MODULE 4: FUELS AND RENEWABLE ENERGY

Fuels: Introduction, definitions of calorific value, lower calorific value, and higher calorific value numerical. Knocking mechanism and octane number, anti-knock additives and biodiesel.

Solar Energy: Introduction, Photovoltaic cells-principle, construction, working and applications of Photovoltaic cell and Perovskite solar cell. Advantages and disadvantages of PV cells.

Green fuel: Introduction, Hydrogen-production (photo catalytic water splitting) and applications, Compressed Natural Gas (CNG), Synthetic Natural Gas (SNG).

FUELS

Chemical fuels: Chemical fuel is a combustible substance containing carbon as the main constituent, which on complete burning produces a large amount of heat which can be used for domestic & industrial purposes".

Calorific Value: It is defined as "the amount of heat liberated when unit weight (or unit volume in the case of a gaseous fuel) of a fuel is completely burnt in excess of air or oxygen".

Gross (Higher) Calorific Value (GCV): It is defined as "the amount of heat released when unit quantity (unit mass of a solid or liquid fuel or unit volume of a gaseous fuel) of a fuel is burnt completely in air and the combustion products are cooled to room temperature".

$$GCV = \frac{(W_1 + W_2) \times S \times \Delta t}{m}$$

W_1 is mass of water taken in calorimeter; W_2 is water equivalent in calorimeter; S is specific heat of water; ⊗t is the raise in the temperature; and m is the mass of the fuel.

Carbon and hydrogen present in fuels are converted into carbon dioxide and steam respectively on combination. On cooling the combination products, steam gets condensed to water and liberate its latent heat. The measured gross calorific value includes the latent heat of steam. Therefore, it is always higher than the net calorific value.

Net (Lower) Calorific value (NCV): It is defined as "the amount of heat liberated when unit mass of a solid or liquid fuels or unit volume of a gaseous fuel is burnt in excess of oxygen & the products formed are allowed to escape without cooling".

NCV = GCV – Latent heat of steam formed (by 1kg of solid or 1m^3 of gaseous fuel)

NC**V =** GCV – (mass of hydrogen x 9 x latent heat of steam)

Because one part of hydrogen produces 9 parts of H_2O. The latent heat of steam is 2456 kJ/kg or 4.2 x 587 kJ/kg.

SI unit of calorific value: The calorific value is normally expressed in calorie per gram (cal/g) in (g) units. It is also expressed in joules per kg (J/ kg) for solid fuels and Joules per cubic meter (J/ m^3) for gaseous fuels in SI units at one atmospheric pressure.

Numerical on GCV and NCV:

1) 0.75 g of coal sample (carbon 90%, H_2 5% and ash 5%) was subjected combustion in Bomb calorimeter. Mass water taken in the calorimeter was 2.5 kg and the water equivalent of calorimeter is 0.65 Kg. The rise in temperature was found to be 3.2 °C. Calculate gross and net calorific values of the sample. Latent heat of Steam = 587 Cal/g and specific heat of water = 4.187KJ/Kg/°C.

Ans:

$$GCV = \frac{(W_1 + W_2) \times S \times \Delta t}{m}$$

$$GCV = \frac{(2.5 + 0.65) \times 4.187 \times 3.2}{0.75 \times 10^{-3}}$$

$$GCV = \frac{42.20}{0.75 \times 10^{-3}}$$

$$GCV = 56266.67 kJ / kg$$

$$NCV = GCV - (0.09 \times H\% \times Latent\_heat\_of\_steam)$$

$$NCV = 56266.67 - (0.09 \times 5 \times 587 \times 4.187)$$

$$NCV = 56266.67 - (1105.60)$$

$$NCV = 55161.07 kJ / kg$$

2) 0.85 g of coal sample (carbon 90%, H_2 5% and ash 5%) was subjected to combustion in a Bomb calorimeter. Mass water taken in the calorimeter was 2000 g and the water equivalent of calorimeter was 600 g. The rise in temperature was found to be 3.5 °C. Calculate gross and net calorific values of the sample. Latent heat of steam = 2457KJ/Kg.

Ans:

$$GCV = \frac{(W_1 + W_2) \times S \times \Delta t}{m}$$

$$GCV = \frac{(2000+600)\ 10^{-3} \times 3.5 \times 2457}{0.85 \times 10^{-3}}$$

$$GCV = \frac{38101.70}{0.85}$$

GCV = 44825.52 KJ/Kg

$$NCV = GCV - (0.09 \times H\% \times Latent\_heat\_of\_steam)$$

$$NCV = 44825.52 - (0.09 \times 5 \times 2457)$$

$$NCV = 44825.52 - (1105.65)$$

NCV= 43719 KJ/Kg

Knocking:

In internal combination engine a mixture of gasoline and air is used as fuel. After the initiation of the combustion reaction by a spark in the cylinder, the flame should spread rapidly and smoothly through the gaseous mixture, there by the expanding gas drives the piston down the cylinder.

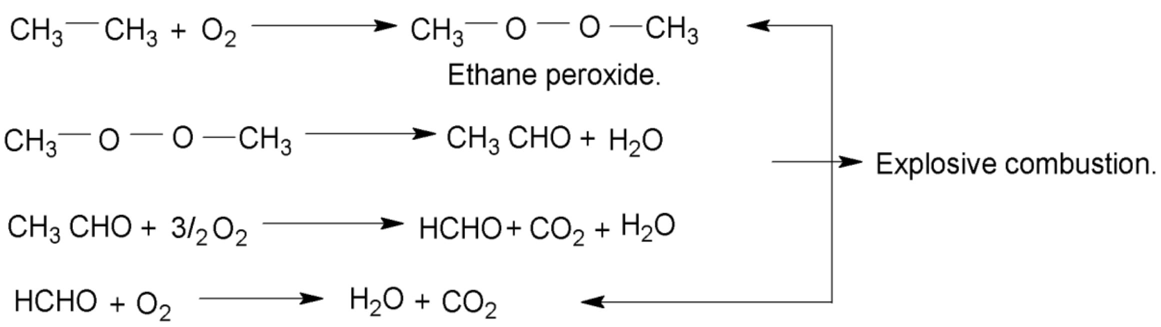
Definition: "Knocking is the explosive combustion of petrol-air mixture beyond a certain compression ratio, which produces shock waves in IC engine, which hit the walls of the cylinder and piston producing a rattling sound." This is due to the presence of certain constituents in petrol.

The efficiency of power production in spark ignited IC engines is related to the compression ratio (CR). The compression ratio is the ratio of the cylinder volume (V_1) at the bottom of its stroke (suction), to the cylinder volume (V_2) when the piston is at the top of its stroke (Compression). The efficiency of an internal combustion engine increases with the increase in compression ratio. This ratio is always greater than one. (Since $V_1 > V_2$).The efficiency of an internal combustion engine with increase in compression ratio. However, a successful high compression ratio is dependent on the nature of constituents present in the gasoline used.

$$\text{Compression Ratio} = \frac{V_1}{V_2}$$

Mechanism of Knocking*:* Under normal conditions there is a slow oxidation of the fuel during which oxygen combines with a few hydrocarbons molecules and activates them by forming peroxides. The activated molecules combine with other hydrocarbon molecules and a chain reaction is set up resulting in smooth combustion. Knocking occurs if the chain reaction proceeds at too fast rate. The unstable peroxides formed decompose explosively giving rise to pressure waves, which knock against the engine walls. The normal and explosive combustion of a fuel (e.g., C_2H_6) may be represented as follows.

$$C_2H_{6\,(g)} + \frac{7}{2}O_{2\,(g)} \rightarrow 2CO_{2\,(g)} + 3H_2O_{(g)}.\quad \text{(Normal combustion)}$$



Adverse effects of Knocking:

1. It produces undesirable rattling noise.
2. It increases the fuel consumption.
3. It results in decreased power output.
4. It causes mechanical damage due to overheating to engine parts such as Spark plug, piston and engine walls & reduces the life of the engine.
5. The driving becomes rather unpleasant.

<u>Octane number:</u>

The knocking characteristic of a petrol sample is described by its Octane number (or anti-knock value).

- Higher the octane number lower is the tendency to knock and better is the quality of petrol.
- Isooctane (2, 2,4-trimethyl pentane) has the least knocking tendency, and its Octane number is arbitrarily fixed as 100.
- n-heptane, a straight chain alkane, has the highest tendency to knock and is assigned an Octane number zero. In general, straight chain hydrocarbons have low octane numbers and those with branched chains have high values.
- Greater the percentage of isooctane better is the efficiency of the fuel. A knocking tendency is related to the chemical structure of the fuels. The decreasing tendency of the fuels to knocking is as follows.

  Straight chain hydrocarbons > Branched chain alkanes > Cycloalkanes > alkenes> aromatics.

The petrol whose octane number is to be determined is compared with reference mixtures of isooctane and n-heptane.

Definition: "The Octane number of a petrol sample is "the percentage of isooctane present in a standard mixture of iso-octane and heptane blend, which has the same knowing characteristic (compression ratio) as the petrol sample under test"

Eg: The octane number of a petrol sample is found to be equivalent to that of a mixture containing 80% by volume of iso-octane and 20% of n-heptane, then the octane number of the petrol sample is 80.

The octane number of petrol is determined with the help of a special single cylinder engine where the compression ratio can be varied for testing the octane value. Automobile petrol's have octane numbers ranging from 76 to 95. Aviation petrol's have much higher-octane values.

Alkenes, cyclo-alkanes, and aromatic compounds have much higher-octane numbers than alkanes containing the same number of carbon atoms.

Anti-knock additives:

Anti-knock value is the measure of resistance to knocking. Anti-knock agent is a gasoline additive used to reduce knocking and increase the fuel's octane rating by raising the temperature and pressure at which auto-ignition occurs. Anti-knock agents are-
Definition: "The substances added to motor or aviation gasoline for controlling and containing the knocking in IC engines are called anti-knowing agents."

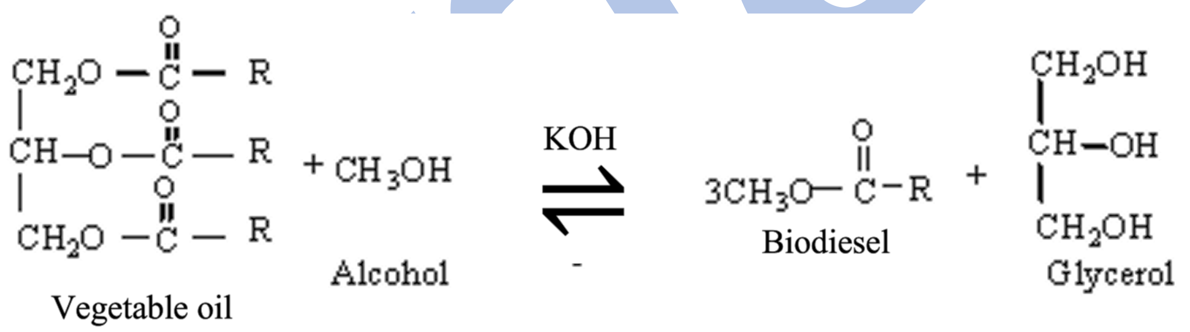
The common commercial anti-knowing agents used are-

(i) Tetraethyl lead (TEL) $Pb(C_2H_5)_4$
(ii) Tetra methyl lead (TME) $Pb(CH_3)_4$
(iii) Mixed methyl ethyl lead.
(iv) Alcohol
(v) Tricarbonyl
(vi) Ferrocene
(vii) Iron pentacarbonyl
(viii) Toluene
(ix) Isooctane

The cheap and more effective in increasing octane rating of fuels is TEL. About 0.5ml of TEL is added per liter of automobile petrol & 1.5ml of TEL per liter is added in aviation fuels. TEL is always used along with ethyl fluid which contains 63% 26% dibromoethane & 9% dichloro ethane. During the combustion of petrol (or gasoline), TEL forms lead and lead oxide may get deposited on engine parts and cause mechanical damage. The function of these halogen compounds is to convert the less volatile Pb and PbO into more volatile $PbBr_2$ or $PbCl_2$, which escapes into air along with, exhaust gases. Petrol containing TEL is called "leaded petrol".

Biodiesel:

Biodiesel is a mixture of monoalkyl esters of long chain fatty acids. It is obtained from the renewable sources such as vegetable oils like **soyabean oil, palm oil, peanut oil, sunflower oil, jathropa oil** and which are essentially triglycerides. Biodiesel is commonly produced by the trans-esterification of the vegetable oil with virtually any alcohol in presence of catalysts like KOH or H_2SO_4. The most commonly used alcohol is methanol to produce methyl esters (commonly referred to as Fatty Acid Methyl Ester-FAME) as it is the cheapest alcohol available. Ethanol can be used to produce an ethyl ester (commonly referred to as Fatty Acid Ethyl Ester FAEE). The products are allowed to settle and from the bottom glycerol layer is drawn off. The upper layer of methyl ester is washed with water and purified further to remove excess of alcohol which finally gives biodiesel.



Cooking oil or animal fat can be converted into biodiesel. Since triglycerides undergo hydrolysis with water forming mono, diglycerides and free fatty acids , the direct esterification in the presence of alkali results in soap formation. It is avoided by first esterifying the free fatty acid in the presence of an acid catalyst followed by base catalyzed trans esterification to produce biodiesel.

Advantages:

(a) It is biodegradable, nontoxic, and free from Sulphur compounds.

(b) Nonedible oils can be used.

(c) Ecofriendly products are formed.

SOLAR ENERGY

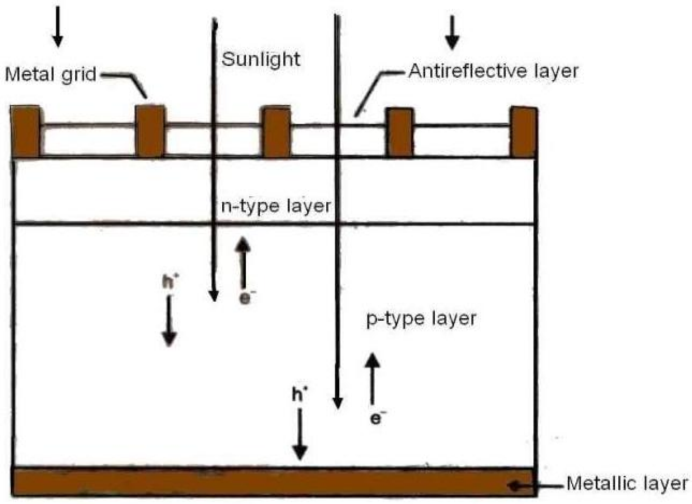
Solar energy is the energy which has the greatest potential of acting as a alternate source of energy because of the reason that the reserves of fossil fuels are very limited and are depleted very fast.

Photovoltaic Cells: (Photo = sunlight, voltaic = electricity)

*Definition: "*Photovoltaic cells or solar cells as they are often referred to are semiconductor devices that convert sunlight into direct-current electricity on illumination." Present day solar cells could convert only 25% solar energy into electricity.

Principle: PV cells works based on the principle of photoelectric effect, i.e., ejection of electron from the surface of metal or semiconductor when photons of sufficient energy fall on it. Energy of photon as evident from Planck quantum equation, $E = hc/\lambda$, **w**here, h is Planck's constant, c is velocity of light and λ is the wavelength of the radiation.

Construction and working: A typical silicon photovoltaic cell is composed of a thin wafer consisting of an ultra-thin layer of Phosphorous doped (n-type) silicon on top and Boron doped (p-type) silicon at the bottom. Hence a p-n junction is formed between the two. A metallic grid forms one of the electrical contacts of the diode and allows light to fall on the semiconductor between the grid lines. An antireflective layer between the grid lines increases the amount of light transmitted to the semiconductor. The electrical contact is formed by a metallic layer on the back of the solar cell.



Solar cell structure

When light radiation falls on the p-n junction diode, electron-hole pairs are generated by the absorption of the radiation. The electrons are drifted to and collected at the n-type end and the holes are drifted to and collected at the p-type end. When these two ends are electrically connected through a conductor, there is a flow of current between the two ends through the external circuit. Thus, photoelectric current is produced and available for use. Solar energy is the energy which has a greatest potential of acting as alternate source of energy because of the reason that the reserves of fossil fuels are very limited and are depleted very fast.

Advantages of PV cells:

(i) Energy source is vast and essentially infinite.
(ii) Solar cells need no recharging like batteries and produce electrical energy as long as sunlight is available.
(iii) Solar cells have no movable parts and hence do not suffer from wear and tear.
(iv) The materials used in PV cells do not corrode and serve for long duration.
(v) They operate at ambient temperature.
(vi) PV cells involve no emissions, no combustion, or radioactive residues for disposal.
(vii) PV cells are environment friendly, do not contribute to global climate change or pollution.
(viii) Low operating costs and quick installation.
(ix) High public acceptance and safety record.

Disadvantages of PV cells:

(i) Poor reliability of auxiliary elements including storage
(ii) The installation cost is high.
(iii) PV cells generate only DC current and must be converted into AC power when used in distribution grids.
(iv) Sun light is diffuse source, i.e , it is relatively low-density energy.
(v) Power generation can be done during daytime.

Applications:

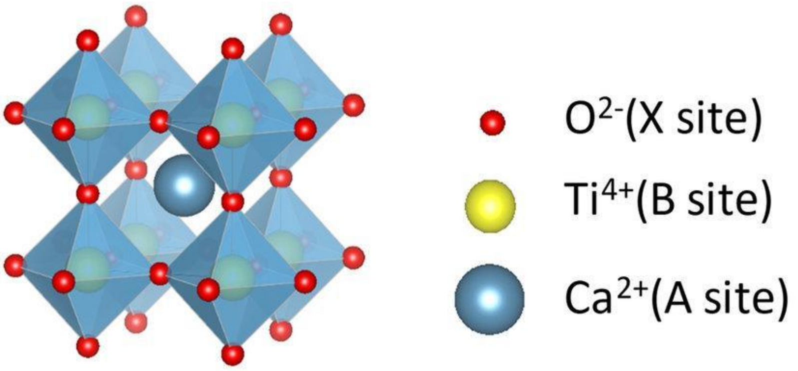
- Useful in remote and isolated locations.
- Streetlight in rural areas.
- Operating water pumps for domestic and agricultural purpose.
- Use in the field of water treatment & pumping.
- Operating radio and TV sets, scientific calculators.
- Lighthouses and offshore drilling rig operations.
- Use in the field of satellites.

Perovskite solar cells (PSV):

Perovskite solar cell (PSC) is a type of solar cell that includes a perovskite-structured compound, most commonly a hybrid organic–inorganic lead or tin halide-based material as the light-harvesting active layer. Perovskite solar cells (PSCs) are relatively a new technology.

Perovskite materials, such as methylammonium lead halides and all-inorganic cesium lead halide, are cheap to produce and simple to manufacture.

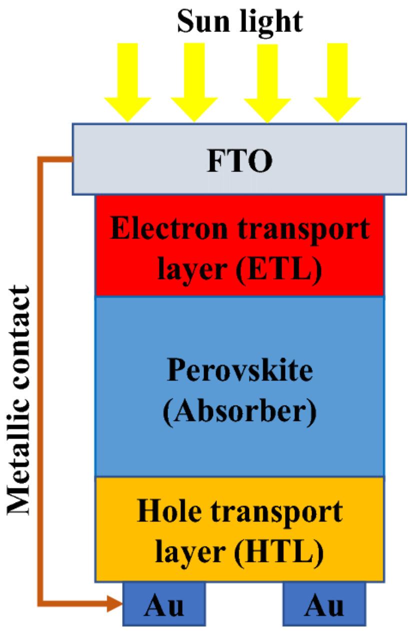
Perovskites are a yellow, brown, or black mineral of calcium titanium oxide $CaTiO_3$ named after the Russian mineralogist Lev Perovski. In practice all crystals having structures of the form AMX_3 (where A and B are cations with A larger than that of B and X is the anion usually oxides or halogens) are classified as perovskite materials.



Structure of $CaTiO_3$ perovskite

Working principle: The working principle of perovskite solar cells: after sunlight irradiates the light absorbing layer (perovskite layer), photons with energy greater than the forbidden band width are absorbed, the energy of the photon excites electrons that were originally bound around the nucleus, producing excitons (electron-hole pairs). Due to the small exciton binding energy of perovskite materials, they can be separated into free carriers (electrons and holes) at room temperature. After the excitons are separated into electrons and holes, the holes enter the hole transport material (HTM) from the perovskite material, electrons enter the electron transport material (ETM) from the perovskite material and flow to the cathode and anode of the battery, respectively.

Construction: The PSC structure is generally composed of five parts from top to bottom: photoanode (FTO/ITO conductive glass), electron transport layer (ETL), perovskite photoactive layer, hole transport layer (HTL) and metal back electrodes (Au, Ag , Al). PSC is a thin-film battery, which is mainly deposited on glass at present. At the same time, different degrees of transparency can be achieved by controlling the thickness and material of each layer of materials, and of course the efficiency will also be reduced.



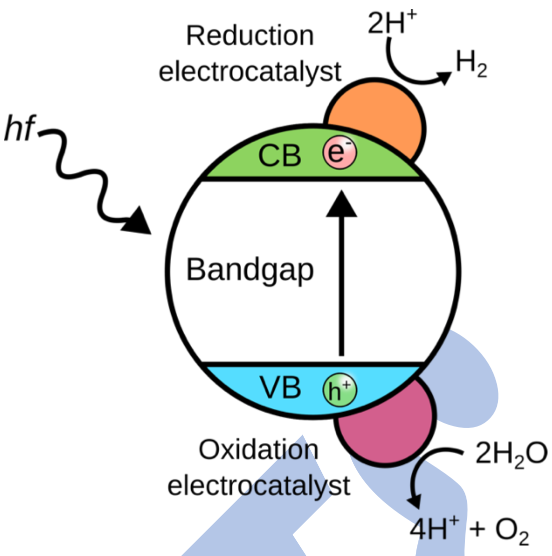
GREEN FUEL

These green fuels are derived from the elements like green hydrocarbons and are generally produced from sources such as biomass. However, the production process relates to several processes such as biological and as well as thermochemical. Several examples are there such as biofuels and fuels of hydrogen. The examples of biofuels cater to several vegetable oils such as methanol, ethanol that are derived from clean energy, biodiesel and carbon dioxide or biomass. Hydrogen energy is mainly derived from renewable energy resources. Unlike fossil fuels, when hydrogen is burned, it generates only water as a byproduct, meaning no harmful greenhouse gas emissions.

<u>Hydrogen-production (photo catalytic water splitting) and applications:</u>

Photocatalytic water splitting is a process that uses photocatalysis for the dissociation of water (H_2O) into hydrogen (H_2) and oxygen (O_2).

Principle: Semiconductor materials are used as photocatalysts for the light-induced redox reaction. Semiconductors are characterized by valence band (VB) and conduction band (CB). For excitation of charge carrier, when a photon (hv) having energy similar to or higher than the band gap (E_g) of semiconductor falls on the semiconductor, electron migrates from the VB to the conduction band, leaving holes behind. In this excited state, either electron of CB or holes in the VB may recombine to dissipate the energy in the form of heat. A photon with an energy greater than 1.23 eV is needed to generate an electron–hole pairs, which react with water on the surface of the photocatalyst. The photocatalyst must have a bandgap large enough to split water.



Construction & Working*:* Titanium dioxide is the common catalyst used for photocatalytic hydrogen evolution. Dissociation of water is not a spontaneous process. The minimum energy required per electron will be 1.23 eV. The dissociation of water comprises two half-reactions, namely, oxidation and reduction of water to oxygen and hydrogen, respectively. The following equations refer to the dissociation of water into oxygen and hydrogen in alkaline media. The overall photocatalytic dissociation of water consists of mainly three steps:

Step 1: electron–hole pair's generation by using the absorption of a photon, $TiO_2 + h\nu \rightarrow 2h^+ + 2e^-$

Step 2: electron–hole separation and migration of electrons to the conduction band

Step 3: reactions between surface species and electron.

Oxidation: $H_2O + 2h^+ \rightarrow 2H^+ + \frac{1}{2} O_2$

Reduction: $2H^+ + 2e^- \rightarrow H_2$

Overall reaction: $H_2O + 1.23\ eV \rightarrow H_2 + \frac{1}{2} O_2$

The first step is photon-physical processes, the second step is the migration of charge carriers, and the third step is the chemical process. Moreover, surface, and bulk recombination of electron–hole may also occur.

Compressed Natural Gas (CNG):

When the natural gas is compressed, it is called compressed natural gas (CNG). It is mainly derived from natural gas. CNG is made by compressing natural gas, which mainly composed of methane, to less than 1% of the volume it occupies at standard atmospheric pressure. It is stored and distributed in hard containers (tank) of a vehicle as compressed natural gas at 200-248 bar(3000 or 3600 psi) pressure usually in cylindrical or spherical shapes.

Constituents	Percentage
Methane	88.5
Ethane	5.5
Propane	3.7
Butane	1.8
Pentane	0.5

Properties of CNG:

(i) CNG is the cheapest, cleanest, and least environmentally impacting alternative fuel.

(ii) Vehicles powered by CNG produce less carbon monoxide and hydrocarbon emission.

(iii) It is less expensive than petrol and diesel.

(iv) The ignition temperature of CNG is about 550 °C.

(v) CNG required more air for ignition.

Advantages of CNG:

(i) CNG produces less pollutants than LPG.

(ii) CNG is cheaper and cleaner than LPG.

(iii) The octane rating of CNG is high, hence the thermal efficiency is more.

(iv) It doesn't evolve Sulphur and nitrogen gas.

(v) It mixes very easily with air than the other gaseous fuels.

(vi) Noise level is much less than diesel.

(vii) CNG vehicle limit 40% less of nitrogen oxide, 90% less of hydrocarbons and 25% less of CO_2.

Applications of CNG:

(i) CNG is a fossil fuel substituent for gasoline (petrol), diesel, or propane/LPG.

(ii) CNG may also be mixed with biogas, produced from landfills or wastewater, which doesn't increase the concentration of carbon in the atmosphere.

(iii) Cars and locomotives.

Synthetic Natural Gas (SNG):

Synthetic natural gas is synthesized by anerobic digestion or methanization of gasified wood. It is a blend of liquified petroleum gas (LPG) and diluent. Diluents include biogas, digester gas, landfill gas, nitrogen, and compressed gas. Since compressed gases are mostly used, it is a direct replacement for natural gas.

Advantages of SNG:

(i) provide convenient, consistent, and high-quality fuel with combustion characteristic similar to natural gas.
(ii) SNG can be used as an alternative in regions where the availability of the natural gas is insufficient or unavailable.
(iii) SNG baseload system provides continuous and uninterrupted fuel supply to meet full load energy demand.
(iv) SNG will provide an ideal standby fuel in the event Natural Gas source is unavailable due to curtailment, maintenance shutdown or catastrophic failure or interruption of Natural Gas supply.
(v) Avoiding investment in dual fuel burners
(vi) Optimization of production capacity
(vii) Low switch over cost and lower risk in
(viii) Save in insurance premium by using SNG as backup.

Applications of SNG:

(i) Large and medium scale industries
(ii) Critical industrial applications like float glass, fiber glass, food, and ceramics
(iii) Utility companies
(iv) Hotels and commercial complexes
(v) District cooling/heating units