Applied Chemistry

Fuels and Combustion

1. Definition of Fuel and Combustion of Fuel

A fuel is defined as a combustible substance which, on burning (combustion) in air or oxygen, produces a large amount of heat energy that can be used economically for domestic, industrial, and other practical purposes, such as heating, generating power, or providing energy for transportation.

Combustion is defined as a rapid chemical reaction between a substance (the fuel) and oxygen, accompanied by the evolution of heat and, usually, light. During combustion, the combustible elements present in the fuel, mainly carbon and hydrogen, combine with oxygen to form carbon dioxide and water, releasing the chemical energy stored in the fuel as heat.

A good fuel should ideally possess characteristics such as a high calorific value, moderate ignition temperature, low moisture and ash content, ease of storage and transport, and combustion products that are not excessively harmful to health or the environment.

2. Classification of Fuels

Fuels can be classified in several ways, most commonly on the basis of their physical state or their occurrence, as summarised below:

Basis of Classification	Types	Examples
Physical State	Solid, Liquid, Gaseous	Coal (solid); Petrol, Diesel (liquid); LPG, CNG (gaseous)
Occurrence	Primary (Natural) Fuel, Secondary (Derived) Fuel	Coal, petroleum, natural gas (primary); Coke, petrol, diesel, LPG, coal gas (secondary, obtained by processing primary fuels)

3. Calorific Values — HCV and LCV

The calorific value of a fuel is defined as the total amount of heat liberated when a unit mass (or unit volume, for a gaseous fuel) of the fuel is completely burnt in oxygen. Calorific value is generally expressed in units such as kilocalories per kilogram (kcal/kg) or kilojoules per kilogram (kJ/kg) for solid and liquid fuels, and kilocalories per cubic metre (kcal/m^3) for gaseous fuels.

Since most fuels contain hydrogen, which combines with oxygen during combustion to form water, the calorific value of a fuel is reported in two forms, depending on whether this water is assumed to remain as vapour or to condense to liquid:

- Higher Calorific Value (HCV) or Gross Calorific Value (GCV): The total heat liberated when a unit mass of fuel is completely burnt, and the water vapour produced during combustion is assumed to condense completely into liquid water, thereby releasing its latent heat of condensation as additional heat.
- Lower Calorific Value (LCV) or Net Calorific Value (NCV): The net heat liberated when a unit mass of fuel is completely burnt, and the water vapour produced during combustion is assumed to escape as vapour, without condensing, so that its latent heat is not recovered as usable heat.

Since the latent heat associated with the condensation of water vapour is not usually recovered in practical combustion equipment (such as boilers and engines), the LCV is generally more representative of the heat actually available for practical use, and is related to the HCV by the approximate relation:

- LCV = HCV − (Latent heat of water vapour × mass of water vapour formed per unit mass of fuel)

3.1 Calculation of HCV and LCV Using Dulong's Formula

Dulong's formula is an empirical formula used to estimate the higher calorific value (HCV) of a solid or liquid fuel from the percentage composition of its combustible elements, as determined by ultimate analysis. Dulong's formula is expressed as:

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

where C, H, O, and S represent the percentage by mass of carbon, hydrogen, oxygen, and sulphur present in the fuel, respectively. The term $(H - O/8)$ accounts for the fact that any oxygen already present within the fuel is assumed to be already combined with a corresponding proportion of the fuel's hydrogen (as if pre-combined in the form of water), so that only the remaining, uncombined hydrogen is available to contribute fully to combustion heat.

Once the HCV has been calculated using Dulong's formula, the corresponding LCV can be obtained using the relation:

- $LCV = HCV - 0.09 \times H \times 587$ kcal/kg (approximately, where H is the percentage of hydrogen in the fuel, and 587 kcal/kg is the latent heat of water vapour, with the factor 0.09 accounting for the mass of water formed per unit mass of hydrogen burnt)

Worked Example:

A sample of coal contains 82% carbon, 5% hydrogen, 8% oxygen, 1% sulphur, and the remainder non-combustible matter. Calculate its higher calorific value (HCV) using Dulong's formula.

Solution: HCV = (1/100) × [8080 × 82 + 34500 × (5 − 8/8) + 2240 × 1] = (1/100) × [662560 + 34500 × (5 − 1) + 2240] = (1/100) × [662560 + 138000 + 2240] = (1/100) × 802800 = 8028 kcal/kg. The higher calorific value of the coal sample is therefore approximately 8028 kcal/kg.

4. Proximate Analysis and Ultimate Analysis of Coal (Solid Fuel)

4.1 Proximate Analysis

Proximate analysis is a relatively simple analytical procedure used to determine the percentage composition of coal in terms of four broad parameters, without identifying the individual chemical elements present. It is widely used for the routine assessment and grading of coal quality, since it is quicker and simpler to carry out than ultimate analysis.

Parameter	What It Represents
Moisture Content	The amount of water present in coal; higher moisture reduces the effective calorific value and heating efficiency of the coal.
Volatile Matter	The gaseous and liquid substances driven off when coal is heated in the absence of air; higher volatile matter generally makes coal easier to ignite but may reduce fixed carbon content.
Ash Content	The incombustible mineral residue left behind after complete combustion of coal; higher ash content reduces the effective calorific value and increases disposal problems.
Fixed Carbon	The solid combustible carbon remaining after moisture, volatile matter, and ash have been accounted for; higher fixed carbon generally indicates a higher-quality fuel with a greater calorific value.

4.2 Ultimate Analysis

Ultimate analysis is a more detailed analytical procedure used to determine the percentage composition of coal in terms of its constituent chemical elements, providing a more precise chemical picture of the fuel than proximate analysis.

Element Determined	Significance
Carbon and Hydrogen	The main combustible elements in coal; higher carbon and hydrogen content generally indicates a higher calorific value.

Nitrogen	An undesirable, non-combustible constituent; contributes nothing to heat production and may form oxides of nitrogen during combustion.
Sulphur	An undesirable constituent; although it contributes slightly to the calorific value, its combustion produces sulphur dioxide, a pollutant, and can also cause corrosion of equipment.
Oxygen	Generally reduces the effective calorific value of the coal, since oxygen already present in the fuel does not need to combine with external oxygen during combustion.
Ash (by difference)	The mineral residue remaining, determined by difference after accounting for the other elements, corresponding closely to the ash content found in proximate analysis.

Together, proximate and ultimate analysis provide essential information for assessing the quality, calorific value, and suitability of a given coal sample for a particular industrial or domestic application.

5. Petrol and Diesel — Fuel Rating (Octane and Cetane Numbers)

Since petrol and diesel are used in different types of internal combustion engines, operating on different combustion principles, their quality is assessed and rated using two distinct numerical scales, summarised below:

Fuel	Rating Used	Significance
Petrol (used in spark-ignition/SI engines)	Octane number	A measure of a petrol's resistance to knocking (premature, uncontrolled ignition) in a spark-ignition engine; a higher octane number indicates greater resistance to knocking and better performance under compression.
Diesel (used in compression-ignition/CI engines)	Cetane number	A measure of the ease with which diesel fuel ignites under compression in a compression-ignition engine; a higher cetane number indicates shorter ignition delay and smoother, more efficient combustion.

A higher octane number in petrol allows an engine to be operated at a higher compression ratio without the fuel prematurely self-igniting (knocking), improving engine efficiency and performance. In contrast, a higher cetane number in diesel is desirable because it allows the fuel to ignite readily and promptly under compression, without a significant ignition delay, resulting in smoother, more efficient, and more complete combustion within the engine.

6. Chemical Composition, Calorific Values and Applications of Gaseous Fuels

Gaseous fuels are widely used for domestic, industrial, and automotive purposes, owing to their ease of transport through pipelines, clean combustion, and convenient control of the combustion process. The chemical composition, approximate calorific value, and typical applications of some commonly used gaseous fuels are summarised below:

Gaseous Fuel	Chemical Composition (Main Constituents)	Approximate Calorific Value	Applications
LPG (Liquefied Petroleum Gas)	Mainly propane (C_3H_8) and butane (C_4H_{10})	High, approximately 45–50 MJ/kg	Domestic and commercial cooking fuel, industrial heating, and as an automotive fuel (autogas)
CNG (Compressed Natural Gas)	Mainly methane (CH_4), compressed to high pressure	High, approximately 50–55 MJ/kg	Automotive fuel for vehicles, and industrial and domestic fuel in areas with piped natural gas supply
Water Gas	Mixture of carbon monoxide (CO) and hydrogen (H_2), produced by passing steam over red-hot coke	Moderate, approximately 11–12 MJ/m³	Industrial heating, and as a raw material (syngas) for chemical synthesis, such as the manufacture of methanol
Coal Gas	Mixture of hydrogen, methane, carbon monoxide, and other gases, obtained by the destructive distillation of coal	Moderate, approximately 18–20 MJ/m³	Industrial and domestic heating and lighting (historically), and as a fuel in areas with piped town gas supply
Producer Gas	Mixture of carbon monoxide and nitrogen (with some hydrogen), produced by passing a limited supply of air over red-hot coke	Low, approximately 5–6 MJ/m³	Industrial heating in furnaces and kilns, valued for being an inexpensive, low-cost fuel gas
Biogas	Mainly methane (CH_4, about 55–65%) and carbon dioxide (CO_2), produced by the anaerobic digestion (bacterial decomposition) of organic waste and animal dung	Moderate, approximately 20–25 MJ/m³	Rural domestic cooking and lighting fuel, and small-scale electricity generation, produced from renewable organic waste

Among these, LPG and CNG, being derived mainly from petroleum and natural gas respectively, have relatively high calorific values and are widely used as clean-burning fuels for cooking and transportation, while producer gas and water gas, being industrially generated fuel gases with lower calorific values, find their main use as economical fuels for large-scale industrial heating applications. Biogas, being generated from organic waste through a renewable, natural biological process, is of particular importance as a sustainable, rural energy source.

7. Multiple Choice Questions (MCQs)

Answer the following questions by selecting the most appropriate option.

1. A fuel is best defined as a substance that:

A) Absorbs heat when burnt

B) Produces a large amount of heat energy on combustion, usable for practical purposes

C) Cannot burn at all

D) Only produces light, not heat

2. Combustion is best described as:

A) A physical change with no heat release

B) A rapid chemical reaction of a substance with oxygen, accompanied by the evolution of heat and usually light

C) The process of dissolving a fuel in water

D) A reaction that always absorbs heat

3. Based on their occurrence, fuels obtained directly from nature without significant processing are called:

A) Secondary fuels

B) Primary (natural) fuels

C) Synthetic fuels

D) Composite fuels

4. The higher calorific value (HCV) of a fuel is measured assuming that the water vapour produced during combustion:

A) Escapes as vapour without condensing

B) Condenses completely, releasing its latent heat

C) Is not formed at all

D) Combines with the fuel again

5. The lower calorific value (LCV) of a fuel is generally:

A) Greater than the HCV

B) Equal to the HCV always

C) Less than the HCV, since the latent heat of water vapour is not recovered

D) Independent of hydrogen content

6. Dulong's formula for calculating the calorific value of a solid or liquid fuel uses the percentage composition of:

A) Carbon, hydrogen, oxygen, and sulphur only

B) Only nitrogen and ash

C) Only moisture content

D) Only carbon content

7. Proximate analysis of coal determines:

A) Only the elemental composition of coal

B) Moisture, volatile matter, ash, and fixed carbon content

C) Only the octane number of coal

D) Only the sulphur content

8. Ultimate analysis of coal determines:

A) Only the moisture content

B) The percentage of elements such as carbon, hydrogen, nitrogen, sulphur, and oxygen present

C) Only the ash content

D) Only the volatile matter

9. A higher fixed carbon content in coal, as determined by proximate analysis, generally indicates:

A) Lower quality and lower calorific value

B) Higher quality and higher calorific value

C) No relation to fuel quality

D) Higher ash content only

10. The octane number of petrol is a measure of its:

A) Resistance to knocking in a spark-ignition engine

B) Ease of ignition under compression in a diesel engine

C) Boiling point

D) Sulphur content

11. The cetane number of diesel is a measure of its:

A) Resistance to knocking in a spark-ignition engine

B) Ease and speed of self-ignition under compression in a diesel engine

C) Viscosity only

D) Colour

12. LPG (Liquefied Petroleum Gas) mainly consists of:

A) Methane and ethane

B) Propane and butane

C) Hydrogen and nitrogen

D) Carbon monoxide and hydrogen

13. CNG (Compressed Natural Gas) mainly consists of:

A) Methane, compressed to high pressure
B) Propane and butane
C) Carbon monoxide and nitrogen
D) Pure hydrogen

14. Producer gas is a mixture mainly of:

A) Methane and carbon dioxide
B) Carbon monoxide and nitrogen
C) Propane and butane
D) Hydrogen and oxygen

15. Biogas, produced by the anaerobic digestion of organic waste, mainly consists of:

A) Methane and carbon dioxide
B) Propane and butane only
C) Carbon monoxide and hydrogen only
D) Pure nitrogen

Answer Key

1. B) Produces a large amount of heat energy on combustion, usable for practical purposes | 2. B) A rapid chemical reaction of a substance with oxygen, accompanied by the evolution of heat and usually light | 3. B) Primary (natural) fuels | 4. B) Condenses completely, releasing its latent heat | 5. C) Less than the HCV, since the latent heat of water vapour is not recovered | 6. A) Carbon, hydrogen, oxygen, and sulphur only | 7. B) Moisture, volatile matter, ash, and fixed carbon content | 8. B) The percentage of elements such as carbon, hydrogen, nitrogen, sulphur, and oxygen present | 9. B) Higher quality and higher calorific value | 10. A) Resistance to knocking in a spark-ignition engine | 11. B) Ease and speed of self-ignition under compression in a diesel engine | 12. B) Propane and butane | 13. A) Methane, compressed to high pressure | 14. B) Carbon monoxide and nitrogen | 15. A) Methane and carbon dioxide

8. Broad / Long Answer and Numerical Questions

1. Define fuel and combustion, and explain the essential requirements of a good fuel.

2. Classify fuels on the basis of their physical state and their occurrence, giving examples of each type.

3. Define higher calorific value (HCV) and lower calorific value (LCV) of a fuel, and explain the difference between them.

4. State Dulong's formula for calculating the calorific value of a solid or liquid fuel, and explain the significance of each term used in it.

5. A sample of coal contains 82% carbon, 5% hydrogen, 8% oxygen, 1% sulphur, and the rest non-combustible matter. Calculate its higher calorific value (HCV) using Dulong's formula: $HCV = [1/100][8080C + 34500(H - O/8) + 2240S]$ kcal/kg.

6. Explain proximate analysis of coal, describing the four parameters determined and their significance in assessing fuel quality.

7. Explain ultimate analysis of coal, describing the elements determined and their significance in assessing fuel quality.

8. Explain the concept of octane number and cetane number as measures of fuel quality for petrol and diesel respectively.

9. Describe the chemical composition, approximate calorific value, and applications of LPG and CNG.

10. Describe the chemical composition, approximate calorific value, and applications of water gas, coal gas, producer gas, and biogas.