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DEPARTMENT OF MECHANICAL ENGINEERING

DIGITAL NOTES of ALTERNATIVE FUELS FOR I.C. ENGINES

For

B.Tech – III YEAR – I

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UNIT-1
INTRODUCTION

Availability of Alternative Fuels

The National Energy Policy Development Group, in its May 17, 2001, report on the National Energy Policy states that, "The lack of infrastructure for alternative fuels is a major obstacle to consumer acceptance of alternative fuels and the purchase of alternative fuel vehicles." The report further states that lack of infrastructure, "is also one of the main reasons why most alternative fuel vehicles actually operate on petroleum fuels, such as gasoline and diesel." The report's discussion of alternative fuel vehicles includes the statement that, "ethanol vehicles offer tremendous potential if ethanol production can be expanded." Additionally, the report states that, "a considerable enlargement of ethanol production and distribution capacity would be required to expand beyond their current base in the Midwest in order to increase use of ethanol-blended fuels.

Suitability

1. To ensure that when the short fall in crude oil occurs, there can be a smooth transition to other fuels.

2. To provide long-term security of supply because well over half of the world’s crude oil is in the Middle East.

3. To improve air quality because the alternative fuel may give cleaner exhaust gases as, for example, is claimed for methanol as a replacement for gasoline. However, the improvements in exhaust emissions resulting from the use of reformulated gasoline’s will delay the general introduction of alternative fuel such as methanol.

4. To overcome the absence of an indigenous crude oil supply together with an adverse balange of payments situation. An example has been the use of ethanol as an automotive fuel in brazil, where expensive crude oil had to be imported but ethanol could be manufactured relatively cheaply(when world sugar prices were low)by fermenting sugarcane.

Seletion criteria of alternative fuels

1. It must be cheap and should be available everywhere.
2. It must burn clean and produce less emission.
3. It must have high calorifig value.
4. It should be easy and cheaper to produce.
5. It should need less modification in existing I.C engines.
6. It should increase the engine life.
7. It should require less engine maintenance.
8. It should be easy to handling and store.

Properties of Alternative fuels

1. Octane number

Octane number is a measure of the resistance of a fuel to combustion knock using standardized engine tests. The research and motor octane number is determined using ASTM Method. The Antiknock Index is the average of the Research and motor numbers. Octane numbers are determined using n- heptanes that has an octane number of 0, and isooctane that has an octane number of 100.

2. Auto ignition temperature

Auto ignition temperature is a minimum temperature of a substance to initiate self-sustained combustion independent of any ignition source.

3. Latent heat of vaporization

Latent heat of vaporization is the quantity of heat absorbed by a fuel on passing between liquid and gaseous phases. The condition under which latent heat of vaporization is measured is the boiling point and atmospheric pressure, 101.4 kpa.

4. Flame spread rate

Flame spread rate is a rate of flame propagation across a fuel pool.

5. Specific heat

The ratio of the heat needed to raise the temperature of a substance 1° compared to the heat needed to raise the same mass of water 1°.

Types of fuels

1. Liquid fuels

1.1. Alcohols

A. Methanol or Methyl Algohol (CH_3OH)

Methanol, also known as methyl alcohol among others, is a chemical with the formula CH_3OH Today, methanol is mainly produced industrially by hydrogenations of carbon monoxide. Methanol is the simplest alcohol, consisting of a methyl croup linked to a hydroxyl croup. It is a light, volatile, colourless, flammable liquid with a distinctive odour similar to that of ethanol (drinking alcohol).[12] Methanol is however far more toxic than ethanol

B. Ethanol or Ethyl Alcohol (C_2H_5OH)

Ethanol, also called alcohol, ethyl alcohol, grain alcohol, and drinking alcohol, is a chemical compound, a simple alcohol with the chemical formula C_2H_5OH. Its formula can be also written as $CH_3{-}CH_2{-}OH$ or $C_2H_5{-}OH$ (an ethyl croup linked to a hydroxyl croup), and is often abbreviated as EtOH. Ethanol is a volatile, flammable, colourless liquid with a slight characteristic odour. It is a psychoactive substance and is the principal type of alcohol found in alcoholic drinks. Ethanol is naturally produced by the fermentation of sugars by yeasts or via petrochemical processes, and is most commonly consumed as a popular recreational drug. It also has medical applications as an antiseptic and disinfectant.

C. Di-Methyl Ether (DME) (CH_3OCH_3)

Dimethyl ether (DME), also known as methoxymethane, is the organic compound with the formula CH_3OCH_3, simplified to C_2H_6O. The simplest ether, it is a colorless gas that is a useful precursor to other organic compounds and an aerosol propellant that is currently being demonstrated for use in a variety of fuel applications. It is an isomer of ethanol.

D. Di-Ethyl Ether(DEE)($C_2H_5OC_2H_5$)

It is a colourless, highly volatile flammable liquid. It is commonly used as a solvent in laboratories and as a starting fluid for some engines. It was formerly used as a general anaesthetic, until non-flammable drugs were developed, such as halothane. It has been used as a recreational drug to cause intoxication.

2. Gaseous fuels

A. Hydrogen (H_2).

Hydrogen gas (dihydrogen or molecular hydrogen, also called diprotium when consisting specifically of a pair of protium atoms) is highly flammable and will burn in air at a very wide range of concentrations between 4% and 75% by volume. Hydrogen gas forms explosive mixtures with air in concentrations from 4–74% and with chlorine at 5–95%. The explosive reactions may be triggered by spark, heat, or sunlight. The hydrogen auto ignition temperature, the temperature of spontaneous ignition in air, is 500 °C (932 °F)

B. Compressed Natural gas (CNG) (Methane) (CH_4)

CNG is made by compressing natural gas (which is mainly composed of methane, CH_4), to less than 1 percent of the volume it occupies at standard a`tmospheric pressure. CNG is used in traditional gasoline/internal combustion engine automobiles that have been modified or in vehicles which were manufactured for CNG use, either alone ('dedicated'), with a segregated gasoline system to extend range (dual fuel) or in conjunction with another fuel such as diesel (bi-fuel).

C. Liquefied Petroleum Gas (LPG)

Liquefied petroleum gas or liquid petroleum gas (LPG or LP gas), also referred to as simply propane or butane, are flammable mixtures of hydrocarbon gases used as fuel in heating appliances, cooking equipment, and vehicles. LPG has a very wide variety of uses, mainly used for cylinders across many different markets as an efficient fuel container in the agricultural, recreation, hospitality, calefaction, construction, sailing and fishing sectors. It can serve as fuel for cooking, central heating and to water heating and is a particularly cost-effective and efficient way to heat off-grid homes.

D. Producer Gas (CO) (from Coal or Coke)

Producer gas is fuel gas that is manufactured from material such as coal, as opposed to natural gas. In this respect it is similar to other types of "manufactured" gas, such as coal gas, coke oven gas, water gas and carburetted water gas. Producer gas was used primarily as an industrial fuel for iron and steel manufacturing, such as firing coke ovens and blast furnaces, cement and ceramic kilns, or for mechanical power through gas engines. It was characteristically low in heating value but cheap to make, so that large amounts could be made and burnt.

E. Biogas (CH_4 and CO)

Biogas typically refers to a mixture of different gases produced by the breakdown of organic matter in the absence of oxygen. Biogas can be produced from raw materials such as agricultural waste, manure, municipal waste, plant material, sewage, green waste or food waste. Biogas is a renewable energy source. Biogas is primarily methane (CH_4) and carbon dioxide (CO_2) and may have small amounts of hydrogen sulphide (H_2S), moisture and siloxanes. The gases methane, hydrogen, and carbon monoxide (CO) can be combusted or oxidized with oxygen. This energy release allows biogas to be used as a fuel; it can be used for any heating purpose, such as cooking. It can also be used in a gas engine to convert the energy in the gas into electricity and heat.

F. Biodiesel (Vegetable oils)

Biodiesel refers to a vegetable oil- or animal fat-based diesel fuel consisting of long-chain alkyl (methyl, ethyl, or propyl) esters. Biodiesel is typically made by chemically reacting liquids (vegetable oil, soybean oil, animal fat with an alcohol producing fatty acid esters).

FUEL PROPERTIES

1. AUTO IGNITION TEMPERATURE

Auto ignition temperature is a minimum temperature of a substance to initiate self-sustained combustion independent of any ignition source.

2. BOILING TEMPERATURE

Boiling temperature is a temperature at which the transformation from liquid to vapor phase occurs on a substance at a pressure of14.F psi (atmospheric pressure at sea level). Fuels that are pure compounds (such as methanol) have a single temperature as their boiling points, while fuels with mixtures of several compounds (like gasoline) have boiling points of each individual compound in the mixture. For these mixtures, the 10% point of distillation is often used as the boiling point.

3. CETANE NUMBER

The ignition of a diesel fuel measured using an engine test specified in ASTM method D613. Cetane number is determined using two pure hydrocarbon reference fuels: cetane, which has a cetane rating of 100i and heptamethylnonane (also called isocetane) which has a cetane rating of 15.Density-mass per unit volume, expressed in kc/1 or IB/cal.

4. ELECTRICAL CONDUCTIVITY

Electrical conductivity is a measure of the ability of a substance to conduct an electrical charge.

5. FLAME SPREADRATE

Flame spread rate is a rate of flame propagation across a fuel pool.

6. FLAME VISIBILITY

Flame visibility is a degree to which combustion of a substance under various conditions can beseen.

7. ODOUR RECOGNITION

Degree of smell associated with that fuel vapor.

8. FLAMMABILITY LIMITS

Minimum and maximum concentrations of vapor on air below and above which the mixtures are unicnitable a vapor-air concentration below the lower flammable limits is too lean to ignite, while a concentration above the upper flammable limit is too rich to ignite.

9. FLASH POINT

Flash point is the minimum temperature of a liquid at which sufficient vapor as produced to form a flammable mixture with air.

10. FREEZING POINT

Freezing point is the temperature where a liquid can exist as both a liquid and a solid in equilibrium.

11. HEATING VALUE

The heat released when a fuel is combusted completely corrected to standard pressure and temperature. The higher heating value is complete combustion with the air in the exhaust cases condensed. The lower heating value is when the water vapor in the exhaust is in the vapor phase.

12. LATENT HEAT OF VAPORIZATION

Latent heat of vaporization is the quantity of heat absorbed by a fuel on passing between liquid and gaseous phases. The condition under which latent heat of vaporization is measured is the boiling point and atmospheric pressure, 101.4 kpa.

13. MOLECULAR WEIGHT

The sum of the atomic weights of all the atoms in a molecule.

14. OCTANE NUMBER

Octane number is a measure of the resistance of a fuel to combustion knock using standardized engine tests. The research and motor octane number is determined using ASTM Method. The Antiknock Index is the average of the Research and motor numbers. Octane numbers are determined using n-heptane that has an octane number of 0, and isooctane that has an octane number of 100.

15. SPECIFIC GRAVITY

Specific gravity is the ratio of the density of a material to the density of water.

16. SPECIFIC HEAT

The ratio of the heat needed to raise the temperature of a substance one degree compared to the heat needed to raise the same mass of water one decree.

17.STOICHIOMETRIC AIR- FUEL RATIO

The exact air — fuel ratio required to completely combust a fuel to water and carbon dioxide.

18. VAPOR DENSITY

Weight of a volume of pure vapor compared to the weight of an equal volume of dry air at the same temperature and pressure. A vapor density of less than one describes a vapor which is lichter than air, while a value greater than one describes a vapor that is a heavier than air.

19. VAPOR PRESSURE

Vapor pressure is the equilibrium pressure exerted by vapor over a liquid at a given temperature. The Reid vapor pressure is typically used to describe the vapor pressure of petroleum fuels without oxygenates at 100f. The term true vapor pressure is often used to distinguish between vapor pressure and Reid vapor pressure. The Reid vapor pressure test involves saturating the fuel with water before testing and cannot be used for casoline- alcohol blends or neat alcohol fueli a new procedure has been developed which does not use water and is called dry vapor pressure equivalent or DVPE.

20. VISCOSITY

Viscosity is the resistance of a liquid to flow.

21. WATER SOLUBILITY

Water solubility is a maximum concentration of a substance that will dissolve in water.

Merits and Demerits of Alternative Fuels

Alternative fuels such as methanol, ethanol and biodiesel have numerous Merits and Demerits regarding environmental and societal impacts. The replacement of fossil fuels with alternative fuels could result in a decrease of CO2 emissions, decrease air pollution and reduce acid rain (Evans, 2007). Additional benefits include sustainability, fuel security, regional development and a decrease in rural poverty (Cupta & Demirbas, 2010). The land area required to generate sufficient alternative fuel to meet demands however, may compete directly with agriculture requirements, water use, may cause pollution from the use of herbicides and pesticides, and could result in the destruction of natural habitats and a decrease in biodiversity (Evans, 2007; Ciampietro & Ulciati, 2005). In developing countries, the expansion of the alternative fuel industry could increase deforestation, decreasing the removal of CO2 from the atmosphere through photosynthesis (Croom, Cray & Townsend, 2008).

UNIT-4

Gaseous Fuels in S.I Engines

Properties of Gaseous Fuels

Gaseous fuels in common use are liquefied petroleum gases (LPG), Natural gas, producer gas, blast furnace gas, coke oven gas etc. The calorific value of gaseous fuel is expressed in Kilocalories per normal cubic meter (kCal/Nm^3) i.e. at normal temperature (20^{o}C) and pressure (760 mm Hg)

Calorific Value

Since most gas combustion appliances cannot utlilize the heat content of the water vapour, gross calorific value is of little interest. Fuel should be compared based on the net calorific value. This is especially true for natural gas, since increased hydrogen content results in high water formation during combustion.

Typical physical and chemical properties of various gaseous fuels are given in Table 1.12. Table 1.12 Typical Physical and Chemical Properties of Various Gaseous Fuels.

Fuel Gas	Relative Density	Higher Heating Value kcal/Nm^3	Air/Fuel ratio- m^3 of air to m^3 of Fuel	Flame Temp. ^{o}C	Flame Speed m/s
Natural Gas	0.6	9350	10	1954	0.290
Propane	1.52	22200	25	1967	0.460
Butane	1.96	28500	32	1973	0.870

Hydrogen as fuel in S.I Engines

Appearance

A colourless, odourless gas. It has the lowest density of all gases.

Uses of hydrogen

Some see hydrogen gas as the clean fuel of the future – generated from water and returning to water when it is oxidised. Hydrogen-powered fuel cells are increasingly being seen as 'pollution-free' sources of energy and are now being used in some buses and cars.

Hydrogen also has many other uses. In the chemical industry it is used to make ammonia for agricultural fertiliser (the Haber process) and cyclohexane and methanol, which are intermediates in the production of plastics and pharmaceuticals. It is also used to remove sulphur from fuels during the oil-refining process. Large quantities of hydrogen are used to hydrogenate oils to form fats, for example to make margarine.

In the glass industry hydrogen is used as a protective atmosphere for making flat glass sheets. In the electronics industry it is used as a flushing gas during the manufacture of silicon chips.

The low density of hydrogen made it a natural choice for one of its first practical uses – filling balloons and airships. However, it reacts vigorously with oxygen (to form water) and its future in filling airships ended when the Hindenburg airship caught fire.

Biological role

Hydrogen is an essential element for life. It is present in water and in almost all the molecules in living things. However, hydrogen itself does not play a particularly active role. It remains bonded to carbon and oxygen atoms, while the chemistry of life takes place at the more active sites involving, for example, oxygen, nitrogen and phosphorus.

Natural abundance

Hydrogen is easily the most abundant element in the universe. It is found in the sun and most of the stars, and the planet Jupiter is composed mostly of hydrogen.

On Earth, hydrogen is found in the greatest quantities as water. It is present as a gas in the atmosphere only in tiny amounts – less than 1 part per million by volume. Any hydrogen that does enter the atmosphere quickly escapes the Earth's gravity into outer space.

Most hydrogen is produced by heating natural gas with steam to form syngas (a mixture of hydrogen and carbon monoxide). The syngas is separated to give hydrogen. Hydrogen can also be produced by the electrolysis of water.

LPG as fuel in S.I engines

Liquefied petroleum gas or liquid petroleum gas (LPG or LP gas),also referred to as simply propane or butane, are flammable mixtures of hydrocarbon gases used as fuel in heating appliances, cooking equipment, and vehicles.It is increasingly used as an aerosol propellant[1] and a refrigerant, replacing chlorofluorocarbons in an effort to reduce damage to the ozone layer. When specifically used as a vehicle fuel it is often referred to as autogas.

LPG may be defined as those hydrocarbons, which are gaseous at normal atmospheric pressure, but may be condensed to the liquid state at normal temperature, by the application of moderate pressures. Although they are normally used as gases, they are stored and transported as liquids under pressure for convenience and ease of handling. Liquid LPG evaporates to produce about 250 times volume of gas.

LPG vapour is denser than air: butane is about twice as heavy as air and propane about one and half times as heavy as air. Consequently, the vapour may flow along the ground and into drains sinking to the lowest level of the surroundings and be ignited at a considerable distance from the source of leakage. In still air vapour will disperse slowly. Escape of even small quantities of the liquefied gas can give rise to large volumes of vapour / air mixture and thus cause considerable hazard. To aid in the detection of atmospheric leaks, all LPG’s are required to be odorized. There should be adequate ground level ventilation where LPG is stored. For this very reason LPG cylinders should not be stored in cellars or basements, which have no ventilation at ground level.

Advantages of LPG

Liquefied petroleum gas or liquid petroleum gas (LPG or LP gas), also referred to as simply propane or butane, are flammable mixtures of hydrocarbon gases used as fuel in heating appliances, cooking equipment, and vehicles.

LPG is an economical fuel source. It burns readily and gives off instant heat. The flame is visible and its size is easily controllable to meet your heating needs. LPG burns very efficiently, with very low combustion emissions and does not create black smoke.

Natural Gas

Methane is the main constituent of Natural gas and accounting for about 95% of the total volume. Other components are: Ethane, Propane, Butane, Pentane, Nitrogen, Carbon Dioxide, and traces of other gases. Very small amounts of sulphur compounds are also present. Since methane is the largest component of natural gas, generally properties of methane are used when comparing the properties of natural gas to other fuels.

Natural gas is a high calorific value fuel requiring no storage facilities. It mixes with air readily and does not produce smoke or soot. It has no sulphur content. It is lighter than air and disperses into air easily in case of leak. A typical comparison of carbon contents in oil, coal and gas is given in the table.

Table 1.13 Comparison of Chemical Composition of Various Fuels

	Fuel Oil	Coal	Natural Gas
Carbon	84	41.11	74
Hydrogen	12	2.76	25
Sulphur	3	0.41	-
Oxygen	1	9.89	Trace
Nitrogen	Trace	1.22	0.75
Ash	Trace	38.63	-
Water	Trace	5.98	-

Uses of Natural gas

Natural gas is a fossil fuel used as a source of energy for heating, cooking, and electricity generation. It is also used as a fuel for vehicles and as a chemical feedstock in the manufacture of plastics and other commercially important organic chemicals.

Natural gas is the right fuel for so many reasons. Here are the best reasons ...

1.convenience

With natural gas, you'll never run out of fuel. Underground pipelines mean there is no disruption of supply due to storms or power outages. Unlike other heat sources that leave ashes and odours, natural gas will never leave a mess. And you'll love the convenience natural gas adds to your home - from instant, cozy heat, to precision cooking, and nice, long showers without running out of hot water.

2. Versatility

Natural gas can do more than heat your home. It can be used for water heating, clothes drying, cooking, and mood-setting fireplaces. It can also be used outdoors for barbecuing, gas lighting, and even to heat your swimming pool or hot tub.

3. Savings

Natural gas can save you money. Visit the appliance section to view cost comparison. Natural Gas is still your best energy buy.

4. Safety

Natural gas is one of the world's safest sources of energy used by over 15 million Canadians to heat their homes and businesses.

5. Consistent, Reliable Supply

Natural gas comes from a pipeline underground. It's always there when you need it and you never have to worry about running out of fuel, or arranging for deliveries. Many natural gas appliances will operate during a power outage so you can still stay warm, have hot water and eat well.

6. Future Possibilities

Once your home is connected to natural gas, it's easy to convert appliances or add additional gas products later on:

outside for your barbecue, pool heater, and gas lights in the basement for your water heater and clothes dryer in the kitchen for your range and/or cooktop in the den and living room for your natural gas fireplace.

7. Environmental Benefits

By all measures natural gas is the best energy alternative for today

8. Abundant Domestic Production

International supply issues will never stand in the way of heating your home. There is a secure supply of natural gas in Canada.

9. Easier, More Affordable Maintenance

Clean burning natural gas heating equipment means less maintenance and repairs over the years.

10. Increased Resale Value of Your Home

Adding natural gas heating, a fireplace and other appliances to your home, farm or cottage will pay dividends down the road when you decide it's time to move.

CNG

Compressed natural gas (CNG) (methane stored at high pressure) is a fuel which can be used in place of gasoline(petrol), Diesel fuel and propane/LPG. CNG combustion produces fewer undesirable gases than the fuels mentioned above. It is safer than other fuels in the event of a spill, because natural gas is lighter than air and disperses quickly when released.

Advantages of CNG

Natural gas vehicle have lower maintenance costs than other hydrocarbon-fuel-powered vehicles.

CNG fuel systems are sealed, preventing fuel losses from spills or evaporation.

Increased life of lubricating oils, as CNG does not contaminate and dilute the crankcase oil. Being a gaseous fuel, CNG mixes easily and evenly in air.CNG is less likely to ignite on hot surfaces, since it has a high auto-ignition temperature (540 °C), and a narrow range (5–15 percent) of flammability.

CNG-powered vehicles are considered to be safer than gasoline-powered vehicles.

Less pollution and more efficiency:

CNG emits significantly less pollution directly than gasoline or oil when combusted (e.g., carbondioxide (CO_2), unburnedhydrocarbons (UHC), carbon monoxide (CO), nitrogen oxides (NO_x), sulfur oxides (SO_x) and PM (particulate matter)). For example, an engine running on petrol for 100 km emits 22 kilograms of CO_2, while covering the same distance on CNG emits only 16.3 kilograms of CO_2.[16]

Due to lower carbon dioxide emissions, switching to CNG can help mitigate greenhouse gas emissions However, natural gas leaks (both in the direct use and in the production and delivery of the fuel) represent an increase in greenhouse gas emissions. The ability of CNG to reduce greenhouse gas emissions over the entire fuel lifecycle will depend on the source of the natural gas and the fuel it is replacing.

The lifecycle greenhouse gas emissions for CNG compressed from California's pipeline natural gas is given a value of 67.70 grams of CO_2-equivalent per megajoule (gCO_2e/MJ) by CARB (the California Air Resources Board), approximately 28 percent lower than the average gasoline fuel in that market (95.86 gCO_2e/MJ).

CNG produced from landfill biogas was found by CARB to have the lowest greenhouse gas emissions of any fuel analyzed, with a value of 11.26 gCO_2e/MJ (more than 88 percent lower than conventional gasoline) in the low-carbon fuel standard that went into effect on January 12, 2010.

Producer Gas

Producer gas is fuel gas that is manufactured from material such as coal, as opposed to natural gas. In this respect it is similar to other types of "manufactured" gas, such as coal gas, coke oven gas, water gas and carburetted water gas. Producer gas was used primarily as an industrial fuel for iron and steel manufacturing, such as firing coke ovens and blast furnaces, cement and ceramic kilns, or for mechanical power through gas engines. It was characteristically low in heating value but cheap to make, so that large amounts could be made and burnt.

Uses

The Uses of Producer Gas. Producer gas is a mixture of flammable and nonflammable gases, mainly carbon monoxide and hydrogen in the former, and carbon dioxide and nitrogen for the latter. It burns with a lower heat than some other gases, but its great benefit is that it can be manufactured simply and relatively cheap.

Bio Gas

Biogas typically refers to a mixture of different gases produced by the breakdown of organic matter in the absence of oxygen. Biogas can be produced from raw materials such as agricultural waste, manure, municipal waste, plant material, sewage, green waste or food waste. Biogas is a renewable energy source.

Biogas can be produced by anaerobic digestion with methanogen or anaerobic organisms, which digest material inside a closed system, or fermentation of biodegradable materials.[1] This closed system is called an anaerobic digester, biodigester or a bioreactor.[2]

Biogas is primarily methane (CH_4) and carbon dioxide (CO_2) and may have small amounts of hydrogen sulphide (H_2S), moisture and siloxanes. The gases methane, hydrogen, and carbon monoxide (CO) can be combusted or oxidized with oxygen. This energy release allows biogas to be used as a fuel; it can be used for any heating purpose, such as cooking. It can also be used in a gas engine to convert the energy in the gas into electricity and heat.

Advantages of Biogas

1. Biogas is Eco-Friendly

Biogas is a renewable, as well as a clean, source of energy. Gas generated through biodigestion is non-polluting; it actually reduces greenhouse emissions (i.e. reduces the greenhouse effect). No combustion takes place in the process, meaning there is zero emission of greenhouse gasses to the atmosphere; therefore, using gas from waste as a form of energy is actually a great way to combat global warming.

Unsurprisingly, concern for the environment is a major reason why the use of biogas has become more widespread. Biogas plants significantly curb the greenhouse effect: the plants lower methane emissions by capturing this harmful gas and using it as fuel. Biogas generation helps cut reliance on the use of fossil fuels, such as oil and coal.

Another biogas advantage is that, unlike other types of renewable energies, the process is natural, not requiring energy for the generation process. In addition, the raw materials used in the production of biogas are renewable, as trees and crops will continue to grow. Manure, food scraps, and crop residue are raw materials that will always be available, which makes it a highly sustainable option.

2. Biogas Generation Reduces Soil and Water Pollution

Overflowing landfills don’t only spread foul smells- they also allow toxic liquids to drain into underground water sources. Consequently, yet another advantage of biogas is that biogas generation may improve water quality. Moreover, anaerobic digestion deactivates pathogens and parasites; thus, it’s also quite effective in reducing the incidence of waterborne diseases. Similarly, waste collection, and management, significantly improve in areas with biogas plants. This, in turn, leads to improvements in the environment, sanitation, and hygiene.

Emissions:

The emissions are also significantly related to fuel boiling point. A high boiling point may comprise fractions or components that are not completely vaporized and/or burnt [15]. A low boiling point, on the other hand, can enhance the fuel combustion and thereby can decrease the CO and UHC emissions.

The first emission control for the spark ignition engines involved adjustments of air-fuel ratio. It was followed by control and adjustment of other engine parameters such as mixture control under idling, acceleration and deceleration, spark timing, precision manufacturing of key engine components such as piston, rings, cylinder head gasket to minimize crevice volume, cams, valves etc. Positive crankcase ventilation (PCV) system was introduced on gasoline vehicles during mid 1960’s to prevent release into atmosphere of hydrocarbon-rich crankcase blow by gases. As the emission standards were tightened, exhaust after treatment devices such as catalytic converters were introduced for the first time in 1974-75 and more advanced modifications in engine design and fuel system were employed. Electronic fuel and engine management become necessary during 1980s to meet the then emission regulations. Further advancements in engine, fuel system and emission control technology have emerged in the meantime. Multi-valve cylinder engines became common and variable valve actuation was applied in production vehicles during late 1980s. In mid 1990s, gasoline direct injection stratified charge (DISC) engines were put into production by Japanese auto-manufacturers.

Besides all-round advancements in engine technology and after treatment systems happening all the time, in the past few years alternative power trains also for vehicles have been developed which provide a higher fuel efficiency in addition to low emissions. Hybrid electric vehicles (HEV) are already in market place. The HEV has IC engine as a primary source of power but employ electric propulsion powered by storage batteries as the main propulsion unit. Fuel cell vehicles using hydrogen as energy source an advanced stage of development and they completely eliminate the use of IC engines as a propulsion system

CHAPTER 3

ALTERNATIVE FUEL

3.1 GENERAL

The rapid depletion of fossil fuels and ever increasing price of crude oil made the researchers to search for alternative source of energy. The scarcity of known petroleum reserves will make renewable energy resources more attractive. The most feasible way to meet this growing demand is by utilizing alternative fuels. The enormous growth of automobiles made the diesel engines to play a vital role in transportation sector. The use of diesel in the transport sector is increasing day by day due to the increase in vehicle population.

In addition, the price of fossil fuel is increasing day by day due to the hike in crude oil price. India is spending huge foreign exchange for the import of crude oil in order to meet the ever increasing demand affecting the economic growth. India is spending around 20 thousand crore of rupees a year on the import of crude oil alone. The demand for crude oil may rise by 5 crore barrels than the present consumption by the year 2010. The share of hydrocarbons is presently estimated at 44.9 per cent (36 per cent for oil and 8.9 per cent for natural gas). The import dependence of oil in India, which is presently about 70 per cent, is likely to increase further during the next 10 years (Tenth Five Year Plan, Government of India). Hence intensive research on alternative fuel is gaining momentum to substitute the fossil fuels and to reduce emissions, particularly NOx.

3.2 NEED FOR ALTERNATIVE FUELS

Alternative fuels which are renewable and eco friendly reduce the dependency on fossil fuels and they help to preserve the atmosphere by reducing the emission levels. The burning of fossil fuels create higher levels of CO_2 and other gases in atmosphere affecting the green house effect. The scarcity of conventional fossil fuels, growing emissions of combustion causing pollutants and their increasing costs will make biomass sources more attractive.

Epidemiological studies have concluded that the long term exposure to diesel exhaust may cause lung cancer and other respiratory diseases. The diesel emission has been classified as human carcinogen. The different kinds of fuels that have been considered as alternative fuels for petroleum based fuel are classified as solid, liquid and gas. The solid fuels are pulverized coal, slurry and charcoal which are not used in IC engines due to their physical properties, handling and storage problems. The liquid fuels are alcohols (ethanol, methanol) and vegetable oils (edible and non edible). The gaseous fuels are LPG, CNG, H_2, biomass and producer gas. Liquid fuels are easy to handle, transport, store and have reasonable calorific values and they are preferred for IC engines.

3.3 ALTERNATIVE LIQUID FUELS

There are few techniques by which alcohol fuels can partially or completely displace diesel fuel. Once it was believed that alcohol was suitable for S.I. engine fuels but not suitable for C.I. engine due to its high octane number. In mid 1970, ethanol and methanol were considered as prime alternative to diesel and the most promising techniques are explored for better engine performance namely power output, thermal efficiency, emissions and operability.

3.3.1 Alcohol as IC Engine Fuel

Many countries like Brazil, Mauritius, US and few European countries are using ethanol blended fuel in automobiles. Ethanol is produced from sugar molasses, wood, maize, beet etc,. Ethanol is processed from any feed stock such as corn, wheat, sugar cane, tapioca and other grains. The grain is first ground and cooked with water to convert the starch to sugar with the enzyme. The sugar is than fermented with yeast to produce raw ethanol and a high protein material. The raw ethanol is distilled to get anhydrous ethanol.

Methanol is produced from coal, natural gas, farm waste, municipal waste etc., The municipal wastes are first shredded and then passed under a magnet to remove the ferrous materials and then gasified with oxygen. The synthesis gas is cleaned by water scrubbing and other means to remove any particulates, H_2S and CO_2. Further CO-shift conversion for H_2-CO-CO_2 adjustment, methanol synthesis and methanol purification are accomplished.

Alcohols are used as blended fuel with petrol for flexible fuel vehicle operation. Since the alcohol structure has O_2 of its own, like Ethanol (C_2H_5OH) and Methanol (CH_3OH), they are called as oxygenated fuels. They are adoptable with little modification by selecting suitable materials to handle them. However the emission reduction were considerable than fossil fuel. Various methods by which alcohol may be converted as IC engine fuel are given below

- Alcohol / diesel fuel solutions
- Alcohol / diesel fuel emulsions

- Alcohol fumigation
- Dual injection
- Spark ignition of alcohols
- Ignition improving additives

Table 3.1 gives the properties of diesel and other alternative liquid and gaseous fuels(Kajitani et al 1998, Brent Bailey et al 1997, Mitsuru Konno et al 1999).

3.3.1.1 Ignition improvers and additives

The main problem associated with all the alternative fuels is that they have high octane ratings, and hence require high compression ratio for diesel engine operation. Alternatively ignition promoters can be added to the fuel to broaden the diesel engine operating range. The same fuel additives used in gaseous fuels to increase the cetane rating can also be used in gasoline, or any of the alternative fuels, to promote ignition in diesel engines. There are a number of additives that have been added to gaseous fuels, and in particular the use of nitrate compounds have been widespread. While many different organic nitrates have been evaluated over the years, only 2-ethyl hexyl nitrate (2-EHN) is currently commercially available and has been added to diesel fuels for over 30 years.

Table 3.1 Properties of Diesel and various Alternate fuels

Properties		Diesel Fuel # 2	DEE	Propane	DME	Methanol	Ethanol	CNG
Formula		$C_n H_{1.8n}$ (C_8 to C_{20})	$C_2H_5OC_2H_5$	C_3H_8	CH_3OCH_3	CH_3O_H	C_2H_5OH	CH_4
Molecular Weight, g/mole		≈ 170	74	44.10	46.1	32.04	46.07	16.4
Boiling Point, at 101.3 kPa,°C.		163-399	34.4	6.5	-25	64.5	78.3	-161.7
Vapor Pressure, at 38°C, kPa.		negligible	110.3	1172	799	31.9	16.0	16547
Auto ignition Temperature,°C		257	160	450	235	464	363	565-582
Cetane Number		40-55	>125	< 3	> 55	5	9	<6
Stoichiometric Air Fuel ratio on Mass Basis		14.5	11.1	15.85	9	6.46	8.98	17.2
Octane rating	Research	30	-	112	-	106	107	120
	Motor			97		92	89	-
Flammability limits, Vol %	Lower	1	1.9	2.1	3.4	6.72	3.28	5.3
	Higher	5	9.5-36.0	9.5	27.0	36.5	18.95	15
Net Heating Value, MJ / Kg		42.5	33.9	46.4	28.2	20	27	49.5
Viscosity, at 20°C Centipoise		2.6-4.1	0.23	-	-	0.59	1.19	
Density at 16°C and 101.3 kPa , kg/m^3		833-881	713	505.9	667	794.6	789.8	128

Ethers and oxygenates are known to be effective cetane improvers. Oxygenates that are widely used are dimethyl ether (DME), dimethoxy methane (DMM) and diethyl ether (DEE). The important properties of these oxygenates are given in the Table 3.2(Fuquan Frank Zhao et al 2003).

Table 3.2 Properties of Various Fuel Additives

Additives	**Chemical Formula**	**Cetane No**	**Boiling Point (°C)**	**LHV (MJ/kg)**
DME	CH_3-O-CH_3	55-60	-25	28.8
DMM	CH_3-O-CH_2-O-CH_3	25-30	42	22.3
DEE	CH_3-CH_2-O-CH_2-CH_3	> 125	34	33.9

In the experimental investigation using biodiesel as a primary fuel, DEE can be admitted into the cylinder through intake manifold. As DEE has high cetane number, DEE was used as an effective ignition enhancer. DEE has excellent properties and it is produced from dehydration of ethanol in the presence of a catalyst, which is analogous to the formation of DME from methanol. It is found to be very effective as a cold-starting aid for diesel engines. Although the cetane rating of DEE is greater than 100, adding DEE to diesel fuel significantly inhibits its ignition.

The advantages of DEE on diesel cold-starting appears to be that DEE acts as a neat fuel and ignites well before the diesel fuel has vaporized. DEE is also an excellent compression ignition fuel with higher energy density, low auto ignition temperature (160°C), non-corrosive nature, highly volatile liquid and has greater heating value (33,900 kJ/kg) than ethanol (27,000 kJ/kg).

3.3.2 Edible Vegetable Oil

In 1911 itself, Rudolf Diesel demonstrated his engine with peanut oil and said that the diesel engine can be fed with vegetable oils and would help considerably in the development of agriculture of the countries which use it. He has also said that the use of vegetable oils for engine fuels would become significant in the long run as the demand for petroleum products go up.

Countries like Europe, South America and East Asia started using vegetable oil as fuel in diesel engines. If the engine is started with diesel, run with vegetable oil and stopped with diesel the fuel system of the engine will function for long time, however the engine components are deposited with severe carbon build up.

Initially, it was believed that vegetable oils could be used directly with minimum processing and preparation. Out of all the alternative fuels, vegetable oil offers an advantage because of its comparable fuel properties with diesel and can be substituted between 20% to 100% depending upon its processing. The various vegetable oils like sunflower oil, safflower oil, soybean oil, rice bran oil, palm oil, peanut oil, cotton seed oil etc. have been tested in the diesel engine. Research in this direction with edible oil yielded encouraging results.

The vegetable oil fuel has gained importance due to the following merits :

- It has high cetane number
- It is renewable
- It is carbon neutral

- It can be abundantly produced at low cost
- It is not harmful to engine
- It is eco friendly
- It aims at reduction in crude import

The vegetable oil has the following demerits:

- It has high viscosity which results in ring sticking, stuffing of cylinder links
- It has unfavorable spray atomization and evaporation
- It has high flash point resulting in slow combustion
- It has severe gum deposits lead to clog in the fuel system
- It has unsaturated components cause deposits in combustion chamber

The Table 3.3 shows the quantity of edible vegetable oil imported by India during the years 2007 to 2010 as given by Ministry of Agriculture, Government of INDIA.

It is seen from the Table 3.3 that we are importing more than 8.6 million tons of edible vegetable oil during the year 2008-2009. It may also go up in the coming years due to increase in the population. India is the world's fourth largest country, having edible oil sources. But still about 43 per cent of edible oil available in India is imported.

India is yet to attain self sufficiency in edible oil production and due to the pressure on edible oils like groundnut, rapeseed, sesame, ricebran, safflower, linseed, castor, mustard, soybean, coconut etc., there is a need to explore non edible oil like karanja (pongamia pinnata), jatropha, mahua, tumba which are evaluated as diesel fuel replacement (Racheman et al 2003).

Table 3.3 Break- up of various oils imported during financial years in Million tonnes

Oil\Year	**2007-08**	**2008-09**	**2009-10**
Soya oil	0.75	1.0	0.90
Palm oil	5.27	6.65	6.90
Sunflower oil	0.03	0.60	0.50
Lauric oils	0.20	0.25	0.25
Vanaspati	0.05	0.05	0.05
Others	---	0.05	------
Total	6.3	8.6	8.6

Table 3.4 shows the production of major oilseeds, availability of edible oils from all domestic sources and consumption of edible oils in India (from Domestic and Import Sources) during the years 2000-01 to 2007-08 (Source: Ministry of Agriculture & Directorate of Vanaspati, Vegetable Oils and Fat, Government of INDIA)

Table 3.4 Production of oilseeds, net availability and consumption of edible oils during the year 2000-2008 in Lakh Tonnes

Year (Nov.-Oct.)	**Production of Oilseeds**	**Net availability of edible oils from all domestic sources**	**Consumption of Edible Oils (from domestic and import sources)**
2000-2001	184.40	54.99	96.76
2001-2002	206.63	61.46	104.68
2002-2003	148.39	46.64	90.29
2003-2004	251.86	71.40	124.30
2004-2005	243.54	72.47	117.89
2005-2006	279.79	83.16	126.04
2006-2007	242.89	73.70	115.87
2007-2008	297.55	86.54	142.62

As India import huge quantity of edible oil and oilseeds to meet the domestic demand, the research on the use of non edible oils like pungamia, jatropha, neem, and madhuca indica have major role as fuel.

3.3.3 Non-Edible Vegetable Oil

If an oil contains aflatoxin contents of pesticides, carcinogenic substances and toxic metal concentration, the oil is labeled as non edible oil. There are several non edible oils such as Jatropha, pungamia oil, madhuca indica, mango seed oil, tobacco seed oil on which the research as alternative fuel has gained momentum.

In our country eventhough number of non edible vegetable oil are available for use in diesel engines as fuel, karanja oil is widely used because it is available in plenty, particularly in southern peninsula. Karanja is the botanical name of pongamia also known as pungam in Tamil.

The pongam/karanja tree belongs to the Leguminiceae family with Magnoliophyta division and Magnoliopsida class. Its Botanical name is Pongamia glabra. Its Scientific name is Pongamia pinnata. Its Common names are Pongam, Pongamia, Puna oil tree, Indian Beech Tree, Honge Tree, Milletia Pinnata, Honge, Panigrahi, Karanji, Calpa and Ponge and in sanskrit it is called as Naktamala. Recent research has suggested that it should be reclassified to genus Millettia.

Table 3.5 Non- edible oil potential in India in the year 2009 given by National Oilseeds and Vegetable Oil Development (NOVOD) Board, Government of India.

Table 3.5 Non- edible oil potential in India

Oil	Botanical name	Oil potential (tonnes)
Mahua	Madhuca indica	180000
Neem	Azadiracht	100000
Karanja	Pongamia pinnata	55000
Mango	Mangifera indica	45000
Kusum	Schleichera oleosa	25000
Tumba	Citrullus collocynthis	21000
Pilu	Salvadora oleoides	17000
Ratanjyot	Jatropha curcus	15000
Phulware	Cheura	3000
Kokum	Garcinia indica	500
Simarouba	Simaruba glauca	-----
Jojoba	Simmondsia chinesis	-----
Chullu	Prunus armeniaca	110

As given in Table 3.5, out of the 13 major non edible vegetable oil sources, the Pongamia pinnata oil places the third position after to neem and mahua oil. Though various non edible oil resources are available in India the scope for karanja oil is in third position which can be used as feed stock for production of non edible biodiesel as alternate fuel.

3.3.3.1 Karanja oil

Karanja oil can be extracted from karanja oil seeds either using Bullock driven expellers or using motorized expellers. Expellers also called as Ghanis are widely used in Asia in rural areas. It is heavy wooden or metal pestle driven in a large metal or wooden mortar. The oil from the raw material is made to come out by the crushing and pressing of the oil seed in between mortar and pestle. This method of oil extraction is a slow process. To speed up the process of oil extraction the expellers are driven by electric motor. An electrical motor is fitted with the driver mechanism. The pestle is connected to the driver. The oil is collected at the bottom. It requires capital investment for large scale production. In this process oil extraction is carried out in batches.

Figure 3.1 Photographic view of Karanja seed

The properties of common raw non edible vegetable oils used as fuel for diesel engine are given in Table 3.6 (Sankaranarayanan et al 2005).

Table 3.6 Properties of common non edible vegetable oils

Vegetable Oil	**Iodine value**	**CN**	**CV (kJ/kg)**	**Viscosity (mm^2/s)**	**CP (°C)**	**PP (°C)**	**FP (°C)**
Neem	--	47	39399	30.3 (30°)	--	--	180
Karanja	--	--	37100	41.8 (30°)	--	--	--
Madhuca Indica	58-70	45	38960	16.9 (30°)	--	--	99
Jetropha	--	40-45	39774	49.9 (38°)	--	--	--
Honne	--	--	33058	35.0 (30°)	--	--	--
Cotton seed	90-140	41.8	39468	33.5 (38°)	1.7	-15.0	234
Sesame	104-120	40.2	39349	35.5 (38°)	-3.9	-9.4	260
Crambe	93	44.6	40482	53.6 (38°)	10	-12.2	274
Rapeseed	94-120	37.6	39709	37.0 (38°)	-3.9	-31.7	246
Linseed	168-204	34.6	39307	27.2 (38°)	1.7	-15.0	241
Diesel	--	47	45000	2.7 (38°)	-15.0	-33.0	52

The various vegetable oils like sunflower oil, safflower oil, soybean oil, rice bran oil, palm oil, peanut oil, cotton seed oil etc., have been tested in the diesel engine. Research in this direction with edible oil yielded encouraging results. But, still India imports huge edible oil and oilseeds to meet the domestic demand, therefore, the research on non edible oils like pungamia, jatropha, neem and madhuca indica have major role as fuel.

3.3.4 Biodiesel

Biodiesel is a kind of fuel produced by a process known as Transesterification. This is a process of transformation of one type of ester into another type of ester. Vegetable oil is a triglyceride. Glycerin is separated from oil ester and alcohol is added and formed as alcohol ester known as bio diesel. Biodiesel or biofuel or esters of vegetable oil is a replacement of diesel fuel.

Biodiesel is defined as the monoalkyl esters of vegetable oils or animal fats. Biodiesel is the best substitute for diesel fuels in diesel engines. The biggest advantage that biodiesel has over gasoline and petroleum diesel is its environmental friendliness. The production and utilization of biodiesel is facilitated firstly through the agricultural policy of subsidizing the cultivation of non-food crops. The higher heating values of biodiesels are closer to that of the petroleum products in the range of 39–41 MJ/kg which is slightly lower than that of gasoline (46 MJ/kg), petrodiesel (43 MJ/kg) or crude petroleum (42 MJ/kg), but higher than coal (32–37 MJ/kg).

Biodiesel burns similar to petroleum diesel as it concerns regulated pollutants. On the other hand, biodiesel probably has better efficiency than gasoline. Important operating disadvantages of biodiesel in comparison with petrodiesel are cold start problems, the lower energy content, higher copper strip corrosion and fuel pumping difficulty from higher viscosity. This increases fuel consumption when biodiesel is used in comparison with application of pure petrodiesel, in proportion to the share of the biodiesel content. Taking into account the higher production value of biodiesel as compared to the petrodiesel, this increase in fuel consumption raises in addition to the overall cost of application of biodiesel as an alternative to petrodiesel. Typical ASTM standards for diesel and biodiesel is given in Table 3.7 as given by Rachel Burton et al 2008.

Table 3.7 Typical ASTM standards of diesel and biodiesel

Property	**ASTM D975 (diesel)**	**ASTM D6751 (biodiesel, B100)**
Flash point	325 K min	403 K
Water and sediment	0.05 max vol%	0.05 max vol%
Kinematic viscosity (at 313 K)	1.3–4.1 mm^2/s	1.9–6.0 mm^2/s
Sulfated ash	—	0.02 max wt%
Ash	0.01 max wt%	—
Sulfur	0.05 max wt%	—
Sulfur	—	0.05 max wt%
Copper strip corrosion	No 3 max	No 3 max
Cetane number	40 min	47 min
Aromaticity	35 max vol%	—
Carbon residue	—	0.05 max mass%
Carbon residue	0.35 max mass%	—
Distillation temp. (90% volume recycle)	555 K min–611 K max	—

The following Table 3.8 shows the % change in mass of different pollutants of an engine running on typical biodiesel mixture when compared to diesel as given by Dincer et al 2008.

Table 3.8 Changes in mass emissions from diesel engines using the biodiesel mixtures

Mixture	**CO**	**NO_x**	**SO_2**	**Particular matter**	**Volatile organic compounds**
B20	−13.1	+2.4	−20	−8.9	−17.9
B100	−42.7	+13.2	−100	−55.3	−63.2

As given in Table 3.8 the use of 20% biodiesel when mixed with 80% diesel reduces 13.1% CO emission when compared to engine running with diesel, SO_2 emission reduces to 20%, particulate matter reduces to 8.9%, volatile matter reduces to 17.9% with the increase in 2.4% NOx emission. When the engine was run with pure biodiesel (i.e. 100% biodiesel) there was 42.7% drop in CO emission, no SO_2 emission at all, drop in particulate matter up to 55.3%, the volatile organic compounds drops to 63.2% with 13.2% increase in NOx emission. Hence the use of biodiesel increases NOx emission with the drop in all the remaining pollutants.

3.3.5 Advantages of Biodiesel

The use of biodiesel gives the following advantages :

- It can be used in any conventional, unmodified diesel engines
- It can be used alone or mixed in any amount with diesel fuel
- It has more lubrication than diesel, so it increases the life of engines
- It has higher cetane number and higher biodegradability
- It is non toxic and it has higher combustion efficiency
- It has high flash point and hence safe to transport and store
- It is an oxygenated fuel and hence clean burning
- It is sulphur free and it reduces the dependency on imported petroleum

- It has low viscosity and hence improved injection and atomization
- Use of Biodiesel gives out reduced HC,CO and smoke emissions
- It has 90% reduction in cancer risk
- It provides domestic, renewable energy
- It provides employment opportunities
- It is of domestic origin
- It is in soluble in water
- It contains 11% oxygen in it

The comparison of properties of various biodiesel fuels are listed in Table 3.9 (Graboski et al 1998, Mittelbach et al 2007, Prakash et al 1998, Reddy et al 2005 and Tyson K. Shaine et al 2001) which is given below

Table 3.9 Properties of diesel and various biodiesel fuels

Fuels\Properties	Cetane number	Total glycerin (% m/m)	Specific gravity	Pour point ° C	Heating value (MJ/kg)	Cloud point ° C	Sulphur content (wt %)	Carbon residue (%)	Fla Flash point ° C	Iodine number	Viscosity @40 ° C(Cst)
Diesel	40-52	-	0.82	-25 to +5	43.4-44.9	-25 to -15	0.05max	0.34-0.37	60-72	8.60	4.2
Soybean oil methyl ester	50.9	0.21	0.885	-3.8	37.0-40.4	-0.5	0.00-0.0024		131	133.20	4.08
Rapeseed oil methyl ester	52.9	< 0.25	0.883	-10.8	37.3-40.7	-4	0.001	-	170	97.40	4.83
Tallow oil methyl ester	58.8	0.1	0.876	9.0	38-40.2	13.9	-	-	117	-	4.80
Used Frying oil methyl ester	49	0.22	0.897	-11	37.5-38.7	-5	0.06	0.33	110	101.50	4.5
Jatropha oil methyl ester	50	0.25	0.885	4	38.4-39.3	10	0.01	0.44	170	-	3.57
Karanja oil methyl ester	48	0.2	0.860	5	39.42	14	0.02	0.65	180	91	4.5
Rice bran oil methyl ester	56.2	0.21	0.874	3	38.72	8.2	0.01	0.23	165	110	4.12
Madhuca indica oil methyl ester	47	0.24	0.87	-9	38.82	6	0.02	186	180	-	4.2
Palm oil methyl ester	48.5	0.22	0.88	5	37.4	-2	-	0.20	164	-	4.7
Rubber seed oil methyl ester	51	0.20	0.924	8.2	39.5	-4	0.04	0.22	135	120.52	5.0
Sunflower oil methyl ester	54-58	0.22	0.88	3 to -3	38.2-39.5	0 - 1.5	0.012	-	170	-	4.39
Canola oil methyl ester	-	0.24	0.881	-10	-	-	0.01	0.01	135.7	-	4.44

3.4 EMULSION

An emulsion is defined as a two phase liquid system consisting of dispersion of one liquid in another in the form of droplets, whose diameter is generally greater than 0.1 micron. The emulsions are classified into two types: water-in-oil type and oil-in-water type.

3.4.1 Water-in-oil emulsion

When water (dispersed phase) and oil (dispersion medium) are vigorously shaken, the former splits into fine droplets surrounded by oil. As water is polar and oil is nearly non-polar and hydrophobic, each water droplet is guided by the other by the dipole – dipole force to cleave the oil barrier, diffuse through oil and finally coalesce. Since there is a repulsive force at the interface of oil and water, the oil wall around the droplet of water might be weak to protect droplets. The droplets, therefore, break the boundary, come out of it and make a random walk in the oil portion, finally reach the other droplet and coalesce.

Hence, the water in oil emulsion is said to be unstable. In order to destroy such force and then to stabilize emulsion, emulsifying agents which inbuilt hydrophilic and hydrophobic properties are added. The water in oil emulsion with an emulsifying agent is shown in the following figure. As the hydrophilic part of the emulsifying agent faces water while hydrophobic part faces oil, the interaction between water droplets through the intervening oil is suppressed and hence emulsion stabilized.

The above discussion is reversed for oil-in-water type emulsion.

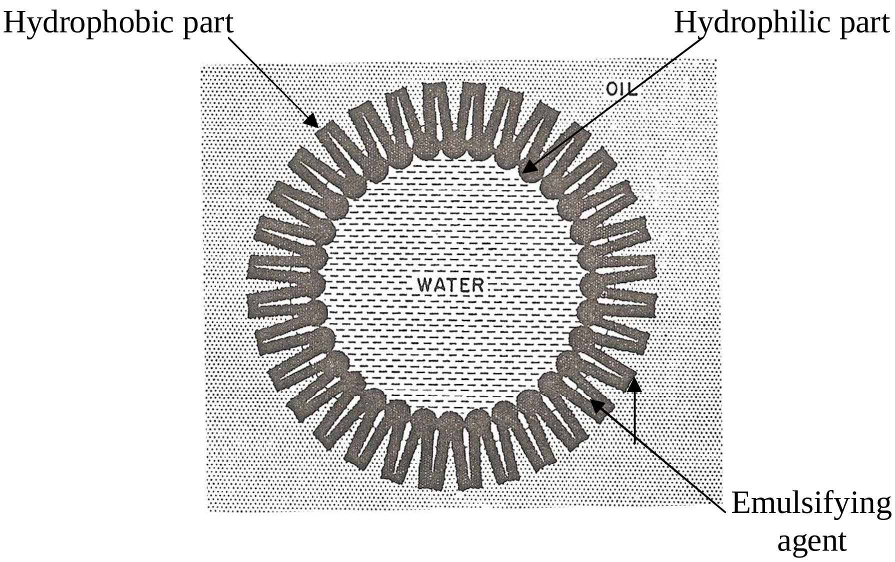


Figure 3.2 (a) Water-in-oil emulsion

3.4.2 Oil-in-water emulsion

In this type of emulsion, water forms the continuous medium whereas oil droplets form a dispersed phase. Typical examples are soap solution and vanishing cream. Figure 3.2(b) shows stabilization of an O/W emulsion by the surfactant.

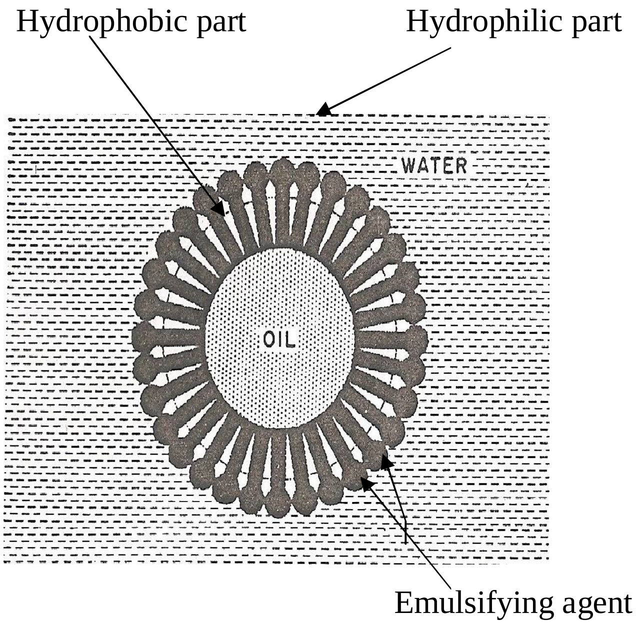


Figure 3.2 (b) Oil -in-water emulsion

The two immiscible phases form an interface, which will be in the high energy condition to separate out. The surfactant added having polar and non-polar sections spread at the interface. In the diagram the rectangular section is the non polar which has higher affinity with water and the circular section is polar which has very good affinity towards oil. The rectangular and circular portions of the surfactant bound the two different phases giving stabilized emulsion. The difference between water-in-oil and oil-in-water emulsion is that in the former one the oil forms a matrix in which the water droplets are dispersed. The binding theory will be the same as discussed below.

Of these two types of emulsions water-in-oil type is best suited for Internal Combustion Engines rather than oil-in-water type (Paul Becher et al 1965). The reason behind the use of W/O emulsion as engine fuel is mainly due to the micro-explosion phenomenon of droplet of water since water has high latent heat of vaporization which cause large fragmentation of the oil and less change in viscosity with water content.

3.4.3 Emulsifying agents

Emulsifying agents are chemicals in the form of liquid which are added in small quantity to biodiesel to provide binding energy between oil and water during the process of emulsion preparation. When two immiscible liquids like oil and water are mixed and shaken together vigorously, a milky like phase will form. But this is stable only for a small period of time. On standing, the two liquids soon separate and the oil reaches the top surface. In order to get stable emulsions of fairly high concentration it is necessary to a binding agent called emulsifier in a small quantity. These emulsifying agents are generally long chain compounds with polar groups such as soaps of various kinds, long chain sulphonic acids and alkyl sulphates. Their function is to lower the interfacial tension between water and oil so as to facilitate the mixing of these two. The soap molecule gets concentrated at the interface between water and oil and their polar end (-CO O-) is pointing to water and hydrocarbon chain (-R) to the oil.

3.4.4 Types of Emulsifier

There are three types of emulsifiers. They are Anionic emulsifier, Cationic emulsifier and Nonionic emulsifier. Only Nonionic emulsifying agents are suggested for preparing emulsified fuel for engine applications owing to its non reactive and non corrosive nature without any source for secondary pollutant formation in engines.

The surfactant molecules may be considered as being made of two distinct section: one possessing polar characteristics the other non-polar. The polar portions of these molecules are characterized by a fair degree of water solubility. On the other hand the non polar portions of these molecules are distinguished by their distinct nonsolubility in water. For this reason the polar portions of the molecule is commonly referred as the hydrophilic (water-loving) group: the nonpolar as hydrophobic (water-hating) or better as lipophilic (oil loving) group. Example OH group-Hydrophilic, H_2SO_4 group-Hydrophobic.

A combination of Hydropholic and Lipophilic nature of the surfactants is very much essential. A balance between the two is referred as HLB (Hydropholic Lipophilic Balance). HLB method finds most successful approach to the selection of emulsifying agent.

3.4.5 Mode of Adding the Emulsifier

Having chosen the appropriate emulsifier there are four recognized ways of incorporating the emulsifier into the system. They are agent in oil method, agent in water method, nascent soap method and alternative addition method. In all the above four methods Agent in Oil method is generally used to prepare W/O emulsion type. In this method the emulsifier is dissolved in the oil and water is gradually added to it.

The common method of preparing emulsion is to apply brute force to break up the interface into fine shreds and globules (dispersion method). This can be achieved by any one of the following methods like Mixing, Colloid milling and Homogenizing. Normally it is seen that the simple mixers have substantially less power requirement than colloid mills or homogenizers of similar capacity.

3.4.6 Emulsion Instability

It has been said that an emulsion is stable only when the large droplets are broken down into fair dispersible droplets. Emulsion can show instability in three ways. They are Breaking, Ceramic and Flocculance.

Breaking

Breaking is the spontaneous joining of small droplets in the emulsion to form larger ones, leading ultimately to two separate liquid layer.

Creaming

Creaming is the rise of dispersed droplets under the action of gravity. It is bound to occur if the phases are not equal in density.

Flocculance

Flocculance is the sticking together of droplets in the formation of three-dimensional clusters without coalescence.

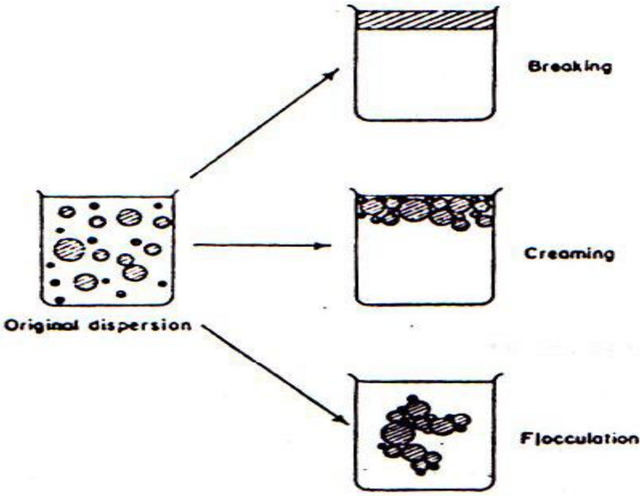


Figure 3.3 Diagrammatic representation of types of instability in emulsion

3.4.7 Stability of Water-in-Oil Emulsion

To check the stability of the emulsion a small quantity of emulsified fuel was placed in a test tube and observed for any phase separation at different time intervals. The phase separation does not occurred till 24 hours of observation. After 24 hours duration slowly the phase separation takes place. Hence the water-biodiesel emulsion was stable without any problem of phase separation even till 24 hours of duration.

3.5 SUMMARY

In the preceeding paragraph, the details about the need for alternative fuels, alcohol as IC engine fuel, ignition improvers and additives, edible and non edible vegetable oil, properties of common vegetable oils, the reason for choosing non edible karanja vegetable oil, non- edible oil potential in India, fatty acid composition and structure of karanja oil, top 10 nations in terms of biodiesel production, biodiesel emulsion, types of emulsion, stability of emulsion are presented. The availability of various alternative fuels were discussed. In the present investigation, biodiesel obtained from the non edible karanja vegetable oil is used due to its potential availability.

UNIT -2

LIQUID FUELS FOR S.I ENGINES

IMPORTANT PROPERTIES OF SI ENGINE FUEL

The fuel characteristics that are important for the performances of Internal combustion engines are

- Volatility of the Fuel
- Detonation Characteristics
- Power and Efficiency of Engines
- Good thermal properties like heat of combustion and heat of evaporation
- Gum Content
- Sulphur Content
- Aromatic Content
- Cleanliness

REQUIRED CHARACTERISTICS OF SI ENGINE FUELS

Every SI engines are designed for a particular fuel having some desired qualities. For a good performance of a SI engine the fuel used must have the proper characteristics. The fundamental requirements of liquid hydrocarbon fuels for spark ignition engines, namely that the fuel should vaporise satisfactorily and burn in a controlled manner.

The followings are requirements of a good SI engine fuels or Gasolines.
It should readily mix with air to make a uniform mixture at inlet, ie. it must be volatile
It must be knock resistant
It should not pre-ignite easily
It should not tend to decrease the volumetric efficiency of the engine.
It should not form gum and varnish
Its Sulphur content should be low as it is corrosive
It must have a high calorific value

Different techniques of utilizing alternative fuels

BLENDS: Mixing of one fuel with the other one so that they combine as a single substance. Such as Ethanol-gasoline blend, Methonal gasoline blend.

Reformed fuels

Reformed gases combustible gases, such as hydrogen or methane. When they are added with air and supplied to the engine reduces the exhaust emissions of the engine and a11ows the engine to operate at 1ean mixtures. As a fue1 for reformation into gas, methano1 is more suitab1e than gaso1ine, and it can a1so perform in the ro1e of main fue1 for the a1goho1 engine in the a1ternative-fue1 age of the future. The major constituents of reformed gas are hydrogen and carbon monoxide.

300° C, 150 atm

$$\mathrm{CH_3OH} \qquad\qquad\qquad 2\mathrm{H_2} + \mathrm{CO}$$

Methano1 Endothermig Reagtion Reformed Cas

Instant of using hydrocarbon fue1s or methano1 in 1iquid phase, we can use these fue1s in gaseous phase in the engines. Then this gaseous phase hydrocarbon fue1s or methano1 is ca11ed reformed gas.

A cata1ytig reforming system has been devised in which a 1iquid fue1 is reformed with a cata1yst into a gombustib1e gas containing compounds such as H_2 and CO and fed to the engine.

Advantages of Reformed gas

- Reduction of exhaust emissions, especia11y CO and NO_x.
- Stabi1ization of Lean-Mixture Combustion.
- Extension of Lean-Operation Range.

Storage of Fuel oil

It can be potentially hazardous to store furnace oil in barrels. A better practice is to store it in cylindrical tanks, either above or below the ground. Furnace oil, that is delivered, may contain dust, water and other contaminants.

The sizing of storage tank facility is very important. A recommended storage estimate is to provide for at least 10 days of normal consumption. Industrial heating fuel storage tanks are generally vertical mild steel tanks mounted above ground. It is prudent for safety and environmental reasons to build bund walls around tanks to contain accidental spillages.

As a certain amount of settlement of solids and sludge will occur in tanks over time, cleaning should be carried out at regular intervals-annually for heavy fuels and every two years for light fuels. A little care should be taken when oil is decanted from the tanker to storage tank. All leaks from joints, flanges and pipelines must be attended at the earliest. Fuel oil should be free from possible contaminants such as dirt, sludge and water before it is fed to the combustion system.

VOLATILITY OF THE FUEL

It is the most important characteristics of a SI engine fuel. Volatility is a physical concept that loosely defined as the tendency to evaporate at a temperature lower than their boiling temperature. It is the most dominant factor that controls the air-fuel ratio inside the combustion chamber.

VOLATILITY AND ITS EFFECT ON ENGINE PERFORMANCES

Volatility greatly affects the engine performances and fuel economy characteristics. The most important of them are

- Cold and Hot starting
- Vapour Lock in fuel delivery system
- Short and Long trip economy
- Acceleration and Power
- Warm Up
- Hot Stalling
- Carburettor Icing
- Crankcase Dilution
- Deposit formation and Spark Plug Fouling

When the percentage evaporation of the fuel is 0% ~ 20%, it is called front end of volatility curves, and there are 3 major problems that we encounter in this region of volatility curves which is also known as Distillation curves. They are

- Cold Starting
- Hot Starting
- Vapour Lock

Introduction ETHANOL

Ethanol is a volatile, flammable, clear, colourless liquid. Ethanol is a good sovent. It is also used as a germicide, beverage, antifreeze, fuel, depressant and chemical intermediate. It can be made by the fermentation process of material that contains sugar or from the compound which can be converted to sugar. Yeast enzyme readily ferment sucrose to ethanol.

Molecular formula- C_2H_5OH Molecular weight- 46.07

(a) Main Reaction

$C_{12}H_{22}O_{11} + H_2O \rightarrow 2C_6H_{12}O_6$

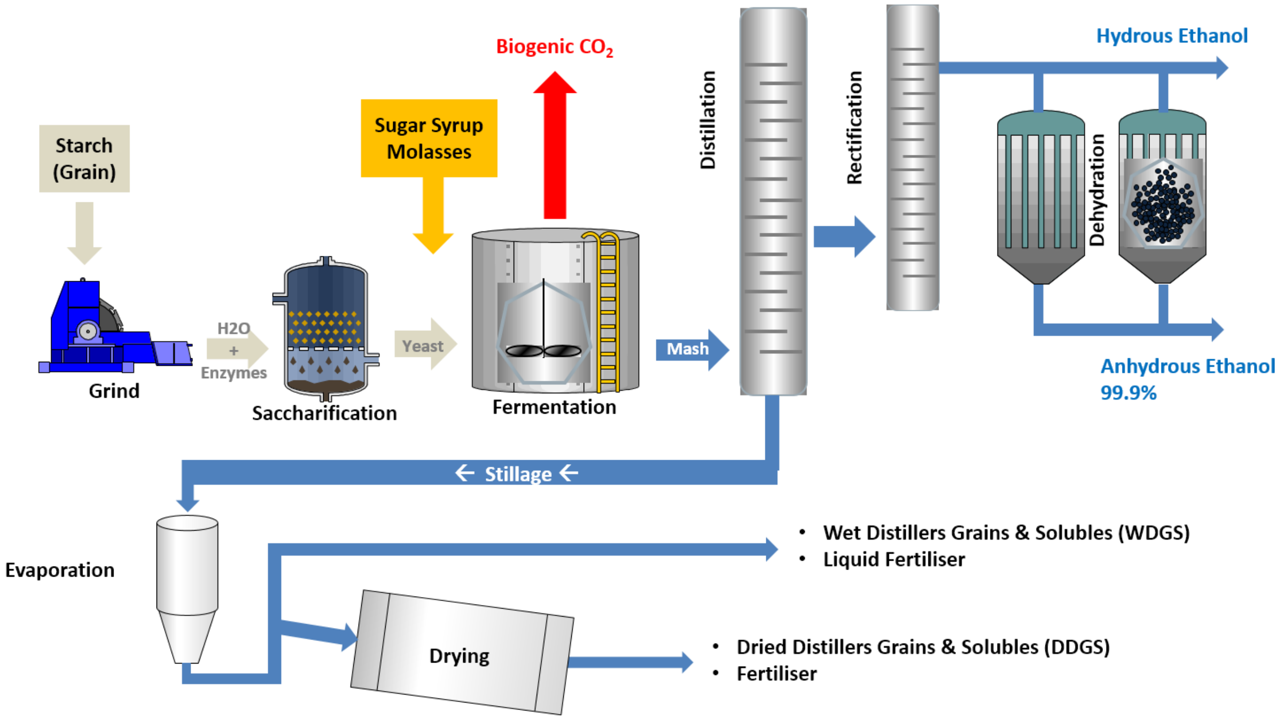
(b) Second Reaction

$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$ $\Delta H = -31.2$ kcal
Glucose Ethanol

Manufacturing of Ethanol:

1. Milling
2. Liquification
3. Saccharification
4. Fermentation
5. Distillation
6. Dehydration
7. Denaturing
8. Co products

In this process the feedstock is first converted into glucose. In the case of sugar this is quite straightforward as the sugar is simply dissolved in water. Starch however requires pre-processing where the starch is transformed into glucose through a process call liquefaction and saccharification. This process through the addition of enzymes frees the glucose bound in the starch and makes it available for fermenting into alcohol.



Effect of Ethanol on S.I.Engine

·Since ethanol is a renewable source of energy and it contributes to lower CO2 emissions, ethanol produced from biomass is expected to increase in use as an alternative fuel.

·It is recognized that for spark ignition (SI) engines ethanol has advantages of high octane number and high combustion speed and has a disadvantage of difficult startability at low temperature.

·This concept investigates the influence of ethanol fuel on SI engine performance, thermal efficiency, and emissions. The combustion characteristics under cold engine conditions are also examined.

·Ethanol has high anti-knock quality due to its high octane number, and high latent heat of evaporation, which decreases the compressed gas temperature during the compression stroke.

·In addition to the effect of latent heat of evaporation, the difference of combustion products compared with gasoline further decreases combustion temperature, thereby reducing cooling heat loss. As a result, torque and thermal efficiency increase compared to gasoline.

·Also, reductions in CO2, NOx, and THC are described. To improve combustion under cold conditions, methods of increasing fuel temperature or the compressed gas temperature during the compression stroke are considered.

·In the latter case, simulation showed valve timing to be effective. Based on simulation results, the effect of valve timing optimization on improving combustion at low temperature is investigated with an engine.

Storage of Ethanol

·The National Fire Protection Association –NFPA has established guidelines for the safe storage and handling of flammable liquids. This code uses flash point to distinguish between different liquids

·Class I liquids have Flash point below 380C and class II liquids have flash points above this level.

·Ethanol and gasoline are class I liquids. This means more stringent storage requirements including more distant location of storage tanks from property lines, buildings, other tanks and vent terminals as well as the mandatory requirement of flame arrestors on all vents. ·Ethanol must be stored and handled like gasoline.

·The end user must be educated that ethanol is properly transported, stored, dispensed and used.

·Soft metals such as Zinc, brass or Aluminium for fuel tank are not compatible with Ethanol.

·In order to store and dispense high volume of Ethanol fiber glass and steel UST must be used.

Transportation and Safety of Ethanol

·There are additional safety requirements for transporting ethanol by truck or for on board vehicle fuel tanks.

·Neat ethanol can produce a flammable mixture in a vehicle fuel tank under a wide range of temperatures.

BIO ETHANOL

Bio ethanol is obtained from the conversion of carbon based feedstock. Agricultural feed stocks are considered renewable because they get energy from the sun using photosynthesis. Ethanol can be produced from a variety of feeds tocks such as sugar cane, bagasse, miscanthus, sugar beet, sorghum, grain sorghum, switch grass, barley, hemp, kenaf, potatoes, sweet potatoes, cassava, sunflower, fruit, molasses, whey or skim milk, corn, stover, grain, wheat, wood, paper, straw, cotton, other biomass, as well as many types of cellulose waste. As of 2006, production is primarily from sugarcane, maize (corn) and sugar beets - and also as of 2006, technology does not yet exist that makes it economically competitive to produce ethanol from cellulosic feedstock.

How is Bioethanol used / Bioethanol Blends

Ethanol is most commonly used to power cars although it is also used to power other vehicles, such as tractors, airplanes and boats. Like Biodiesel, engine old starting can be effected when using high blends of Bioethanol fuel in cars. EU markets have adopted E85 (85 percent Ethanol / 15 percent Gasoline) as the maximum blend to be used and this is the common standard which manufactures work to when making their cars run Bioethanol or “flexi- fuel”. In some colder climate its it recommended that an E70 blend is used.

Manufacturing of Ethanol

The basic steps for large scale production of ethanol are: fermentation of sugars, distillation, dehydration and denaturing (optional). Prior to fermentation, some crops require saccharification or hydrolysis of carbohydrates such as cellulose and starch into sugars. Saccharification of cellulose is called cellulolysis (see cellulosic ethanol). Enzymes are used to convert starch into sugar.

Fermentation

Ethanol is produced by microbial fermentation of the sugar. Microbial fermentation will currently only work directly with sugars. Two major components of plants, starch and cellulose, are both made up of sugars, and can in principle be converted to sugars for fermentation. Currently, only the sugar (e.g. sugar cane) and starch (e.g. corn) portions can be economically converted. However, there is much activity in the area of cellulosic ethanol, where the cellulose part of a plant is broken down to sugars and subsequently converted to ethanol.

Distillation

For the ethanol to be usable as a fuel, water must be removed. Most of the water is removed by distillation. The purity is limited to 95-96% due to the formation of a low-boiling water-ethanol azeotrope. This may be used as fuel alone but unlike anhydrous ethanol it is immiscible in Petrol meaning it can not be mixed i.e. E85. The water fraction is typically removed in further treatment in order to burn with in combination with petrol in petrol engines.

Dehydration

Currently, the most widely used purification method is a physical absorption process using a molecular sieve, for example, ZEOCHEM Z3-03 (a special 3A molecular sieve for EtOH dehydration). Another method, azeotropic distillation, is achieved by adding the hydrocarbon benzene which also denatures the ethanol (to render it undrinkable for duty purposes). A third method involves use of calcium oxide as a desiccant.

METHONAL:

Methanol is an alternative fuel for internal combustion and other engines, either in combination with gasoline or directly ("neat"). It is used in racing cars in many countries. In the U.S., methanol fuel has received less attention than ethanol fuel as an alternative to petroleum-based fuels.

·When methanol/gasoline fuel blends being used, the engine emissions of carbon monoxide (CO) and hydrocarbon (HC) decrease, nitrogen oxides (NO*x*) changes little prior to three-way catalytic converter (TWC). After TWC, the conversion efficiencies of HC, CO and NO*x* are better.

·The non-regulated emissions, unburned methanol and formaldehyde, increase with the fraction of methanol, engine speed and load, and generally the maximum concentrations are less than 200 ppm. Experimental tests further prove that methanol and formaldehyde can be oxidized effectively by TWC.

During the cold start and warming-up process at 5 °C, with methanol addition into gasoline, HC and CO emissions decrease obviously.HC emission reduces more than 50% in the first few seconds (cold start period) and nearly 30% in the following warming-up period, CO reduces nearly 25% when the engine is fueled with M30. Meanwhile, the temperature of exhaust increases, which is good to activate TWC.

Emissions:

The emissions are also significantly related to fuel boiling point. A high boiling point may comprise fractions or components that are not completely vaporized and/or burnt [15]. A low boiling point, on the other hand, can enhance the fuel combustion and thereby can decrease the CO and UHC emissions.

The first emission control for the spark ignition engines involved adjustments of air-fuel ratio. It was followed by control and adjustment of other engine parameters such as mixture control under idling, acceleration and deceleration, spark timing, precision manufacturing of key engine components such as piston, rings, cylinder head gasket to minimize crevice volume, cams, valves etc. Positive crankcase ventilation (PCV) system was introduced on gasoline vehicles during mid 1960's to prevent release into atmosphere of hydrocarbon-rich crankcase blow by gases. As the emission standards were tightened, exhaust after treatment devices such as catalytic converters were introduced for the first time in 1974-75 and more advanced modifications in engine design and fuel system were employed. Electronic fuel and engine management become necessary during 1980s to meet the then emission regulations. Further advancements in engine, fuel system and emission control technology have emerged in the meantime. Multi-valve cylinder engines became common and variable valve actuation was applied in production vehicles during late 1980s. In mid 1990s, gasoline direct injection stratified charge (DISC) engines were put into production by Japanese auto-manufacturers.

Besides all-round advancements in engine technology and after treatment systems happening all the time, in the past few years alternative power trains also for vehicles have been developed which provide a higher fuel efficiency in addition to low emissions. Hybrid electric vehicles (HEV) are already in market place. The HEV has IC engine as a primary source of power but employ electric propulsion powered by storage batteries as the main propulsion unit. Fuel cell vehicles using hydrogen as energy source an advanced stage of development and they completely eliminate the use of IC engines as a propulsion system.

CHAPTER-5
USE OF HYDROGEN AS FUEL IN C.I ENGINE

In this chapter use of hydrogen as fuel in I.C. engine is discussed on the basis of literature survey. Prospects of use of hydrogen in C.I. engine have been discussed. The methods of use of hydrogen as fuel in C.I. engine are also discussed.

5.1 Fuel Properties of hydrogen

Fuel properties of hydrogen play very important role in combustion and during transportation.

5.1.1. Calorific value

Every fuel liberates a fixed amount of energy when it reacts completely with oxygen. This energy content is measured experimentally and is quantified by a fuel’s higher heating value (HHV) and lower heating value (LHV). The difference between the HHV and the LHV is the “heat of vaporization” and represents the amount of energy required to vaporize a liquid fuel into a gaseous fuel, as well as the energy used to convert water to steam.

5.1.2. Flash point

All fuels burn only in a gaseous or vapour state. Fuels like hydrogen and methane are already gasses at atmospheric conditions, whereas other fuels like gasoline or diesel that are liquids must convert to a vapour before they burn. The characteristic that describes how easily these fuels can be converted to a vapour is the flash point. The flashpoint is defined as the temperature at which the fuel produces enough vapours to form an ignitable mixture with air at its surface. If the temperature of the fuel is below its flashpoint, it can not produce enough vapours to burn since its evaporation rate is too slow. Whenever a fuel is at or above its flashpoint, vapours are present. The flashpoint is not the temperature at which the fuel bursts into flames; that is the autoignition temperature.

5.1.3. Flammability range

The flammability range of gas is defined regarding its lower flammability limit (LFL) and its upper flammability limit (UFL). The LFL of gas is the lowest gas concentration that will support a self-propagating flame when mixed with air and ignited. Below the LFL, there is not enough fuel present to support combustion; the fuel/air mixture is too lean. Hydrogen is flammable over a very wide range of concentrations in air (4 – 75%), and it is explosive over a wide range of concentrations (15 –59%) at standard atmospheric temperature. The flammability limits increase with temperature as illustrated in Figure 1-6. As a result, even small leaks of hydrogen have the potential to burn or explode. Leaked hydrogen can concentrate in an enclosed environment, thereby increasing the risk of combustion and explosion.

5.1.4. Auto-ignition temperature

The autoignition temperature is the minimum temperature required to initiate self-sustained combustion in a combustible fuel mixture in the absence of a source of ignition. In other words, the fuel is heated until it bursts into flame. Each fuel has a unique ignition temperature. For hydrogen, the autoignition temperature is relatively high at 585ºC. This makes, it difficult to ignite a hydrogen/air mixture by heat alone without some additional ignition source.

5.1.5. Electro-conductivity

Hydrogen has the added property of low electroconductivity so that the flow or agitation of hydrogen gas or liquid may generate electrostatic charges that result in sparks. For this reason, all hydrogen conveying equipment must be thoroughly grounded.

5.1.6. Ignition energy

Ignition energy is the amount of external energy that must be applied to ignite a combustible fuel mixture. Energy from an external source must be higher than the autoignition temperature and be of sufficient duration to heat the fuel vapor to its ignition temperature. Common ignition sources are flames and sparks Although hydrogen has a higher autoignition temperature than methane, propane or gasoline, its ignition energy is 0.02 mJ, therefore, more easily ignitable. Even an invisible spark or static electricity discharge from a human body (in dry conditions) may have enough energy to cause ignition.

5.1.7. Burning speed

Burning speed is the speed at which a flame travels through a combustible gas mixture. Burning speed is different from flame speed. The burning speed indicates the severity of an explosion since high burning velocities has a greater tendency to support the transition from deflagration to detonation in long tunnels or pipes. Flame speed is the sum of burning speed and displacement velocity of the unburned gas mixture. Burning speed varies with gas concentration and drops off at both ends of the flammability range. Below the LFL and above the UFL the burning speed is zero. The burning speed of hydrogen at 2.65–3.25 m/s is nearly an order of magnitude higher than that of methane or gasoline (at stoichiometric conditions). Thus hydrogen fires burn quickly and, as a result, tend to be relatively short-lived

5.1.8. Quenching gap

The quenching gap (or quenching distance) describes the flame extinguishing properties of fuel when used in an internal combustion engine. Specifically, the quenching gap relates to the distance from the cylinder wall that the flame extinguishes due to heat losses. The quenching gap has no specific relevance for use with fuel cells. The quenching gap of hydrogen (at 0.064 cm) is approximately 3 times less than that of other fuels, such as gasoline. Thus, hydrogen flames travel closer to the cylinder wall before they are extinguished making them harder to quench than gasoline flames. This smaller quenching distance can also increase the tendency for backfire since the flame from a hydrogen-air mixture can more readily get past a nearly closed intake valve than the flame from a hydro carbon-air mixture.

5.2. Hydrogen use in I.C. engine

Hydrogen has a potential to be used in an internal combustion engine with some modification and safety measure. Fuel properties of hydrogen are not same as gasoline or Diesel fuel. So researchers are focusing on using hydrogen in internal combustion engine. A lot of research work has been carried out to use hydrogen in S.I. engine. Researchers are targeting to explore the possibility to use hydrogen as a fuel in Diesel engine.

5.2.1. Hydrogen use in C.I. engines

There are several reasons for applying hydrogen as an additional fuel to accompany diesel fuel in the internal combustion (IC) compression-ignition (CI) engine. Use of hydrogen in compression ratio combustion engine improve the H/C ratio of the charge. High diffusivity of hydrogen along with air and diesel reduces the heterogeneity in the combustion chamber and make the combustion mixture better premixed and more uniform, Szwaja et al. (2009). Hence the formation of unburnt hydrocarbon, Carbon monoxide, and carbon dioxide during the combustion can be reduced drastically. Self-ignition temperature of hydrogen is very high that is the reason; it cannot be used as sole fuel in C.I. engine, Saravanan et al. (2009). Hydrogen cannot be used in C.I. engine without a spark plug or glow plug. However, Hydrogen can be used in dual fuel mode. In a dual fuel engine, the primary fuel is induced or injected into the intake air while combustion is initiated by diesel fuel that acts as an ignition source. The quantity of hydrogen may be in the range of 10–30% while diesel fuel supplies the rest of the energy. Hydrogen operated dual fuel engine has the characteristics to operate at leaner equivalence ratios at part loads, which results in NOx reduction and increase in thermal efficiency thereby reducing the fuel consumption. Oxides of nitrogen (NOx) are the major problem in hydrogen operated dual fuel engine, Saravanan et al. (2009).

One method that has been used to reduce NOx emissions successfully is exhausted gas recirculation (EGR). EGR is very effective in reducing NOx emissions due to the dilution effect of, where the oxygen concentration of the intake charge is reduced. Also, volumetric efficiency reductions with increasing EGR rates are significant (reductions of about 15% compared with hydrogen dual-fuel operation without EGR are recorded). At the same time, EGR addition to hydrogen dual-fuel operation can increase particulate emissions compared with hydrogen dual-fuel operation without EGR. As a result, hydrogen dual-fuel operation with EGR produces smoke levels similar to normal CI engine operation. In addition to reducing NOx, increases in unburned HC, CO and CO_2 emissions with EGR addition are also recorded.

Second method is by introducing liquid water into the combustion chamber. Water injection can also prevent knocking and pre-ignition during hydrogen combustion. Here water acts in a similar manner to diluents such as EGR, cooling the charge and reducing the combustion rate. However, water injected into the intake manifold reduces volumetric efficiency, Korakianitis et al. (2010).

Conventional diesel engines can be converted to operate on hydrogen–diesel dual mode with up to about 38% of full-load energy substitution without any sacrifice on the performance parameters such as power and efficiency, Das et al. (2002).

5.2.2 Hydrogen use in S.I. engines

Hydrogen can be used as a fuel directly in an internal combustion engine, almost similar to a spark-ignited (SI) gasoline engine. Most of the past research on H_2 as a fuel focused on its application in SI engines. Hydrogen is an excellent candidate for use in SI engines as a fuel having some unique and highly desirable properties, such as low ignition energy, and very fast flame propagation speed, wide operational range. The hydrogen fuel, when mixed with air, produces a combustible mixture which can be burned in a conventional spark ignition engine at an equivalence ratio below the lean flammability limit of a gasoline/air mixture. The resulting ultra-lean combustion produces low flame temperatures and leads directly to lower heat transfer to the walls, higher engine efficiency and lower exhaust of NOx emission, Wahab et al. (2009) & Abdelghaffar et al. (2010).

Therefore, the extensive research pure H_2 as fuel has led to the development and successful marketing of hydrogen engine. For example, Ford developed P2000 hydrogen engine, which was used to power Ford’s E-450 Shuttle Bus. BMW developed a 6 liter, a V-12 engine using liquid H_2 as fuel. With an external mixture formation system, this engine has a power out about 170 kW and an engine torque of 340 Nm, Wahab et al. (2009).

5.2.3 Hydrogen use with natural gas as fuel mixture in engines

Natural gas is considered to be one of the favourable fuels for engines, and the natural gas powered engine has been realized in both the spark-ignited engine and the compression-ignited driving force. However, due to the slow burning velocity of the natural gas and the have-not's lean-burn capability, the natural gas spark ignited engine has the disadvantage of significant cycle-by-cycle variations and poor lean-burn capability, and these will decrease the engine power output and increase fuel consumption, Huang et al. (2006).

Due to these restrictions, natural gas with hydrogen for use in an internal combustion engine is an effective method to improve the burning velocity, with a laminar burning velocity of 2.9 m/s for hydrogen versus a laminar burning velocity of 0.38 m/s for methane. This can improve the cycle-by-cycle variations caused by relatively poor lean-burn capabilities of the natural gas engine. Thus, natural gas engines can reduce the exhaust emissions of the fuel, especially the methane and carbon monoxide emissions. Also, the fuel economy and thermal efficiency can also be increased by the addition of hydrogen. The thermal efficiency of hydrogen-enriched natural gas is covered. There are some challenges when it comes to using the hydrogen-natural gas mixture as a fuel. One of the biggest challenges using HCNG as a fuel for engines is determining the most suitable hydrogen/natural gas ratio. When the hydrogen fraction increases above certain extent, abnormal combustion such as pre-ignition, knock, and backfire, will occur unless the spark timing and air-fuel ratio are adequately adjusted. This is due to the low quench distance and higher burning velocity of hydrogen which causes the combustion chamber walls to become hotter, which causes more heat loss to the cooling water. With the increase of hydrogen addition, the lean operation limit extends and the maximum brake torque (MBT) decreases, which means that there are interactions among hydrogen fraction, ignition timing and excess air ratio, Fanhua et al. (2010).

5.3 Hydrogen fuel induction techniques in I.C. engine:

As far as the development of a practical hydrogen engine system is concerned, the mode of fuel induction plays a very critical role. Three different fuel induction mechanisms are observed in the literature. 1. Fuel Carburetion Method (CMI) 2. Inlet Manifold and Inlet

Port Injection 3. Direct Cylinder Injection (DI), the engine was operated using all these fueling modes.

5.3.1 Fuel carburetion method (CMI)

Carburetion by the use of a gas carburetor has been the simplest and the oldest technique. This system has advantages for a hydrogen engine. Firstly, central injection does not require the hydrogen supply pressure to be as high as for other methods. Secondly, central injection or carburetors are used on gasoline engines, making it easy to convert a standard gasoline engine to hydrogen or a gasoline/hydrogen engine. The disadvantage of central injection in internal combustion engine, the volume occupied by the fuel is about 1.7% of the mixture, whereas a carbureted hydrogen engine, using gaseous hydrogen, results in a power output loss of 15%. Thus, carburetion is not at all suitable for hydrogen engine, because it gives rise to uncontrolled combustion at unscheduled points in the engine cycle. Also the greater amount of hydrogen/air mixture within the intake manifold compounds the effects of pre-ignition. If pre-ignition occurs while the inlet valve is open in a premixed engine, the flame can propagate past the valve and the fuel-air mix in the inlet manifold can ignite or backfire. In a carbureted hydrogen engine, a considerable portion of the inlet manifold contains a combustible fuel-air mix and extreme care must be taken to ensure that ignition of this mix does not occur. Serious damage to the engine components can result when back fire occurs, Overend et al. (1999) & White et al. (2006).

5.3.2 Hydrogen inducted in inlet manifold and inlet port injection

The port injection fuel delivery system injects fuel directly into the intake manifold at each intake port by using mechanically or electronically operated injector, rather than drawing fuel in at a central point. Typically, the hydrogen is injected into the manifold after the beginning of the intake stroke. Electronic injectors are robust in design with greater control over the injection timing and injection duration with quicker response to operating under high-speed conditions. In port injection, the air is injected separately at the beginning of the intake stroke to dilute the hot residual gasses and cool any hot spots (Saravanan 2010). Since less gas (hydrogen or air) is in the manifold at any one time, any pre-ignition is less severe. The inlet supply pressure for port injection tends to be higher than for carbureted or central injection systems, but less than for direct injection systems COD (2001). Inlet manifold and inlet port injection, Overend et al. (1999). Inlet manifold or port injection methods of fuel induction, the induced volume of air per cycle is kept constant, and the power output can be controlled by the amount of fuel injected into the air stream, thus allowing lean operation. The fuel can either be metered by varying the injection pressure of the hydrogen, or by changing the injection duration by controlling the signal pulse to the injector, Overend et al. (1999).

Di-ethyl ether as ignition source for hydrogen in dual fuel mode -Self-ignition temperature of hydrogen fuel is very high. It is very difficult to ignite the combustion in compression ignition engine. So there is a need of external igniter to initiate the combustion. There are many oxygenated based ignition improvers available i.e. Dimethyl ether, Dimethoxymethane (DMM), Diethyl ether and Di-tertiary butyl peroxide etc.-Ethyl ether is one of the good ignition improvers that can be used for hydrogen fuel.

5.3.3 Direct injection of hydrogen in cylinder

Hydrogen is injected directly into the combustion chamber with the required pressure at the end of compression stroke. As hydrogen diffuses quickly, the mixing of hydrogen takes flame instantaneously. For ignition either diesel or spark plug is used as a source. The problem of drop in power output in manifold induction/injection can be completely eliminated by in-cylinder ignition. During idling or part load condition, the efficiency of the engine may be reduced slightly. This method is the most efficient one compared to other methods of using hydrogen. The power output of a direct injected hydrogen engine was 20% more than for a gasoline engine and 42% more than a hydrogen engine using a carburetor.

With hydrogen directly injected into the combustion chamber in a compression-ignition (CI) engine, the power output would be approximately double that of the same engine operated in the pre-mixed mode (Antunes 2009). The power output of such an engine would also be higher than that of a conventionally fueled engine, since the stoichiometric heat of combustion per standard kilogram of air is higher for hydrogen (approximately 3.37 MJ for hydrogen compared with 2.83 MJ for gasoline). While direct injection solves the problem of pre-ignition in the intake manifold, it does not necessarily prevent pre-ignition within the combustion chamber. In addition, due to the reduced mixing time of the air and fuel in a direct injection engine, the air/fuel mixture can be non-homogenous, Masood et al. (2007).

5.4 Abnormal combustion

The same properties that make hydrogen such a desirable fuel for internal combustion engines also bear responsibility for abnormal combustion events associated with hydrogen. In particular, the wide flammability limits, low required ignition energy, and high flame speeds can result in undesired combustion phenomena summarized as-as combustion anomalies. These anomalies include surface ignition and backfiring as well as auto ignition, Verhelst et al. (2009).

The suppression of abnormal combustion in hydrogen has proven to be quite a challenge and measures taken to avoid abnormal combustion have significant implications for engine design, mixture formation, and load control. Three regimes of abnormal combustion exist: knock (autoignition of the end gas region), pre-ignition (uncontrolled ignition induced by a hot spot, premature back flash, flashback, and induction ignition; this is a premature ignition during the intake stroke, which could be seen as an early form of pre-ignition) and backfire, Verhelst et al. (2009).

5.4.1 Pre-ignition

Pre-ignition is often encountered in hydrogen engines because of the low ignition energy and wide flammability limits of hydrogen. As a premature ignition causes the mixture to burn mostly during the compression stroke, the temperature in the combustion chamber rises, which causes the hot spot that led to the pre-ignition to increase in temperature, resulting in another earlier pre-ignition in the next cycle, Verhelst et al. (2005). This advancement of the pre-ignition continues until it occurs during the intake stroke and causes backfire. Due to the dependence of minimum ignition energy on the equivalence ratio, pre-ignition is more pronounced when the hydrogen–air mixtures approach stoichiometric levels. Also, operating conditions at increased engine speed and engine load are more prone to the occurrence of pre-ignition due to higher gas and component temperatures. In-cylinder pressure trace as well as the crank angle resolved intake manifold pressure for a combustion cycle in which pre-ignition occurred. A regular combustion event is shown for comparison. The data were taken on an automotive-size single cylinder hydrogen research engine at an engine speed of 3200 rpm and an IMEP of 7 bars for the regular combustion. It is interesting to note that the peak pressure for the pre-ignition case is higher than the regular combustion cycle. However, due to the early pressure rise that starts around 80° CA BTDC. The intake pressure trace for the pre-ignition case does not show any significant difference from the regular trace, because the pre-ignition occurred after the intake valves closed, Verhelst et al. (2009).

5.4.2 Backfire

Backfire is a violent consequence of the pre-ignition phenomena. Should pre-ignition occur at a point when the inlet valve is open, the inflamed charge can travel past the valve and into the inlet manifold, resulting in backfire. This problem is particularly dangerous in pre-mixed fuel inducted engines where there is the possibility that an ignitable fuel-air mix is present in the inlet manifold, Overend et al. (1999). The main difference between backfiring and pre-ignition is the timing at which the anomaly occurs. Pre-ignition takes place during the compression stroke with the intake valves already closed whereas backfiring occurs with the intake valves open. This result in combustion and pressure rise in the intake manifold, which is not only clearly audible but can also damage or destroy the intake system. Due to the lower ignition energy, the occurrence of backfiring is more likely when mixtures approach stoichiometric. Limited information available on combustion anomalies also indicates that pre-ignition and backfiring are closely related with pre-ignition as the predecessor for the occurrence of backfiring. Pre-ignition thereby heats up the combustion chamber, which ultimately leads to backfiring in a consecutive cycle. Consequently, any measures that help avoid pre-ignition also reduce the risk of backfiring. Another work has been done on optimizing the intake design and injection strategy to avoid backfiring. Although trends identified on hydrogen research engines indicated that combustion anomalies significantly limit the operation regime, optimization of the fuel injection strategy in combination with variable valve timing for both intake and exhaust valves, Verhelst et al. (2001).

5.4.3 Auto-ignition

When the end gas conditions (pressure, temperature, time) are such that the end gas spontaneously auto-ignites, there follows a rapid release of the remaining energy generating high-amplitude pressure waves, mostly referred to as engine knock. The amplitude of the pressure waves of heavy engine knock can cause engine damage due to increased mechanical and thermal stress. The tendency of an engine to knock depends on the engine design as well as the fuel-air mixture properties, Verhelst et al. (2009,). Knocking combustion is a common problem found in hydrogen-fuelled engines. It is detectable by the human ear as an audible knocking sound and by oscillations in pressure during combustion. There are many theories about how knock occurs and different types of knocking combustion have been categorized. The most common, detonation knock, describes an effect due to the self-ignition and explosion of the end gas - the unburned gas ahead of the flame.

5.5 Performance

Performance and emission of engine using hydrogen as fuel are discussed below.

5.5.1 Power output

The theoretical maximum power of a hydrogen engine depends on the air/fuel ratio and fuel injection method. Stoichiometric air/fuel ratio for hydrogen is 34:1. At this air/fuel ratio, hydrogen will displace 29% of the combustion chamber leaving only 71% for the air. As a result, the energy content of this mixture will be less. Since both the carbureted and port injection methods mix the fuel and air prior to it entering the combustion chamber, these systems limit the maximum theoretical power obtainable to approximately 85% of that of gasoline engines. For direct injection systems, which mix the fuel with the air after the intake valve has closed (and thus the combustion chamber has 100% air), the maximum output of the engine can be approximately 15% higher than that for gasoline engines. However, at a stoichiometric air/fuel ratio, the combustion temperature is very high and as a result it will form a significant amount of nitrogen oxides (NOx), which is a dangerous pollutant. Since one of the reasons for using hydrogen is low exhaust emissions, hydrogen engines are not normally designed to run at a stoichiometric air/fuel ratio, COD, Moduel-3.

5.5.2 Emissions

The combustion of hydrogen with oxygen produces water as its only product: $2H_2 + O_2 = 2H_2O$ The combustion of hydrogen with air however can also produce oxides of nitrogen (NOx): $2H_2 + O_2 + N_2 \rightarrow H_2O + N_2 + NO_x$ The oxides of nitrogen are created due to the high temperatures generated within the combustion chamber during combustion.

Oxides of nitrogen is the major problem in hydrogen operated dual fuel engine, which can be reduced by some of the following techniques:

- Exhaust gas recirculation
- Water injection
- Nitrogen / Helium addition
- Increased coolant flow rate
- High conductivity materials to dissipate heat
- Effective scavenging system
- Catalytic reduction

The following observation are drawn based on the review of earlier work on the exhaust gas recirculation:

- EGR cause an increase in ignition delay and a shift in the location of the start of combustion. This makes the products of combustion, spending shorter period at high temperatures, which lowered the NO_X formation rate.
- The shift of combustion towards expansion stroke results in smooth quenching of combustion process, which results in shorter combustion duration.

- Shorter combustion period yields a higher level of incomplete combustion products in the exhaust.
- If low NO_X emissions (< 5 ppm) are the requirement, the EGR strategy can produce 23 - 29 % more torque than the lean burn approach.
- By adopting EGR, CO increases by 6 times and HC decreases.
- Higher levels of soot can be produced due to increased rates of fuel pyrolysis at high temperatures prevailing during combustion.
- The heat losses to the walls increase with an increase in EGR rate.

Based on the literature survey conducted using various ignition enhancers, the following observations are made:

- DEE has a high cetane number of 125 and high energy density than diesel fuel.
- DEE for starting may vary from (57 % by mass) compared to an entire range of operation (2.5 % at full load to 3 % at no load).
- The improvement in brake thermal efficiency is around 19 - 48 % at full load conditions.
- The rate of increase in pressure rise is 3.2 bar/ CA at no load to 5.6 bar/ CA at full load for operated ethanol engine compared to diesel operation of 3 bars/ CA at no load and 5.2 bars/ CA at with full load
- DEE results in shorter ignition delay which lowers the maximum cylinder pressure.
- NO_X emission reduces significantly with DEE operation.
- LPG/DME mixture can operate quietly for a wide load range of from 2.1 to 5.2

Based on the literature survey conducted using Fuel Injection for Hydrogen, the following observations are made:

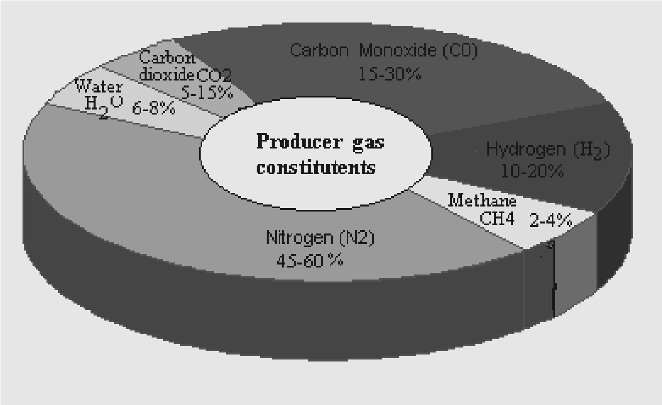
- Backfire and pre-ignition problems are severe in carburation system.

- The volumetric efficiency of the hydrogen-operated engine using carburation technique is 30 % less, due to the replacement of air by gaseous hydrogen in the intake manifold.
- The peak pressure of the hydrogen-operated engine is higher which leads to NO_X emission, noise, and vibration.
- In-cylinder injection type systems give the maximum volumetric efficiency of 78 % compared to port injection system of 60 %.
- NO_X concentration in the in-cylinder injection is higher than that of intake port injection system at the same equivalence ratio.
- Leak in the in-cylinder injector is a problem.
- Optimum injection timing is necessary for hydrogen injection system to get the best efficiency and power output.
- Proper injection duration, determines proper mixing of fuel with air. Hence injection duration needs optimization.
- Electrically controlled injectors are more versatile compared to hydraulically operated or mechanically operated injectors regarding performance, response, and flexibility in timings.
- The addition of diluents (Nitrogen, helium, water) improves the knock limited engine operation.
- The optimum diluents for highest brake thermal efficiency and power output are 30 % for Nitrogen, 10 % for helium and 2460 ppm for water.
- The performance of in-cylinder injection is superior to the intake port injection as the fuel-air equivalence ratio goes to stoichiometry.

PRODUCER GAS

PRODUCER GAS AND ITS CONSTITUENTS

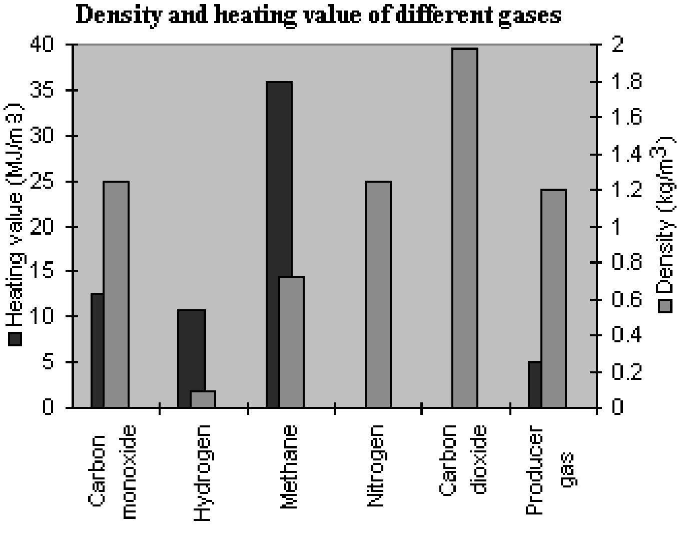
Producer gas is the mixture of combustible and non-combustible gases. The quantity of gases constituents of producer gas depends upon the type of fuel and operating condition.



PROPERTIES OF PRODUCER GAS

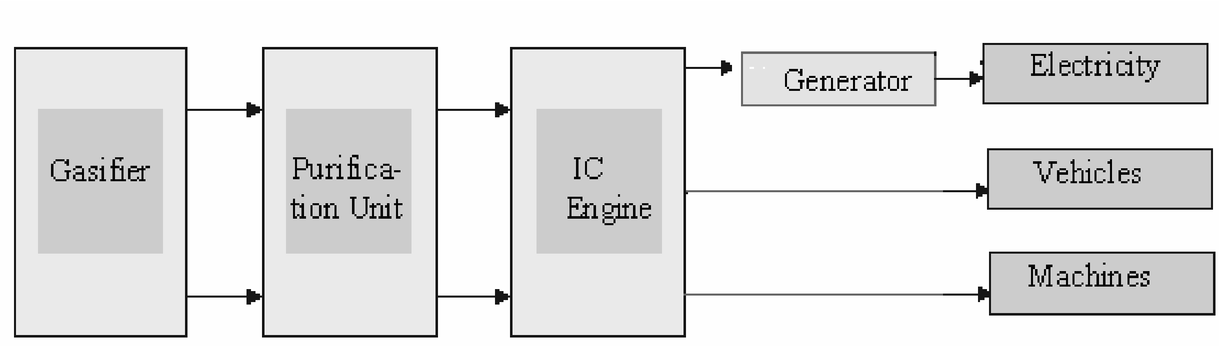
The heating value of producer gas varies from 4.5 to 6 MJ/m³ depending upon the quantity of its constituents. Carbon monoxide is produced from the reduction of carbon dioxide and its quantity varies from 15 to 30 % by volume basis. Although carbon monoxide possesses higher octane number of 106, its ignition speed is low. This gas is toxic in nature. Hence, human operator need to careful while handling gas.

Hydrogen is also a product of reduction process in the gasifier. Hydrogen posses the octane number of 60-66 and it increases the ignition ability of producer gas. Methane and hydrogen are responsible for higher heating value of producer gas. Amount of methane present in producer gas is very less (up to 4 %). Carbon dioxide and nitrogen are non-combustible gases present in the producer gas. Compared to other gas constituents, producer gas contains highest amount (45-60 %) of nitrogen. The amount of carbon dioxide varies from 5 to 15 %. Higher percentage of carbon dioxide indicates incomplete reduction. Water vapor in the producer gas occurs due to moisture content of air introduced during oxidation process, injection of steam in gasifier or moisture content of biomass fuels.



GASIFICATION

Gasification is basically a thermo chemical process which converts biomass materials into gaseous component. The results of gasification are the producer gas, containing carbon monoxide, hydrogen, methane and some other inert gases. Mixed with air, the producer gas can be used in gasoline or diesel engine with little modifications. The complete gasification system consists of gasification unit (gasifier), purification unit and energy converter - burners or internal combustion engine.



PRODUCTION OF PRODUCER GAS

Producer gas is essentially a mixture of Combustible gases, carbon monoxide and hydrogen, associated with large percent of non-combustible gases, N_2, CO_2, etc. It is prepared by passing air mixed with a little steam (about 0.35 kg / kg of coal) over a red hot coal or coke bed maintained at about 1,100^{0}C in a special reactor, called 'gas producer'.

It consists of a steelvessel, about 3m in diameter and 4 m in height. The vessel is lined inside with refractory bricks. It is provided with a cup and cone feeder at the top and a side opening for producer gas exit. At the base, it has inlets for passing air and steam. Moreover, the producer at the base is provided with an exit for the ash formed.

REACTIONS

The producer gas production reactions can be divided into four zones as follows:

(1) Ash zone is the lowest zone (about 0.8 m thick) consisting mainly of ash. The ash protects the grate (of the producer plant) from the intense heat of combustion. Moreover, the temperature of supplied air and steam is increased as they pass through this zone.

(2) Combustion Zone is the zone next to the ash zone. It is known as oxidation zone. Here the carbon burns and forms CO and CO_2. The temperature of this zone is about 1,100^{0}C.

$$C + O_2 \qquad CO_2$$

$$C + \tfrac{1}{2}\, 0_2 \qquad CO$$

(3) Reduction Zone :

Here carbon dioxide and steam combines with the red-hot coke and liberates free hydrogen and carbon monoxide.

$$CO_2 + C \qquad\qquad 2\ CO$$

$$C + H_2O \qquad\qquad CO + H_2$$

$$C + 2\ H_2O \qquad\qquad CO_2 + 2\ H_2$$

All these reduction reactions are endothermic, so the temperature in the reduction zone is about 1,000^{0}C. If no steam is supplied, the temperature of the producer further rises and this may **fuse** the ash refractory lining. To avoid these troubles and to producer richer gas, a little steam admixed with air is used. In actual practice, a balance between the air and steam supply is struck so as to maintain proper temperature of about 1,000^{0}C.

(4) Distillation zone:

Distillation zone in this zone (400 to800˚C), the down coming coal is heated by the out going gases, since as the gases give their sensible heat to the coal. The heat given by the gases and heat radiated from the reduction zone helps to distil the fuel, thereby volatile matter of coal is added to the out going gas.

Composition:

The average composition of producer gas is CO = 22 to 30%, H_2 = 8 to 12%, N_2 = 52 to 55%, and CO_2 = 3%. Its calorific value is about 1300 kcal/m^3.

Use:

It is cheap, clean and easily pre-parable gas and is used for heating open hearth furnaces (in steel and glass manufacture), muffle furnaces, retorts (used in coke and coal gas manufacture), etc., and as a reducing agent in metallurgical operations.

PRODUCER GAS ENGINES

Producer gas is used in internal combustion engine for power or electricity generation. Internal combustion engines are normally designed to run on diesel or gasoline fuel. Properties of producer gas- mixture are different from that of diesel or gasoline. Use of producer gas in internal combustion engines affects performance and other maintenance features of engines. This sections deals with various following issues concerned with use of producer gas in internal combustion engines.

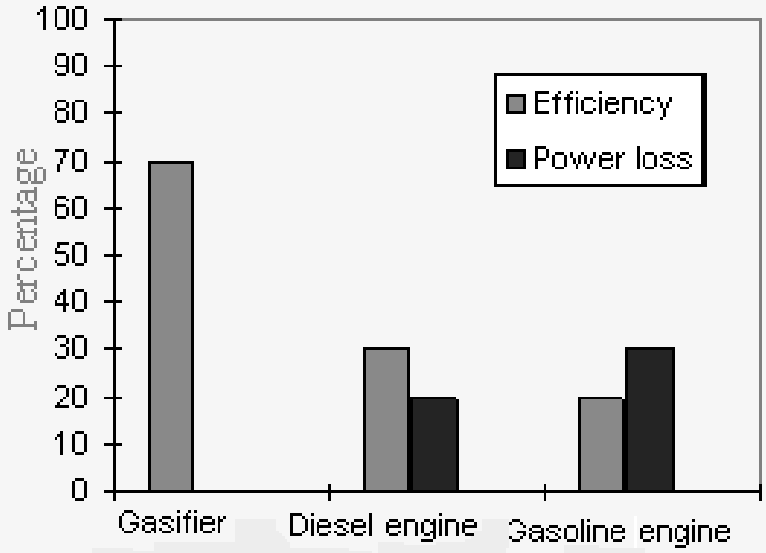
PEFORMANCE OF GASIFIER-ENGINE SYSTEM

Cold gas efficiency of producer gas in favorable condition can be 70%. In gasifier-engine system, losses also occur at different stages. Engine performance is expressed in terms of brake thermal efficiency. Overall efficiency of the system is the product of gasifier efficiency and brake thermal efficiency.

The actual efficiency of engine varies with design, size and running condition. Efficiency of diesel and gasoline engines under good condition is considered to be 30% and 20% respectively. The efficiency of engine run with producer gas goes down owing to lower density of gas-air mixture and other power losses associated with suction of mixture in engines.

Theoretically, gasoline and diesel engine operated on producer gas suffer a power loss of 30% and 20 % respectively. In practice, considering a wide range of producer gas quality, a power drop ranging from 25 % to 60 % can be expected when diesel or gasoline engine is run with producer gas

A typical composition of 4.5% CO_2, 27 % CO, 14% H_2, 3 % CH_4 and 51% N_2 has a lower heating value of 5.7 MJ/m^3 at normal ambient condition of 15^o C and pressure of 1 atm. The stoichiometric gas-mixture has an energy density of 2.5 MJ/m^3 compared to 3.5 MJ/m^3 for gasoline-air mixture and 3.3 MJ/m^3 diesel-air mixture.



Theoretical efficiency and power loss in different gasifier-engine system

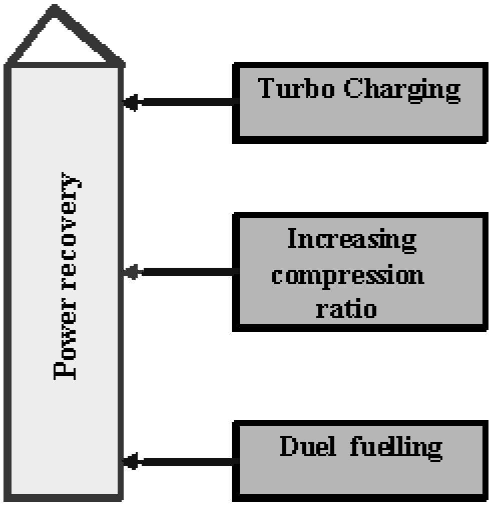
Operational difference between diesel and gasoline engine

There is significant difference between diesel and spark ignition engine system with respect to it's suitability for producer gas. In diesel engine, diesel is injected at the end of compression stroke and gets ignited immediately without any spark ignition. These will not the case with producer gas- air mixture. In fact, diesel engine cannot operate alone on producer gas as temperature and pressure is not sufficient to ignite gas-air mixture. Hence, during the injection of producer-gas mixture, some quantity of diesel is also injected in combustion chamber.

In gasoline engine, air-fuel mixture is sucked during suction stroke and mixture is ignited with a spark at the end of compression stroke. Gasoline engine running on producer gas can operate on producer gas alone without any injection of gasoline. This is certainly convenient in remote rural areas, where gasifier-engine system is used for power or electricity generation. In general, low speed engines with large displacement and combustion place have advantage over today's compact and high speed engines.

Conversion of gasoline engine to producer gas

Unaltered gasoline engine run with producer gas experiences the power loss of 30-50% depending upon the producer gas quality. Unaltered gasoline engine run with producer gas sound good from economical point of view. This approach is beneficial, for some application such as irrigation pump, which works at constant load and even at low load also. This approach is not practically workable for tractor or any other automobile which has to work under different loading condition.



In case already installed gasoline engine is converted to producer gas drive, some of the power can be recovered through supercharging or turbo charging. The turbocharger would be required to deliver the gas-air mixture into existing unaltered engine at differential pressure of 1 atm to achieve equivalent of compression ratio increase from 5 to 10. This compression can be achieved by reciprocating type of pump. The power for pump shall be provided by turbine run on exhaust of engine.

Compression ratio

Power loss in gasoline engine run on producer gas be recovered by increasing the compression ratio. Commercially built gas producers were usually operated at the compression ratio of 6.5 to 7.5. Keeping in mind hydrogen content in producer gas and its effect on flame speed, compression ratio as high as 10 is said to be technically and economical feasible. There are other operational problems with higher compression ratio. Engine with higher compression ratio are difficult to start, creates vibrations, and increases wear and tear on piston, reducing the life of the system.

BIO GAS

The general composition of biogas from farm waste is

Methane CH_4 = 55% to 70%

Carbon dioxide CO_2 = 27% to 44%

Hydrogen H_2 = 1%

Hydrogen Sulfide H_2S = 1% to 2 %

Biomethanation

Biomethanation is the process of conversion of organic matter in the waste (liquid or solid) to biogas and manure by microbial action in the absence of air.

Properties

Biogas has a higher octane number (120) compared to 87 of gasoline. The auto ignition temperature (650° C) is higher than petrol (257 ° C) which makes it a safer fuel. Since calorific value of biogas (19550 kJ/kg) is lesser than gasoline (42000 kJ/kg), and has higher octane number it is possible to use higher compression ratio for same size of engine to generate same amount of power.

Also other properties of biogas are, its stoichiometric air / fuel ratio is 6.68:1 and Flammability limit is 5 to 15 % volume in air gas mixture. Density of biogas is 1.1 kg/m^3.

System required for the use of BIOGAS in engines:

Gas carburetor

A gas carburettor, especially designed for biogas, was used to mix the gas and the air. It contains a control valve and a T-tube with a venturi throat. Figure shows its schematic diagram. The amount of biogas was controlled by the throttle valve of the carburettor to improve the properties of biogas and air mixture. Figure presents a schematic diagram of the gas supply system. The gas carburettor was installed in the inlet manifold. In this way, the biogas was first mixed with air from air filter inside venturi throat of the gas carburettor. And then, the mixture of biogas and air was introduced to the combustion chamber of the engine.

Installing a spark ignition system

The original fuel injection system was eliminated. A spark plug was installed in the position of the original diesel injector orifice. The spark plug should be considerably chosen so that its electrodes could be located at a proper position of the combustion chamber.

Appending a biogas control apparatus

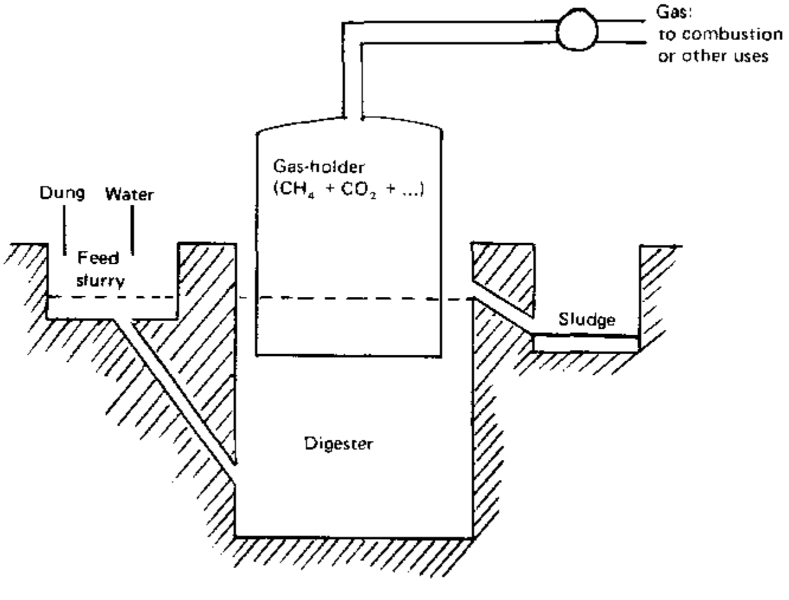
A conical valve was used in order to control the amount of biogas admitted to the gas carburettor. In addition, a linkage which connects the conical throttle of the gas carburettor and governor of the engine was mounted on the engine. Moreover, a main valve was used for controlling the flow of biogas. A gas flow meter was used for measuring the flow rate of biogas. And a U-shape manometer was used for measuring the pressure of biogas, and a pressure regulator for maintaining pressure of biogas was installed on the engine.

Gobar Gas Plant with neat sketch.

Biogas is produced by the degradation of biological matter by the bacterial action (of anaerobic bacteria's) in the absence of free oxygen. Probably the cheapest and easily obtainable biogas is gobar gas (or dung gas), which is produced by the anaerobic fermentation of cattle dung. Biogas can also be produced from the sewage waste and other organic wastes.

GOBAR GAS:

The raw material for the gas is called dung, which is subjected to anaerobic fermentation (i.e., fermentation in the absence of free air, caused by fresh cattle dung and water, is poured. Anaerobic bacteria's (i.e., which can survive and function in the absence of free air), present in the dung, digest this slurry forming mainly methane and carbon dioxide. The optimum temperature for this fermentation is 34 – 48^{0}C. The gas generated is collected in a steel gas is holder, placed on the top of digestion tank. The average composition of gobar gas is: CH_4 = 55%; H_2 = 7.4%; CO_2 = 35.0%, N_2 = 2.6%; and traces of H_2S. Its average gross calorific value is 1200 kcal/m^3.



The essentials of gobar gas plant are:

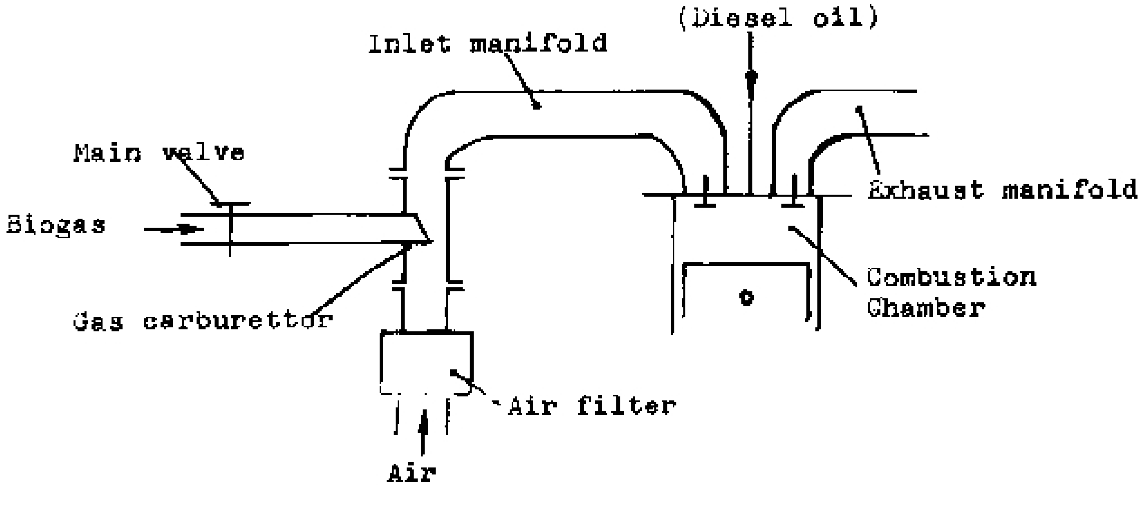
- (i) A 'digester', a well constructed of masonry work, dug and built usually below the ground level:
- (ii) A 'gas holder', made up of weld steel sheets, which covers digester,
- (iii) A pipeline.

Advantages

1. It has been found that 4.25 kg of fresh cattle dung (or 1kg dry cattle dung) gives approximately 160 liters of gobar gas, which can supply 188 kcal of heat. On other hand, 1 kg of dry dung or direct burning gives only 23.4 kcal of effective heat. Thus, gobar gas production is highly economical.
2. The gas has all the advantages of gaseous fuel (such as flexibility, optimum utilization of waste, cleanliness of utensils and surrounding areas, absence of smoke, dust, dirt, etc.).
3. It does not contain the poisonous gas, carbon monoxide, as an ingredient.
4. It can provide the flame temperature of 540^0C, with proper burners.
5. Gobar gas also gives simultaneously excellent yield of good manure. The nitrogen content of the manure is 2% as against 0.75% in farm yard manure.

Use of Bio Gas in diesel engines.

The biogas can be used in C.I engine as a dual fuel. The biogas can be introduced in the engine with air during suction stroke and compressed. A small quantity of diesel fuel (15 – 20%) is injected towards the end of compression, to initiate the combustion of biogas – air mixture. The diesel fuel ignites first and heat released by combustion leads to the combustion of biogas air mixture. The air flow rate is kept constant as in normal diesel engine and gas flow rate is regulated to achieve different outputs. Diesel fuel injected is always fixed amount. The gas flow rate is controlled by a throttle and diesel fuel flow rate by rack in the fuel pump. These two are linked together by an automatic governor.



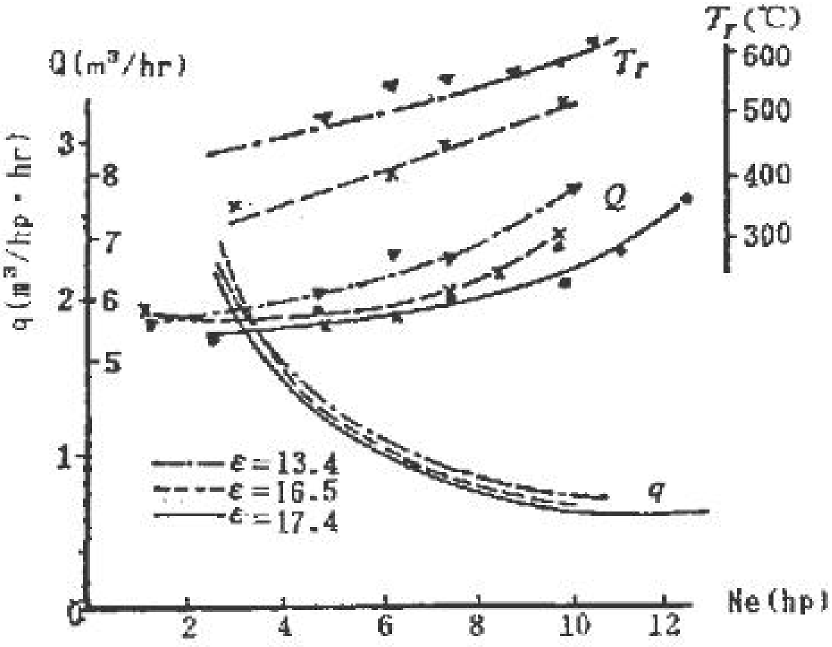
In dual fuel C.I engine, biogas can substitute for about 80% of the normal diesel fuel consumption. Existing diesel engines in the rural areas like power pumping sets and small generators can be easily modified as biogas diesel dual fuel engines.

A small valve controlled pipe can introduce biogas into the inlet manifold of diesel engine. Initially the engine is started as a diesel engine and brought up to the required output. Then the gas valve slowly opened manually, allowing the gas to flow into inlet manifold and mix with air. If a speed governor is fitted in the engine, it automatically educes diesel flow rate. (If there is no speed governor, diesel flow is reduced manually) Gas flow rate can be gradually increased until diesel flow rate is just above minimum required.

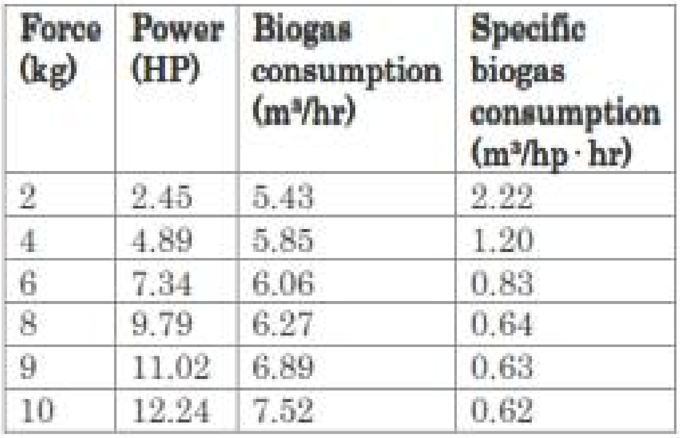
Before stopping engine, gas flow is gradually reduced and shut off and engine is run on diesel fuel alone for few minutes. This is to prevent gas from remaining in the inlet manifold.

Load Performance of the engine:

The load performances of the engine at three compression ratios were tested. The results are shown in Figure Specifically, when the engine using biogas alone operated at 2000 RPM with 39.2° rank angle of spark timing and compression ratio being 17.4: 1, its load performance data are shown in Table.



The load performances of the engine at three compression ratios



Force (kg)	Power (HP)	Biogas consumption (m^3/hr)	Specific biogas consumption ($m^3/hp \cdot hr$)
2	2.45	5.43	2.22
4	4.89	5.85	1.20
6	7.34	6.06	0.83
8	9.79	6.27	0.64
9	11.02	6.89	0.63
10	12.24	7.52	0.62

The load performance of diesel engine using biogas

From the Figure and the Table, it can be seen that the maximum power of the engine operating on biogas alone was about the 90 percent that of the engine's original power. The temperature of the exhaust gases were ranged within 550 °C to 610"C, which was slightly higher than the usual temperature level. The heat consumption rate was 3000 kcal/hp · hr.

Stability of engine performance at low speed

The engine using biogas alone showed a stable operation at a low speed. No vibration occurred. And the engine running with biogas alone performed well at low speed (around 400-500 RPM).

Start performance

The engine using biogas alone could be started well as other gasoline engines do. No other fuels were needed to start the engine.

Discussion

The compression ratio has a great effect on thermal efficiency and combustion performance of the engine. High compression ratio means a high thermal efficiency. However, too big in an increase of the compression ratio may cause detonation of the engine. It was unknown what the maximum compression ratio was. However, according to experiments, when the compression ratio reached 17.4: 1, no severe combustion and detonations were observed. From the Figure, it can be seen that the specific biogas consumption was not very high within a very wide load range when the combustion ratio was 17.4. And the power was also not lower than that of engine's original power. This suggests that biogas has a higher anti-detonation value. Therefore, to increase compression ration is an effective way for improving the performance of the engine operating on biogas alone.

LPG (Liquefied Petroleum Gas)

The additives added with LPG are

1. Hydrogen (H_2)
2. Methane (CH_4)
3. Methanol (CH_3 OH)
4. Carbon monoxide (CO)

Major constituents of LPG:

LPG (Liquefied Petroleum Gas) is predominantly propane with iso-butane and n-butane.

LPG fuel is mainly a mixture of propane and butane stored in steel cylinders in liquid form under a pressure of approximately 7 kg/cm^2.

Advantages of LPG

1. Propane has low cold-start emissions due to its gaseous state.
2. Propane has lower peak pressure during combustion than conventional fuels, which generally reduces noise and improves durability.
3. LPG fuel systems are sealed and evaporative losses are negligible.
4. Propane is easily transportable and offers 'stand-alone' storage
5. LPG vehicles do not require special catalysts.
6. Propane contains negligible toxic components.
7. LPG has lower particulate emissions and lower noise levels relative to diesel, making propane attractive for urban areas. Noise levels can be less than 50% of equivalent engines using diesel.
8. Propane's emissions are low in greenhouse gases and low in NOx, thus they are low in ozone precursors.
9. Increases in future demand for LPG can be easily satisfied from both natural gas fields and oil refinery sources.
10. Emissions of PAH and aldehydes are much lower than those of diesel-fuelled vehicles.
    It is cheaper than gasoline.
12. It gives better manifold distribution and mixes easily with air.
13. It is highly knock resistant.
14. Residue and oil contamination is small, as it burns cleanly.
15. Crankcase oil dilution is small, thereby resulting in increased engine life.

Limitations of LPG

Although LPG has a relatively high energy content per unit mass, its energy content per unit volume is low which explains why LPG tanks take more space than diesel fuel tanks of the same energy storage capacity.

1. Propane tanks are pressure vessels and thus weigh more than the equivalent diesel tank.
2. Propane is heavier than air, which requires appropriate handling.
3. Propane vapor flammability limits in air are wider than those of petrol, which makes LPG, ignite more easily.
4. Propane has a high expansion coefficient so that tanks can only be filled to 80% of capacity.
5. Propane in liquid form can cause cold burns to the skin in case of inappropriate use.
6. Due to its faint odor, leakage cannot be easily detected.
7. LPG is advantageous only in engines working under high compression ratios.
8. Its octane number is quite low and the load sensitivity is very high.

Modifications required for Diesel Engine for the use of LPG:

In the case of using LPG as a diesel replacement, a difficulty arises as it has a low cetane number and thus the auto-ignition temperature is considerably higher than that of diesel. To achieve ignition temperatures, the compression ratio must be increased to impractically high levels (~25:1). To overcome this it is necessary to convert the engine to spark ignition which also requires decreasing the compression ratio to ~13:1, hence also reducing the thermal efficiency and increasing the greenhouse emissions as compared to a diesel only system.

Alternatively using a relatively complicated dual-fuel system in which a small quantity of diesel (~15% of the total fuel blend by volume) is injected into the cylinder to act as a source of ignition for the LPG. In this way the benefits of improved efficiency and reduced emissions from the higher compression ratios can be captured while using LPG.

Diesel engines can be converted to run partly on LPG, partly on diesel. This method uses the combustion of the diesel to ignite the LPG. The benefits include large increases in power and reduction in emissions, particularly the black smoke often associated with diesels. Typically a ratio of 30% LPG to 70% diesel is possible.

No adjustments are required to the diesel injection system and fuel savings come from the fact that throttle openings are lower due to the greatly increased power, which basically means you do not have to press the accelerator as hard to get the same performance. Fuel savings upwards of 30% are possible with the increased power levels seen as a major benefit to users.

Performance and emmission characteristics:

Performance Charateristics

The air: fuel volumetric ratio affects the quantities of fuel and oxygen that independently enter the combustion chamber which in turn affects both the engine power output and the tailpipe emissions.

Under given conditions of atmospheric pressure, ambient temperature, engine speed etc, a modern vehicle engine designed to operate on petrol inducts air into the combustion chamber (cylinder) and the fuel is injected as a mist either into the inlet manifold or directly into the combustion chamber.

When the engine is converted to operate on LPG, the gas is normally metered into the inlet manifold which has two main effects.

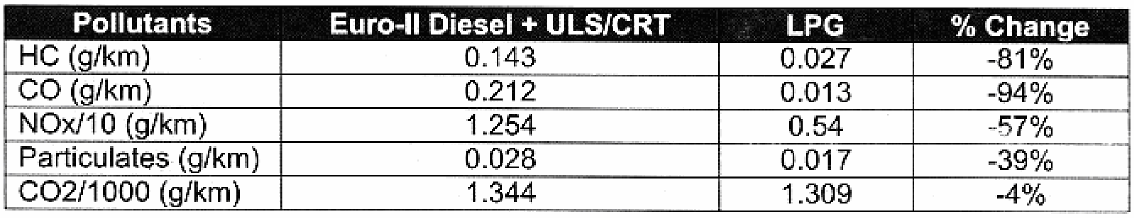
Since the volume of gas is considerably larger than that of the liquid fuel otherwise injected, it will displace a significant proportion of the air volume and thus reduce the total air: fuel mixture resulting in a significant loss of power.

Improved mixing of the air: LPG mixture may lead to a slight improvement in combustion and hence engine efficiency.

E

Emission characteristics

The main constituent of LPG is propane. Lower carbon-to-hydrogen ratio, higher octane rating and its ability to form a homogeneous mixture inside the combustion chamber enable it to produce lesser emissions compared to conventional fuels. Table gives a comparative emissions status from diesel and LPG fuel.



Pollutants	Euro-II Diesel + ULS/CRT	LPG	% Change
HC (g/km)	0.143	0.027	-81%
CO (g/km)	0.212	0.013	-94%
NOx/10 (g/km)	1.254	0.54	-57%
Particulates (g/km)	0.028	0.017	-39%
CO2/1000 (g/km)	1.344	1.309	-4%

CNG(Compressed Natural Gas)

CNG (Compressed Natural Gas) is usually around 70-90% methane with 10-20% ethane, 2-8% propane's, and decreasing quantities of the higher HCs up to butane.

Limitations

The major disadvantage of compressed gas is the reduced range. Vehicles may have between one to three cylinders (25 MPa, 90-120 liter capacity), and they usually represent about 50% of the gasoline range.

As natural gas pipelines do not go everywhere, most conversions are dual-fuel with gasoline. The ignition timing and stoichiometry are significantly different, but good conversions will provide about 85% of the gasoline power over the full operating range, with easy switching between the two fuels. Concerns about the safety of CNG have proved to be unfounded.

Natural Gas in CI Engine:

Natural gas is used in diesel engines in two methods. In one method the diesel engine is made to work on dual fuel mode. In the other method it works in full natural gas mode.

In dual fuel mode the engine runs with diesel as well as natural gas. The engine starts and ideals as normal diesel engine. And after some speed and load the engine switches to dual fuel mode automatically.

In full natural gas mode the diesel engine is converted to a spark ignited engine. This requires replacement of diesel fuel system by spark ignition system, fitment of gas carburetor, and reduction in compression ratio. However, switch back to diesel operation is not possible.

Engine Modifications Required to use natural gas in Diesel Engine

To run existing diesel engines in natural gas some modifications to be done. They are:

1. Removal of Diesel fuel injection system.
2. Introduction of Spark ignition system.
3. Fitting spark plugs Instead of injectors.
4. Connecting Gas carburetor to engine.
5. Fitment of turbo charger.

To run existing petrol engines in natural gas some modifications to be done. The conversion kit is available in the market it consist of following items. They are:

1. CNG storage tank

2. Pressure regulator
3. Gas carburetor
4. Fuel selection switch
5. Gas filling valve
6. Petrol solenoid

So these are the new components to be installed in the existing petrol engine to run the engine either by CNG or petrol. Hardly will it take an hour to modify the existing petrol engine to CNG operated engine.

Because of its characteristics, natural gas can be used in spark ignition engines, but in compression ignition engines a proportion of diesel fuel is usually required to trigger ignition. Alternatively, diesel engines can be converted to spark ignition for natural gas use.

For diesel engines, the conversion to a compression ignition dual (Mixed) fuel configuration involves use of a pilot supply of diesel to ignite the natural gas. This requires the addition of a gas fuel system alongside the existing diesel fuel system, together with a mechanism for regulating the proportion of diesel and gas for the engine speed and load conditions.

The engine efficiency for this configuration is about the same as that for a diesel engine. The efficiency of dual (mixed) fuel systems can be equal to or higher than for diesel at high loads, but lower at part loads. For this reason, the overall efficiency in service is lower than for diesel. This chapter deals with single fuel vehicles so that dual fuel vehicles have not been examined. It is to be expected, based on results of LPG dual fuel vehicles, that emissions reductions from dual fuel vehicles will not be as large as those from single fuel vehicles.

Conversion of diesel engines to spark ignition engines running solely on natural gas requires more extensive modification, in that the diesel fuel injectors in the cylinder head will be replaced by spark plugs, and an ignition system added to the engine. A compression ratio lower than that of the diesel is likely to be required. Also, a larger cylinder capacity than that required for a dual (mixed) fuel system may be needed, to provide the same energy content.

Most components of the kit are common for both CI and SI engines except that CI engine kit has a festo valve, rack limiter and airline are also added. The engine is started as a diesel engine and gradually, proportionally to the load, the engine starts using natural gas at a particular speed called change over speed. A small quantify of diesel fuel (pilot fuel) is used as ignition source. In order to achieve more power, the natural; gas addition to the intake air is increased. The gas is metered by the venture through a load regulator.

Conversion Kits for the Diesel Engine to use Dual Fuel

I. Cylinder Tank : Cylindrical tanks designed for storage of CNG at a pressure of 200 bar. A typical tank capacity is 60 liters and 4 such tanks give a range of 200 km.

II. Refueling Connection : Multistage pressure regulator in which the gas pressure is reduced from the CNG filling station to the CNG tanks.

III. CNG pressure regulator: Multistage pressure regulator in which the gas pressure is reduced from the CNG tank pressure to a pressure just below the atmospheric pressure. Thus natural gas flow from this pressure regulator, when the engine is not running has overcome by its design.

IV. Over speed limiter: Pneumatically operated safety value which will close the gas supply to the engine if the engine speed reaches maximum allowable speed.

V. Load Regulator: Gas valve linked to the accelerator pedal which controls the gas flow as per engine load.

VI. Diesel fuel limited: Allows full load diesel flow up to a certain speed and reduces diesel flow to the pilot valve (about 30% of the full load) beyond the speed called changeover speed.

VII. Venturi: Gas air mixing and metering device located at the downstream of the engine air filter. This meters the gas flow proportionate to the engine speed.

VIII. Change over switch: Actuate the electrical circuits in the system to automatically change the mode of operation from diesel to pilot injection mode at the changeover speed of the engine.

Performance of CNG Engine :

The efficiency of at full load is usually equal or better than that of the original diesel engine. At part load, the efficiency is lower, but still better than that of a spark ignited (Otto) engine. The use of 20% to 25% pilot diesel fuel is preferable to avoid poorer part load efficiency and overheating of injectors.

Comparision of properties of natural gas with conventional fuel:

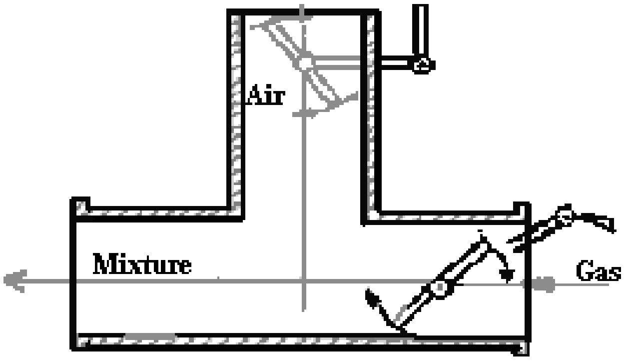
The auto ignition temperature of methane is about twice as high as that of gasoline, suggesting less chance o ignition due to contact with hot surfaces.

The flammability limits of methane are higher and wider than those of gasoline or diesel fuel.

The storichiometric ratio of methane is higher than gasoline or diesel fuel because methane has a higher percentage of hydrogen.

Gas-fuel mixture

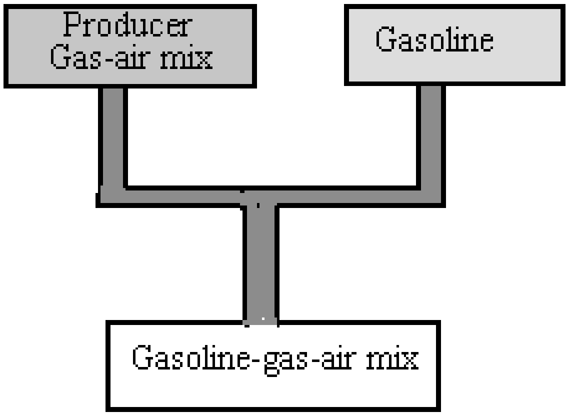
In the case of engine run on gasoline, gasoline-air mixture is adjusted automatically by carburetor and controlled by accelerator. Finding the correct gas-air ratio in producer gas drive engine is difficult as gas composition changes over a run, sometimes drastically. There are different kinds of valves ranging from simple hand operated valve to fully automatic valve for control of gas-air mixture.



Hand operated valve

Due fuelling

One of the most widely used and convenient method to increase the power output of engine is duel fuelling. Dual fuelling is good compromise between gasoline savings, convenience and ease of operations. In dual fuelling, gas-air mixture is injected with small amounts of gasoline. Degree of dual fuelling depends upon the engine load and independence one need in use of producer gas.



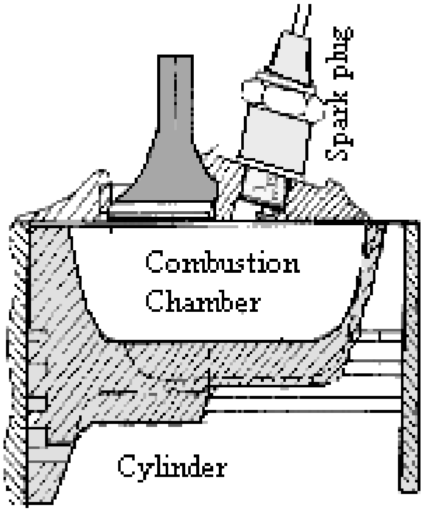
Three commonly used dual fuelling methods are:

1. Dual fuelling on continuous basis, meaning small amounts of gasoline with gas-air mixture.
2. Starting the engine on gasoline and then switching over to producer gas drive.
3. Dual fuelling when additional power is needed to overcome the load, for instance, on hills.

*CONVERSION OF DIESEL ENGINE TO **PRODUCER** GAS*

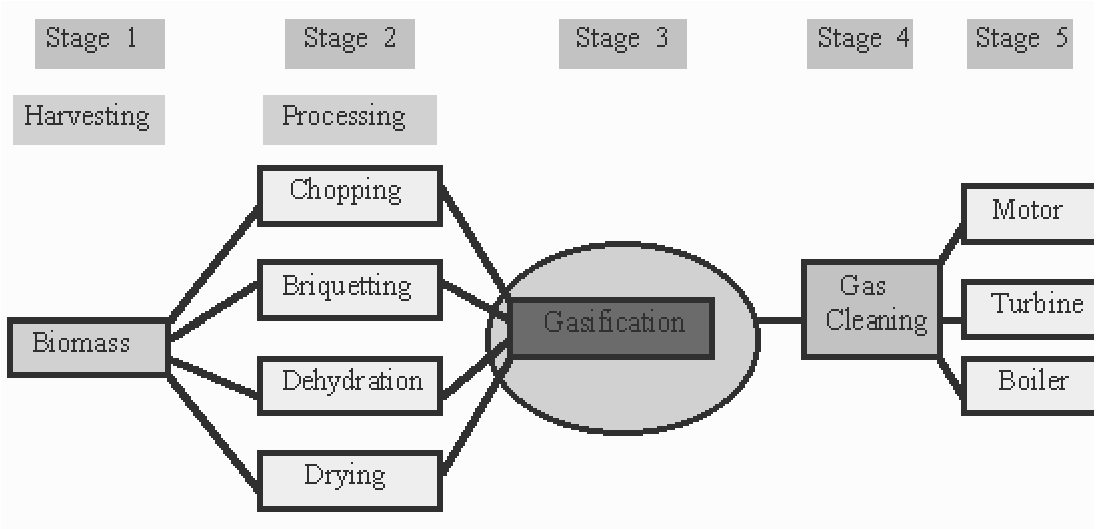
Diesel engines are compression ignition engines with compression ratio of 16-24 depending on whether they are direct combustion chamber, pre-combustion chamber, four strokes or two strokes. Fuel is ignited by high gas air temperature. As diesel engine cannot be operated on producer gas alone, it need to be operated on dual fuel or converted completely into spark ignition engine.

Complete rebuilding of entire engine is expensive and time consuming job. Power drop in diesel engine converted to spark ignition is not as sever as gasoline engine running on producer gas. In case of dual fuelling, modification is confined to a special induction manifold and gas-air mixer as converted in gasoline engines. The pilot injection of diesel amounted to 10 - 25% of original consumption. For economical reason, it is best to inject the amount of diesel necessary for smooth operation of engine.



Complete conversion of diesel engine to gas drive

GASIFICATION



Complete Gasification Process

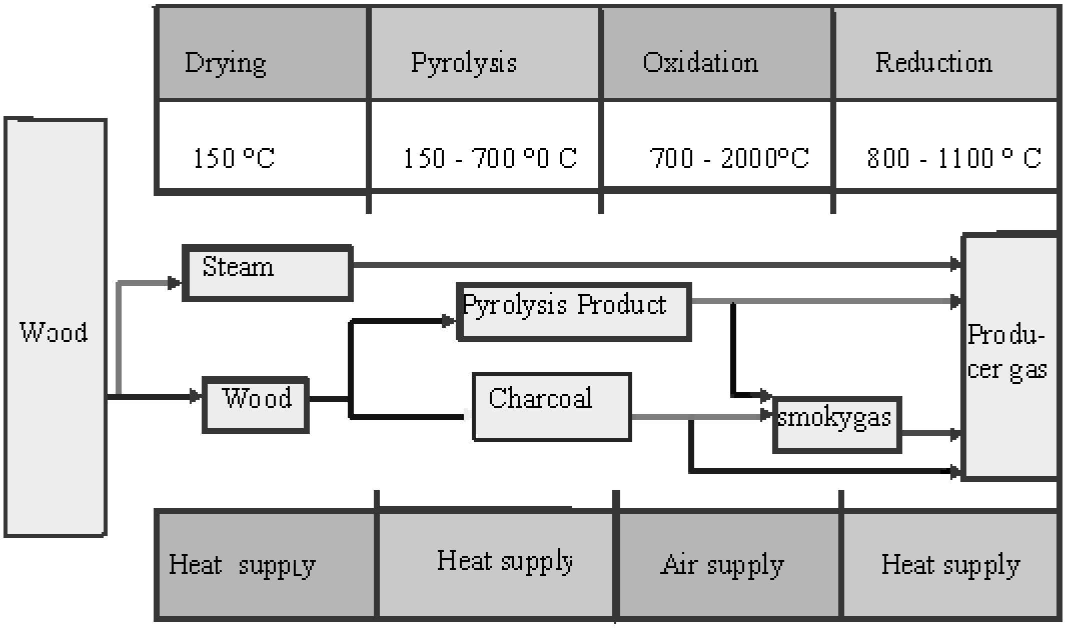
The essence of gasification process is the conversion of solid carbon fuels into carbon monoxide by thermo chemical process. The gasification of solid fuel is accomplished in air sealed, closed chamber, under slight suction or pressure relative to ambient pressure. Gasification is quite complex thermo chemical process. Splitting of the gasifier into strictly separate zones is not realistic, but nevertheless conceptually essential. Gasification stages occur at the same time in different parts of gasifier.

DRYING

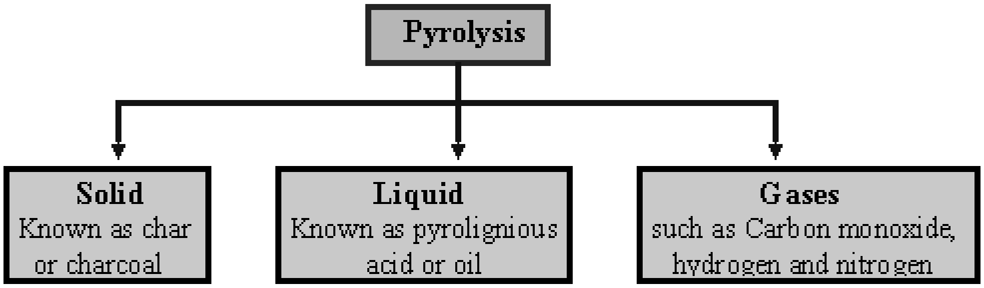
Biomass fuels consist of moisture ranging from 5 to 35%. At the temperature above 100 °C, the water is removed and converted into steam. In the drying, fuels do not experience any kind of decomposition.

PYROLYSIS

Pyrolysis is the thermal decomposition of biomass fuels in the absence of oxygen. Pyrolysis involves release of three kinds of products: solid, liquid and gases. The ratio of products is influenced by the chemical composition of biomass fuels and the operating conditions. The heating value of gas produced during the pyrolysis process is low (3.5 - 8.9 MJ/m^3). It is noted that no matter how gasifier is built, there will always be a low temperature zone, where pyrolysis takes place, generating condensable hydrocarbon.



Conversion of biomass into producer gas



OXIDATION

Introduced air in the oxidation zone contains, besides oxygen and water vapors, inert gases such as nitrogen and argon. These inert gases are considered to be non-reactive with fuel constituents. The oxidation takes place at the temperature of 700-2000°c.

Heterogeneous reaction takes place between oxygen in the air and solid carbonized fuel, producing carbon monoxide. Plus and minus sign indicate the release and supply of heat energy during the process respectively.

$$C + O_2 = CO_2 + 406 \text{ [MJ/kmol]}$$

In reaction 12.01 kg of carbon is completely combusted with 22.39 m^3 of oxygen supplied by air blast to yield 22.26 m^3 of carbon dioxide and 393.8 MJ of heat.

Hydrogen in fuel reacts with oxygen in the air blast, producing steam.

$$H_2 + \frac{1}{2} O_2 = H_2O + 242 \text{ [MJ/kmol]}$$

REDUCTION

In reduction zone, a number of high temperature chemical reactions take place in the absence of oxygen. The principal reactions that take place in reduction are mentioned below.

Boudouard reaction

$$CO_2 + C = 2CO - 172.6 \text{ [MJ/kmol]}$$

Water-gas reaction

$$C + H_2O = CO + H_2 - 131.4 \text{ [MJ/kmol]}$$

Water shift reaction

$$CO_2 + H_2 = CO + H_2O + 41.2 \text{ [MJ/kmol]}$$

Methane production reaction

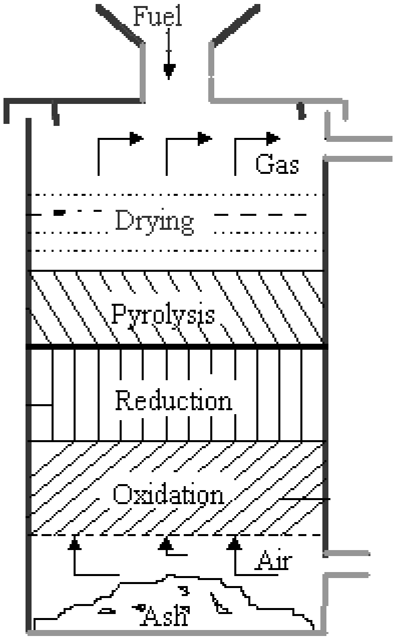
$$C + 2H_2 = CH_4 + 75 \text{ [MJ/kmol]}$$

Main reactions show that heat is required during the reduction process. Hence, the temperature of gas goes down during this stage. If complete gasification takes place, all the carbon is burned or reduced to carbon monoxide, a combustible gas and some other mineral matter is vaporized. The remains are ash and some char (unburned carbon)

GASIFIERS

Design of gasifier depends upon type of fuel used and whether gasifier is portable or stationary. Gas producers are classified according to how the air blast is introduced in the fuel column. History of gasification reveals several designs of gasifiers.

UPDRAFT GAS PRODUCER



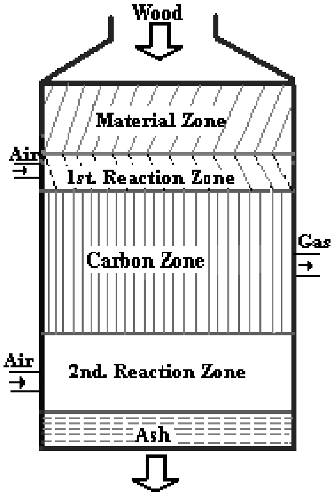
An updraft gasifier has clearly defined zones for partial combustion, reduction, and pyrolysis. Air is introduced at the bottom and act as countercurrent to fuel flow. The gas is drawn at higher location. The updraft gasifier achieves the highest efficiency as the hot gas passes through fuel bed and leaves the gasifier at low temperature. The sensible heat given by gas is used to preheat and dry fuel. Disadvantages of updraft gas producer are excessive amount of tar in raw gas and poor loading capability. Hence it is not suitable for running vehicle.

DOWNDRAFT GAS PRODUCER

In the updraft gasifier, gas leaves the gasifier with high tar vapor which may seriously interfere the operation of internal combustion engine. This problem is minimized in downdraft gasifier. In this type, air is introduced into downward flowing packed bed or solid fuels and gas is drawn off at the bottom. A lower overall efficiency and difficulties in handling higher moisture and ash content are common problems in small downdraft gas producers. The time (20-30 minutes) needed to ignite and bring plant to working temperature with good gas quality is shorter than updraft gas producer. This gasifier is preferred to updraft gasifier for internal combustion engines.

TWIN FIRE GAS PRODUCER

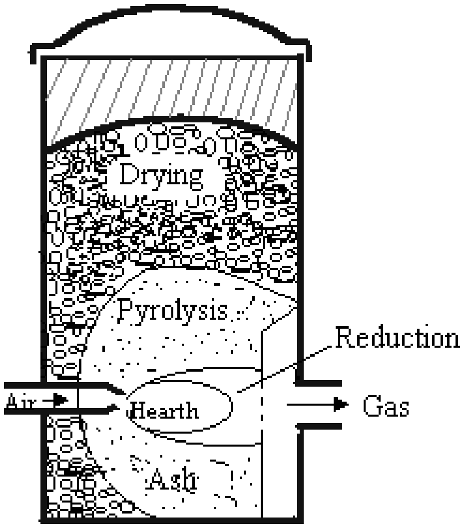
The advantage of co-current and counter-current gasifiers are combined in a so a called twin-fire gasifier. It consists of two defined reaction zones. Drying, low-temperature carbonization, and cracking of gases occur in the upper zone, while permanent gasification of charcoal takes in lower zone. The gas temperature lies between 460 to 520^{o} C. Total process takes place with under pressure of -30 mbar. Twin-fire gasifier produces fairly clean gas.



CROSSDRAFT GAS PRODUCER

Cross draft gas producers, although they have certain advantages over updraft and downdraft gasifiers, they are not of ideal type. The disadvantages such as high exit gas temperature, poor CO_2 reduction and high gas velocity are the consequence of the design. Unlike downdraft and updraft gasifiers, the ash bin, fire and reduction zone in cross draft gasifiers are separated. These design characteristics limit the type of fuel for operation to low ash fuels such as wood, charcoal and coke.

The load following ability of cross draft gasifier is quite good due to concentrated partial zones which operates at temperatures up to 2000 ^{o} c. Start up time (5-10 minutes) is much faster than that of downdraft and updraft units. The relatively higher temperature in cross draft gas producer has an obvious effect on gas composition such as high carbon monoxide, and low hydrogen and methane content when dry fuel such as charcoal is used. Cross draft gasifier operates well on dry air blast and dry fuel.



9.3.5. Hydrogen

A number of companies have built automobiles with prototype or modified engines which operate on hydrogen.

— A H_2-powered car being developed in Melbourne University Department of Mechanical Engineering is achieving 40 percent energy saving over conventional petrol engine. The car is a converted Ford Cortina Wagon which carries enough fuel in 4-cylinders to travel upto 50 km at a speed of 130 km/h.

— German cars are so developed that they can be converted for driving either gasoline or H_2 by making a few simple adjustments. Presently a few vehicles are running on road as there are very few public filling stations for liquid H_2. Many more are planned for future.

Advantages of hydrogen as I.C. engine fuel :

1. *Low emissions.* Essentially no CO or HC in the exhaust as there is no carbon in the fuel. Most exhaust would be H_2O and N_2.
2. *Fuel availability.* There are a number of different ways of making hydrogen, including electrolysis of water.
3. Fuel leakage to environment is *not a pollutant.*
4. High energy content per volume when stored as liquid. This would give a large vehicle range for a given fuel tank.
5. Hydrogen-air mixture burns *ten-times faster* compared to gasoline-air mixture. Since the burning rate is considerably high, it is *more preferred in high speed engines.*
6. Hydrogen-ignition limits are much wider than gasolines. So it can burn easily and *give considerably higher efficiency.*
7. Hydrogen has high self-ignition temperature (S.I.T.) but very *little energy* (1/50 th of gasoline) is *required to ignite it.*
8. The exhaust heat can be used to *extract H_2 from the hybride reducing the load engine.*
9. Besides being a relatively clean burning renewable source, H_2 as I.C. engine fuel is *very efficient* as there are *no losses associated with throttling.*

Disadvantages :

1. The *handling of H_2 is more difficult* and *storage requires high capital and running cost particularly for liquid H_2.*
2. *Difficult to refuel.*
3. *Poor engine volumetric efficiency.* Any time a gaseous fuel is used in an engine, the fuel will displace some of the inlet air and poorer volumetric efficiency will result.
4. Fuel cost would be high at present day technology and availability.
5. Can detonate.
6. High NO_x emissions because of high flame temperature.
7. *In hydrogen engines there is a danger of back fire and induction ignition which can melt the carburettor. Therefore in H_2-fuel system, flame traps, flask back arresters are necessary. Additionally, crankcases must be vented to prevent accumulation of explosive mixtures.*

9.3.6. Natural Gas (Methane)

- *Natural gas* is a mixture of components, consisting mainly of **methane** (60–98%) with *small amounts of other hydrocarbon fuel components.* In *addition it contains various amounts of N_2, CO_2, He and traces of other gases.* Its sulphur content ranges from very little (sweet) to larger amounts (sour).

An *ideal composition of CNG* as an automative fuel is as follows :

Methane = 90% (minimum) ; *Ethane content* = 4% (maximum) ; *Propane content* = 1.7% (maximum) ; C_4 *and higher* = 0.7% (maximum) ; C_6 *and higher* = 0.2% (maximum) ; $(CO_2 + N_2)$ = 0.2% (maximum) ; *Hydrogen* = 0.1% (maximum) ; *Carbon monoxide* = 0.1% (maximum) ; *Oxygen* = 0.5% (maximum) ; *Sulphur* = 10% ppm (maximum).

- It is stored as **Compressed Natural Gas (CNG)** at pressures of 7 to 21 bar and a temperature around –160°C.
- *As a fuel it works best in an engine system with a single-throttle body fuel injector. This gives a longer mixing time, which is needed by this fuel.*
- Tests using CNG in various sized vehicles continue to be conducted by government agencies and private industry.

Properties of CNG :

The properties of CNG are almost similar to that of methane :

- Methane has very good antiknock qualities which means it *does not ignite readily. Anti-knock Octane number of CNG is nearly 130, so it burns at much higher temperature compared with petrol unleaded (Octane No = 95) and diesel which have low octane number.*
- Owing to better antiknock quality of CNG it can be safely used in engines with a compression ratio as high as 12 : 1 compared with petrol (maximum 10 : 1).
  - *The CNG fuel used engines have higher thermal efficiencies* than *those fuelled by gasoline.* In addition to this, the reduction in the pollutants emitted by CNG engine is noticeable.
- CNG is *non-toxic* and *lighter than air so when leakage occurs it quickly disappears* unlike gasoline which paddles and evaporates.
- The presence of ethane and propane even in small percentages (5% and 2%, respectively) affect the burning properties of CNG. Both the gases try to lower the Octane characteristics and causes pre-ignition and reduced fuel efficiency.

Advantages of CNG :

(*i*) *High octane number* makes it a *very good S.I. engine fuel.*
(*ii*) *Low engine emissions.* Less aldehydes than with methanols.
(*iii*) It is cheap (It costs about 25 to 50% less than gasoline and more than 50% less than other alternative fuels, such as methanol and ethanol.
(*iv*) It is engine friendly.
(*v*) It is safe in operation.
(*vi*) Fuel fairly abundant world-wide. Natural gas is the second most abundant fuel available in India after coal.
(*vii*) Easy to tap.
(*viii*) It is odourless.
(*ix*) It is clean.

Disadvantages of CNG :

(*i*) Low energy density resulting in low engine performance.
(*ii*) Low engine volumetric efficiency because it is a gaseous fuel.
(*iii*) Need for large pressurised fuel storage tank.
(*iv*) Inconsistent fuel properties.
(*v*) Refueling is a slow process.
(*vi*) The storage cylinder takes a lot of space as the gas once filled has to travel at least of 400 km. But now a days there are byfuel and duel-fuel engines which can run on CNG and other fuel.

9.3.7. LPG and LNG

- **LPG** (*Liquified Petroleum Gas*) is mainly *propane* but may also contain a small proportion of butane and possibly, some ethane and a little pentane in heavier vapour form. The heavier fractions tend to occur in LPG produced by distillation of crude oil.
  - — Propane has a higher octane number, burns more clearly and saves on maintenance costs.
  - — Propane is gaining as a gasoline substitute because it costs 60% of petrol and gives 90% mileage of its fellow gasoline.
- **LNG** (*Liquified Natural Gas*) comes from dry natural reservoirs *mainly* CH_4 with very small percentages of ethane and propane.
  - — The major difficulty encountered in the use of this gas is its boiling temperature – 161.5°C.

9.3.8. Biogas

9.3.8.1. Introduction

- The biogas is generally produced from by dung from different beasts as **cow**, *buffalo, goat, sheep, horse, donkey* and *elephant*. Some other sources are :

(*i*) Sewage
(*ii*) Crop residue
(*iii*) Vegetable wastes
(*iv*) Water hyacinth
(*v*) Alga
(*vi*) Poultry droppings
(*vii*) Pig manure
(*viii*) Ocean kelp.

- Biogas is produced by *digestion, pyrolysis* or *hydrogasification*. **Digestion** is a biological process that occurs in absence of oxygen and in the presence of anaerobic organism at ambient pressures and temperatures of 35–70°C. The container in which digestion takes place is known as the *digester*. Biogas plants have been built in various designs.

9.3.8.2. Composition and Properties of Biogas

- Its main combustible component is CH_4 and another major component is CO_2 *which reduces its octane number*. The components of biogas with composition are given below :

Component	*Composition (% volume)*
CH_4	50—60
CO_2	30—45
H_2 and N_2	5—10
H_2S and O_2	Traces

Octane rating : 110 with CO_2
130 without CO_2

- Biogas *possesses excellent antiknock properties* with an equivalent Octane number in excess of 120 compared with 87 for regular petrol.
- Its auto-ignition temperature is higher than petrol which makes it a *safer fuel*.
- Being a gas it mixes readily with air even at low temperature, therefore, there is no need to provide rich mixture during starting or idling.
- Although its calorific value is lesser than petrol, it is possible to use higher compression ratio for the same size engine thus making it possible to generate the same amount of power.

Use of biogas in S.I. engines :

S.I. engines can be operated on biogas after starting the engine by using petrol. Biogas can be used in these engines in *two forms* as :

(*i*) To run the engine entirely on biogas.

(*ii*) Duel fuel engine where engine can run on both fuels. (This arrangement is preferred these days).

9.3.8.3. Advantages of using biogas as fuel in C.I. engine

The biogas can be used in C.I. engine as a duel fuel and improves engine performance.

The following are the *advantages* of using biogas as fuel in C.I. engine :

(*i*) A uniform gas-air mixture is available in multi-cylinder engine at all times.

(*ii*) Due to clean operation of the engine there is virtually no CO-emission in exhaust.

(*iii*) When biogas is used as a fuel, NO_x emissions are reduced by about 60 per cent.

(*iv*) Soot is virtually eliminated and exhaust is found to have less pungent odour than that obtained while operating the engine with diesel oil.

WORKED EXAMPLES

Air-Fuel Ratio and Analysis of Products of Combustion

Example 9.1. *Calculate the amount of theoretical air required for the combustion of 1 kg of acetylene (C_2H_2) to CO_2 and H_2O.*

Solution. For combustion of acetylene (C_2H_2) the stoichiometric equation is written as

$$C_2H_2 + xO_2 \longrightarrow a\,CO_2 + b\,H_2O \qquad ...(i)$$

Balancing the *carbon atoms* on both sides of the combustion equation (*i*), we get

$$2C = a\,C \quad i.e. \quad a = 2$$

Now balancing *hydrogen atoms* on both sides, we get

$$2H = 2bH$$
$$b = 1$$

Thus, equation (*i*) becomes

$$C_2H_2 + x\,O_2 \longrightarrow 2CO_2 + H_2O$$

Now, balancing *oxygen atoms* in the above equation

$$2x = 2 \times 2 + 1 = 5 \quad i.e. \quad x = 2.5$$

Hence, the final combustion equation (*i*) is

$$C_2H_2 + 2.5O_2 \longrightarrow 2CO_2 + H_2O \qquad ...(ii)$$

Thus, for combustion of C_2H_2 in air, we get

$$C_2H_2 + 2.5O_2 + 2.5\left(\frac{79}{21}\right) N_2 \longrightarrow 2CO_2 + H_2O + 2.5\left(\frac{79}{21}\right) N_2$$

On a mass basis, this becomes

$$(2 \times 12 + 2 \times 1)\ C_2H_2 + 2.5\ (2 \times 16)\ O_2 + 2.5\left(\frac{79}{21}\right)(2 \times 14)\ N_2$$

$$\longrightarrow 2\ (12 + 2 \times 16)\ CO_2 + (1 \times 2 + 1 \times 16)\ H_2O + 2.5\left(\frac{79}{21}\right)(2 \times 14)\ N_2$$

$$26 \text{ kg } C_2H_2 + 80 \text{ kg } O_2 + 263.3\ N_2 \longrightarrow 88 \text{ kg } CO_2 + 18 \text{ kg } H_2O + 263.3 \text{ kg } N_2$$

or $$1 \text{ kg } C_2H_2 + 3.076 \text{ kg } O_2 + 10.12 \text{ kg } N_2 \longrightarrow 3.38 \text{ kg } CO_2 + 0.69 \text{ kg } H_2O + 10.12 \text{ kg } N_2$$

i.e., Amount of air = 3.076 + 10.12 = 13.196 kg of air per kg of C_2H_2

Hence amount of theoretical air required for combustion of 1 kg acetylene

= 13.196 kg. (Ans.)

Example 9.2. *Determine the gravimetric analysis of the products of complete combustion of acetylene with 200 per cent stoichiometric air.*

Solution. The Stoichiometric air equation (Example 9.1) is written as :

$$C_2H_2 + 2.5\ O_2 + 2.5\left(\frac{79}{21}\right) N_2 \longrightarrow 2CO_2 + H_2O + 2.5\left(\frac{79}{21}\right) N_2$$

If *200 per cent* stoichiometric air is used, the combustion equation for C_2H_2 becomes

$$C_2H_2 + (2)\ (2.5)\ O_2 + (2)\ (2.5)\left(\frac{79}{21}\right) N_2 \longrightarrow 2CO_2 + H_2O + (2)\ (2.5)\left(\frac{79}{21}\right) N_2 + (1)\ (2.5)\ O_2$$

$$(2 \times 12 + 2 \times 1) \text{ kg } C_2H_2 + (2)\ (2.5)\ (2 \times 16) \text{ kg } O_2 + (2)\ (2.5)\left(\frac{79}{21}\right)(2 \times 14) \text{ kg } N_2$$

$$\longrightarrow 2\ (12 + 2 \times 16) \text{ kg } CO_2 + (2 \times 1 + 16) \text{ kg } H_2O + (2)\ (2.5)\left(\frac{79}{21}\right)(2 \times 14) \text{ kg } N_2 + (1)\ (2.5)\ (2 \times 16) \text{ kg } O_2$$

or $\quad 26 \text{ kg } C_2H_2 + 160 \text{ kg } O_2 + 526.6 \text{ kg } N_2 \longrightarrow 88 \text{ kg } CO_2 + 18 \text{ kg } H_2O + 526.6 \text{ kg } N_2 + 80 \text{ kg } O_2$

or $\quad 1 \text{ kg } C_2H_2 + 6.15 \text{ kg } O_2 + 20.25 \text{ kg } N_2 \longrightarrow 3.38 \text{ kg } CO_2 + 0.69 \text{ kg } H_2O + 20.25 \text{ kg } N_2 + 3.07 \text{ kg } O_2$

Thus for 1 kg of fuel, the products will consist of

$$CO_2 = 3.38 \text{ kg}$$
$$H_2O = 0.69 \text{ kg}$$
$$O_2 = 3.07 \text{ kg}$$
$$N_2 = 20.25 \text{ kg}$$

Total mass of products $= 27.39$ kg

∴ Mass fractions are :

$$CO_2 = \frac{3.38}{27.39} = 0.123$$

$$H_2O = \frac{0.69}{27.39} = 0.025$$

$$O_2 = \frac{3.07}{27.39} = 0.112$$

$$N_2 = \frac{20.25}{27.39} = 0.739.$$

Hence the gravimetric analysis of the complete combustion is :

$CO_2 = 12.3\%$, $H_2O = 2.5\%$, $O_2 = 11.2\%$, $N_2 = 73.9\%$. (Ans.)

Example 9.3. *Calculate the theoretical air-fuel ratio for the combustion of octane, C_8H_{18}. The combustion equation is :*

$$C_8H_{18} + 12.5\ O_2 + 12.5\left(\frac{79}{21}\right) N_2 \longrightarrow 8CO_2 + 9H_2O + 12.5\left(\frac{79}{21}\right) N_2.$$

Solution. The air-fuel ratio on a mole basis is

$$A/F = \frac{12.5 + 12.5\left(\frac{79}{21}\right)}{1} = 59.5 \text{ mol air/mol fuel}$$

The theoretical air-fuel ratio on a mass basis is found by introducing the molecular weight of the air and fuel

$$A/F = \frac{59.5\,(28.97)}{(8 \times 12 + 1 \times 18)} = \mathbf{15.08\ kg\ air/kg\ fuel.} \quad \textbf{(Ans.)}$$

Example 9.4. *One kg of octane (C_8H_{18}) is burned with 200% theoretical air. Assuming complete combustion determine :*

(*i*) *Air-fuel ratio*

(*ii*) *Dew point of the products at a total pressure 100 kPa.*

Solution. The equation for the combustion of C_8H_{18} with theoretical air is

$$C_8H_{18} + 12.5\ O_2 + 12.5\left(\frac{79}{21}\right) N_2 \longrightarrow 8CO_2 + 9H_2O + 12.5\left(\frac{79}{21}\right) N_2$$

For *200% theoretical air* the combustion equation would be

$$C_8H_{18} + (2)\,(12.5)\ O_2 + (2)\,(12.5)\left(\frac{79}{21}\right) N_2$$

$$\longrightarrow 8CO_2 + 9H_2O + (1)\,(12.5)\ O_2 + (2)\,(12.5)\left(\frac{79}{21}\right) N_2$$

Mass of fuel = (1) (8 × 12 + 1 × 18) = 114 kg/mole

$$\text{Mass of air} = (2)\,(12.5)\left(1 + \frac{79}{21}\right) 28.97 = 3448.8 \text{ kg/mole of fuel}$$

(*i*) **Air-fuel ratio :**

$$\text{Air-fuel ratio, A/F} = \frac{\text{Mass of air}}{\text{Mass of fuel}} = \frac{3448.8}{114} = 30.25$$

i.e., **A/F = 30.25. (Ans.)**

(*ii*) **Dew point of the products, t_{dp} :**

Total number of moles of products

$$= 8 + 9 + 12.5 + (2)\,(12.5)\left(\frac{79}{21}\right) = 123.5 \text{ moles/mole fuel}$$

$$\text{Mole fraction of } H_2O = \frac{9}{123.5} = 0.0728$$

Partial pressure of H_2O = 100 × 0.0728 = 7.28 kPa

The saturation temperature corresponding to this pressure is 39.7°C which is also the dew-point temperature.

Hence **t_{dp} = 39.7°C. (Ans.)**

Note. The water condensed from the products of combustion usually contains some dissolved gases and therefore may be quite *corrosive*. For this reason the products of combustion are often *kept above the dew point until discharged to the atmosphere.*

Example 9.5. *One kg of ethane (C_2H_6) is burned with 90% of theoretical air. Assuming complete combustion of hydrogen in the fuel determine the volumetric analysis of the dry products of combustion.*

Solution. The complete combustion equation for C_2H_6 is written as :

$$C_2H_6 + 3.5\ O_2 \longrightarrow 2CO_2 + 3H_2O$$

The combustion equation for C_2H_6 for 90% theoretical air is written as :

$$C_2H_6 + (0.9)\,(3.5)\ O_2 + (0.9)\,(3.5)\left(\frac{79}{21}\right) N_2 \longrightarrow a\ CO_2 + b\ CO + 3H_2O + (0.9)\,(3.5)\left(\frac{79}{21}\right) N_2$$

By balancing *carbon atoms* on both the sides, we get

$$2 = a + b \quad ...(i)$$

By balancing *oxygen atoms* on both the sides, we get

$$(0.9)(3.5)(2) = 2a + b + 3 \quad ...(ii)$$

Substituting the value of b ($= 2 - a$) from eqn. (*i*) in eqn. (*ii*), we get

$$(0.9)(3.5)(2) = 2a + 2 - a + 3$$

$$6.3 = a + 5$$

$$\therefore \quad a = 1.3$$

and $$b = 2 - a = 2 - 1.3 = 0.7$$

Thus the combustion equation becomes :

$$C_2H_6 + (0.9)(3.5)\,O_2 + (0.9)(3.5)\left(\frac{79}{21}\right)N_2$$

$$\longrightarrow 1.3\,CO_2 + 0.7\,CO + 3H_2O + (0.9)(3.5)\left(\frac{79}{21}\right)N_2$$

Total number of moles of *dry products* of combustion

$$= 1.3 + 0.7 + (0.9)(3.5)\left(\frac{79}{21}\right)$$

$$= 1.3 + 0.7 + 11.85 = 13.85 \text{ moles/mole of fuel}$$

Volumetric analysis of dry products of combustion is as follows :

$$\mathbf{CO_2} = \frac{1.3}{13.85} \times 100 = \mathbf{9.38\%.} \quad \textbf{(Ans.)}$$

$$\mathbf{CO} = \frac{0.7}{13.85} \times 100 = \mathbf{5.05\%.} \quad \textbf{(Ans.)}$$

$$\mathbf{N_2} = \frac{11.85}{13.85} \times 100 = \mathbf{85.56\%.} \quad \textbf{(Ans.)}$$

☞**Example 9.6.** *Methane (CH_4) is burned with atmospheric air. The analysis of the products on a 'dry' basis is as follows :*

$$CO_2 = 10.00\%,\ O_2 = 2.37\%,\ CO = 0.53\%,\ N_2 = 87.10\%.$$

(*i*) *Determine the combustion equation;* (*ii*) *Calculate the air-fuel ratio;*
(*iii*) *Percent theoretical air.*

Solution. (*i*) **Combustion equation :**

From the analysis of the products, the following equation can be written, keeping in mind that this analysis is on a *dry basis.*

$$x\,CH_4 + y\,O_2 + z\,N_2 \longrightarrow 10.0\,CO_2 + 0.53\,CO + 2.37\,O_2 + a\,H_2O + 87.1\,N_2$$

To determine all the unknown co-efficients let us find balance for each of the elements.

Nitrogen balance : $z = 87.1$

Since all the nitrogen comes from the air,

$$\frac{z}{y} = \frac{79}{21}\ ;\ y = \frac{87.1}{(79/21)} = 23.16$$

Carbon balance : $x = 10.00 + 0.53 = 10.53$

Hydrogen balance : $a = 2x = 2 \times 10.53 = 21.06$

Oxygen balance. All the unknown co-efficients have been solved for, and in this case the oxygen balance provides a check on the accuracy. Thus, y can also be determined by an oxygen balance

$$y = 10.00 + \frac{0.53}{2} + 2.37 + \frac{21.06}{2} = 23.16$$

Substituting these values for x, y, z and a, we have,

$$10.53\ CH_4 + 23.16\ O_2 + 87.1\ N_2 \longrightarrow 10.0\ CO_2 + 0.53\ CO + 2.37\ O_2 + 21.06\ H_2O + 87.1\ N_2$$

Dividing both sides by 10.53 we get the **combustion equation** per mole of fuel

$$\mathbf{CH_4 + 2.2\ O_2 + 8.27\ N_2 \longrightarrow 0.95\ CO_2 + 0.05\ CO + 2H_2O + 0.225\ O_2 + 8.27\ N_2.} \quad \textbf{(Ans.)}$$

(*ii*) **Air-fuel ratio A/F :**

The air-fuel ratio on a *mole basis* is

$$2.2 + 8.27 = \textbf{10.47 moles air/mole fuel.} \quad \textbf{(Ans.)}$$

The air-fuel ratio on a *mass basis* is found by introducing the molecular weights

$$\text{A/F} = \frac{10.47 \times 28.97}{(12 + 1 \times 4)} = \textbf{18.96 kg air/kg fuel.} \quad \textbf{(Ans.)}$$

The theoretical air-fuel ratio is found by writing the combustion equation for theoretical air.

$$CH_4 + 2O_2 + 2\left(\frac{79}{21}\right) N_2 \longrightarrow CO_2 + 2H_2O + (2)\left(\frac{79}{21}\right) N_2$$

$$\text{A/F}_{\text{theo.}} = \frac{\left[2 + (2)\left(\frac{79}{21}\right)\right] 28.97}{(12 + 1 \times 4)} = \textbf{17.24 kg air/kg fuel.} \quad \textbf{(Ans.)}$$

(*iii*) **Percent theoretical air :**

$$\text{Percent theoretical air} = \frac{18.96}{17.24} \times 100 = \textbf{110\%.} \quad \textbf{(Ans.)}$$

Example 9.7. *The gravimetric analysis of a sample of coal is given as 82% C, 10% H_2 and 8% ash. Calculate :*

(*i*) *The stoichiometric A/F ratio;* (*ii*) *The analysis of the products by volume.*

Solution. (*i*) **The stoichiometric A/F ratio :**

1 kg of coal contains 0.82 kg C and 0.10 kg H_2

$\therefore$ 1 kg of coal contains $\dfrac{0.82}{12}$ moles C and $\dfrac{0.10}{2}$ moles H_2

Let the oxygen required for complete combustion = x moles

Then the nitrogen supplied with the oxygen = $x \times \dfrac{79}{21} = 3.76x$ moles

For 1 kg of coal the combustion equation is therefore as follows :

$$\frac{0.82}{12}\ C + \frac{0.10}{2}\ H_2 + x\ CO_2 + 3.76x\ N_2 \longrightarrow a\ CO_2 + b\ H_2O + 3.76x\ N_2$$

Then, ***Carbon balance :*** $\dfrac{0.82}{12} = a \qquad \therefore \quad a = 0.068$ moles

Hydrogen balance : $2 \times \dfrac{0.10}{2} = 2b \qquad \therefore \quad b = 0.05$ moles

Oxygen balance : $2x = 2a + b \qquad \therefore \quad x = \left(\dfrac{2 \times 0.068 + 0.05}{2}\right) = 0.093$ moles

The mass of 1 mole of oxygen is 32 kg, therefore, the mass of O_2 supplied per kg of coal

$$= 32 \times 0.093 = 2.976 \text{ kg}$$

i.e.,
$$\textit{Stoichiometric A/F ratio} = \frac{2.976}{0.233}$$

(where air is assumed to contain 23.3% O_2 and 76.7% N_2 by mass)

Total moles of products $= a + b + 3.76x = 0.068 + 0.05 + 3.76 \times 0.093 = 0.467$ moles

(*ii*) **Analysis of the products by volume :**

The analysis of the products by volume is :

$$\mathbf{CO_2} = \frac{0.068}{0.467} \times 100 = \mathbf{14.56\%}. \quad \textbf{(Ans.)}$$

$$\mathbf{H_2} = \frac{0.05}{0.467} \times 100 = \mathbf{10.7\%}. \quad \textbf{(Ans.)}$$

$$\mathbf{N_2} = \frac{(3.76 \times 0.093)}{0.467} \times 100 = \mathbf{74.88\%}. \quad \textbf{(Ans.)}$$

☞**Example 9.8.** *Calculate the stoichiometric air-fuel ratio for the combustion of a sample of dry anthracite of the following composition by mass :*

Carbon (C) = 88 per cent	*Hydrogen (H_2) = 4 per cent*
Oxygen (O_2) = 3.5 per cent	*Nitrogen (N_2) = 1 per cent*
Sulphur (S) = 0.5 per cent	*Ash = 3 per cent*

If 30 per cent excess air is supplied determine :

(*i*) *Air-fuel ratio*

(*ii*) *Wet dry analysis of the products of combustion by volume.*

Solution. Stoichiometric air-fuel (A/F) ratio :

In case of a fuel with several constituents a *tubular method* is advisable, as shown below. Each constituent is taken separately and the amount of oxygen required for complete combustion is found from the chemical equation. The oxygen in the fuel is included in the column headed '*oxygen required*' as a *negative quantity.*

	Mass per kg coal	*Combustion equation*	*Oxygen required per kg of coal*	*Products per kg of coal*
C	0.88	$C + O_2 \longrightarrow CO_2$ $12 \text{ kg} + 32 \text{ kg} \longrightarrow 44 \text{ kg}$	$0.88 \times \frac{32}{12} = 2.346$ kg	$0.88 \times \frac{44}{12} = 3.23$ kg CO_2
H_2	0.04	$2H_2 + O_2 \longrightarrow 2H_2O$ $1 \text{ kg} + 8 \text{ kg} \longrightarrow 9 \text{ kg}$	$0.04 \times 8 = 0.32$ kg	$0.04 \times 9 = 0.36$ kg H_2O
O_2	0.035	—	– 0.035 kg	—
N_2	0.01	—	—	0.01 kg N_2
S	0.005	$S + O_2 \longrightarrow SO_2$ $32 \text{ kg} + 32 \text{ kg} \longrightarrow 64 \text{ kg}$	$0.005 \times \frac{32}{32} = 0.005$ kg	$0.005 \times \frac{64}{32} = 0.01$ kg SO_2
Ash	0.03	—	—	—
			Total O_2 = 2.636 kg	

From table :

O_2 required per kg of coal = 2.636 kg

$\therefore$ Air required per kg of coal $= \dfrac{2.636}{0.233} = 11.31$ kg

(where air is assumed to contain 23.3% O_2 *by mass*)

N_2 associated with this air = 0.767 × 11.31 = 8.67 kg

$\therefore$ Total N_2 in products = 8.67 + 0.01 = 8.68 kg

The stoichiometric A/F ratio = 11.31/1. (Ans.)

When 30 per cent excess air is used :

(*i*) **Actual A/F ratio :**

Actual A/F ratio $= 11.31 + 11.31 \times \dfrac{30}{100} = \mathbf{14.7/1.}$ **(Ans.)**

(*ii*) **Wet and dry analyses of products of combustion by volume :**

As per actual A/F ratio, N_2 supplied = 0.767 × 14.7 = 11.27 kg

Also O_2 supplied = 0.233 × 14.7 = 3.42 kg

(where air is assumed to contain N_2 = 76.7% and O_2 = 23.3)

In the products then, we have

$$N_2 = 11.27 + 0.01 = 11.28 \text{ kg}$$

and $$\text{excess } O_2 = 3.42 - 2.636 = 0.784 \text{ kg}$$

The products are entered in the following table and the analysis by volume is obtained :

- In column 3 the percentage by mass is given by the mass of each product divided by the total mass of 15.66 kg.
- In column 5 the moles per kg of coal are given by equation $n = \dfrac{m}{M}$. The total of column 5 gives the total moles of wet products per kg of coal, and by subtracting the moles of H_2O from this total, the total moles of dry products is obtained as 0.5008.
- Column 6 gives the proportion of each constituent of column 5 expressed as a percentage of the total moles of the wet products.
- Similarly column 7 gives the percentage by volume of the dry products.

Product	*Mass/kg coal*	*% by mass*	*M*	*Moles/kg coal*	***% by vol. wet***	***% by vol. dry***
1	*2*	*3*	*4*	*5*	*6*	*7*
CO_2	3.23	20.62	44	0.0734	**14.10**	**14.66**
H_2O	0.36	2.29	18	0.0200	**3.84**	—
SO_2	0.01	0.06	64	0.0002 (say)	**0.04**	**0.04**
O_2	0.78	4.98	32	0.0244	**4.68**	**4.87**
N_2	11.28	72.03	28	0.4028	**77.34**	**80.43**
	15.66 kg			Total wet = 0.5208 – H_2O = 0.0200 Total dry = 0.5008	100.00	100.00 **(Ans.)**

Example 9.9. *The following analysis relate to coal gas :*

$H_2 = 50.4$ *per cent* $CO = 17$ *per cent*
$CH_4 = 20$ *per cent* $C_4H_8 = 2$ *per cent*
$O_2 = 0.4$ *per cent* $N_2 = 6.2$ *per cent*
$CO_2 = 4$ *per cent.*

(*i*) *Calculate the stoichiometric A/F ratio.*

(*ii*) *Find also the wet and dry analyses of the products of combustion if the actual mixture is 30 per cent weak.*

Solution. The example is solved by a tabular method ; a specimen calculation is given below :

For CH_4 :

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

i.e., 1 mole CH_4 + 2 moles $O_2 \longrightarrow$ 1 mole CO_2 + 2 moles H_2O

There are 0.2 moles of CH_4 per mole of the coal gas, hence

0.2 moles CH_4 + 0.2 × 2 moles $O_2 \longrightarrow$ 0.2 moles CO_2 + 0.2 × 2 moles H_2O

∴ O_2 required for the CH_4 in the coal gas = 0.4 moles per mole of coal gas.

The oxygen in the fuel (0.004 moles) is included in column 4 as a *negative quantity*.

Product	*Moles/mole fuel*	*Combustion equation*	*O_2 moles/ mole fuel*	*Products CO_2*	*H_2O*
1	*2*	*3*	*4*	*5*	*6*
H_2O	0.504	$2H_2 + O_2 \longrightarrow 2H_2O$	0.252	—	0.504
CO	0.17	$2CO + O_2 \longrightarrow 2CO_2$	0.085	0.17	—
CH_4	0.20	$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$	0.400	0.20	0.40
C_4H_8	0.02	$C_4H_8 + 6O_2 \longrightarrow 4CO_2 + 4H_2O$	0.120	0.08	0.08
O_2	0.004	—	– 0.004	—	—
N_2	0.062	—	—	—	—
CO_2	0.04	—	—	0.04	—
			Total = 0.853	0.49	0.984

(*i*) **Stoichiometric A/F ratio :**

$$\text{Air required} = \frac{0.853}{0.21} = 4.06 \text{ moles/mole of fuel}$$

(where air is assumed to contain 21% O_2 by volume)

∴ *Stoichiometric A/F ratio* = **4.06/1 by volume. (Ans.)**

(*ii*) **Wet and dry analysis of the products of combustion if the actual mixture is 30% weak :**

Actual A/F ratio with 30% weak mixture

$$= 4.06 + \frac{30}{100} \times 4.06 = 1.3 \times 4.06 = 5.278/1$$

Associated N_2 = 0.79 × 5.278 = 4.17 moles/mole fuel
Excess oxygen = 0.21 × 5.278 – 0.853 = 0.255 moles

Total moles of N_2 in products = 4.17 + 0.062 = 4.232 moles/mole fuel.

Analysis by volume of wet and dry products

Product	*Moles/mole fuel*	*% by vol. (dry)*	*% by vol. (wet)*
CO_2	0.490	**9.97**	**8.31**
H_2O	0.984	—	**16.68**
O_2	0.255	**5.19**	**4.32**
N_2	4.170	**84.84**	**70.69**
	Total wet = 5.899	100.00	100.00 **(Ans.)**
	$- H_2O = 0.984$		
	Total dry = 4.915		

Example 9.10. *Find the stoichiometric air-fuel ratio for the combustion of ethyl alcohol (C_2H_6O), in a petrol engine. Calculate the air-fuel ratios for the extreme mixture strengths of 80 per cent and 130 per cent. Determine also the wet and dry analyses by volume of the exhaust gas for each mixture strength.*

Solution. The equation for combustion of ethyl alcohol is as follows :

$$C_2H_6O + 3O_2 \longrightarrow 2CO_2 + 3H_2O$$

- Since there are two atoms of carbon in each mole of C_2H_6O then there must be two moles of CO_2 in the products, giving two atoms of carbon on each side of the equation.
- Similarly, since there are six atoms of hydrogen in each mole of ethyl alcohol then there must be three moles of H_2O in the products, giving six atoms of hydrogen on each side of the equation.
- Then balancing the atoms of oxygen, it is seen that there are (2 × 2 + 3) = 7 atoms on the right hand side of the equation, hence seven atoms must appear on the left hand side of the equation. There is one atom of oxygen in ethyl alcohol, therefore a further six atoms of oxygen must be supplied, and hence three moles of oxygen are required as shown.

Since the O_2 is supplied as air, the associated N_2 must appear in the equation,

i.e.,
$$C_2H_6O + 3O_2 + 3 \times \frac{79}{21} N_2 \longrightarrow 2CO_2 + 3H_2O + 3 \times \frac{79}{21} N_2$$

One mole of fuel has a mass of (2 × 12 + 1 × 6 + 16) = 46 kg. Three moles of oxygen have a mass of (3 × 32) = 96 kg.

$$\therefore\ O_2 \text{ required per kg of fuel} = \frac{96}{46} = 2.09 \text{ kg}$$

$$\therefore\ \textbf{Stoichiometric A/F ratio} = \frac{2.09}{0.233} = \textbf{8.96/1.} \quad \textbf{(Ans.)}$$

Considering a mixture strength of 80% :

$$\text{Now, mixture strength} = \frac{\text{Stoichiometric A/F ratio}}{\text{Actual A/F ratio}}$$

i.e.,
$$0.8 = \frac{8.96 / 1}{\text{Actual A/F ratio}}$$

$$\therefore\ \textbf{Actual A/F ratio} = \frac{8.96}{0.8} = \textbf{11.2/1.} \quad \textbf{(Ans.)}$$

This means that 1/0.8 or 1.25 times as much air is supplied as is necessary for complete combustion. The exhaust will therefore contain 0.25 stoichiometric oxygen.

i.e., $$C_2H_6O + 1.25\left(3O_2 + 3 \times \frac{79}{21} N_2\right) \longrightarrow 2CO_2 + 3H_2O + 0.25 \times 3O_2 + 1.25 \times 3 \times \frac{79}{21} N_2$$

i.e., The products are :

$$2 \text{ moles } CO_2 + 3 \text{ moles } H_2O + 0.75 \text{ moles } O_2 + 14.1 \text{ moles } N_2$$

The total moles = 2 + 3 + 0.75 + 14.1 = 19.85

Hence wet analysis is :

$$\mathbf{CO_2} = \frac{2}{19.85} \times 100 = \mathbf{10.08\%.} \quad \textbf{(Ans.)}$$

$$\mathbf{H_2O} = \frac{3}{19.85} \times 100 = \mathbf{15.11\%.} \quad \textbf{(Ans.)}$$

$$\mathbf{O_2} = \frac{0.75}{19.85} \times 100 = \mathbf{3.78\%.} \quad \textbf{(Ans.)}$$

$$\mathbf{N_2} = \frac{14.1}{19.85} \times 100 = \mathbf{71.03\%.} \quad \textbf{(Ans.)}$$

The total dry moles = 2 + 0.75 + 14.1 = 16.85

Hence dry analysis is :

$$\mathbf{CO_2} = \frac{2}{16.85} \times 100 = \mathbf{11.87\%.} \quad \textbf{(Ans.)}$$

$$\mathbf{O_2} = \frac{0.75}{16.85} \times 100 = \mathbf{4.45\%.} \quad \textbf{(Ans.)}$$

$$\mathbf{N_2} = \frac{14.1}{16.85} \times 100 = \mathbf{83.68\%.} \quad \textbf{(Ans.)}$$

Considering a mixture strength of 130% :

Now, $$1.3 = \frac{\text{Stoichiometric ratio}}{\text{Actual A/F ratio}}$$

$\therefore$ **Actual A/F ratio** $= \dfrac{8.96}{1.3} = \mathbf{6.89/1.}$ **(Ans.)**

This means that $\dfrac{1}{1.3}$ or 0.769 of the stoichiometric air is supplied. *The combustion cannot be complete, as the necessary oxygen is not available. It is usual to assume that all hydrogen is burned to H_2O, since hydrogen atoms have a greater affinity for oxygen than carbon atoms. The carbon in the fuel will burn to CO and CO_2, but the relative proportions have to be determined.*

Let, a = Number of moles of CO_2 in the products, and

b = Number of moles of CO in the products

Then the combustion equation is as follows :

$$C_2H_6O + 0.769\left(3O_2 + 3 \times \frac{79}{21} N_2\right) \longrightarrow a\, CO_2 + b\, CO + 3H_2O + 0.769 \times 3 \times \frac{79}{21} N_2$$

To find a and b a balance of carbon and oxygen atoms can be made,

i.e., ***Carbon balance :***

$$2 = a + b \qquad \text{...}(i)$$

and ***Oxygen balance :***

$$1 + 2 \times 0.769 \times 3 = 2a + b + 3$$

or

$$2.614 = 2a + b \qquad \text{...}(ii)$$

From eqn. (i) and (ii), we get $a = 0.614$, $b = 1.386$

i.e., The products are : 0.614 moles CO_2 + 1.386 moles CO + 3 moles H_2O + 8.678 moles N_2

The total moles = 0.614 + 1.386 + 3 + 8.678 = 13.678.

Hence wet analysis is :

$$\mathbf{CO_2} = \frac{0.614}{13.678} \times 100 = \mathbf{4.49\%.} \qquad \textbf{(Ans.)}$$

$$\mathbf{CO} = \frac{1.386}{13.678} \times 100 = \mathbf{10.13\%.} \qquad \textbf{(Ans.)}$$

$$\mathbf{H_2O} = \frac{3}{13.678} \times 100 = \mathbf{21.93\%.} \qquad \textbf{(Ans.)}$$

$$\mathbf{N_2} = \frac{8.678}{13.678} \times 100 = \mathbf{63.45\%.} \qquad \textbf{(Ans.)}$$

The total dry moles = 0.614 + 1.386 + 8.678 = 10.678

Hence dry analysis is :

$$\mathbf{CO_2} = \frac{0.614}{10.678} \times 100 = \mathbf{5.75\%.} \qquad \textbf{(Ans.)}$$

$$\mathbf{CO} = \frac{1.386}{10.678} \times 100 = \mathbf{12.98\%.} \qquad \textbf{(Ans.)}$$

$$\mathbf{N_2} = \frac{8.678}{10.678} \times 100 = \mathbf{81.27\%.} \qquad \textbf{(Ans.)}$$

Example 9.11. *For the stoichiometric mixture of example 9.10 calculate :*

(*i*) *The volume of the mixture per kg of fuel at a temperature of 50°C and a pressure of 1.013 bar.*

(*ii*) *The volume of the products of combustion per kg of fuel after cooling to a temperature of 130°C at a pressure of 1 bar.*

Solution. As before,

$$C_2H_6O + 3O_2 + 3 \times \frac{79}{21} N_2 \longrightarrow 2CO_2 + 3H_2O + 3 \times \frac{79}{21} N_2$$

$\therefore$ Total moles reactants $= 1 + 3 + 3 \times \frac{79}{21} = 15.3$

From equation, $pV = nR_0T$

$$V = \frac{nR_0T}{p} = \frac{15.3 \times 8.314 \times 10^3 \times (50 + 273)}{1.013 \times 10^5} = 405.6 \text{ m}^3\text{/mole of fuel}$$

In 1 mole of fuel there are (2 × 12 + 6 + 16) = 46 kg (*i*) ∴ **Volume of reactants per kg of fuel** $= \dfrac{405.6}{46}$ $=$ **8.817 m³. (Ans.)**

When the products are cooled to 130°C the H_2O exists as steam, since the temperature is well above the saturation temperature corresponding to the partial pressure of the H_2O. (This must be so since the saturation temperature corresponding to the *total* pressure is 99.6°C, and the *saturation temperature decreases with pressure.* The total moles of the products is

$$= \left(2 + 3 + 3 \times \frac{79}{21}\right) = 16.3$$

From equation, $pV = nR_0T$

$$V = \frac{nR_0T}{p} = \frac{16.3 \times 8.314 \times 10^3 \times (130 + 273)}{1 \times 10^5} = 546.14 \text{ m}^3\text{/mole of fuel.}$$

(*ii*) ∴ **Volume of products per kg of fuel** $= \dfrac{546.14}{46}$ $=$ **11.87 m³. (Ans.)**

☞**Example 9.12.** *The following is the composition of coal gas supplied to a gas engine :*

$H_2 = 50.6$ per cent ; $CO = 10$ per cent ; $CH_4 = 26$ per cent ; $C_4H_8 = 4$ per cent ; $O_2 = 0.4$ per cent ; $CO_2 = 3$ per cent ; $N_2 = 6$ per cent.

If the air-fuel ratio is 7/1 by volume, calculate the analysis of the dry products of combustion. It can be assumed that the stoichiometric A/F ratio is less than 7/1.

Solution. Since it is given that the actual *A/F ratio is greater than the stoichiometric,* therefore it follows that *excess air has been supplied.* The products will therefore consist of CO_2, H_2O, O_2 and N_2.

The combustion equation can be written as follows :

$$0.506H_2 + 0.1CO + 0.26CH_4 + 0.04C_4H_8 + 0.004O_2 + 0.03CO_2 + 0.06N_2 + 0.21 \times 7O_2 + 0.79 \times 7N_2 \longrightarrow a\,CO_2 + b\,H_2O + c\,O_2 + d\,N_2$$

Then,

Carbon balance : $0.1 + 0.26 + 4 \times 0.04 + 0.03 = a$ $\quad \therefore a = 0.55$

Hydrogen balance : $2 \times 0.506 + 4 \times 0.26 + 8 \times 0.04 = 2b$ $\quad \therefore b = 1.186$

Oxygen balance : $0.1 + 2 \times 0.004 + 2 \times 0.03 + 0.21 \times 7 \times 2 = 2a + b + 2c$ $\quad \therefore c = 0.411$

Nitrogen balance : $2 \times 0.06 + 2 \times 0.79 \times 7 = 2d$ $\quad \therefore d = 5.59$

∴ Total moles of dry products = 0.55 + 0.411 + 5.59 = 6.65

Then analysis by volume is :

$$\mathbf{CO_2} = \frac{0.55}{6.55} \times 100 = \mathbf{8.39\%.} \qquad \textbf{(Ans.)}$$

$$\mathbf{O_2} = \frac{0.411}{6.55} \times 100 = \mathbf{6.27\%.} \qquad \textbf{(Ans.)}$$

$$\mathbf{N_2} = \frac{5.59}{6.55} \times 100 = \mathbf{85.34\%.} \qquad \textbf{(Ans.)}$$

Example 9.13. *The following is the analysis (by weight) of a chemical fuel :*

Carbon = 60 per cent ; Hydrogen = 20 per cent ; Oxygen = 5 per cent ; Sulphur = 5 per cent and Nitrogen = 10 per cent.

Find the stoichiometric amount of air required for complete combustion of this fuel.

Solution. On the basis of 100 kg fuel let us assume an equivalent formula of the form :

$$C_aH_bO_cN_dS_e$$

From the given analysis by weight, we can write

$$12a = 60 \quad \text{or} \quad a = 5$$
$$1b = 20 \quad \text{or} \quad b = 20$$
$$16c = 5 \quad \text{or} \quad c = 0.3125$$
$$14d = 10 \quad \text{or} \quad d = 0.7143$$
$$32e = 5 \quad \text{or} \quad e = 0.1562$$

Then the formula of the fuel can be written as

$$C_5H_{20}O_{0.3125}N_{0.7143}S_{0.1562}$$

The combustion equation is

$$C_5H_{20}O_{0.3125}\,N_{0.7143}S_{0.1562} + x\,O_2 + x\left(\frac{79}{21}\right)N_2 \longrightarrow p\,CO_2 + q\,H_2O + r\,SO_2 + s\,N_2$$

Then,

Carbon balance : $5 = p \quad \therefore \quad p = 5$

Hydrogen balance : $20 = 2q \quad \therefore \quad q = 10$

Sulphur balance : $0.1562 = r \quad \therefore \quad r = 0.1562$

Oxygen balance : $0.3125 + 2x = (2p + q + 2r)$

i.e.,
$$x = p + \frac{q}{2} + r - \frac{0.3125}{2} = 5 + \frac{10}{2} + 0.1562 - \frac{0.3125}{2} = 9.99$$

Nitrogen balance : $0.7143 + 2x \times \frac{79}{21} = 2s$

$$\therefore \quad s = \frac{0.7143}{2} + x \times \frac{79}{21} = \frac{0.7143}{2} + 9.99 \times \frac{79}{21} = 37.94$$

Hence the combustion equation is written as follows :

$$C_5H_{20}O_{0.3125}N_{0.7143}S_{0.1562} + 9.99O_2 + 9.99\left(\frac{79}{21}\right)N_2 \longrightarrow 5CO_2 + 10H_2O + 0.1562SO_2 + 37.94N_2$$

$$\therefore \textbf{Stoichiometric air required} = \frac{9.99 \times 32 + 9.99 \times \left(\frac{79}{21}\right) \times 28}{100} = \textbf{13.7 kg/kg of fuel. (Ans.)}$$

(**Note.** This example can also be solved by tabular method as explained in example 9.8.).

Example 9.14. *A sample of fuel has the following percentage composition by weight :*

Carbon = 84 per cent *Hydrogen = 10 per cent*
Oxygen = 3.5 per cent *Nitrogen = 1.5 per cent*
Ash = 1 per cent

(*i*) *Determine the stoichiometric air fuel ratio by mass.*

(*ii*) *If 20 per cent excess air is supplied, find the percentage composition of dry flue gases by volume.*

Solution. (*i*) **Stoichiometric air fuel ratio :**

On the basis of 100 kg of fuel let us assume an equivalent formula of the form :

$$C_aH_bO_cN_d$$

From the given analysis by weight, we can write

$$12a = 84 \quad i.e., \quad a = 7$$
$$1b = 10 \quad i.e., \quad b = 10$$
$$16c = 3.5 \quad i.e., \quad c = 0.218$$
$$14d = 1.5 \quad i.e., \quad d = 0.107$$

The formula of fuel is $C_7H_{10}O_{0.218}N_{0.107}$

The combustion equation is written as

$$C_7H_{10}O_{0.218}N_{0.107} + x\,O_2 + x\left(\frac{79}{21}\right)N_2 \longrightarrow p\,CO_2 + q\,H_2O + r\,N_2$$

Then,

Carbon balance : $7 = p \quad i.e., \quad p = 7$

Hydrogen balance : $10 = 2q \quad i.e., \quad q = 5$

Oxygen balance : $0.218 + 2x = (2p + q)$

or $0.218 + 2x = 2 \times 7 + 5 \quad i.e. \quad x = 9.39$

Nitrogen balance : $0.107 + 2x\left(\frac{79}{21}\right) = 2r$

or $$0.107 + 2 \times 9.39 \times \frac{79}{21} = 2r \; i.e., \; r = 35.4$$

Hence the combustion equation becomes

$$C_7H_{10}O_{0.218}N_{0.107} + 9.39O_2 + 9.39\left(\frac{79}{21}\right)N_2 \longrightarrow 7CO_2 + 5H_2O + 35.4N_2$$

$\therefore$ **Stoichiometric A/F ratio** $= \dfrac{9.39 \times 32 + 9.39 \times \frac{79}{21} \times 28}{100} = \mathbf{12.89.}$ **(Ans.)**

(*ii*) **Percentage composition of dry flue gases by volume with 20 per cent excess air :**

If 20 per cent excess air is used, the combustion equation becomes

$$C_7H_{10}O_{0.218}N_{0.107} + (1.2)(9.39)\,O_2 + (1.2)(9.39)\left(\frac{79}{21}\right)N_2$$
$$\longrightarrow 7CO_2 + 5H_2O + (0.2)(9.39)\,O_2 + (1.2)(35.4)\,N_2$$

Total number of moles of dry products of combustion

$$n = 7 + (0.2)(9.39) + (1.2)(35.4)$$
$$= 7 + 1.878 + 42.48 = 51.358$$

$\therefore$ **Percentage composition of dry flue gases by volume is as follows :**

$$CO_2 = \frac{7}{51.358} \times 100 = \mathbf{13.63\%.} \qquad \textbf{(Ans.)}$$

$$O_2 = \frac{1.878}{51.358} \times 100 = \mathbf{3.66\%.} \qquad \textbf{(Ans.)}$$

$$N_2 = \frac{42.48}{51.358} \times 100 = \mathbf{82.71\%.} \qquad \textbf{(Ans.)}$$

Example 9.15. *Orsat analysis of the products of combustion of a hydrocarbon fuel of unknown composition is as follows :*

Carbon dioxide (CO_2) *= 8%* *Carbon monoxide (CO) = 0.5%*
Oxygen (O_2) *= 6.3%* *Nitrogen* (N_2) *= 85.2%*

Determine the following :

(*i*) *Air-fuel ratio*

(*ii*) *Percent theoretical air required for combustion.*

Solution. From the given Orsat analysis the combustion equation is written as follows :

$$a\,\text{C} + b\,\text{H} + c\,\text{O}_2 + \left(\frac{79}{21}\right) c\,\text{N}_2 = 8\text{CO}_2 + 0.5\text{CO} + 6.3\text{O}_2 + x\,\text{H}_2\text{O} + 85.2\text{N}_2$$

Then,

Carbon balance : $a = 8 + 0.5 = 8.5$ *i.e.*, $a = 8.5$

Nitrogen balance : $\frac{79}{21}\text{C} = 85.2$ *i.e.*, $c = 22.65$

Oxygen balance : $\text{C} = 8 + \frac{0.5}{2} + 6.3 + \frac{x}{2}$

or $22.65 = 8 + 0.25 + 6.3 + \frac{x}{2}$ *i.e.*, $x = 16.2$

Hydrogen balance : $b = 2x = 2 \times 16.2 = 32.4$ *i.e.*, $b = 32.4$

(*i*) **Air-fuel ratio :**

The air supplied per 100 moles of dry products is

$$= 22.65 \times 32 + \left(\frac{79}{21}\right) \times 22.65 \times 28 = 3110.6 \text{ kg}$$

$\therefore$ **Air-fuel ratio** $= \frac{3110.6}{8.5 \times 12 + 32.4 \times 1}$ **= 23.1 kg of air/kg of fuel. (Ans.)**

(*ii*) **Per cent theoretical air required for combustion :**

Mass fraction of carbon $= \frac{12 \times 8.5}{12 \times 8.5 + 32.4 \times 1} = 0.759$

Mass fraction of hydrogen $= \frac{32.4 \times 1}{12 \times 8.5 + 32.4} = 0.241$

Considering 1 kg of fuel, the *air required for complete combustion* is

$$= \left[0.759 \times \left(\frac{8}{3}\right) \times \frac{100}{23.3}\right] + \left[0.241 \times 8 \times \frac{100}{23.3}\right] = 16.96 \text{ kg}$$

$\therefore$ **Percent theoretical air required for combustion** $= \frac{23.1}{16.96} \times 100 =$ **136.2%. (Ans.)**

Example 9.16. *The following is the volumetric analysis of the dry exhaust from an internal combustion engine :*

$CO_2 = 8.9\%$; $CO = 8.2\%$; $H_2 = 4.3\%$; $CH_4 = 0.5\%$ *and* $N_2 = 78.1\%$.

If the fuel used is octane (C_8H_{18}) *determine air-fuel ratio on mass basis :*

(*i*) *By a carbon balance.* (*ii*) *By a hydrogen oxygen balance.*

Solution. (*i*) As per analysis of dry products, the combustion equation is written as

$$a\,C_8H_{18} + 78.1N_2 + 78.1\left(\frac{21}{79}\right)O_2 \longrightarrow 8.9CO_2 + 8.2CO + 4.3H_2 + 0.5CH_4 + 78.1N_2 + x\,H_2O$$

Carbon balance : $8a = 8.9 + 8.2 + 0.5 = 17.6$ *i.e.* $a = 2.2$

$$\therefore \quad \textbf{Air-fuel (A/F) ratio} \quad = \frac{78.1 \times 28 + 78.1 \times \frac{21}{79} \times 32}{2.2(8 \times 12 + 1 \times 18)}$$

$$= \frac{2186.8 + 664.3}{250.8} = \frac{2851.1}{250.8} = \mathbf{11.37.} \quad \textbf{(Ans.)}$$

(*ii*) In this case the combustion equation is written as

$$a\,C_8H_{18} + b\,O_2 + b\left(\frac{79}{21}\right)N_2 \longrightarrow 8.9CO_2 + 8.2CO + 4.3H_2 + 0.5CH_4 + b\left(\frac{79}{21}\right)N_2 + x\,H_2O$$

Carbon balance : $8a = 8.9 + 8.2 + 0.5 = 17.6$ *i.e.,* $a = 2.2$

Hydrogen balance : $18a = 4.3 \times 2 + 0.5 \times 4 + 2x$

or $18 \times 2.2 = 8.6 + 2 + 2x$ *i.e.,* $x = 14.5$

Oxygen balance : $2b = 8.9 \times 2 + 8.2 + x$

or $2b = 17.8 + 8.2 + 14.5$ *i.e.,* $b = 20.25$

$$\therefore \quad \textbf{Air-fuel (A/F) ratio} = \frac{(20.25 \times 32) + (20.25)\left(\frac{79}{21}\right) \times 28}{2.2(8 \times 12 + 1 \times 18)} = \frac{2781}{250.8} = \mathbf{11.09.} \quad \textbf{(Ans.)}$$

☞**Example 9.17.** *The exhaust from an engine running on benzole was measured with the help of Orsat apparatus. Orsat analysis showed a CO_2 content of 12%, but no CO. Assuming that the remainder of the exhaust contains only oxygen and nitrogen, calculate the air-fuel ratio of the engine.*

The ultimate analysis of benzole is C = 88% and H_2 = 12%.

Solution. 1 kg of fuel, consisting of 0.88 kg C and 0.12 kg H_2, can be written as 0.88/2 moles C and 0.12/2 moles H_2. Therefore, considering 1 mole of *dry exhaust gas* (D.E.G.) we can write the combustion equation as follows :

$$X\left(\frac{0.88}{12}C + \frac{0.12}{2}H_2\right) + Y\,O_2 + \frac{79}{21}\,Y\,N_2 \longrightarrow 0.12CO_2 + a\,O_2 + (0.88 - a)\,N_2 + b\,H_2O$$

[Let the D.E.G. contain a moles of O_2. The moles of CO_2 in 1 mole of D.E.G. are 0.12. Therefore the D.E.G. contains $(1 - a - 0.12) = (0.88 - a)$ moles of N_2.]

where,
X = Mass of fuel per mole D.E.G.,
Y = Moles of O_2 per mole D.E.G.,
a = Moles of *excess* O_2 per mole D.E.G., and
b = Moles of H_2O per mole D.E.G.

Now,

Carbon balance : $\frac{0.88}{12}X = 0.12$ $\quad \therefore \; X = 1.636$

Hydrogen balance : $0.06X = b$ $\quad \therefore \; b = 0.06 \times 1.636 = 0.098$

Oxygen balance : $2Y = 2 \times 0.12 + 2a + b$ or $2Y = 0.24 + 2a + 0.098$

$\therefore \; Y = 0.169 + a$

Nitrogen balance : $\frac{79}{21}Y = (0.88 - a)$ $\therefore\ Y = 0.234 - 0.266a$

Equating the expressions for Y gives

$$0.234 - 0.266a = 0.169 + a \qquad \therefore\ a = 0.0513$$

i.e., $$Y = 0.169 + 0.0513 = 0.2203$$

$\therefore$ O_2 supplied = 0.2203 × 32 kg/mole D.E.G.

i.e., Air supplied = $\frac{0.2203 \times 32}{0.233}$ = 30.26 kg/mole D.E.G.

Since $X = 1.636$, then, the fuel supplied per mole D.E.G. is 1.636 kg

$\therefore$ **A/F ratio =** $\frac{30.26}{1.636}$ **= 18.5/1. (Ans.)**

Example 9.18. *The analysis of the dry exhaust from an internal combustion engine is as follows :*

Carbon dioxide (CO_2) *= 15 per cent* *Carbon monoxide (CO) = 3 per cent*

Methane (CH_4) *= 3 per cent* *Hydrogen* (H_2) *= 1 per cent*

Oxygen (O_2) *= 2 per cent* *Nitrogen* (N_2) *= 76 per cent*

Calculate the proportions by mass of carbon to hydrogen in the fuel, assuming it to be a pure hydrocarbon.

Solution. Let 1 kg of fuel contain x kg of carbon (C) and y kg hydrogen (H_2). Then considering 1 mole of D.E.G. and introducing X and Y, we can write

$$X\left(\frac{x\,C}{12} + \frac{y}{2}H_2\right) + Y\,O_2 + \frac{79}{21}Y\,N_2 \longrightarrow 0.15CO_2 + 0.03CO + 0.03CH_4$$
$$+ 0.01H_2 + 0.02O_2 + a\,H_2O + 0.76N_2$$

Then,

Nitrogen balance : $\frac{79}{21}Y = 0.76$ $\therefore\ Y = 0.202$

Oxygen balance : $Y = 0.15 + \frac{0.03}{2} + 0.02 + \frac{a}{2}$

or $$0.202 = 0.15 + 0.015 + 0.02 + \frac{a}{2} \qquad \therefore\ a = 0.034$$

Carbon balance : $\frac{Xx}{12} = 0.15 + 0.03 + 0.03$ $\therefore\ Xx = 2.52$ ...(*i*)

Hydrogen balance : $\frac{Xy}{2} = 2 \times 0.03 + 0.01 + a = 0.06 + 0.01 + 0.034$

$\therefore$ $Xy = 0.208$ ...(*ii*)

Dividing equations (*i*) and (*ii*), we get

$$\frac{Xx}{Xy} = \frac{2.52}{0.208} \quad \text{or} \quad \frac{x}{y} = 12.1$$

i.e., **Ratio of C to H_2 in fuel =** $\frac{x}{y} = \mathbf{\frac{12.1}{1}}$. **(Ans.)**

Internal Energy and Enthalpy of Combustion

Example 9.19. *ΔH_0 (enthalpy of combustion at reference temperature T_0) for benzene vapour (C_6H_6) at 25°C is – 3301000 kJ/mole with the H_2O in the liquid phase. Calculate ΔH_0 for the H_2O in the vapour phase.*

Solution. If H_2O remains as a vapour the heat transferred to the surroundings will be less than when the vapour condenses by the amount due to the change in enthalpy of the vapour during condensation at the reference temperature.

$$\Delta H_0 \text{ (vapour)} = \Delta H_0 \text{ (liquid)} + m_s\, h_{fg0}$$

where, m_s = Mass of H_2O formed, and

h_{fg0} = Change in enthalpy of steam between saturated liquid and saturated vapour at the reference temperature T_0

= 2441.8 kJ at 25°C

For the reaction :

$$C_6H_6 + 7.5O_2 \longrightarrow 6CO_2 + 3H_2O$$

3 moles of H_2O are formed on combustion of 1 mole of C_6H_6 ; 3 moles of H_2O

$$= 3 \times 18 = 54 \text{ kg } H_2O$$

$\therefore$ **ΔH_0 (vapour)** $= -3301000 + 54 \times 2441.8 =$ **$-$ 3169143 kJ/mole. (Ans.)**

Example 9.20. *Calculate ΔU_0 in kJ/kg for the combustion of benzene (C_6H_6) vapour at 25°C given that $\Delta H_0 = -3169100$ kJ/mole and the H_2O is in the vapour phase.*

Solution. Given : $\Delta H_0 = -3169100$ kJ

The combustion equation is written as

$$C_6H_6 + 7.5O_2 \longrightarrow 6CO_2 + 3H_2O \text{ (vapour)}$$

$$n_R = 1 + 7.5 = 8.5,\ n_P = 6 + 3 = 9$$

Using the relation, $\Delta U_0 = \Delta H_0 - (n_P - n_R)R_0T_0$

$$= -3169100 - (9 - 8.5) \times 8.314 \times (25 + 273)$$

$$= -3169100 - 1239 = -3170339 \text{ kJ/mole}$$

(It may be noted that ΔU_0 is negligibly different from ΔH_0)

1 mole of $C_6H_6 = 6 \times 12 + 1 \times 6 = 78$ kg

$$\therefore \quad \mathbf{\Delta U_0} = \frac{-3170339}{78} = \mathbf{-\ 40645\ kJ/kg.} \quad \textbf{(Ans.)}$$

Example 9.21. *ΔH_0 for CO at 60°C is given as – 285200 kJ/mole. Calculate ΔH_0 at 2500°C given that the enthalpies of gases concerned in kJ/mole are as follows :*

Gas	*60°C*	*2500°C*
CO	*9705*	*94080*
O	*9696*	*99790*
CO_2	*10760*	*149100*

Solution. The reaction equation is given by

$$CO + \tfrac{1}{2}\, O_2 \longrightarrow CO_2$$

Refer Fig. 9.34.

It can be seen from the property diagram of Fig. 9.34 that the enthalpy of combustion at temperature T, ΔH_T can be obtained from ΔH_0 and T_0 by the relationship

$$-\Delta H_T = -\Delta H_0 + (H_{R_T} - H_{R_0}) - (H_{P_T} - H_{P_0}) \quad ...(i)$$

where, $H_{R_T} - H_{R_0}$ = increase in enthalpy of the *reactants* from T_0 to T

and $H_{P_T} - H_{P_0}$ = increase in enthalpy of the *products* from T_0 to T.

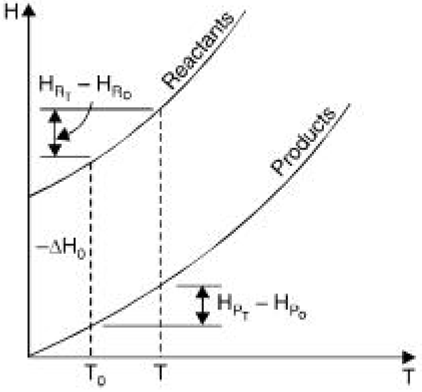


Fig. 9.34

Now, from the given data, we have

$$H_{R_0} = 1 \times 9705 + \tfrac{1}{2} \times 9696 = 14553 \text{ kJ}$$

$$H_{R_T} = 1 \times 94080 + \tfrac{1}{2} \times 99790 = 143975 \text{ kJ}$$

$$H_{P_0} = 1 \times 10760 = 10760 \text{ kJ}$$

$$H_{P_T} = 1 \times 149100 \text{ kJ} = 149100 \text{ kJ}$$

Using equation (*i*), we get

$$-\Delta H_T = +285200 + (143975 - 14553) - (149100 - 10760)$$

$$= 285200 + 129422 - 138340 = 276282$$

$\therefore$ **ΔH_T = – 276282 kJ/mole. (Ans.)**

Heating Values of Fuels

Example 9.22. *The lower heating value of propane at constant pressure and 25°C is 2044009 kJ per kg mole. Find the higher heating value at constant pressure and at constant volume.*

Solution. (*i*) **Higher heating value at constant pressure, $(\mathbf{HHV})_p$:**

The combustion reaction for propane is written as

$$C_3H_8 + 5O_2 = 3CO_2 + 4H_2O$$

Now $$(\text{HHV})_p = (\text{LHV})_p + mh_{fg}$$

where , HHV = Higher heating value at constant pressure

LHV = Lower heating value

m = Mass of water formed by combustion

= 4 × 18 = 72 kg per kg mole

h_{fg} = Latent heat of vapourisation at given temperature per unit mass of water

= 2442 kJ/kg at 25°C

$\therefore$ **$(\text{HHV})_p$** = 2044009 + 72 × 2442 = **2219833 kJ/kg. (Ans.)**

(*ii*) **Higher heating value at constant volume, $(\mathbf{HHV})_v$:**

Now $$(\Delta U) = \Delta H - \Delta n R_0 T$$

or $$-(\text{HHV})_v = -(\text{HHV})_p - \Delta n R_0 T$$

or $$(\text{HHV})_v = (\text{HHV})_p + \Delta n R_0 T$$

where, R_0 = Universal gas constant = 8.3143 kJ/kg mol K

$\Delta n = n_P - n_R$

$$\begin{bmatrix} n_P = \text{Number of moles of gaseous products} \\ n_R = \text{Number of moles of gaseous reactants} \end{bmatrix}$$

Now, the reaction for higher heating value is

$$C_3H_8 + 5O_2 = 3CO_2 + 4H_2O \text{ (liquid)}$$

$$\Delta n = 3 - (1 + 5) = -3$$

$\therefore$ **$(\text{HHV})_v$** = 2219833 – 3(8.3143)(25 + 273) = **2212400 kJ/kg. (Ans.)**

Example 9.23. *Calculate the lower heating value of gaseous octane at constant volume if* $(\Delta U)_{25°C} = -5494977$ *kJ for the reaction :*

$$[C_8H_{18} \text{ (gas)} + 12.5O_2 \text{ (gas)}] = [8CO_2 \text{ (gas)} + 9H_2O \text{ (liquid)}].$$

Solution. The given value of ΔU corresponds to the *higher heating value* at constant volume because the water in the products is in *liquid phase.*

$$\text{HHV} = 5494977 \text{ kJ/kg}$$

$$(\text{LHV})_v = (\text{HHV})_v - m(u_g - u_f)$$

$$m = 9 \times 18 = 162 \text{ kg/kg mole } C_8H_{18}$$

$$(u_g - u_f) = 2305 \text{ kJ/kg at } 25°\text{C}$$

∴ $$\mathbf{(LHV)_v} = 5494977 - 162(2305) = \mathbf{5121567 \text{ kJ/kg.}} \quad \textbf{(Ans.)}$$

Example 9.24. *Calculate the lower and higher heating values at constant pressure per kg of mixture at 25°C, for the stoichiometric mixtures of :*

(*i*) *Air and benzene vapour* (C_6H_6) *and*

(*ii*) *Air and octane vapour* (C_8H_{18}).

Given that the enthalpies of combustion at 25°C are :

$$C_6H_6 = -3169500 \text{ kJ/mole}$$

$$C_8H_{18} = -5116200 \text{ kJ/mole}$$

Both the above figures are for the case where the water in the products is in the vapour phase.

Solution. (*i*) **Air and benzene vapour :**

For benzene, the combustion equation is as follows :

$$C_6H_6(g) + 7.5O_2(g) + 7.5\left(\frac{79}{21}\right)N_2(g) = 6CO_2(g) + 3H_2O(g) + 7.5\left(\frac{79}{21}\right)N_2(g)$$

Since the water in the products is in *vapour phase*, therefore, the given value of enthalpy of combustion corresponds to the *lower heating* value at constant pressure.

i.e. $$(\text{LHV})_p = 3169500 \text{ kJ/mole}$$

$$\textbf{(LHV)}_\mathbf{v} \textbf{ per kg of mixture} = \frac{3169500}{(12 \times 6 + 6 \times 1) + (7.5 \times 32) + 7.5\left(\frac{79}{21}\right)(28)}$$

$$= \frac{3169500}{78 + 240 + 790} = \mathbf{2861 \text{ kJ/kg.}} \quad \textbf{(Ans.)}$$

Now, $$(\text{HHV})_p = (\text{LHV})_p + mh_{fg}$$

where, $(\text{HHV})_p$ = Higher heating value at constant pressure,

$(\text{LHV})_p$ = Lower heating value at constant pressure,

m = Mass of water formed by combustion,

= 3 × 18 = 54 kg/kg mole of fuel, and

h_{fg} = Latent heat of vapourisation at given temperature per unit mass of water

= 2442 kJ/kg at 25°C.

∴ $$(\text{HHV})_p = 3169500 + 54 \times 2442 = 3301368 \text{ kJ/mole}$$

Thus, $$\textbf{(HHV)}_\mathbf{p} \textbf{ per kg of mixture} = \frac{3301368}{78 + 240 + 790} = \mathbf{2980 \text{ kJ/kg.}} \quad \textbf{(Ans.)}$$

(*ii*) **Air and octane vapour :**

$$(\text{LHV})_p = 5116200 \text{ kJ/mole of } C_8H_{18}$$

For octane, the combustion equation is written as follows :

$$C_8H_{18}(g) + 12.5O_2(g) \longrightarrow 8CO_2(g) + 9H_2O(g) + 12.5\left(\frac{79}{21}\right) N_2(g)$$

(LHV)$_p$ per kg of mixture $= \dfrac{5116200}{(12 \times 8 + 18 \times 1) + 12.5 \times 32 + 12.5 \times \dfrac{79}{21} \times 28}$

$= \dfrac{5116200}{114 + 400 + 1317}$ **= 2794 kJ/kg. (Ans.)**

$$(HHV)_p = (LHV)_p + mh_{fg}$$

$$m = 9 \times 18 = 162 \text{ kJ/kg mole of fuel}$$

$\therefore$ $(HHV)_p = 5116200 + 162 \times 2442 = 5511804$

Hence, **(HHV)$_p$ per kg of mixture** $= \dfrac{5511804}{114 + 400 + 1317}$ **= 3010 kJ/kg. (Ans.)**

☞**Example 9.25.** *The higher heating value of kerosene at constant volume whose ultimate analysis is 88% and 12% hydrogen, was found to be 45670 kJ/kg. Calculate the other three heating values.*

Solution. Combustion of 1 kg of fuel produces the following products :

$$CO_2 = \frac{44}{12} \times 0.88 = 3.23 \text{ kg}$$

$$H_2O = \frac{18}{2} \times 0.12 = 1.08 \text{ kg}$$

At 25°C : $(u_g - u_f)$ *i.e.* $u_{fg} = 2304$ kJ/kg

$h_{fg} = 2442$ kJ/kg

(*i*) **(LHV)$_v$:**

$$(LHV)_v = (HHV)_v - m(u_g - u_f)$$

$$= 45670 - 1.08 \times 2304 = 43182 \text{ kJ/kg}$$

Hence **(LHV)$_v$ = 43182 kJ/kg. (Ans.)**

(*ii*) **(HHV)$_p$:, (LHV)$_p$:**

The combustion equation is written as follows :

$$1 \text{ mole fuel} + \frac{x}{32} O_2 \longrightarrow \frac{3.23}{44} CO_2 + \frac{1.08}{18} H_2O$$

i.e., $\dfrac{x}{32} = \dfrac{3.23}{44} + \dfrac{1.08}{18 \times 2}$

or $x = 3.31$ kg

i.e., 1 kg fuel + 3.31 kg O_2 = $3.23CO_2 + 1.08H_2O$

Also, $\Delta H = \Delta U + \Delta n R_0 T$

i.e., $-(HHV)_p = -(HHV)_v + \Delta n R_0 T$

or $(HHV)_p = (HHV)_v - \Delta n R_0 T$

where, $\Delta n = n_p - n_R$

$$= \left(\frac{3.23}{44} - \frac{3.31}{32}\right) \quad \begin{bmatrix} n_p = \text{Number of moles of gaseous products} \\ n_R = \text{Number of moles of gaseous reactants} \end{bmatrix}$$

Since in case of higher heating value, H_2O will appear in liquid phase

$$\textbf{(HHV)}_\textbf{p} = 45670 - \left(\frac{3.23}{44} - \frac{3.31}{32}\right) \times 8.3143 \times (25 + 273)$$

$$= \textbf{45744 kJ/kg.} \quad \textbf{(Ans.)}$$

$$\textbf{(LHV)}_\textbf{p} = (\text{HHV})_p - 1.08 \times 2442 = 45774 - 1.08 \times 2442$$

$$= \textbf{43107 kJ/kg.} \quad \textbf{(Ans.)}$$

Example 9.26. *The reaction equation of a fuel is represented by*

$$C_nH_m + aO_2 + bN_2 = 8CO_2 + 0.9CO + 8.8O_2 + dH_2O + 82.3\ N_2$$

Determine :

(*i*) *The actual air-fuel ratio and the chemical formula of the fuel ;*

(*ii*) *The stoichiometric air-fuel ratio and the percent theoretical air used.*

You may assume N_2/O_2 ratio in air = 3.76 : **(Bombay University)**

Solution. $C_nH_m + aO_2 + bN_2 = 8CO_2 + 0.9\ CO + 8.8O_2 + dH_2O + 82.3N_2$

Equating coefficients, we have

C : $n = 8 + 0.9 = 8.9$ ...(*i*)

H : $m = 2d$ ...(*ii*)

O_2 : $a = 8 + \frac{0.9}{2} + 8.8 + \frac{d}{2}$ ...(*iii*)

N_2 : $b = 82.3$ ...(*iv*)

Assume N_2/O_2 ratio in air = 3.76

It means $\frac{b}{a} = 3.76$

or $b = 3.76\ a$ ...(*v*)

On solving eqns. (*i*), (*ii*), (*iii*), (*iv*) and (*v*), we get

$$a = 21.89, \quad b = 82.3, \qquad d = 9.28$$

$$m = 18.56, \quad n = 8.9$$

(*i*) **Chemical formula of fuel is : $C_{8.9}H_{18.56}$ (Ans.)**

$$\textbf{Actual air-fuel ratio} = \frac{m_a}{m_f} = \frac{21.89 \times 32 + 82.3 \times 28}{8.9 \times 12 + 18.56 \times 1} = \textbf{23.97.} \quad \textbf{(Ans.)}$$

(*ii*) **Stoichiometric air-fuel ratio :**

Stoichiometric air-fuel ratio can be found by finding the theoretical air required for complete combustion of 1 kg of fuel. Hence,

$$C_{8.9}\ H_{18.56} + 13.54\ O_2 = 8.9\ CO_2 + 9.28\ H_2O$$

Mass of oxygen required for combustion of 1 kg fuel

$$= \frac{13.54 \times 32}{8.9 \times 12 + 18.56 \times 1} = 3.456$$

Mass of air required for complete combustion of 1 kg fuel

$$= \frac{3.456}{0.23} = 15.03 \text{ kg}$$

Stoichiometric air-fuel ratio = 15.03 kg

Percentage theoretical air used $= \dfrac{23.97}{15.03} \times 100 =$ **159.48%. (Ans.)**

HIGHLIGHTS

Chemical Thermodynamics

1. A *chemical reaction* may be defined as the rearrangement of atoms due to redistribution of electrons. '*Reactants*' comprise of initial constituents which start the reaction while '*products*' comprise of final constituents which are formed by the chemical reaction.

2. A chemical fuel is a substance which releases heat energy on combustion.

3. The total number of atoms of each element concerned in the combustion remains constant, but the atoms are rearranged into groups having different chemical properties.

4. The amount of excess air supplied varies with the type of the fuel and the firing conditions. It may approach a value of 100 per cent but modern practice is to use 25% to 50% excess air.

5. *Stoichiometric* (or chemically correct) *mixture* of air and fuel is one that contains just sufficient oxygen for complete combustion of the fuel.

6. Mixture strength $= \dfrac{\text{Stoichiometric A / F ratio}}{\text{Actual A / F ratio}}$.

7. When analysis of combustion products is known air fuel ratio can be calculated by the following methods :

(*a*) Fuel composition known
  (*i*) Carbon balance method
  (*ii*) Hydrogen balance method
  (*iii*) Carbon hydrogen balance method
(*b*) Fuel composition unknown
  (*i*) Carbon hydrogen balance method.

8. The most common means of analysis of the combustion products is Orsat apparatus.

9. The *enthalpy of formation* (ΔH_f) is the increase in enthalpy when a compound is formed from its constituent elements in their natural form and in a standard state. The standard state is 25°C and 1 atm. pressure (but it must be borne in mind that not all substances can exist in natural form, *e.g.* H_2O cannot be a vapour at 1 atm. and 25°C).

10.
$$(\text{HHV})_p = (\text{LHV})_p + m\,h_{fg}$$
$$(\text{HHV})_v = (\text{LHV})_v + m(u_g - u_f)$$

where, HHV = higher heating value
LHV = lower heating value
m = mass of water formed by combustion
h_{fg} = enthalpy of vapourisation of water, kJ/kg
u_g = specific internal energy of vapour, kJ/kg
u_f = specific internal energy of liquid, kJ/kg.

11. In a given combustion process, that takes place adiabatically and with no work or changes in kinetic or potential energy involved, the temperature of the products is referred to as the '*adiabatic flame temperature*'.

12. For a given fuel and given pressure and temperature of the reactants, the maximum adiabatic flame temperature that can be achieved is with a 'stoichiometric' mixture.

Conventional Fuels

13. The constituents petroleum are classified into the following four groups :

(*i*) Paraffins
(*ii*) Olefins
(*iii*) Naphthenes
(*iv*) Aromatics.

14. The process of separating petroleum into useful fractions and removal of undesirable impurities is called *refining.*

15. *Volatility* is commonly defined as the *evaporating tendency of a liquid fuel.* The volatility of gasoline is generally characterised by the following two laboratory tests :

(*i*) ASTM distillation test (*ii*) Reid vapour test.

16. *Vapour lock* is a situation where too lean a mixture is supplied to the engine. The vapour lock tendency of the gasoline is related to front end volatility.

17. When self-ignition does occur in S.I. engine higher than desirable, pressure pulses are generated. The higher above self-ignition temperature which the fuel is heated, the shorter will be ignition delay.

18. The *highest useful compression ratio* (HUCR) is the highest compression ratio at which a fuel can be used without detonation in a specified test-engine under specified operating conditions and the ignition and mixture strength being adjusted to give best efficiency.

19. The property of a fuel which describes how fuel will or will not self-ignite is called the *Octane number* or just *Octane.* Engines with low compression ratios can use fuels with lower octane number, but high-compression engines must use high-octane fuel to avoid self-ignition and knock.

20. The difference in octane number between reseach method and motor method octane numbers is known as the *fuel sensitivity.*

21. Antiknock index $= \frac{\text{RON} + \text{MON}}{2}$.

22. High octane fuels (upto 100) can be produced by *refining techniques*, but it is done more cheaply, and more frequently, by the use of antiknock *additives* such as *tetraethyl lead.*

23. Cetane number of diesel fuel is a measure of its ignition quality.

In general, lower the cetane number higher are the hydrocarbon emissions and noise levels. In general, a high octane value implies a low cetane value.

24. Diesel index (D.I.) = Aniline point (°F) $\times \frac{\text{API gravity (deg)}}{100}$

Alternative Fuels

25. Some alternative fuels which can replace conventional fuels in I.C. engine are :

(*i*) Alcohol (methyl and ethyl) (*ii*) Hydrogen

(*iii*) Natural gas (*iv*) LPG and LNG

(*v*) Biogas.

26. The power output of ethanol engine is higher compared to gasoline engine at all speeds.

27. The CNG fuel used engines have higher thermal efficiencies than those fuelled by gasoline.

28. Biogas possesses excellent antiknock properties with an equivalent octane number in excess of 120 compared with 87 for regular petrol.

OBJECTIVE TYPE QUESTIONS

A. Choose the Correct Answer :

1. The smallest particle which can take part in a chemical change is called

(*a*) atom (*b*) molecule

(*c*) electron (*d*) compound.

2. A chemical fuel is a substance which releases ...... on combustion.

(*a*) chemical energy (*b*) heat energy

(*c*) sound energy (*d*) magnetic energy.

3. The most important solid fuel is

(*a*) wood (*b*) charcoal

(*c*) coal (*d*) all of the above.

4. For each mole of oxygen, number of moles of nitrogen required for complete combustion of carbon are
(*a*) 20/21
(*b*) 2/21
(*c*) 77/21
(*d*) 79/21.

5. Modern practice is to use ...... excess air.
(*a*) 5 to 10 per cent
(*b*) 15 to 20 per cent
(*c*) 20 to 25 per cent
(*d*) 25 to 50 per cent.

6. Stoichiometric air-fuel ratio by mass for combustion of petrol is
(*a*) 5
(*b*) 10
(*c*) 12
(*d*) 15.05.

7. An analysis which includes the steam in the exhaust is called
(*a*) dry analysis
(*b*) wet analysis
(*c*) dry and wet analysis
(*d*) none of the above.

8. The Orsat apparatus gives
(*a*) volumetric analysis of the dry products of combustion
(*b*) gravimetric analysis of the dry products of combustion
(*c*) gravimetric analysis of products of combustion including H_2O
(*d*) volumetric analysis of products of combustion including H_2O.

9. In the Orsat apparatus KOH solution is used to absorb
(*a*) carbon monoxide
(*b*) carbon dioxide
(*c*) oxygen
(*d*) none of the above.

10. Enthalpy of formation is defined as enthalpy of compounds at
(*a*) 25°C and 10 atmospheres
(*b*) 25°C and 1 atmosphere
(*c*) 0°C and 1 atmosphere
(*d*) 100°C and 1 atmosphere.

11. Bomb calorimeter is used to find the calorific value of ...... fuels.
(*a*) solid
(*b*) gaseous
(*c*) solid and gaseous
(*d*) none of the above.

12. When the fuel is burned and the water appears in the vapour phase, the heating value of fuel is called
(*a*) enthalpy of formation
(*b*) lower heating value
(*c*) higher heating value
(*d*) none of the above.

13. Heat released in a reaction at constant pressure is called
(*a*) entropy change
(*b*) enthalpy of reaction
(*c*) internal energy of reaction
(*d*) none of the above
(*e*) all of the above.

14. When the fuel is burned and water is released in the liquid phase, the heating value of fuel is called
(*a*) higher heating value
(*b*) lower heating value
(*c*) enthalpy of formation
(*d*) none of the above.

15. Choose the *correct* statement :
(*a*) Number of atoms of each constituent are not conserved in a chemical reaction.
(*b*) The mass of all the substances on one side of the equation may not be equal to the mass of all the substances on the other side.
(*c*) The number of atoms of each constituent are conserved in a chemical reaction.
(*d*) The number of moles of the reactants in a chemical equation are equal to the number of moles of the products.

ANSWERS

1. (*a*) **2.** (*b*) **3.** (*c*) **4.** (*d*) **5.** (*d*) **6.** (*d*) **7.** (*b*)
8. (*a*) **9.** (*b*) **10.** (*b*) **11.** (*a*) **12.** (*b*) **13.** (*b*) **14.** (*a*)
15. (*c*).

B. Fill in the Blanks or Say "Yes" or "No" :

1. The liquid fuels find ...... use in I.C. engines.

2. ...... gas is manufactured by heating soft coal in closed vessel.

3. Water gas is formed by using steam.

4. ...... gas is a by-product of steel plants.

5. Benzol is obtained as a by-product of high temperature coal carbonization.

6. Olefins are compounds with one or more double bonded carbon atoms in straight chain.

7. Diolefins are more ...... than mono-olefins.

8. Napthenes are ...... structured compounds.

9. Napthenes are unsaturated compounds.

10. Paraffins are most suitable fuels for ...... engines.

11. Aromatics are most suitable fuels for ...... engines.

12. The process of separating petroleum into useful fractions and removal of undesirable impurities is called ....

13. ...... is the evaporating tendency of a liquid fuel.

14. The ...... of petrol is also defined in terms of Reid vapour pressure.

15. ...... is a situation where too lean a mixture is supplied to the engine.

16. The vapour lock tendency of gasoline is related to ...... end volatility.

17. When self-ignition does occur in S.I. engine higher than desirable, ... pulses are generated.

18. The higher above S.I.T. which the fuel is heated, the longer will be ignition delay.

19. Ignition delay is generally a very small fraction of a second.

20. The property of fuel which describes how fuel will or will not self-ignite is called the ...... number.

21. The higher the octane number of fuel, the less likely it will self-ignite.

22. The difference in octane number between research method and the motor method octane numbers is known as the ....

23. Fuel sensitivity is a good measure of how sensitive knock characteristics of a fuel will be to engine geometry.

24. Anti-knock index = $\dfrac{\text{RON} - \text{MON}}{2}$.

25. The cetane number of a diesel fuel is a measure of its ignition quality.

26. Higher the cetane rating of the fuel lesser is the propensity for diesel knock.

27. In general, a high octane value implies a high cetane value.

28. Methanol is very corrosive on metals.

29. Ethanol has less HC emissions than gasoline but more than methanol.

30. The CNG used engines have lower thermal efficiencies than those fuelled by gasoline.

ANSWERS

1. abundant **2.** coal **3.** Yes **4.** Blast furnace **5.** Yes
6. Yes **7.** unstable **8.** ring **9.** No. **10.** C.I.
11. S.I. **12.** refining **13.** Volatility **14.** Volatility **15.** Vapour lock
16. front **17.** pressure **18.** No. **19.** Yes **20.** octane
21. Yes **22.** fuel sensitivity **23.** Yes **24.** No **25.** Yes
26. Yes **27.** No **28.** Yes **29.** Yes **30.** No.

THEORETICAL QUESTIONS

Chemical Thermodynamics

1. What is chemical thermodynamics ?

2. What is a chemical fuel ?

3. What are primary fuels ? List some important primary fuels.

4. What are secondary fuels ? List some important secondary fuels.

5. Write a short note on 'excess air'.

6. What do you mean by stoichiometric air fuel (A/F) ratio ?

7. Enumerate the methods by which air fuel ratio can be calculated when analysis of combustion products is known.

8. How is analysis of exhaust and flue gas carried out ?

9. Derive relations for internal energy and enthalpy of reaction.

10. What is enthalpy of formation $(\Delta H_f) = ?$

11. Define heating value of fuel.

12. What is the difference between higher heating value (HHV) and lower heating value (LHV) of the fuel ?

13. Describe with the help of neat sketches the following calorimeters used for the determination of heating values :

(*i*) Bomb calorimeter (*ii*) Junkers gas calorimeter.

14. What is 'adiabatic flame temperature' ?

15. Write a short note on chemical equilibrium.

Conventional Fuels

16. What are the desirable properties of good I.C. engines fuels ?

17. Enumerate and describe briefly the gaseous fuels.

18. How are constituents of petroleum classified ?

19. Explain briefly the chemical structure of petroleum.

20. What are five primary hydrocarbon families found in petroleum ? Which are chain types ? Which are ring types ? Which of primary families tends to be better S.I. engine fuel and C.I. engine fuel ?

21. What are different kinds of fuels used in an I.C. engine ?

22. What are the important properties which S.I. engine fuel possess ?

23. What are requirements of an ideal gasoline fuel ?

24. What is volatility ?

25. Discuss the significance of distillation curve.

26. Why volatility is an important quality of S.I. engine fuels ?

27. Explain briefly the following in regard to a fuel :

(*i*) Vapour lock characteristics.

(*ii*) Crankcase dilution.

28. "While volatility of the fuel is a determining factor in the selection of fuels for S.I. engines, ignition quality of the fuel is the primary deciding factor for C.I. engines". Discuss briefly the statements.

29. Distinguish clearly between 'Octane Numbers' and 'Cetane Number'. What is their significance in rating of fuels for S.I. and C.I. engines ?

30. What are the reference fuels for 'Octane Number' ?

31. What are the reference fuels for 'Cetane Number' ?

32. What is performance number (PN) ?

33. What is the significance of ASTM distillation curve ?

34. Explain the effect of fuel viscosity on diesel engine performance.

35. What qualities are desired in fuels to inhibit detonation ?

36. Give the advantages of using alternate fuels.

37. Discuss different properties of ethanol and methanol and compare them with gasoline.

38. Why blends of either ethanol or methanol are preferred over pure alcohol fuels ?

39. Give the advantages of alcohol as a fuel.

40. List the advantages of methanol as a fuel.

41. What modifications in engine are required when blends are used ?

42. State the advantages and disadvantages of hydrogen as I.C. engine fuel.

43. What is natural gas ?

44. What are the properties of CNG ?

45. What are the advantages and disadvantages of CNG ?

46. Explain briefly LPG and LNG.

47. What is Biogas ?

48. What are the properties of biogas ?

UNSOLVED EXAMPLES

1. Determine the gravimetric analysis of the products of complete combustion of acetylene (C_2H_2) with 125 per cent stoichiometric air. [**Ans.** CO_2 = 19.5%, H_2O = 3.9%, O_2 = 4.4%, N_2 = 72.2%]

2. One kg of ethane (C_2H_6) is burned with 80% of theoretical air. Assuming complete combustion of the hydrogen in the fuel determine the volumetric analysis of the dry products of combustion.
[**Ans.** CO_2 = 4.8%, CO = 11.2%, N_2 = 84%]

3. The gravimetric analysis of a sample of coal is given as 80% C, 12% H_2 and 8% ash. Calculate the stoichiometric A/F ratio and the analysis of the products by volume.
[**Ans.** CO_2 = 13.6%, H_2 = 12.2%, N_2 = 74.2%]

4. Calculate the stoichiometric air fuel ratio for the combustion of a sample of dry anthracite of the following composition by mass :
C = 90 per cent ; H_2 = 3 per cent ; N_2 = 1 per cent ; Sulphur = 0.5 per cent ; ash = 3 per cent.
If 20 per cent excess air is supplied determine :
(*i*) Air fuel ratio
(*ii*) Wet analysis of the products of combustion by volume.
[**Ans.** 11.25/1 (*i*) 13.5/1 ; (*ii*) CO_2 = 16.3%, H_2O = 0.03%, SO_2 = 3.51%, N_2 = 80.3%]

5. The following is the analysis of a supply of coal gas :
H_2 = 49.4 per cent ; CO = 18 per cent ; CH_4 = 20 per cent ; C_4H_8 = 2 per cent ; O_2 = 0.4 per cent ; N_2 = 6.2 per cent ; CO_2 = 4 per cent.
(*i*) Calculate the stoichiometric A/F ratio.
(*ii*) Find also the wet and dry analysis of the products of combustion if the actual mixture is 20 per cent weak. [**Ans.** (*i*) 4.06/1 by volume ; (*ii*) Wet analysis : CO_2 = 9.0%, H_2O = 17.5%, O_2 = 3.08%, N_2 = 70.4%. Dry analysis : CO_2 = 10.9%, O_2 = 3.72%, N_2 = 85.4%]

6. Find the stoichiometric air fuel ratio for the combustion of ethyl alcohol (C_2H_6O), in a petrol engine. Calculate the air fuel ratios for the extreme mixture strengths of 90% and 120%. Determine also the wet and dry analysis by volume of the exhaust gas for each mixture strength.
[**Ans.** 8.96/1 ; 9.95/1 ; 7.47/1, Wet analysis : CO_2 = 11.2%, H_2O = 16.8%, O_2 = 1.85%, N_2 = 70.2%
Dry analysis : CO_2 = 13.45%, O_2 = 2.22%, N_2 = 84.4%
Wet analysis : CO_2 = 6.94%, CO = 6.94%, H_2 = 20.8%, N_2 = 65.3%
Dry analysis : CO_2 = 8.7%, CO = 8.7%, N_2 = 82.5%]

7. For the stoichiometric mixture of Example 7.10 calculate :
(*i*) The volume of the mixture per kg of fuel at a temperature of 65°C and a pressure of 1.013 bar.
(*ii*) The volume of the products of combustion per kg of fuel after cooling to a temperature of 120°C at a pressure of 1 bar. [**Ans.** (*i*) 9.226 m^3 ; (*ii*) 11.58 m^3]

8. The chemical analysis of a fuel by weight is as follows :

Carbon = 50 per cent ; Hydrogen = 25 per cent ; Oxygen = 10 per cent ; Sulphur = 5 per cent and Nitrogen = 10 per cent.

Find the stoichiometric amount of air required for complete combustion of this fuel. [**Ans.** 14.26 kg]

9. The percentage composition of a fuel by weight is as follows :

Carbon = 89.3 per cent ; Hydrogen = 5 per cent ; Oxygen = 4.2 per cent ; Nitrogen = 1.5 per cent and the remainder ash. Determine the stoichiometric air fuel ratio by mass.

If 30 per cent excess air is supplied, find the percentage composition of dry flue gases by volume.

[**Ans.** 11.74 ; CO_2 = 14.3%, O_2 = 4.9%, N_2 = 80.8%]

10. Orsat analysis of the products of combustion of hydrocarbon fuel of unknown composition is as follows :

Carbon dioxide (CO_2) = 9% Carbon monoxide (CO) = 0.6%

Oxygen (O_2) = 7.3% Nitrogen (N_2) = 83.1%

Determine the following :

(*i*) Air-fuel ratio (*ii*) Per cent theoretical air required for combustion.

[**Ans.** (*i*) 22.1, (*ii*) 146.2%]

11. An Orsat analysis of the exhaust from an engine running on benzole showed a CO_2 content of 15 per cent, but no CO. Assuming that the remainder of the exhaust contains only oxygen and nitrogen, calculate the air-fuel ratio of the engine.

The ultimate analysis of benzole is C = 90 per cent and H_2 = 10%.

[**Ans.** 15.2/1]

12. The analysis of the dry exhaust from and internal-combustion engine gave :

CO_2 = 12 per cent ; CO = 2 per cent ; CH_4 = 4 per cent ; H_2 = 1 per cent ; O_2 = 4.5 per cent and the remainder nitrogen.

Calculate the proportions by mass of carbon to hydrogen in the fuel, assuming it to be a pure hydrocarbon.

[**Ans.** 7.35/1]

13. The following is the percentage analysis by mass of a fuel :

Hydrogen (H_2) = 10 per cent Oxygen (O_2) = 2 per cent

Sulphur (S) = 1 per cent Nitrogen (N_2) = 3 per cent

Determine the following :

(*i*) The amount of air required to completely burn 1 kg of this fuel

(*ii*) The products of combustion as a percentage by mass.

[**Ans.** 13.17 kg ; CO_2 = 21.7% ; H_2O = 6.35% ; SO_2 = 0.141% ; N_2 = 71.75%]

14. An Orsat analysis of the products of combustion resulting from the burning in air of a hydrocarbon fuel yielded the following :

Carbon dioxide (CO_2) = 12.2% Oxygen (O_2) = 1.1%

Carbon monoxide (CO) = 0.5% Nitrogen (N_2) = 86.2%

Determine : (*i*) The mass fraction of carbon in the fuel.

(*ii*) Air-fuel ratio.

(*iii*) Percent of air theoretically needed for complete combustion.

[**Ans.** (*i*) 80.4%, (*ii*) 16.57/1, (*iii*) 103.9%]

15. If the higher heating value at constant pressure (C_6H_6) at 25°C is 3298354 kJ/kg mole, determine its lower calorific value at constant pressure. [**Ans.** 316647 kJ/mole]

16. The lower heating value of propane at constant pressure and 25°C is 2042055 kJ/kg mole. Find the higher heating value at constant pressure and at constant volume.

[**Ans.** 2217816 kJ/kg mole, 2210333 kJ/kg mole]

17. The higher heating value of kerosene at constant volume whose ultimate analysis is 86% carbon and 14% hydrogen, was found to be 46890 kJ/kg. Calculate the other three heating values.

[**Ans.** $(LHV)_v$ = 43987 kJ/kg ; $(HHV)_p$ = 46977 kJ/kg ; $(LHV)_p$ = 43900 kJ/kg]