised from Li to Li⁺ (0 to 1 oxidation state) in the lithiated graphite anode.

Consequently, oxidation reaction occurs at anode to give lithium ions with the release of electrons.

$$LiC_6 \rightarrow C_6 + Li^+ + e^-$$
 (at anode)



Working of Lithium-ion Batteries:

$$LiC_6 \rightarrow C_6 + Li^+ + e^-$$
 (at anode)

The lithium ions are small enough to be able to move through micro-permeable separator between the anode and cathode. Lithium ions move through the electrolyte by diffusion and electrons through the external circuit towards the cathode where these electrons recombine with the cathodic material. The electrolyte provides a conductive medium for lithium ions but does not take part in the electrochemical reaction. The electrolyte facilitates the flow of ions, balancing the charge within the cell.



Working of Lithium-ion Batteries:

• Cathode (Lithium cobalt oxide) undergoes reduction, accepting these electrons. Migrated lithium ions from the anode are incorporated into lithium cobalt oxide through the following reaction, which reduces cobalt from Co⁴⁺ to Co³⁺ i.e. +4 to +3 oxidation state.

$$Li^+ + CoO_2 + e^- \rightarrow LiCoO_2$$
 (at cathode)

https://youtu.be/VxMM4g2Sk8U



Working of Lithium-ion Batteries:

• **Recharge Cycle or Charging:** During the recharge, an external power source reverses the chemical reactions. Consequently, an external electric current drives lithium ions from the cathode through the electrolyte into the anode. The electrons flow through the external circuit to balance the charge, and lithium ions are intercalated (inserted) into the graphite layers of the anode. During charging, cobalt gets oxidised from Co³⁺ to Co⁴⁺.

 $LiCoO_2 \rightarrow Li^+ + CoO_2 + e^-$ (at cathode)



Working of Lithium-ion Batteries:

Recharge Cycle or Charging: During the recharge, an external power source reverses the chemical reactions. Consequently, an external electric current drives lithium ions from the cathode through the electrolyte into the anode. The electrons flow through the external circuit to balance the charge, and lithium ions are intercalated (inserted) into the graphite layers of the anode. During charging, cobalt gets oxidised from Co³⁺ to Co⁴⁺.

$$LiCoO_2 \rightarrow Li^+ + CoO_2 + e^-$$
 (at cathode)
 $C_6 + Li^+ + e^- \rightarrow LiC_6$ (at anode)



Reactions of Lithium-ion Batteries:

$$\text{LiCoO}_2 \rightarrow \text{Li}^+ + \text{CoO}_2 + \text{e}^- \text{ (at cathode)}$$

 $\text{C}_6 + \text{Li}^+ + \text{e}^- \rightarrow \text{LiC}_6 \text{ (at anode)}$

Net Reaction:

$$LiC_6 + CoO_2 \rightleftharpoons C_6 + LiCoO_2$$

Here, **forward reaction** indicates the **discharging** of battery while **backward reaction indicates the charging** of battery.



Advantages of Lithium-ion Batteries:

- **High Energy Density**: Lithium-ion batteries can store a large amount of energy in a small and lightweight package, making them ideal for portable devices like smartphones, wrist watches, laptops, and electric vehicles. It is due to the relatively light weight and low density of lithium.
- **Long Cycle Life**: These batteries can be recharged hundreds to thousands of times before their capacity significantly degrades, offering a long lifespan compared to other rechargeable batteries. It is due to the small radii of lithium ions, which causes fewer disruptions of the electrode structure during ion transfer.
- **Low Self-Discharge**: Lithium-ion batteries have a low self-discharge rate, meaning they lose their charge slowly when not in use, making them more reliable for long-term storage.
- **No Memory Effect**: Unlike some other rechargeable batteries (like nickel-cadmium batteries), lithium-ion batteries do not suffer from the memory effect, where partial discharge followed by recharging reduces the usable capacity.



Disadvantages of Lithium-ion Batteries:

- **Safety Concerns:** Lithium-ion batteries can overheat, leading to thermal runaway, fires, or explosions if damaged, overcharged, or exposed to high temperatures. However, modern batteries include safety mechanisms to mitigate these risks.
- **Cost:** The materials and manufacturing processes involved in lithium-ion batteries are relatively expensive, though costs have been decreasing as technology advances.
- **Limited Lifespan:** Although they have a long cycle life, lithium-ion batteries do eventually degrade over time, with capacity gradually reducing after many charge-discharge cycles.
- **Environmental Impact:** The extraction of lithium and other materials used in these batteries can have significant environmental impacts, though recycling efforts are being developed to mitigate this.



Applications of Lithium-ion Batteries:

- **Consumer Electronics:** Laptops, tablets, smartphones, cameras and other portable devices such as smart wrist watches, fitness trackers and other wearable devices offering long battery life in a compact form.
- **Electric Vehicles:** Powering the electric cars, buses, bikes and other vehicles.
- **Power Tools:** Power drills, saws and other battery operated tools.
- Implanted Medical devices: Portable medical equipment such as pacemakers and defibrillators.
- **Power storage:** Used for solar and wind power storage.
- **Aerospace technologies:** Due to their light weight, they are used in aerospace technologies such as satellites and space probes.



- ➤ Fuel cells represent the new generation of high efficiency, environmentally friendly energy systems.
- Fuel cells are the direct generators of power which take chemical substances from the external source and convert them into electrical energy by electrochemical reaction.
- Consequently fuel cell is an electrochemical device that converts chemical energy from a fuel into electrical energy through a chemical reaction with oxygen or another oxidising agent.

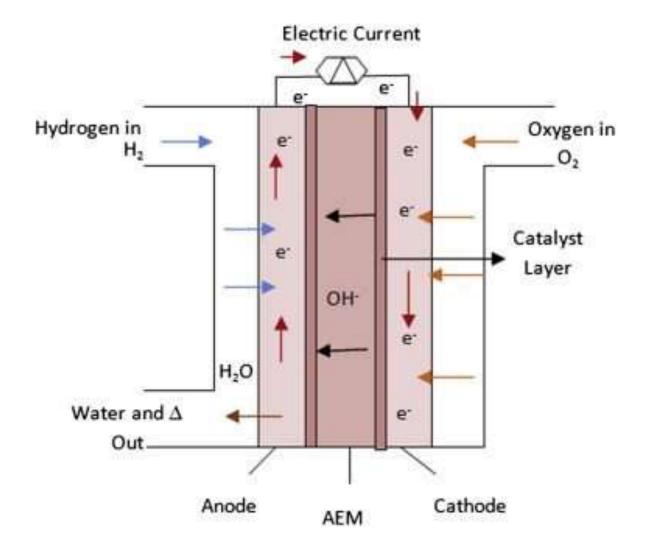


- Fuel cells are different than the battery, as in battery the chemical substances are an integral part of a storage battery whereas in fuel cells chemical substances are fed into the cells whenever energy is required. Fuel cells do not need recharge periodically, but instead continue to produce electricity as long as fuel source is provided.
- ➤ Hence fuel cell is also called as Flow Battery.
- Fuel cells are clean, efficient, reliable and quiet source of power.



- Components of fuel cell:
- **Electrodes:** In fuel cells, the electrodes are generally used are inert materials like graphite, platinum etc. but have catalytic properties. Two types of electrodes:
- **Anode (negative electrode):** The anode is where the fuel, typically hydrogen, is supplied. At the anode, the fuel undergoes oxidation, releasing electrons and creating positively charged ions.
- **Cathode (positive electrode)**: The cathode is where the oxidant, usually oxygen from the air, is supplied. Here, the reduction reaction occurs, where electrons from the external circuit combine with the oxidant and the positively charged ions.
- **Electrolyte:** The electrolyte allows ions (but not electrons) to move between the anode and cathode. The type of electrolyte used determines the type of fuel cell and its operating temperature.
- **Catalyst**: Catalysts are often used at the anode and cathode to speed up the chemical reactions. Platinum is a common catalyst in many fuel cells, particularly those using hydrogen.







Working of fuel cell:

- A typical fuel cell works by passing hydrogen through the anode of a fuel cell and oxygen through the cathode.
- At the anode site, a catalyst splits the hydrogen molecules into electrons and protons.

Anodic Reaction: Oxidation of fuel (Hydrogen)

$$H_2 \rightarrow 2H^+ + 2e^-$$
 (at anode)

- The protons pass through the porous electrolyte membrane, while the electrons are forced through a circuit, generating an electric current and excess heat.
- At the cathode, the protons, electrons, and oxygen combine to produce water molecules.

Cathodic Reaction: Reduction of Oxygen

$$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \ (at \ cathode)$$

Overall Reaction:

$$2H_2 + O_2 \rightarrow 2H_2O$$



Types of fuel cell:

Electrolyte plays very important role in fuel cells. Based on the electrolyte used and the temperature of operation, fuel cells are classified as:

- Alkaline H_2 O_2 Fuel Cell
- Solid Oxide Fuel Cell
- Phosphoric Acid Fuel Cell
- Molten Carbonate Fuel Cell
- Phosphoric Acid Fuel Cell
- Polymer Electrolyte Fuel Cell



Construction: H_2 - O_2 fuel cell consists of anode, cathode and electrolyte. The electrodes used are anode and cathode which consists of **porous graphite** (carbon) impregnated with finely divided platinum or a 75/25 alloy of palladium(Pd) with silver(Ag) or **nickel** (Ni), which acts as catalyst. Electrolyte used is alkali solution like aqueous 25% (to 40%) KOH or NaOH, working at temperature **below 100°C**. Hydrogen as a fuel is bubbled through the anode and oxygen as an oxidant is passed through cathode.



Electrodes:

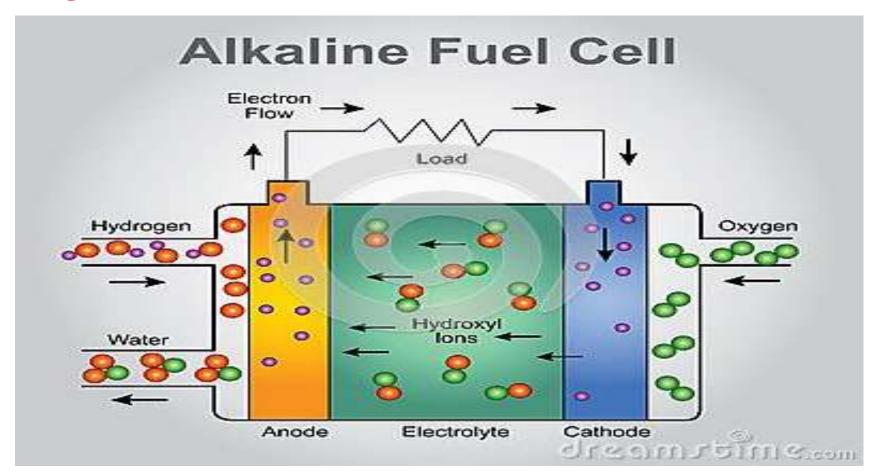
Anode (negative electrode): The anode is where the fuel (Hydrogen) is supplied. Made up of **porous graphite** (carbon) impregnated with finely divided platinum or a 75/25 alloy of palladium(Pd) with silver(Ag) or **nickel** (Ni), which acts as catalyst. At the anode, the hydrogen undergoes oxidation, releasing electrons and creating positively charged hydrogen ions.

Cathode (positive electrode): The cathode is where the oxidant(Oxygen), from the air, is supplied. Similar to anode, it is also made up of **porous** graphite (carbon) impregnated with finely divided platinum or a 75/25 alloy of palladium(Pd) with silver(Ag) or **nickel** (Ni), which acts as catalyst. Here, the reduction reaction occurs, where electrons from the external circuit combine with the oxygen and the positively charged hydrogen ions.

Electrolyte: The electrolyte in AFC is an aqueous alkali solution like **aqueous 25%** (**to 40%**) **KOH or NaOH**, operating at temperature **below 100°C**. It allows hydroxide ions (but not electrons) to move between the anode and cathode. Consequently, it is responsible for conducting hydroxide ions (OH⁻) from the cathode to the anode during the reaction.



Diagram



https://in.pinterest.com/pin/330451691394072719/Ref.



Working of Alkaline Fuel Cell

Fuel (H_2) is introduced at anode & O_2 /Air is supplied at the cathode.

Anodic Reaction: Hydrogen is oxidized, splitting into protons (H⁺) and electrons (e⁻). Hydrogen reacts with hydroxide ions from the electrolyte to form water and release the electrons.

$$2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$$

Cathodic Reaction: Oxygen is reduced by combining with water and electrons to form hydroxide ions. The reaction is:

$$O_2+2H_2O+4e^-\rightarrow 4OH^-$$

Net Reaction:

$$2H_2 + O_2 \rightarrow 2H_2O$$

Water is the only byproduct, and electricity is generated as electrons flow through the external circuit.



Applications Fuel Cell

Transportation: Fuel cell vehicles (FCVs) are a type of electric vehicle that employs fuel cell technology to generate electricity onboard.

Fuel cell vehicles (FCVs) offer an alternative to conventional internal combustion engine vehicles by producing zero-emission power.

Hydrogen-powered FCVs boast
longer ranges and shorter
refuelling times compared
to electric vehicles, making
them a promising contender
for a cleaner future on the roads.





2. Energy Generation

Alternative to Electricity

Can be deployed as distributed power sources, providing electricity to homes, businesses, and even remote areas. Additionally, fuel cells can be integrated into existing power grids, offering stability during peak demand periods.

Backup Power

Fuel cells are well-suited for backup power applications. They offer a reliable energy source during grid failures and emergencies, ensuring essential services continue without interruption.

Portable and Remote Power

Portable fuel cells power a range of devices, from laptops and smartphones to camping equipment. Moreover, in remote and off-grid areas, fuel cells provide a sustainable energy solution, supporting communities without access to traditional power infrastructure.



3. Aerospace Industry

• Fuel cells have found applications in the aerospace sector, powering unmanned aerial vehicles (UAVs) and space missions. Their high energy density and lightweight nature make them ideal for aircraft where every kilogram counts.

4. Spacecraft Power Systems

• Fuel cells have been used in space missions to generate electricity for spacecraft. For example, fuel cells have been used on space shuttles and space stations to provide power and water for crew members.

5. Marines Systems

Fuel cells have been used in sub-marines to generate electricity.



Advantages of Fuel Cell

1. Environmental Benefits

Fuel cells stand out for their environmental advantages, producing only water and heat as byproducts. This minimal impact on air quality makes them a key player in combatting climate change and reducing greenhouse gas emissions.

2. High Efficiency

Fuel cells are highly efficient, converting a significantly higher percentage of energy stored in fuel to electricity compared to traditional combustion engines. This efficiency leads to reduced fuel consumption and increased overall sustainability.



Advantages of Fuel Cell

3. Versatility

Fuel cells come in various shapes and sizes, offering versatility in their applications. From powering vehicles to generating electricity for stationary use, fuel cells cater to a wide range of needs.

4. Reliability

Fuel cells boast high reliability due to their minimal moving parts and lower maintenance requirements. This characteristic makes them a dependable source of power in critical situations.

5. Noise Reduction

Compared to traditional engines, the fuel cells operate quietly, reducing noise pollution in both urban and remote areas. This aspect is particularly advantageous for transportation modes, promoting a more pleasant and serene environment. Bhavna M. Vyas



Disadvantages of Fuel Cell

- **Cost**: Fuel cells, especially those using platinum catalysts, can be expensive.
- **Hydrogen Infrastructure**: Hydrogen fuel cells require hydrogen, which is not yet widely available. Storing and transporting hydrogen also presents
- challenges.
- **Durability**: Some types of fuel cells have shorter lifespans and may degrade faster than conventional power generation systems.
- Electrode gets poisoned easily
- Fuel and oxygen supplied must be pure and free from CO₂

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Thank You