Chemical Fuels

5.1 Introduction

Chemical fuel is a combustible carbonaceous material which on proper burning in air gives large amount of heat that can be used economically for domestic and industrial purposes.

The examples of chemical fuels include wood, charcoal, coal, kerosene, petrol, diesel, producer gas, water gas, natural gas, etc.,

The main elements invariably present in chemical fuels are C and H. During the process of combustion of a chemical fuel, C and H combine with oxygen of air to form CO_2 and H_2O respectively. Since the heat content of combustion products (CO_2, H_2O, etc.) being lower than that of reactants (C, H, etc. of fuel), the chemical fuel release heat during their combustion process.

5.2 Classification

On the basis of their origin chemical fuels are classified as primary and secondary fuels. These are again subdivided into solid, liquid and gaseous according to the physical state.

A primary (Natural) fuel is one which occurs naturally and requires no chemical processing before utilization.

Secondary (Derived) fuels are produced from naturally occurring substances by subjecting them in to treatments which alter their chemical composition and often improve their quality.

The various types of fuels are tabulated in Table-1.

Table-1.Classification of Fuels

Physical state	Primary fuel	Secondary fuel
Solid	Wood, Peat, Lignite, Coal	Charcoal, Coke
Liquid	Crude petroleum	Petrol, Kerosene, Diesel, Synthetic petrol
Gas	Natural gas	Producer gas, Coal gas, Water gas, biogas, LPG

5.3 Characteristics of a Good Fuel

The following are the desirable properties of a good chemical fuel:

i) The fuel should have high calorific value i.e. high heat content.

ii) It should have moderate ignition temperature. The fuel having very low ignition temperature can cause fire hazards during their handling, storage and transportation. It is rather difficult to ignite fuel if its ignition temperature is too high.

iii) A fuel should have low moisture content, because high percentage of moisture in fuel reduces the heat content of the fuel. It also increases the ignition temperature and fuel cost.

iv) A fuel should have low content of non-combustible matter, because non-combustible matter also reduces the heating value.

v) In case of solid fuel, the ash content should be less and the size should be uniform.
vi) A good fuel should be readily available in bulk at low cost.
vii) Products of combustion should not be harmful.
viii) Combustion should be easily controllable.
ix) It should be safe, convenient and economical for storage and transport.

5.4 Calorific value

Calorific value is an important property of a fuel.

Calorific value of a fuel is defined as “the amount of heat liberated when unit mass (or unit volume in the case of a gaseous fuel) of fuel is completely burnt in air or oxygen”

In the case of solid or liquid fuels the weight sufficiently defines the quantity of the fuel present. However, in the case of gaseous fuels, it is necessary to specify both temperature and pressure in order to define this quantity.

The calorific value is generally expressed in calorie per gram (cal/g), kilo calorie per kilo gram (kcal/kg) or joule per kilogram (J/kg) in case of solid and liquid fuels. In case gaseous fuels, the units used are kilocalorie per cubic meter (kcal/m^3) or joules per cubic meter (J/m^3).

Gross or Higher calorific value

The Gross or Higher calorific value is defined as “the amount of heat liberated when unit mass / volume of the fuel is burnt completely in air and the products of combustion are cooled to room temperature”

When a fuel containing hydrogen is burnt, the hydrogen present undergoes combustion and will be converted into steam. As the products of combustion are cooled to room temperature the steam gets condensed into water and the latent heat is evolved. Then the latent heat of condensation of steam is also included in the measured calorific value.

Net or Lower calorific value

Net or Lower calorific value is defined as “the amount of heat produced when unit mass/volume of fuel is completely bunt in air and the products of combustion are allowed to escape into the atmosphere”

In actual practice the combustion products (steam, etc.) are not cooled to room temperature but simply let off into the atmosphere. Hence, a lesser amount of heat is available. Since this calorific value does not include the latent heat of condensation of steam, Net calorific value is always lower than Gross calorific value.

$$\begin{aligned}\text{Net calorific value} &= \text{Gross calorific value} - \text{Latent heat of condensation of steam}\\ &= \text{Gross calorific value} - \text{Mass of hydrogen} \times 9 \times \text{latent heat of steam}\\ &= \text{Gross calorific value} - \frac{9 \text{ x } \% \text{ of hydrogen}}{100} \times \text{latent heat of steam}\end{aligned}$$

Because1g hydrogen gives 9g of water. Latent heat of steam is 587cal/g.

5.5 Determination of calorific value

By Bomb Calorimeter

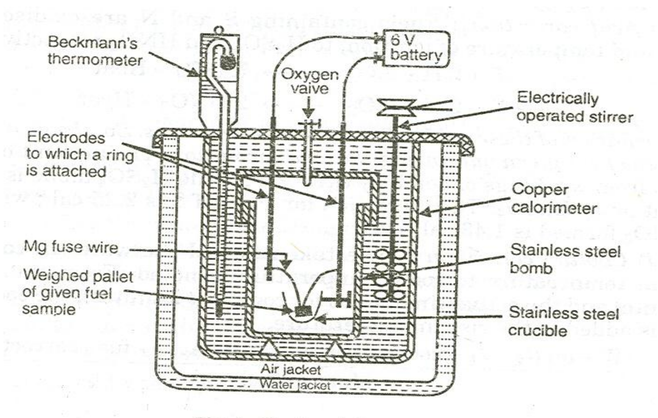


Fig. 1. Bomb calorimeter.

It is apparatus to find the calorific value of solid and liquid fuels. A simple sketch of bomb calorimeter is shown in Fig.1. It consists of a stainless steel air tight sealed cylindrical bomb in which the combustion of fuel is made to take place. The bomb lid is provided with two stainless steel electrodes and an oxygen inlet valve. To one of the electrodes, a small ring is attached and over which a nickel or stainless steel crucible can be supported. The bomb is placed in a copper calorimeter, which is surrounded by an air-jacket and water-jacket to prevent heat loses due to radiation. The copper calorimeter is provided with an electrically operated stirrer and Beckmann's thermometer, which can read accurately temperature difference up to 1/100th of a degree.

Principle: A known mass of the fuel sample is burnt completely in excess of oxygen. The liberated heat is absorbed by water and calorimeter. Thus the heat lost by burning fuel is the heat gained by water and calorimeter. The calorific value of the fuel is calculated from the measured data.

Procedure: A known mass (about 0.5 to 1.0g) of the given fuel is taken in a clean nickel crucible. The crucible is then supported over the ring, attached to one of the electrodes. A fine magnesium wire, touching the fuel sample, is then stretched across the electrodes. The bomb lid is tightly screwed. The bomb is filled with oxygen to 25 atmospheric pressure and then placed in a copper calorimeter containing known mass of water. The stirrer is worked and initial temperature of water in the copper calorimeter is noted. The electrodes are then connected to a 6V battery and the circuit is completed. The sample burns and heat is liberated. Uniform stirring of water is continued and the maximum temperature attained is noted.

m x Higher (Gross) calorific value of fuel = $(W + w)(t_2 - t_1)$

or Higher (Gross) calorific value of fuel = $\frac{(W + w)(t_2 - t_1)}{m}$ cal/g

$$= \frac{(W + w)(t_2 - t_1)}{m} \times 4.184 \times 10^3 \text{ J/kg}$$

Calculation of Lower (Net) calorific value:

If H = Percentage of hydrogen in fuel, then:

Water formed by combustion of 1g of fuel = $\frac{18}{2} \text{ x } \frac{H}{100} = 0.09H$ g

Latent heat of water formed = $0.09H \times 587$ cal/g

Lower(Net) calorific value = Higher (Gross) calorific value – Latent heat of water formed

= Higher (Gross) calorific value – $0.09H \times 587$ cal/g

Cracking

An average grade crude oil on fractionation yields about 20-30% gasoline, 30-45% intermediate oils and 25-50% residual fuel oils. Among these fractions, gasoline (which is called "straight run petrol") has the highst demand. This resulted in the surplus of heavier fractions. Further, the quality of the "straight run petrol" is not so good and hence is used only after suitable blending. Because of these reasons, a process of thermal decomposition known as cracking was developed by means of which the surplus stocks of higher boiling fractions (e.g., fuel oil and heavy oil) are converted into more valuable lower boiling fractions (gasoline). Thus, the objective of cracking is to obtain greater yields of improved gasoline by thermal decomposition of the surplus heavier fractions. It was noticed that cracked gasoline give better engine performance (less knocking) than gasoline obtained from fractional distillation of crude oil.

Cracking is defined as the process of decomposition of higher molecular weight hydrocarbons (higher boiling) into lower molecular weight hydrocarbons (low boiling)

Cracking process involves breaking of C-C and C-H bonds. It produces low boiling alkanes and alkenes. In addition to this a small amount of carbon and hydrogen are also produced.

$$C_{10}H_{12} \xrightarrow{\text{Cracking}} C_5H_{12} + C_5H_{10}$$

Decane Pentane Petene

Cracking is usually done by two methods, namely, thermal cracking and catalytic cracking.

Thermal cracking: In thermal cracking, the heavy oil is subjected to high temperature and pressure in the absence of catalyst. The cracked vapors are fractionated to get gasoline and other low molecular weight fractions. This is the old method and less efficient one.

Catalytic cracking: In this method cracking is carried out in presence of a catalyst at much lower temperatures and pressures. Catalytic cracking methods are now replacing the old and less efficient thermal cracking methods because of their inherent advantages.

The main advantages of catalytic cracking are: (a) The octane number of gasoline produced is high. (b) The yield of gasoline is also high. (c) The process can be better controlled. (d) The product contains a very little amount of undesirable sulphur. (e) There is a saving in production costs since high temperatures and high pressures are not needed. (f) In catalytic cracking, external fuel is not required. The necessary heat is obtained by burning off the coke deposited on the catalyst itself, during the regeneration process. (g) The gasoline formed contains much less gum and gum forming compounds. (h) Catalysts are selective in their action, and therefore, they permit cracking of only high boiling hydrocarbons.

There are two types of catalytic cracking methods- (i) Fixed-bed catalytic cracking and (ii) Fluidized (moving) bed catalytic cracking. Of the two, the fluidized bed catalytic cracking method has some advantages over fixed bed catalytic cracking. Catalytic cracking is normally carried out in vapour phase. In order to have an intimate contact between the solid catalyst and vapours the catalyst should have a large surface area. Accordingly the catalyst used is in the form of powder or pellets.

Fixed-bed catalytic cracking: The catalyst (Al_2O_3 + SiO_2) in the form of powder or pellets is placed on the grid in the catalytic chamber. The vapours of the feed stocks (Heavy oil, gas oil, etc.) are passed through the bed of catalyst maintained at 450-500^0 C. About 50% of the feed stock is converted into gasoline together with elemental carbon which gets deposited on the surface of the catalyst. Cracked vapours are next subjected to fractionation in a fractionating column wherein gasoline is separated from uncracked heavy oil. The catalyst loses its activity because of the deposition of carbon and also due to the adsorption of oil vapours. Accordingly, the catalyst requires regeneration after 8-10 hours. During regeneration time, the cracking process is interrupted and the adsorbed oil is stripped off by passing steam while deposited carbon is burnt off by a hot air blast.

Fluidized (moving) bed catalytic cracking: In fluidized-bed catalytic cracking, the finely divided catalyst is kept agitated by gas streams (feed stock vapour) so that it can be handled like a fluid system i.e., it can be pumped as a true liquid. The advantage of fluidized-bed cracking process is that a high degree of mixing is achieved and consequently a good contact is established between the catalyst and the feed stock vapours. This results in a higher yield. The regeneration of the inactive catalyst can be carried out continuously without interrupting the production of gasoline unlike in fixed-bed cracking method

Process: The finely divided catalyst bed (Al_2O_3 + SiO_2) is fluidized by the upward passage of feed stock vapours (Heavy oil, gas oil, etc) in a cracking chamber (called Reactor) maintained at 550^0 C. Near the top of the reactor (Fig.3),there is a centrifugal separator (called cyclone), which allows only the cracked oil vapours to pass onto the fractionating column but retains the catalyst powder in the reactor itself. The catalyst powder gradually becomes heavier due to the deposition of carbon and settles to the bottom, from where it is forced by an air blast to the regenerator (maintained at 600^0 C). After cracking, the products are fractionated into gases, gasoline, gas oils and residual oils (unconverted). The heavier oil fractions may be cracked in a second-stage cracking, thereby increasing the over all yield of the cracked products.

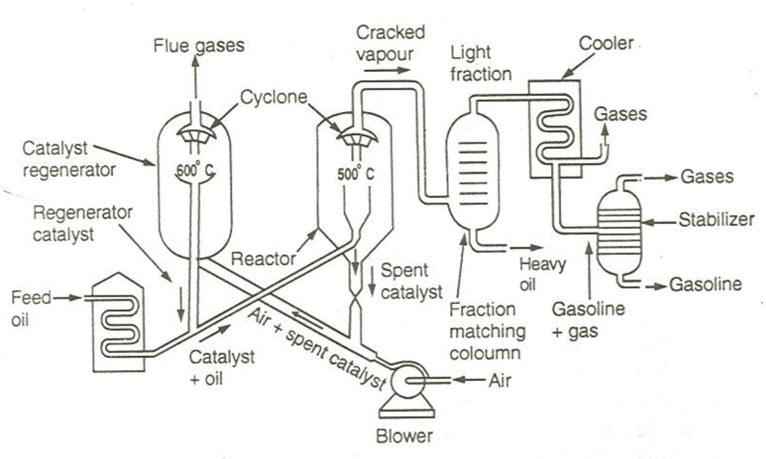


Fig. 9. Moving-bed type catalytic cracking.

In regenerator, the spent catalyst is stripped of the adsorbed oil by passing steam and then decarbonized by a hot air blast, under controlled conditions. The heat liberated during this regeneration is used to raise steam and to preheat the catalyst.

Reforming of Petrol

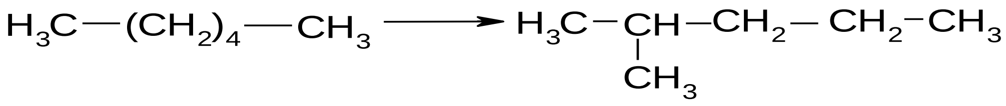
Straight run gasoline obtained from primary distillation of crude oil contains mainly straight chain hydrocarbons. As such, it has very low octane number, not greater than 60. But internal combustion engines require a gasoline of octane number above 90 in USA and 75-85 in India. It is found that branched chain hydrocarbons have higher octane numbers than the corresponding straight chain hydrocarbons. Aromatic hydrocarbons have higher octane numbers than non-aromatic hydrocarbons. It is therefore, follows that if the percentage of branched chain hydrocarbons and aromatic hydrocarbons can be increased, the octane rating will be improved. This improvement can be achieved by catalytic reforming process. The gasoline obtained is called stabilized gasoline.

Catalytic Reforming: Catalytic reforming is a process of upgrading gasoline (increasing its octane number) in presence of a catalyst. The increase in octane number of straight run gasoline occurs through structural modifications such as conversions of straight hydrocarbons into branched, cyclic and aromatic hydrocarbons.

Reforming Process: The feed stock (straight run gasoline) is preheated to remove sulphur and nitrogen content to acceptable limits to avoid platinum catalyst being poisoned. The vapours of the feed stock is mixed with hydrogen and preheated to 500^0 C. The mixture is compressed (15-50 atmosphere) and then fed into a series of three cylindrical reactors containing the platinum catalyst supported on alumina-silica base. The reformed products are fractiona CH_2 -ted to get stabilized gasoline.

Reforming reactions: The main reactions taking place during catalytic reforming process are:

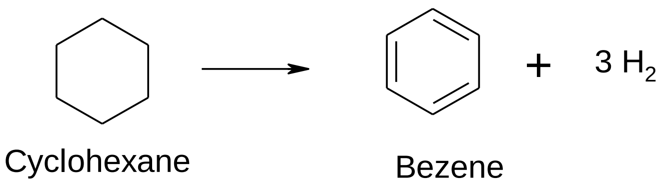
i) Isomerisation: The straight chain hydrocarbons are converted into branched chain hydrocarbons.

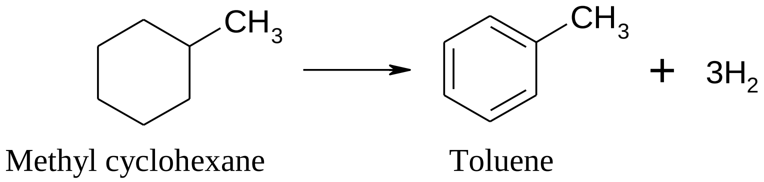


$$H_3C-(CH_2)_4-CH_3 \longrightarrow H_3C-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_2-CH_3$$

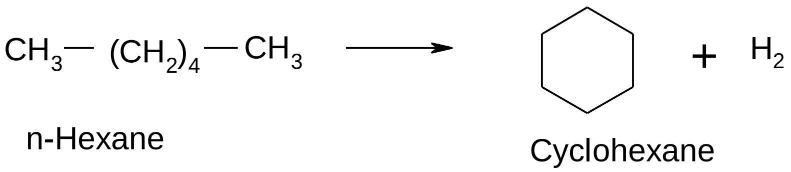
n-hexane 2-methyl petane

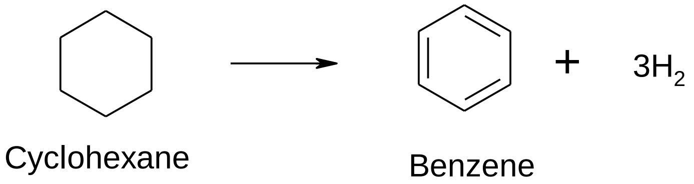
ii) Dehydrogenation: Cycloalkanes undergo dehydrogenation to produce aromatic compounds.





iii) Cyclisation and dehydrogenation: Straight chain hydrocarbons undergo cyclisation followed by dehydrogenation to produce aromatic hydrocarbons.





iv) Hydrocracking: n-Paraffins undergo hydrocracking (cracking in the presence of hydrogen and catalyst) to produce light gases that are removed from gasoline fraction.

$$CH_3-(CH_2)_8-CH_3 + H_2 \xrightarrow{Cat} 2\ CH_3-(CH_2)_3-CH_3$$

n-Decane n-Pentane

Knocking

The efficiency of power production in spark ignited internal combustion (IC) engines is related to the compression ratio (CR). The CR is the ratio of the cylinder volume (V_1) at the end of the suction stroke to the volume (V_2) at the end of the compression stroke of the piston. This ratio is always greater than one since V_1 being greater than V_2. Theoretically, the power output and efficiency of an IC engine should increase continuously with increase in the CR. However, H.R.Ricardo, with the help of a variable compression engine showed that in actual practice, the power increases to a maximum and then falls rapidly with further increase in the CR. The CR, corresponding to the maximum power output, is known as highest useful compression ratio (HUCR).

In IC engines, the mixture of gasoline and air is drawn into the cylinder. The fuel-air mixture is compressed by the piston and is ignited by an electric spark. As the flame front travels towards feed end of the combustion chamber, rapidly expanding combustion gases, compress the remaining unburnt fuel ahead of flame front and raise its temperature. If the flame front travels rapidly at optimum speed, the combustion of unburnt fuel takes place but smoothly. On the other hand, if the flame front travels too slowly, the entire last portion of the fuel-air mixture may get heated up beyond its ignition temperature and undergo instantaneous explosive combustion. This produces thermal shock wave which hits cylinder walls and piston. This result in emitting of characteristic rattling sound called knocking or pinking. The tendency of knocking increases with CR. The mechanism of the chemical reactions that lead to knocking is not clear. It is believed that chemical reactions that are of importance are cracking and the oxidation of the hydrocarbons. Probably the reactions proceed by a chin reaction. It was recognized that the structures of the fuel hydrocarbons determines largely their knocking tendency. The tendency to knock decreases as follows: n-alkanes> mono substituted alkanes> cycloalkanes > alkenes > poly substituted alkanes > aromatics.

The tendency to knock depends not only on the fuel used but also on the engine design, shape of head, location of plug, etc., and also upon the running conditions.

The adverse effects of gasoline knock are: i) It increases the fuel consumption, ii) It results in decreased power output, iii) It causes mechanical damage by overheating of the cylinder parts, iv)The driving becomes rather unpleasant.

The knocking in IC engines can be minimized through the following measures:

i) A suitable change in engine design, ii) By using critical compression ratio, iii)By using high rating gasoline, iv)By using anti-knocking agents.

Octane Number

The resistance to knocking offered by gasolines cannot be defined in absolute terms, but in terms of an arbitrary scale, octane rating, proposed by Graham Edger in 1926. Among alkanes, n-heptane knocks severely, while under identical conditions, 2,2,4-trimethyl pentane (iso-octane) has a high resistance to knocking. For the scale proposed to indicate the anti-knock properties of gasoline, n-heptane was arbitrarily assigned an octane number of zero and iso-octane was arbitrarily assigned a value of 100. By blending these two hydrocarbons in various proportions, primary reference fuels were prepared and the knocking tendency of the gasoline sample could be determined. In the same engine under the same set of conditions and the same critical CR, various blends of the n-heptane and iso-octane are burnt and the percentage of iso-octane by volume in blend that knocks under these conditions is the octane number of the gasoline.

Thus octane number is defined as the percentage by volume of iso-octane in a mixture of iso-octane and n-heptane blend, which has the same knocking characteristics as the gasoline sample, under the same set of conditions.

Thus a gasoline with an octane number of 90, has the same knocking characteristics as a mixture of iso-octane and n-heptane containing 90% by volume of iso-octane. Since iso-octane has good ant-knock properties, it is clear that greater the octane number, greater is the resistance to knocking.

Automobile gasolines have octane number ranging from 75 to 95. Aviation gasolines have a greater knock resistance and their octane numbers are greater than 100. In such cases the octane numbers are computed using the relationship,

$$\text{Octane number} = \left[\frac{\text{Power number} - 100}{3} \right] + 100$$

Where, power number is an arbitrary number proportional to the power being extracted by the engine.

It has been found that in the case of alkanes, the octane number increases with the number of branches in the chain and decreases with increase in chain length. Alkenes have higher octane number than alkanes containing the same number of carbon atoms. Cycloalkanes have a higher octane rating than alkanes with same number of carbon atoms. The highest octane numbers are associated with the aromatic hydrocarbons.

Anti-knocking Agents

The use of high compression ratio in modern IC engines demands gasoline with high octane rating. The octane rating of gasoline samples can be increased by the addition of certain organometallic compounds called anti-knocking agents and the process is called "doping".

An extensively used anti-knocking agent is tetraethyl lead (TEL), $Pb(C_2H_5)_4$. About 0.5 ml of TEL per liter is added for motor fuel and about 1 ml of TEL per liter is generally added for aviation petrol.

It is believed that during combustion of gasoline, TEL forms Pb and PbO. These species act as free-radical chain inhibitors and thus curtail the propagation of the explosive chain reaction and thereby minimizing knocking. However, if TEL alone is used, the species Pb and PbO may get deposited on engine parts and cause mechanical damage. Further the vapours of Pb and PbO may pollute the air. In order to minimize the air pollution and damage to engine parts, TEL is always used along with ethylene dibromide or ethylene di chloride. The functions of these ethylene derivatives is to convert the less volatile Pb and PbO into more volatile $PbBr_2$ or $PbCl_2$ which escapes into air along with exhaust gases.

Unleaded Petrol

Unleaded petrol is one which does not contain any lead compounds (like TEL). To improve its octane number, concentration of high octane components (like isopentane, isooctane, ethylbenzene, isopropylbenzene, etc) is increased by the process of reforming. In addition to it, compounds like methyl tertiary butylether (MTBE) is added to improve octane number of unleaded petrol. MTBE provides oxygen (of ether group) for combustion of petrol in IC engines, thereby reducing considerably the formation of peroxy compounds (which causes knocking).

Petrol wherein the enhancement of octane rating is accomplished without the addition of lead compounds is referred to as unleaded petrol.

The advantages of unleaded petrol are: (i) The harmful effects of discharge of poisonous lead and its compounds through the exhaust of automobiles is avoided, (ii) One of the major advantages of using unleaded petrol is that it permits the attachment of a catalytic converter to the exhaust pipe in automobiles. Catalytic converter contains a rhodium catalyst which converts the toxic gases such as CO and NO to harmless CO_2 and N_2. It also oxidizes hydrocarbons into CO_2 and H_2O. However, leaded petrol cannot be used in automobiles equipped with catalytic converter as the lead present poisons the catalyst thus destroying the active sites.