Unit 2
Organic Fuels

SOLID FUELS

Solid fuels are materials in solid state that can undergo combustion to produce heat energy. These fuels have been used by humans for centuries, from the earliest use of wood to modern uses of coke and coal. They are primarily made up of carbon and hydrogen but may also contain oxygen, nitrogen, sulphur, ash, and moisture. Solid fuels play a vital role in domestic heating, industrial furnaces, and power generation.

Examples of Solid Fuels

- *Wood:* A renewable biomass fuel commonly used in rural and underdeveloped areas.
- *Coal:* A fossil fuel formed from plant matter over millions of years under high pressure and temperature.
- Coke: A solid carbonaceous residue derived from the destructive distillation of coal.
- *Charcoal:* Made by heating wood in a limited oxygen supply; used for cooking and metallurgy.

COAL

Coal is a combustible black or brownish-black sedimentary rock formed from fossilized plant matter. It contains carbon, hydrogen, sulphur, oxygen, nitrogen, moisture, and ash.

Formation of Coal

Coal originates from the accumulation and decomposition of plant material in swampy environments. Over time, heat and pressure convert this biomass into peat and then into various ranks of coal.

Types / Classification of Coal

Coal is classified based on its carbon content, calorific value, moisture content, and volatile matter:

1. *Peat:* Earliest form, low carbon (~50-60%), high moisture, low heating value.
2. *Lignite (Brown Coal):* Carbon content (~60-70%), moisture 30-50%, low calorific value.
3. *Sub-bituminous Coal:* Intermediate between lignite and bituminous coal.
4. *Bituminous Coal:* Carbon content (~70-85%), used for electricity generation and industrial use.
5. *Anthracite:* Highest rank, carbon content (>90%), low volatile matter, hard and shiny, high calorific value.

COMPOSITION OF COAL

The performance and efficiency of coal as a fuel depends on its chemical composition, analysed through:

1. Proximate Analysis

Determines moisture, volatile matter, ash, and fixed carbon:

- *Moisture:* Reduces combustion efficiency, causes handling issues.
- *Volatile Matter:* Influences ignition and combustion.
- *Ash:* Non-combustible residue; excessive ash reduces efficiency.
- *Fixed Carbon:* Actual combustible portion providing heat.

2. Ultimate Analysis

Determines elemental composition:

- *Carbon (C):* Primary heat-producing element.

- *Hydrogen (H):* Combines with oxygen during combustion to release heat.
- *Oxygen (O):* Reduces calorific value as it combines with carbon and hydrogen.
- *Nitrogen (N):* Inert; forms NOx pollutants.
- *Sulphur (S):* Combusts to form SO2 and SO3; causes pollution and corrosion.

CALORIFIC VALUE OF COAL

It is the amount of heat released by the complete combustion of a unit mass of coal.

Types

1. *Gross Calorific Value (GCV) or Higher Calorific Value (HCV):*
   - Includes the latent heat of vaporization of water.
   - Heat produced when products of combustion are cooled and steam condenses.
2. *Net Calorific Value (NCV) or Lower Calorific Value (LCV):*
   - Excludes latent heat of steam.
   - Water formed remains in vapor state.

Formula

$$NCV = GCV - (Mass\ of\ water \times Latent\ heat\ of\ vaporization)$$

DETERMINATION OF CALORIFIC VALUE: BOMB CALORIMETER

In a bomb calorimeter, a known mass of coal is burned in an oxygen-filled sealed bomb. The heat released raises the temperature of the surrounding water. From this, the calorific value is determined.

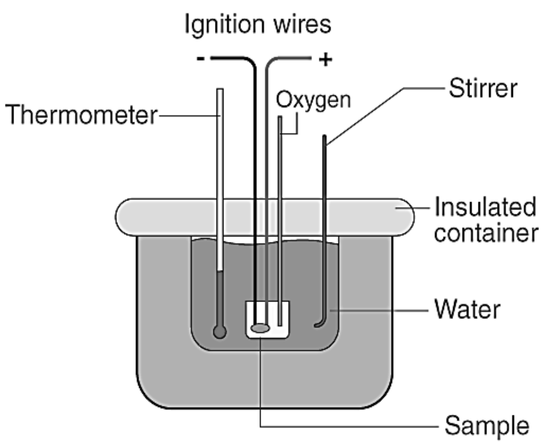
Apparatus

- Bomb (sealed steel chamber)
- Calorimeter vessel
- Water bath
- Thermometer
- Ignition system
- Oxygen supply

Procedure

1. Place weighed coal in crucible.
2. Fill bomb with oxygen at high pressure.
3. Seal bomb and immerse in calorimeter with known mass of water.
4. Ignite coal using ignition coil.
5. Record temperature rise.
6. Calculate GCV using:

$$GCV = [(Mass\ of\ water + water\ equivalent) \times Temp\ rise] \,/\, Mass\ of\ fuel$$



COAL CARBONIZATION

Coal carbonization is the process of heating coal in the absence or limited supply of air to produce coke, gases, tar, and other by-products.

Types of Carbonizations

1. *Low-Temperature Carbonization (LTC):*
   - 500–600°C
   - Produces soft coke with high volatile matter.
   - Used as domestic fuel.
2. *High-Temperature Carbonization (HTC):*
   - 900–1200°C
   - Produces hard coke (metallurgical coke).
   - High carbon, low volatile content.

Metallurgical Coke

Metallurgical coke is a strong, porous, high-carbon material used in blast furnaces to reduce iron ore.

Properties:

- High thermal strength
- Low impurities
- Porous structure

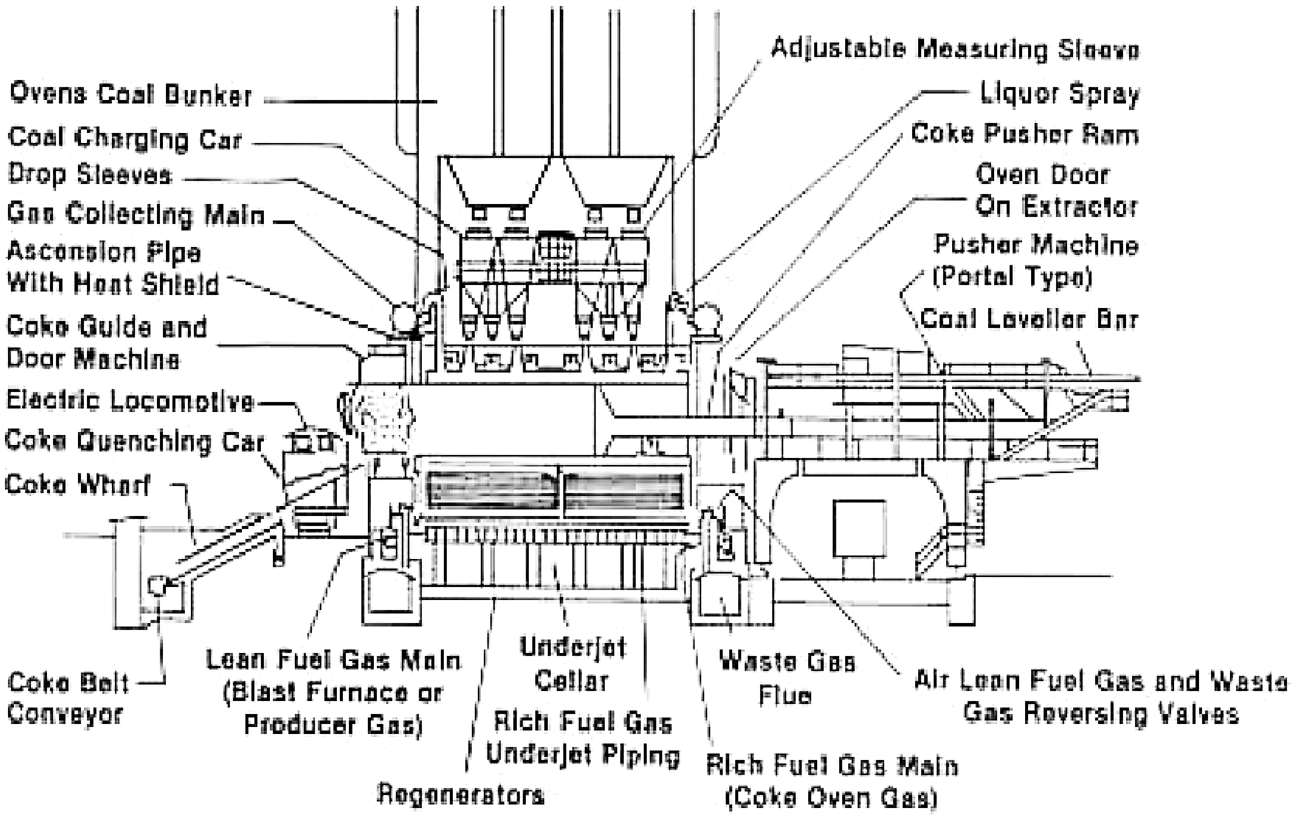
Uses:

- Reducing agent in blast furnace
- Source of carbon and heat

Otto-Hoffman Coke Oven Process

Construction:

- Series of narrow silica brick chambers
- Coal charged from top, heated externally
- Heating gas passes between the walls of chambers



Working:

1. Coal is fed and heated in the absence of air.
2. Carbonization lasts 18–20 hours.
3. Coke is removed and quenched.
4. By-products are collected through off-gas system.

By-product Recovery:

- Coal gas: Used as fuel
- Tar: Raw material for dyes, paints
- Ammonia: Used in fertilizers
- Benzene, Toluene, Xylene: Solvents and chemical feedstock
- Naphthalene: Used in mothballs and organic synthesis

Advantages of Otto-Hoffman Method:

- Recovery of valuable chemicals
- High-quality coke production
- Environmentally safer than traditional beehive ovens

LIQUID FUELS

Liquid fuels are combustible or energy-generating substances that exist in liquid form at room temperature. They are predominantly derived from petroleum or are synthetic in nature. Liquid fuels are widely used due to their ease of storage, transportation, controlled combustion, and high energy output.i

TYPES OF LIQUID FUELS

Liquid fuels can be broadly classified into two categories:

A. Natural Liquid Fuels:

These are obtained directly from natural sources like crude petroleum.

- *Petroleum (Crude Oil):* A complex mixture of hydrocarbons found in earth's crust.
- *Gasoline (Petrol):* A volatile and flammable fraction of petroleum used mainly in spark-ignition engines.
- *Diesel Oil:* A less volatile liquid fuel used in compression-ignition engines.
- *Kerosene:* Used for heating, lighting, and sometimes in jet engines.
- *Fuel Oil:* Used in furnaces and boilers for industrial heating.

B. Artificial (Synthetic) Liquid Fuels:

These are prepared from solid or gaseous fuels through chemical processes.

- *Alcohols (Methanol, Ethanol):* Often blended with petrol.
- *Bergius Process Fuel:* Synthetic petrol from hydrogenation of coal.
- *Fischer-Tropsch Fuel:* Synthetic hydrocarbons from water gas ($CO + H2$).

ADVANTAGES OF LIQUID FUELS

Liquid fuels are preferred over solid and gaseous fuels due to the following reasons:

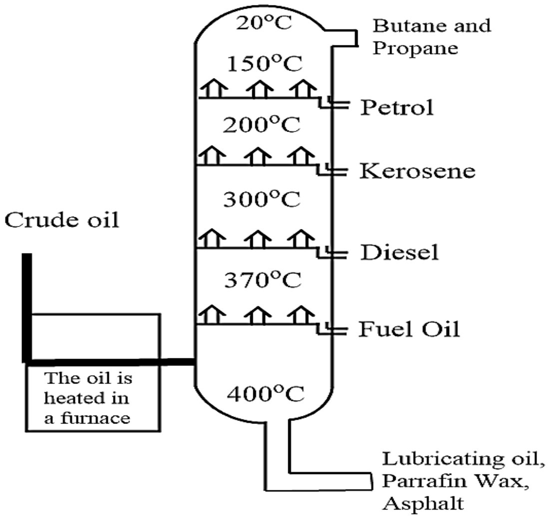
1. *High calorific value:* They generate more energy per unit mass.
2. *Ease of transportation:* Can be easily pumped through pipelines.
3. *Ease of storage:* Requires less space and can be stored in tanks.
4. *Uniform combustion:* Enables better control and efficiency.
5. *Clean handling:* No dust or ash problems as in solid fuels.
6. *Low maintenance cost:* Less wear and tear on equipment.
7. *Automation friendly:* Can be used in automated systems.

REFINING OF PETROLEUM

Petroleum refining is the process of transforming crude oil into useful products like petrol, diesel, kerosene, lubricants, and petrochemicals. The main stages of petroleum refining include:

(a) Fractional Distillation

- Crude oil is heated to about 400°C and passed into a fractionating column.
- Different components condense at different heights according to their boiling points.
- The column has a temperature gradient: hottest at the bottom and coolest at the top.



Major fractions obtained:

- Gases (LPG) at the top
- Gasoline (petrol)
- Naphtha
- Kerosene
- Diesel oil
- Lubricating oil
- Fuel oil and bitumen at the bottom

(b) Cracking Process

Cracking is the decomposition of complex, heavy hydrocarbons into lighter, more valuable products like gasoline and olefins.

Types of Cracking:

1. Thermal Cracking: Uses high temperature and pressure.
2. Catalytic Cracking: Uses catalysts (e.g., zeolites) at moderate conditions. More efficient and selective.

Example reaction:

$$\mathrm{C_{16}H_{34}} \rightarrow \mathrm{C_8H_{18}}\ (octane) + \mathrm{C_8H_{16}}\ (alkene)$$

SYNTHETIC PETROL

Synthetic petrol is a man-made liquid fuel produced from coal or natural gas through chemical processes. It was developed due to limited petroleum reserves and demand for alternative sources.

(a) Bergius Process

- Finely powdered coal is mixed with heavy oil and heated to 400–450°C.
- Hydrogen gas is introduced under high pressure (200–250 atm).
- Catalyst like tin or nickel is used.
- Produces a mixture of hydrocarbons that is refined to obtain petrol.

Reaction:

$$C + 2\mathrm{H}_2 \rightarrow C\mathrm{H}_4\ (Simplified)$$

(b) Fischer-Tropsch Process

- Water gas ($CO + H_2$) is passed over iron/cobalt catalyst at 200–300°C and 5–10 atm.
- Produces hydrocarbons and water.

Reaction:

$$nCO + (2n+1)\mathrm{H}_2 \rightarrow \mathrm{C_nH_{2n}} + 2 + n\mathrm{H}_2O$$

Advantages of Synthetic Petrol

- Useful in countries lacking petroleum resources.
- Can utilize abundant coal reserves.
- Provides independence from imported oil.

PETROL QUALITY TERMS

(a) Octane Number

- Indicates the anti-knocking quality of petrol in spark-ignition engines.
- Higher the octane number, better the fuel resists knocking.
- Defined as the percentage of iso-octane in a mixture with n-heptane that has the same knocking property.

Examples:

- Iso-octane = 100 (high anti-knock)
- n-heptane = 0 (poor anti-knock)

A fuel with octane number 90 behaves like a mixture of 90% iso-octane and 10% n-heptane.

(b) Anti-Knock Agents

To improve octane number and prevent knocking, additives are blended with petrol.

Common anti-knock agents include:

1. Tetraethyl Lead (TEL): Increases octane number but causes lead pollution.
2. MTBE (Methyl Tertiary Butyl Ether): Oxygenate that boosts octane without pollution.
3. Alcohols (ethanol, methanol): Renewable, clean-burning additives.

GASEOUS FUELS

Gaseous fuels are combustible substances that exist in a gaseous state at ambient temperature and pressure. They are either found naturally or produced by chemical processes. Gaseous fuels are extensively used for domestic cooking, industrial heating, and power generation due to their ease of combustion, higher thermal efficiency, and minimal environmental pollution.

Unlike solid and liquid fuels, gaseous fuels mix easily with air, leading to uniform and complete combustion. The ease of transportation through pipelines and accurate control over combustion temperature makes gaseous fuels a preferred choice in many sectors.

TYPES OF GASEOUS FUELS

Gaseous fuels can be classified into two broad categories:

A. Natural Gaseous Fuels:

- *Natural Gas:* Found in deep underground rock formations, natural gas mainly consists of methane (CH_2), with smaller quantities of ethane, propane, butane, carbon dioxide, nitrogen, and hydrogen sulphide.

- *Liquefied Petroleum Gas (LPG):* A mixture of propane (C3H8) and butane (C4H10), stored under pressure in a liquid state and used for cooking, heating, and in vehicles.

B. Manufactured Gaseous Fuels:

- *Coal Gas:* Produced by the destructive distillation of coal in the absence of air. It consists of hydrogen, methane, carbon monoxide, and small quantities of other gases.
- *Producer Gas:* Generated by blowing air (or a mixture of air and steam) over red-hot coke. It mainly consists of CO, N_2, and small amounts of H_2.
- *Water Gas:* Produced by passing steam over red-hot coke or coal. The reaction produces hydrogen and carbon monoxide.
- *Synthetic Gas (Syngas):* A mixture of carbon monoxide and hydrogen, obtained from coal, biomass, or natural gas.

ADVANTAGES OF GASEOUS FUELS

- **Clean Burning:** Produces minimal soot and ash, leading to a clean environment.
- **High Calorific Value:** Provides more heat per unit mass compared to many solid fuels.
- **Uniform Combustion:** Burns with a controlled and steady flame.
- **Easy Transport and Storage:** Can be transported via pipelines and stored in pressurized tanks.
- **Quick Start and Stop:** No need for preheating or waiting for ignition.
- **Automation Friendly:** Suitable for automatic systems in industries.

MANUFACTURING AND COMPOSITION OF GASEOUS FUELS

a) Coal Gas:

- Produced by heating coal in the absence of air (destructive distillation).
- Collected gas contains hydrogen, methane, ethylene, carbon monoxide, and hydrogen sulphide.
- It is cleaned by removing tar, ammonia, and hydrogen sulphide.

b) Producer Gas:

- Formed by blowing air over red-hot coke:
  - $C + O_2 \rightarrow CO_2\ (Exothermic)$
  - $CO_2 + C \rightarrow 2CO\ (Endothermic)$
- Composition: ~26% CO, ~60% N_2, ~10% H_2, traces of CH_4.

c) Water Gas:

- Formed by passing steam over red-hot carbon:
  - C + H_2O → CO + H_2 (Endothermic)
- Composition: ~40-50% H_2, ~40-45% CO, ~10% CO_2.

d) Natural Gas:

- Extracted from petroleum wells.
- Composition: ~85-90% methane, rest ethane, propane, butane.

e) LPG:

- Obtained from crude oil refining or natural gas processing.
- Stored as liquid under pressure.
- Composition: Propane (C_3H_8) and Butane (C_4H_{10}).

CALORIFIC VALUE OF GASEOUS FUELS

Calorific value is the amount of heat produced when a unit volume of gas is completely burned in air or oxygen.

Types:

- *Gross Calorific Value (GCV):* Total heat released including latent heat of steam.
- *Net Calorific Value (NCV):* Heat released excluding latent heat of steam.

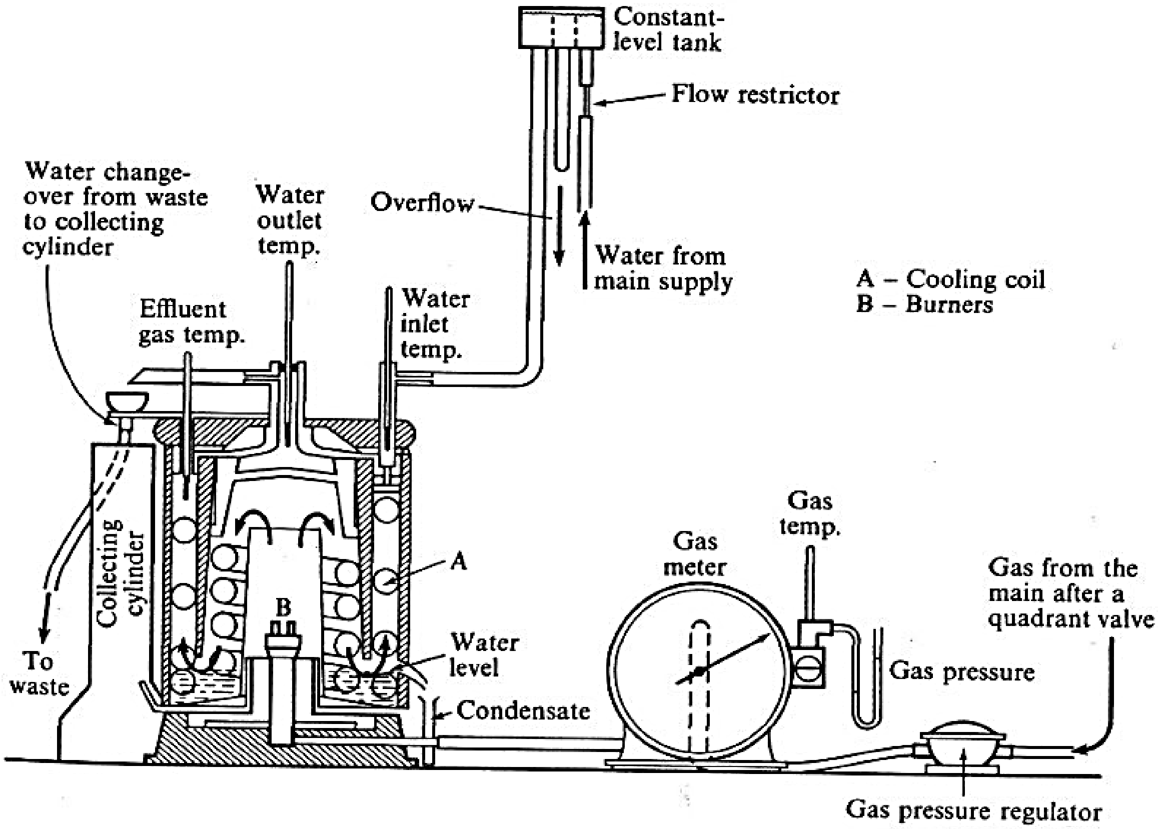
Typical calorific values:

- Natural gas: ~8500 to 9000 kcal/m3
- LPG: ~11000 kcal/kg
- Producer gas: ~1200-1400 kcal/m3
- Water gas: ~2800 kcal/m3

DETERMINATION OF CALORIFIC VALUE (JUNKER'S GAS CALORIMETER)

Principle:

- A known volume of gas is burned.
- Heat produced is used to raise the temperature of a known quantity of water.



Construction:

- Gas burner inside a water-jacketed chamber.
- Water flows at a constant rate.
- Thermometers at water inlet and outlet.
- Gas meter records volume.

Procedure:

1. Water is allowed to flow through calorimeter.
2. Burner is lit and gas is burned at a constant rate.
3. Measure temperature rise in water.
4. Measure volume of gas burned.

Formula:

$$GCV = (Mass\ of\ water \times Temperature\ rise \times Specific\ heat)\ /\ Volume\ of\ gas$$

COMBUSTION OF FUEL

Combustion is the chemical reaction between a fuel and an oxidant, resulting in the release of heat and light.

Complete Combustion:

$$Fuel + O_2 \rightarrow CO_2 + H_2O + Heat$$

Incomplete Combustion:

Occurs due to insufficient air, resulting in CO and soot.

Proper air-fuel ratio is essential for efficient combustion. Gaseous fuels ensure better control of this ratio due to their mixability.

DULONG'S FORMULA FOR CALCULATING CALORIFIC VALUE

Dulong's formula estimates the GCV based on fuel's elemental composition:

$$GCV\ (kcal/kg) = (1/100) \times [8080 \times C + 34500 \times (H - O/8) + 2240 \times S]$$

Where:

- C = % of Carbon
- H = % of Hydrogen
- O = % of Oxygen
- S = % of Sulphur

The formula helps in determining the theoretical calorific value of gaseous fuels when ultimate analysis is known.