

Unit-III

CHEMICAL FUELS

INTRODUCTION TO ENERGY:

Energy is an important aspect of human activity. In the early days energy demands were met primarily by muscular effort, wind and water currents, fuel, wood, direct solar warming and such other sources. With the progress of industrial civilization, these sources became less important and fossil fuels such as coal, lignite, petroleum and natural gas began to play a vital role as sources of energy. Chemical process industries are largest consumers of energy. At present, the major energy sources are hydroelectric, coal, petroleum, natural gas and the products of their processing water, biomass and nuclear. A part of the energy needs is also met with by sun, wind and tides. The energy sources can be broadly classified into two types namely,

- (i) Fuels: e.g., coal, petroleum, natural gas, peat, biomass, uranium
- (ii) Nonfuels: e.g., hydro, solar, wind, tidal, geometrical energy.

Energy sources can also be classified into renewable and nonrenewable sources. The non-fuels and biomass are renewable sources because they can be grown. The fossil fuels and uranium are non-renewable sources as these resources get depleted with mining.

FUELS:

Definition: A fuel is defined as a naturally occurring or an artificially manufactured combustible carbonaceous material, which serves particularly as a source of heat and light and also in a few cases as a source of raw material.

Classification: On the basis of their origin fuels are classified as primary and secondary fuels. These are again subdivided into solid, liquid and gaseous according to the state of phase. A primary fuel is the one, which occurs naturally and requires no chemical processing before utilization. Examples of primary fuels include wood, coal, peat, crude petroleum and natural gas. Secondary fuels are produced from naturally occurring substances by subjecting them to treatments, which alter their chemical composition and often improve their calorific value and utility. Examples of secondary fuels include coke, coal gas and gasoline. The various types of fuels are tabulated in Table 1

Table-1

| State of phase | Primary | Secondary |
|----------------|---------------------------------------|--|
| Solid | Wood, peat, lignite, coal, anthracite | Charcoal, coke |
| Liquid | Crude petroleum | Petrol, kerosene, fuel oil, diesel oil |
| Gaseous | Natural gas | Coal gas, water gas, producer gas, biogas. |

IMPORTANCE OF HYDROCARBON FUELS:

Coal, petroleum, and natural gas are excellent hydrocarbon fuels. They are called 'fossil fuels' (nonrenewable energy sources) formed from plant and animal remains buried deeply under high pressure, about 345 million years ago. These fuels are excellent hydrocarbon fuels as they contain carbon and hydrogen as major elements. When they are burnt in adequate supply of air, they are oxidized to CO_2 and water and release significant amount of energy in the form of heat which can be converted into suitable form to perform useful work. Among fossil fuels, natural gas is relatively inexpensive. It is superior fuel and have many advantages over coal and petroleum. It burns cleanly, leaves no residue and produces less CO_2 per unit energy than other two fossil fuels. Further, unlike coal, petroleum, it produces no NO_x , SO_x , CO, etc., as pollutants. It is therefore, the safest and excellent fuel available. The present day world is heavily dependent on coal, petroleum and natural gas for most of energy needs such

as transportation (vehicles, trains, aeroplanes), industrial processes, heating, cooling building (refrigeration) and generating electrical power (thermal power plant).

Eighty percent of world's energy demand is supplied by these hydrocarbon fossil fuels. The reserves of these fuels are fast depleting because of the high rate of consumption.

Calorific value of a fuel:

An important parameter of fuels is calorific value. It gives useful information about its heating efficiency. The performance of a fuel is expressed in terms of its calorific value

Definition: Calorific value of a fuel is defined as the amount heat released when unit quantity (mass or volume) of a fuel is burnt completely in air or oxygen.

Units of calorific value:

The calorific value is generally expressed calorie/gram (cal/g) or kilocalorie/kg (kcal/kg) in cgs units. It is also expressed in joules per kg (J/kg) for solid fuels and joules per cubic meter (J/m³) for gaseous fuels in SI units.

Types of calorific value:

(i) Gross calorific value (GCV) or Higher calorific value (HCV): GCV is defined as the total amount of heat produced when unit quantity (mass/volume) of the fuel is burnt completely in air or oxygen and the products of combustion are cooled to ambient temperature (288K).

Usually, all fuels contain some hydrogen and when calorific value of hydrogen containing fuel is determined experimentally, the hydrogen is converted into steam. If the products of combustion are condensed to the room temperature (15°C), the latent heat of condensation of steam also gets included in the measured heat, which is then called 'higher or gross calorific value'.

(ii) Net calorific value (NCV) or Lower calorific value (LCV): NCV is defined as the amount of heat produced when a unit amount of a fuel is burnt completely in air and products of combustion are permitted to escape.

In actual practice, the combustion products are not cooled to room temperature, but simply let off into the atmosphere. Since this calorific does not include the latent heat of steam, net calorific value is always lower than gross calorific value.

Net calorific value = Gross calorific value – Latent heat of water vapour formed.

= Gross calorific value – Mass of hydrogen × 9 × Latent heat of steam.

Because 1 part by mass of hydrogen produces 9 parts by mass of water.

Latent heat of steam = 587 kcal/kg or 2454 kJ kg⁻¹.

$$\text{NCV} = \text{GCV} - 9 \times \text{H \%} \times \text{Latent heat of steam} / 100.$$

Determination of calorific value of a solid (or liquid) fuels using Bomb calorimeter:

Principle: A known mass of solid or liquid fuel is completely burnt in excess of oxygen in a bomb calorimeter. The heat liberated is absorbed by surrounding water and calorimeter. Thus the heat lost by burning fuel is the heat gained by water and copper calorimeter.

Construction: A simple sketch of bomb calorimeter is shown in Fig.1. It consists of a strong cylindrical stainless steel bomb in which the combustion of fuel is made to take place. The bomb has a lid, which can be screwed to the body of bomb so as to make a perfect gas tight seal. The lid is provided with two stainless steel electrodes and an oxygen inlet valve. To one of the electrodes, a small ring is attached. In this ring, a nickel or stainless steel crucible can be supported. The bomb is placed in a copper calorimeter, which is surrounded by air-jacket and water-jacket to prevent heat losses due to radiation. The calorimeter is provided with an

electrically operated stirrer and Beckmann's thermometer, which can read accurately temperature difference up to $1/100^{\text{th}}$ of a degree.

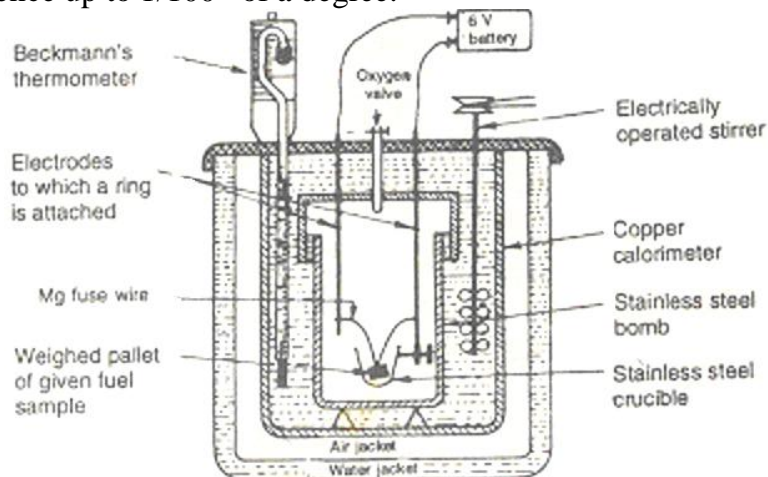


Fig.1. Bomb calorimeter

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

Calculation: Mass of the fuel sample taken in the crucible = 'm' grams.

Mass of water in the calorimeter = W_1 grams.

Water equivalent of calorimeter, stirrer, thermometer, bomb, etc. = W_2 grams.

Initial temperature of water in calorimeter = $t_1^{\circ}\text{C}$.

Final temperature of water in calorimeter = $t_2^{\circ}\text{C}$.

Higher calorific value of the fuel = Q cal/g or kcal/kg.

Heat liberated by burning of fuel = mQ .

Heat absorbed by water and apparatus etc. = $(W_1 + W_2)(t_2 - t_1)$.

But heat liberated by the fuel = Heat absorbed by water, apparatus

$$\text{i.e., } mQ = (W_1 + W_2)(t_2 - t_1)$$

$$\text{Therefore, } Q = (W_1 + W_2)(t_2 - t_1) / m \text{ cal/g or kcal/kg}$$

$$\text{or } Q = (W_1 + W_2) \times S \times (t_2 - t_1) / m \text{ kJ/kg; } S = \text{Specific heat in kJ/kg}^{\circ}\text{C}$$

Net calorific value = GCV – 0.09 × H × latent heat steam.

PETROLEUM:

Petroleum or crude oil (petra = rock; oleum = oil) is a dark greenish-brown, viscous oil found deep in earth's crust. It is composed mainly of various hydrocarbons (like straight-chain paraffins, cycloparaffins, naphthalenes, olefins and aromatics), together with small amounts of organic compounds containing oxygen, nitrogen and sulphur. The average composition of crude petroleum is C = 79.5 to 87.1%; H = 11.5 to 14.8%; S = 0.1 to 3.5%; N + O = 0.1 to 0.5%. The oil is, usually, found floating upon a layer of brine and has a layer of gas on top of it. Mining of petroleum done by drilling holes in the earth's crust and sinking pipes upto the oil-bearing porous rocks. Oil, usually, gushes out itself due to hydrostatic pressure of natural gas. Alternatively, it may be mechanically pumped up by using either lift pump or air-lift pump.

REFINING OF PETROLEUM:

The process of separation of crude oil into different useful fractions on the basis of their boiling points is called refining or fractionation.

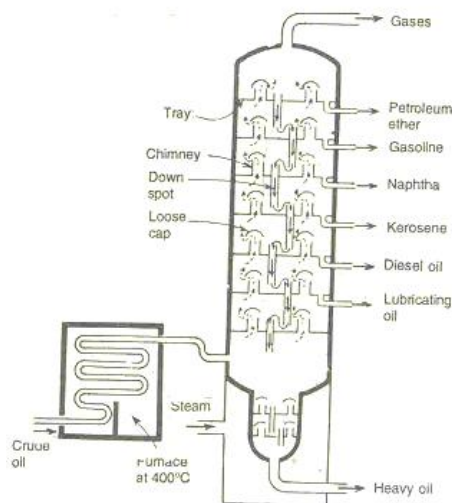


Fig.2. Fractional distillation of crude petroleum

First water, dirt and sulphur are removed from crude oil. It is then heated to about 400°C in iron retort. The hot vapours are then passed through a fractionating column which is huge cylindrical tower, containing a number of horizontal stainless steel trays as shown in Fig.2. The fractionating column permits separation of petroleum into a number of fractions having definite boiling point ranges.

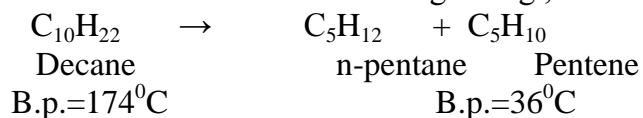
The more volatile component condenses on the upper plates of the fractionating column, while the less volatile fraction is collected on the lower plates. The various fractions condensed and collected at the different parts of the column are continuously withdrawn and some of them are fractionated and processed. Various principal fractionation products thus obtained are given in table-2

Table-2. Fraction by distillation of crude oil

| Name of the fraction | Boiling range | Approx. composition in terms of hydrocarbon containing C-atoms. | Uses. |
|---|-----------------------------|--|--|
| 1. Uncondensed gas | Below 30°C | C_1 to C_4 (such as ethane, propane, isobutene). | As a domestic fuel or industrial fuel under the name L.P.G. |
| 2. Petroleum ether | $30 - 70^{\circ}\text{C}$ | $\text{C}_5 - \text{C}_7$ | As a solvent |
| 3. Gasoline or petrol | $40 - 120^{\circ}\text{C}$ | $\text{C}_5 - \text{C}_9$ | As a motor fuel, solvent and in dry cleaning |
| 4. Naphtha or solvent spirit | $120 - 180^{\circ}\text{C}$ | $\text{C}_9 - \text{C}_{10}$ | As solvent and in dry cleaning. |
| 5. Kerosene oil | $180 - 250^{\circ}\text{C}$ | $\text{C}_{10} - \text{C}_{16}$ | As illuminant, jet engine fuel and for preparing laboratory gas. |
| 6. Diesel oil or fuel oil or gas oil | $250 - 320^{\circ}\text{C}$ | $\text{C}_{10} - \text{C}_{18}$ | Diesel engine fuel. |
| 7. Heavy oil This on refractionation gives | $320 - 400^{\circ}\text{C}$ | $\text{C}_{17} - \text{C}_{30}$ | For getting gasoline by cracking process. |
| (a). Lubricating oil | - | - | As lubricant. |
| (b). Petroleum jelly (Vaseline) | - | - | As lubricant and in cosmetics and medicines. |
| (c). Grease | - | - | As lubricant. |
| (d). Paraffin wax | - | - | In candles, boot polishes, wax paper etc. |
| 8. Residue may be either | Above 400°C | C_{30} and above | |
| (a) Asphalt | - | - | Water-proofing of roofs and road making. |
| or | | | |
| (b) Petroleum coke | - | - | As a fuel and in moulding arc light rods. |

CRACKING:

Cracking is defined as “the decomposition of bigger hydrocarbon molecules into simpler, low boiling hydrocarbons of lower molecular weight” e.g.,



Cracking process aims at:

- To convert low demand, high boiling fraction into low boiling fractions suitable for automobiles.
- To produce raw materials for petrochemical industries.

There are two different methods for cracking, namely, thermal cracking and catalytic cracking.

(a) Thermal cracking: In this method, the feed stock heavy oil subjected to high pressure and temperature (upto 700°C) in absence of air and catalyst. The cracked vapours are fractionated to get gasoline and other low molecular weight alkanes and alkenes.

(b) Catalytic cracking: In this method, cracking is brought in the presence of a catalyst at very low temperature and pressure. The quality and yield of gasoline produced by cracking can be greatly improved using a suitable catalyst like aluminium silicate or alumina (Al_2O_3).

There are two methods of catalytic cracking in use

(i) Fixed-bed catalytic cracking and (ii) Moving-bed (fluidized) catalytic cracking

Fluidized (moving-bed) catalytic cracking (Fig.3): The solid catalyst aluminum silicate or alumina is very finely powdered, so that it behaves almost as a fluid, which can be circulated in gas stream. The vapours of cracking stock (gas oil, heavy oil, etc) mixed with fluidized catalyst is forced up into a large reactor bed maintained at 500°C in which cracking of the heavier into lighter molecules occurs. Near the top of the reactor, there is a centrifugal separator (called cyclone), which allows only the cracked oil vapours to pass on to the fractionating column, but retains all the catalyst powder in the reactor itself. The catalyst powder gradually becomes heavier, due to coating with carbon, and settles to the bottom, from where it is forced by an air blast to regenerator maintained at 600°C .

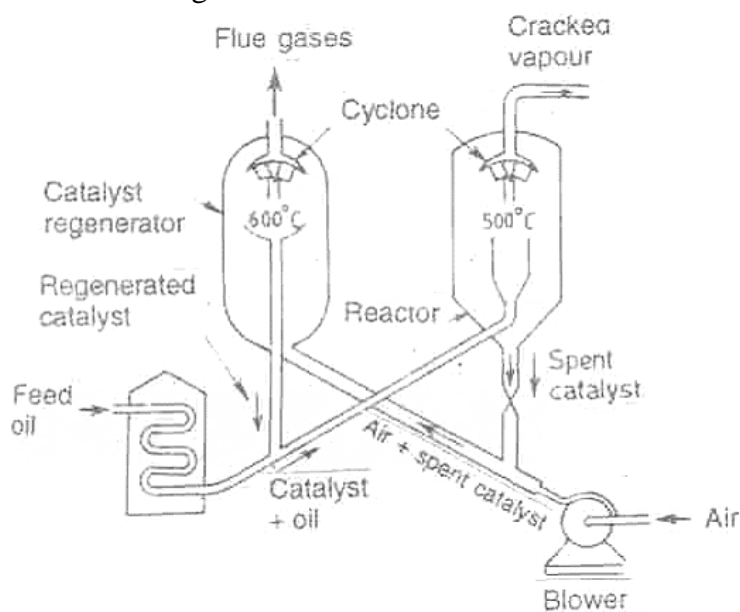


Fig.3. Moving bed type catalytic cracking.

In regenerator, carbon is burnt and the regenerated catalyst then flows through a stand-pipe for mixing with fresh batch of incoming cracking oil. At the top of the regenerator, there is a separator, which permits only gases (CO₂ etc.) to pass out, but holds black catalyst particles.

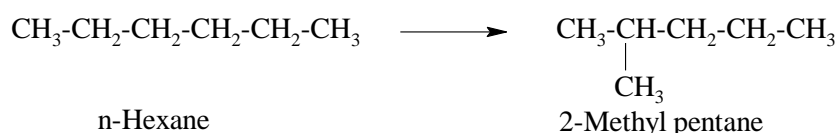
The advantage of fluidized cracking process is that a high degree of mixing is achieved and consequently a good contact is established between the catalyst and the vapour. This results in a higher yield. The bulk of petrol that is used is obtained by the cracking process. It also gives several gaseous hydrocarbons employed in the manufacture of petrochemicals.

REFORMING:

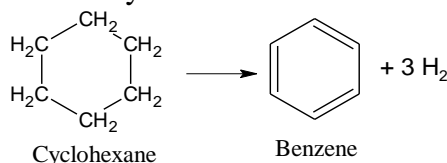
Reforming is a chemical process involves molecular rearrangement of hydrocarbons without any change in the number of carbon atoms to form new compounds. Reforming is usually brought about by passing the petroleum fraction at about 500⁰C over platinum coated on alumina catalyst in the presence of hydrogen. The object of reforming is to enhance the octane number of petrol fraction and to produce aromatic hydrocarbons for use as feed stocks in the synthesis of petrochemicals.

A few important reforming reactions are given below:

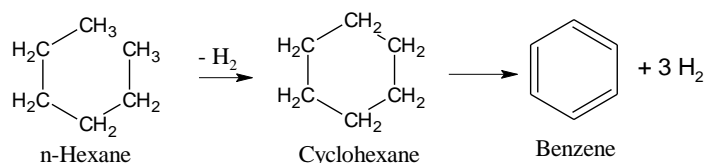
(i) *Isomerization*: Conversion of straight chain hydrocarbons into branched chain hydrocarbons.



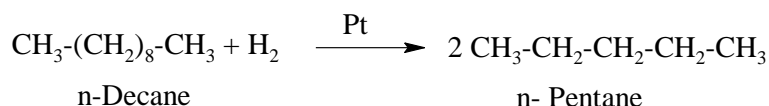
(ii) *Dehydrogenation*: Conversion of cycloalkanes into aromatic compounds.



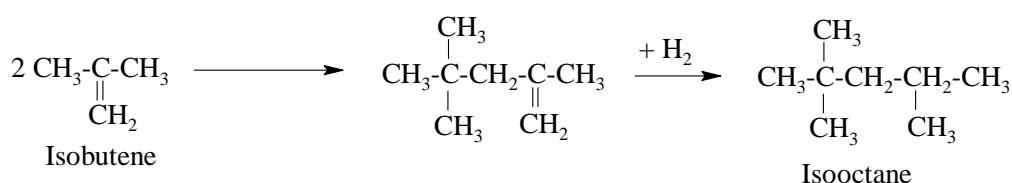
(iii) *Dehydrocyclization (Cyclization and dehydrogenation)*: Conversion of straight chain hydrocarbons into cyclic compounds followed by dehydrogenation of cycloalkanes to aromatic hydrocarbons.



(iv) *Hydrocracking*: n-Paraffin's undergo hydrocracking (cracking in the presence of H₂ and catalyst) to produce light gases that are removed from gasoline to improve the octane number.



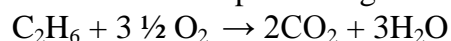
(v) *Conversion* of alkenes to form branched hydrocarbons of high molecular mass.



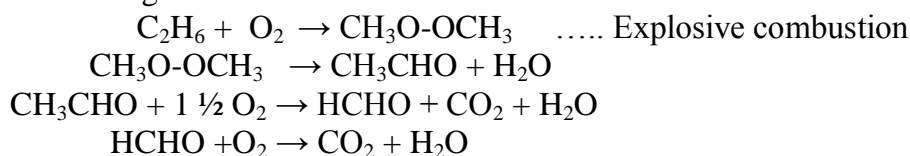
KNOCKING AND ITS MECHANISM:

Definition: Explosive combustion of air-petrol vapour mixture produces shock waves which hit the cylinder wall and piston of IC engine, creating rattling sound is known as knocking.

Mechanism: In an internal combustion engine, a mixture of gasoline vapour and air is used as a fuel. After the initiation of the combustion reaction, by spark in the cylinder, the flame should spread rapidly and smoothly through the gaseous mixture; thereby the expanding gas drives the piston down the cylinder. The ratio of the gaseous volume in the cylinder at the end of the suction-stroke to the volume at the end of compression-stroke of the piston is known the 'compression ratio'. Increase of compression ratio not only increases the efficiency of the engine but also saves the fuel which dependent on the nature of constituents present in the gasoline used. When petrol undergoes combustion under normal conditions the pressure inside the cylinder generally rises and rate of flame propagation is about $20\text{-}25\text{ ms}^{-1}$. Under these conditions, there is a slow oxidation of the fuel during which oxygen combines with a few hydrocarbon molecules and activates them. The activated molecules combine with hydrocarbon molecules and a chain reaction is set up resulting in a smooth combustion.



However, beyond a particular compression ratio, the petrol-air mixture suddenly bursts into flames and flame propagation rises to 2500 ms^{-1} . The chain reactions proceed at a very fast rate. The hydrocarbon molecules combine with oxygen to form peroxides. The unstable peroxides decompose readily to give a number of gaseous compounds. This gives rise to pressure waves which knock against the engine walls. This process is accompanied by a sharp knock in the engine due to explosive combustion producing a shock wave which dissipates its energy by hitting the cylinder wall and piston. As a result, rattling sound is heard which is referred to as the knocking.



Knocking increase *fuel consumption reduces efficiency of the engine and damages the engine parts and reduces the life of the engine.*

Chemical structure and knocking:

The tendency of fuel constituents to knock is in the following order:

Straight-chain paraffins > branched-chain paraffins (iso-paraffins) > olefins > cycloparaffins (i.e., naphthalenes) > aromatics.

OCTANE NUMBER: The knocking characteristics of petrol sample are described by the octane number or antiknock value. Higher the octane number, lower is the tendency to knock and better is the quality of petrol.

Isooctane (2,2,4-trimethyl pentane) has the least knocking tendency and its octane number is arbitrarily fixed as 100.

n-Heptane, a straight chain hydrocarbon, has highest tendency to knock and is assigned an octane number zero.

In general, straight chain hydrocarbons have low octane numbers and those with branched chains have high values. The petrol whose octane number is to be determined is compared with reference mixtures of isooctane and n-heptane.

Definition: The *octane number* of a petrol sample is defined as the percentage of isooctane in a mixture of isooctane and n-heptane which matches the petrol fuel under test in knocking characteristics.

For example, the octane number of automobile petrol is found to be equivalent to that of a mixture containing 70% by volume of isooctane and 30% by volume of n-heptane. Its octane number is said to be 70. The octane number of petrol is determined with the help of a special single cylinder engine where the compression ratio can be varied for testing the octane. Automobile petrols have octane number ranging from 76 to 95.

In alkanes, the octane number increases with the number of branches in the chain and decreases with increase in the chain length. Alkenes have higher octane number than alkanes containing same number of carbon atoms; among alkenes, the octane number increases with a shift in the position of double bond to the centre of the molecules. Cycloalkanes have a higher octane rating than alkanes with the same number of carbon atoms. The highest octane numbers are associated with the aromatic hydrocarbons.

Prevention of knocking: (Improving the octane number): The knocking can be reduced or prevented by using (a) Antiknocking agents (b) Unleaded petrol

(a) Antiknocking agents: Knocking of a petrol may be reduced by addition of organolead compounds into it. The substance added to control knocking is called antiknocking agent. The common commercial antiknocking agents used are

- (i) Tetraethyl lead, $(C_2H_5)_4Pb$, TEL; (ii) Tetramethyl lead, $(CH_3)_4Pb$, TML
- (iii) A mixture of TEL and TML

An extensively used antiknock agent is tetraethyl lead. Tetraethyl lead is added in the form of ethyl fluid and petrol containing ethyl fluid is known as leaded (ethylated) petrol. Ethyl fluid contains 63% TEL, 26% dibromoethane and 9% dichloroethane. TEL is believed to react with the peroxy compounds and decompose them. Thus knocking is prevented. Dibromoethane and dichloroethane are added to remove lead as volatile lead halides which escape with other gases through the exhaust. Addition of 1-2 cm³ of ethyl fluid to a litre of petrol increases the octane value of the petrol by 8-10 units.

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

Advantages of unleaded petrol: (i) The harmful effects of discharge of poisonous lead compounds through exhaust of automobiles is avoided. This in turn eliminates the pollution level of lead in atmosphere. (ii) Unleaded petrol permits the attachment of catalytic converters (containing rhodium catalyst) to the exhaust pipe in automobiles. The catalyst converts the toxic gases like CO and NO to non-toxic gases to CO₂ and N₂ respectively. Consequently, pollution level is reduced to a great extent.

Note: Leaded petrol cannot be used in automobile exhaust pipes fitted with catalytic converter, since the released lead compounds poisons the catalyst itself, thereby destroying its catalytic activity.

POWER ALCOHOL:

Power alcohol is gasoline blends containing ethanol which can be used as a fuel in internal combustion engines. Blend containing up to 25% of alcohol with petrol are used. The main objective of the power alcohol was to reduce oil imports and provide an alternative to non-renewable energy source, gasoline.

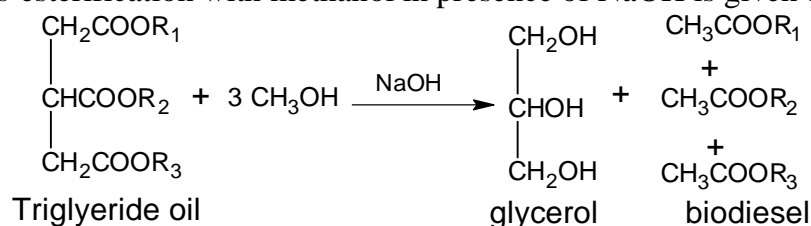
Advantages:

- (i) Alcohol has an octane number of 90; while petrol has octane number of 60-70. Consequently, addition of alcohol to petrol increases the octane number. Hence it possesses better anti-knock properties.
- (ii) Because of the higher octane number, it can be used in engines with higher compression ratio. This compensates for the lower heating value of alcohol in the blend.
- (iii) It has lesser starting difficulties.
- (iv) Alcohol-petrol blend has the same lubrication as petrol.
- (v) Addition of alcohol to petrol reduces the emission of CO and volatile organic compounds.

BIODIESEL:

Biodiesel is a source of energy obtained from renewable sources of plant origin. It is produced from vegetable oils such as soybean, jatropha, corn, sunflower, rapeseed, cotton seed, rice brain and rubber seed oil. It can be used as an alternative fuel to diesel in automobiles.

Biodiesel is commonly produced by the trans-esterification of the vegetable oil. This process involves combining any natural oil (vegetable or animal) with virtually any alcohol (methanol or ethanol) and a catalyst (base). The resulting mixture of monoalkyl esters of fatty acids is referred to as biodiesel. Thus, biodiesel is mixture of *monoalkyl esters of long chain fatty acids*. The trans-esterification with methanol in presence of NaOH is given below.



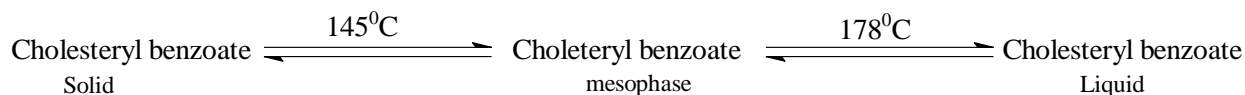
Where R_1 , R_2 and R_3 are the long chain fatty acids in the oil. Glycerol is soluble in water and can be separated from the reaction mixture.

Advantages:

- (i) It is made using renewable sources and feedstocks.
- (ii) Readily undergoes biodegradation.
- (iii) It has higher flash point than diesel but lower ignition point.
- (iv) Biodiesel has higher cetane number (48-60) compared to diesel (40-45)
- (v) Fewer harmful emissions compared to diesel.
- (vi) Use of biodiesel reduces greenhouse gases.

LIQUID CRYSTALS

INTRODUCTION: The study of liquid crystals began with an observation made by Austrian botanist, Freindrich Reinitzer in 1888. He observed that solid cholesteryl benzoate on heating becomes a turbid liquid at 145°C which on further heating turns into a clear, transparent liquid at 178°C . The above changes are reversed on cooling. The changes are generally represented as



Cholesteryl benzoate is said to exit a liquid crystal between 145°C and 178°C . The first temperature at which solid changes into turbid liquid is known as **transition point** and second temperature at which turbid liquid changes into clear liquid is known as **melting point**. Thus, liquid crystal is a distinct phase observed between crystalline solid state and isotropic liquid state.

Definition: Liquid crystals may be described as a distinct state of matter in which the degrees of molecular ordering lie intermediate between the ordered crystalline state and the completely disordered isotropic liquid state.

The liquid crystal state is also referred to as **mesophase**. The compounds which exhibit mesophase are also called **mesogens**. Liquid crystals exhibit optical anisotropy, i.e., they possess different optical properties when light is incident in different directions. Liquids, however, exhibit optical isotropy i.e., they exhibit same optical property irrespective of the direction of incident light.

POSITIONAL AND ORIENTATIONAL ORDER: Most liquid crystals are composed of organic molecules. In solid state, the molecules are highly ordered. Each molecule occupies a definite position in a more or less rigid arrangement and is immobile. In solid state not only do the molecules occupy specific positions but also tend to orient in a preferred direction which is already existing. In liquid state, however, the molecules neither occupy specific positions nor remain oriented in a particular manner. The molecules are somewhat free to move at random and collide with one another abruptly changing their positions. Intermediate between the solid and the liquid crystal phase, wherein the molecules free to move but are oriented in a particular manner.

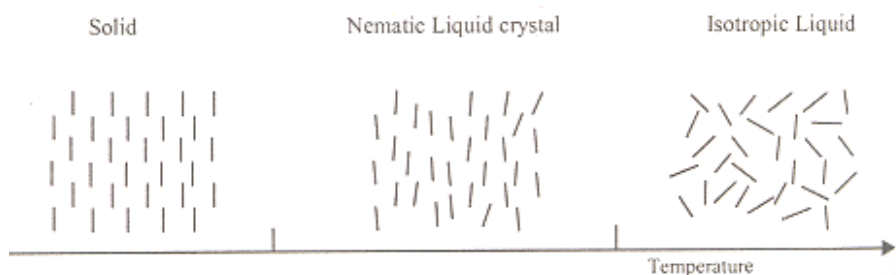


Fig.1 Representation of solid, liquid crystal and liquid states (molecules are represented as thin lines)

Thus, solid phases possess positional order and orientational order. Liquid phases possess neither positional nor orientational order while in liquid crystal phase some orientational order is retained through there is a loss of positional order as shown in Fig.1

DIRECTOR: In a liquid crystal, the molecules possess orientational prder i.e., the molecules tend to remain oriented in a particular direction. The direction of preferred orientation in a liquid crystal is called **director** and may be imagined to be directed towards the top or bottom of the page. Since the molecules are in constant motion, in liquid crystal phase they spend

more time pointing along the director than along any other direction. The extent of orientational order can be described by taking the average. A snapshot of the liquid crystal at any instant of time will give the angle made by each molecule with the director at any instant of time. If we consider a representative group of molecules and measure the angles using the snapshot, the average angle gives the measure of orientational order. An average of 0° indicates perfect orientation and can be expected in solids. An average of greater than 45° indicates no orientational order as found in liquids. However, in liquid crystals a smaller average angle with the director is observed which indicates some orientational order (Fig.2).

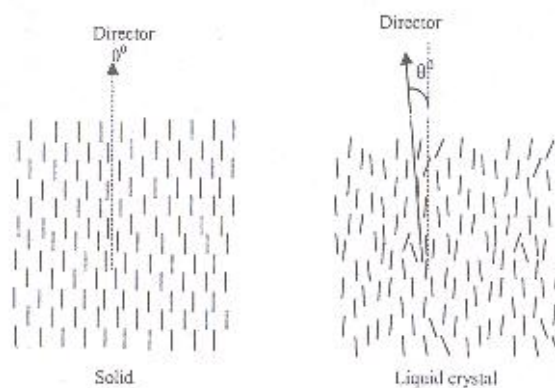


Fig.2 A snapshot showing the orientation of the molecules in the liquid crystal phase as compared to its solid phase. In the liquid crystal phase, the molecules orient in a preferred direction along the director with an average angle of θ^0 . Change in the positional order could be seen.

CLASSIFICATION OF LIQUID CRYSTALS:

Liquid crystals are classified into two main categories, namely,

1. Thermotropic liquid crystals
2. Lyotropic liquid crystals.

1. Thermotropic liquid crystals: The class of compounds that exhibit liquid crystalline behaviour on variation of temperature alone are referred to as thermotropic liquid crystals. The temperature range at which some liquid crystal are stable are given below:

| | Solid | | Liquid crystal | | Liquid |
|----------------------|-------|-------------|----------------|-------------|--------|
| Cholesteryl Benzoate | | 145° | | 178° | |
| p-Azoxyphenetole | | 137° | | 167° | |
| p-Azoxyanisole | | 116° | | 135° | |

2. Lyotropic liquid crystals: Some compounds transform to a liquid crystal phase when mixed with a solvent. They have a lyophilic and a lyophobic end that is they are amphiphilic compounds. They are usually obtained by mixing the compound in a solvent and increasing the concentration of compound till liquid crystal phase is observed. Such liquid crystals are called lyotropic liquid crystals. The formation of lyotropic mesophases is dependent on the concentration of either the component or the solvent. Variation of temperature also affects the formation of these mesogens.

Examples: (i) soap (soap-water mixture) molecules

(ii) Phospholipids (biologically important molecules where each cell membrane owes its structure to the liquid crystalline nature of the phospholipid-water mixture).

Lyotropic mesogens are typically obtained from amphilic compounds comprising of both lyophilic (solvent attracting) and lyophobic (solvent repelling) parts in the same molecule. In the presence of solvent the lyophobic ends come together while the lyophilic ends

directed towards water forming micelles. The formation of micelles takes place only beyond a particular concentration of the solution called critical micelle concentration (CMC). When the concentration of the solution is increased (beyond cmc) the micelles increase in size and eventually coalesce to form liquid crystalline phase.

MOLECULAR ORDERING IN LIQUID CRYSTALS (TYPES OF MESOPHASES):

(1) Nematic phase: Nematic (Greek; nematos = thread like) liquid crystals are formed by compounds that are optically inactive. The molecules have elongated shape and are approximately parallel to one another (Fig.3). Nematic phase is characterized by the total loss of positional order and a near normal flow behaviour similar to its liquid phase.

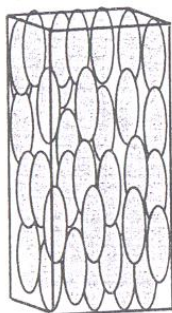


Fig.3 Nematic liquid crystal

Examples: (i) p-Azoxy anisole ($116-135^{\circ}$); (ii) p-Azoxy phenetole ($137-167^{\circ}\text{C}$); (iii) p-Anisaldehyde ($165-180^{\circ}\text{C}$).

(2) Chiral (Twisted) Nematic Phase (Fig.4): Chiral nematic liquid crystals also referred to as cholesteric liquid crystals or twisted nematic liquid crystals (TNLC), formed from optically active compounds having chiral centres. Unlike in a nematic phase where all the molecules are approximately parallel to one another, in chiral nematic phase, the molecules arrange themselves in such a way that they *form a helical structure*. In this mesophase, the director is therefore not fixed in space as in a nematic phase, but rotates through the sample forming a helical pattern as it changes its direction just like the motion of a nut on a screw. The distance traveled by the director as it completes one full turn is called the pitch of the liquid crystal. In other words, the pitch length is the distance traveled by the director when it gets turned by 360° . The twisted pattern repeats itself through the liquid crystal phase.

The most striking feature of cholesteric mesophase is its strong optical activity and selective light reflection, which are attributed to the twisted structure. The twist present in chiral nematic liquid crystal imparts spectacular optical properties which are made use of as thermochromic materials. The pitch is also temperature dependent and hence cholesterics are used in thermography.

Examples: (i) Cholesteryl benzoate; (ii) Cholesteryl myristate and (iii) Cholesteryl formate etc.

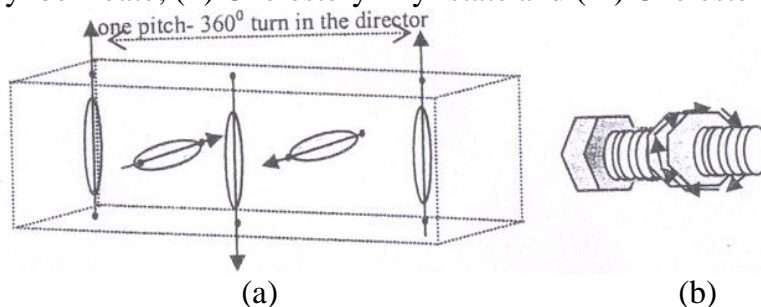


Fig. 4(a) Illustration of the twisted structure in a chiral nematic phase of a liquid crystal as shown by the change in the direction of the director. Arrows show the orientation of the molecules. Pitch is shown as the distance traveled for the director to come back to its original direction. (b) A nut moves a certain distance when it makes a full turn (one pitch) and comes back to its original direction as shown by the arrows.

(3) Smectic mesophase: Substances that form smectic phases are soap-like (in Greek, smectos means soap). In fact, the soft substance that is left at the bottom of a soap dish is a kind of smectic liquid crystal phase. In smectic mesophase, there is a small amount of orientational order and also a small amount of positional order. The molecules tend to point along the director and arrange themselves in layers. A snapshot would reveal that more number of molecules position in regularly spaced planes and a few molecules lie between the planes (Fig.5). That is, any one molecule would spend more time in these planes than between the planes. Based on the orientation of the director there are many types of smectic phases. If the director is perpendicular to the planes it is called smectic A (Fig. 5a) and smectic C if the director makes an angle other than 90° (Fig.5b). In smectic B phase, the director is perpendicular to the plane with the molecules arranging themselves into a network of hexagons within the layer.

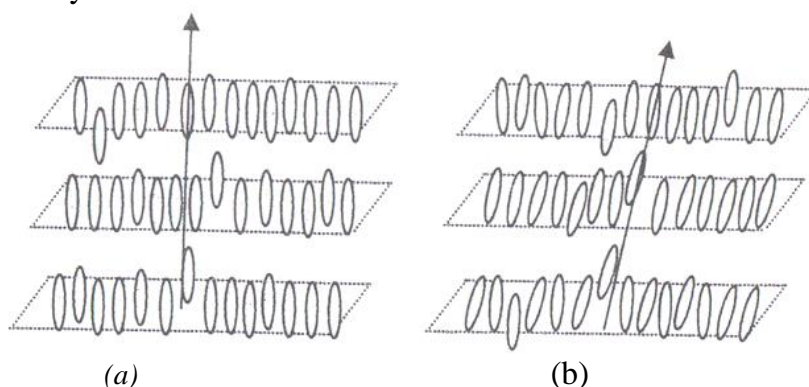


Fig.5 Schematic representation of smectic mesophase where molecules lie on regularly spaced planes (in the form of layers). (a) Smectic A where molecules is perpendicular to the layer planes. (b) Smectic C where the molecules are tilted with respect to the layer planes.

Examples: (i) 4-n-Butyloxybenzylidene aminopropiophenone (smectic-A); (ii) 4,4'-di-n-Heptyloxyazoxybenzene (smectic-C); (iii) Terephthalidene-bis-4-n-butylaniline (smectic-B).

(4) Discotic or Columnar Liquid crystalline Phase: Liquid crystals formed by molecules which have disk-like or plate-like structure are referred to as discotic or columnar liquid crystals.

The simplest discotic phase is also called discotic nematic phase because there is orientational order but no positional order (Fig.6a). There is random motion of the molecules, but on an average, the axis perpendicular to the plane of each molecule tends to orient along the director.

In the discotic or columnar phase, in addition to the orientational order present in the nematic discotic phase, most of the molecules tend to position themselves in columns (Fig.6b). The columns are arranged in a hexagonal lattice resembling a set of coins stacked as shown below (note: the coins in a stack have a great deal of positional order i.e., the coins are equidistant whereas the molecules in a columnar phase are stacked in random fashion).

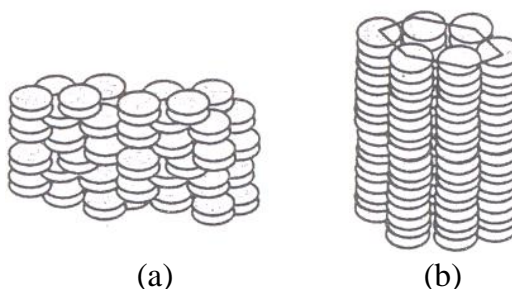
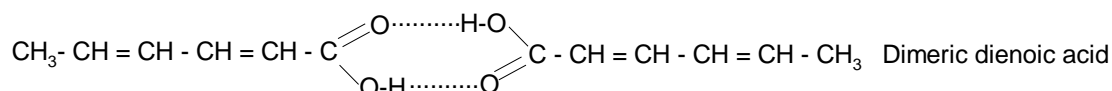
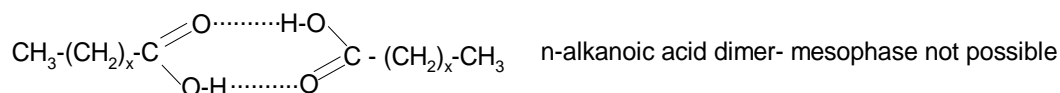


Fig.6. Schematic representation of disc like molecules arranged in (a) Discotic nematic (b) discotic columnar liquid crystal phases

Example: Benzene-hexa-n-alkanoate

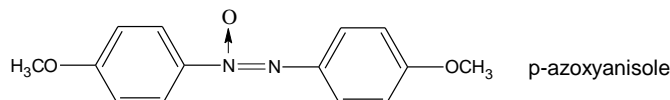
CHEMICAL CONSTITUTION OF LIQUID CRYSTALS:

Liquid crystalline behaviour is dependent on the rigidity at the central portion of the elongated molecule. If the molecule lacks rigidity, bending may occur along its length destroying parallel arrangement of the molecules resulting in no liquid crystal formation. For example, long chain n-alkanes can have elongated conformations, but the flexible alkyl chain can coil and bend, and hence no liquid crystals can be formed for them. Even long chain n-alkanoic acids cannot form liquid crystals because they are flexible. On the other hand, introduction of a double bond makes formation of mesophase possible because the conjugated part makes the molecule rigid.

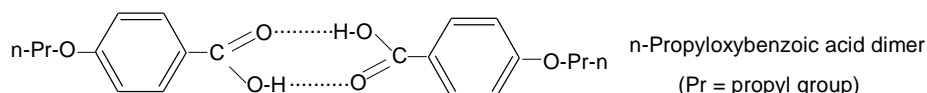


Introduction of double bonds in the side chain makes the formation of liquid crystal phase possible

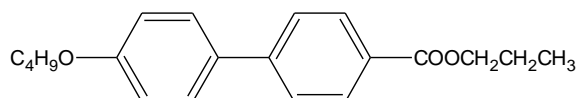
Aromatic compounds are polarizable, have a planar structure and are rigid. Introduction of alkyl groups in suitable positions makes the molecule elongated and hence such compounds can exhibit mesophase. Thus, for benzene nuclei, substituents at *para* positions make mesophase possible if substitutions are such that linking of two such benzene nuclei at the other end is possible. The requirement for liquid crystal formation in compounds with benzene rings is therefore (i) the central part which links the two benzene nuclei should itself be rigid and (ii) the entire molecule, i.e., the two rings and the central part should constitute a rod like structure. For example, in *para* azoxyanisole the central group consisting of azoxy group makes the central part rigid.



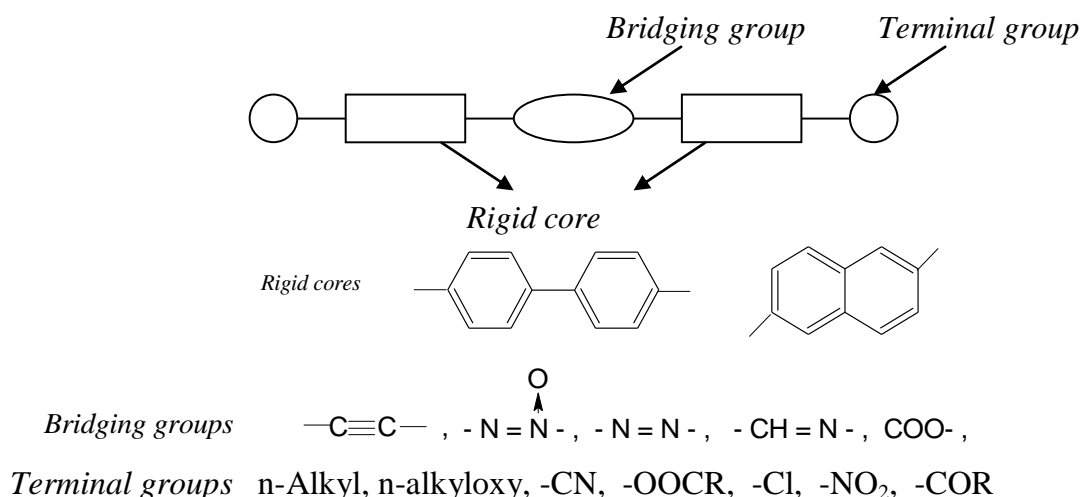
The central groups may also involve a ring formed by dimerization as in the case of *n*-propyloxy benzoic acid which easily forms a mesophase. The ring in the central part makes it rigid due to hydrogen bonding on dimerization.



If the benzene rings are linked through *para* substituents, mesophase formation is favoured. But linkage through *meta* or *ortho* positions is not favourable for mesophase formation. However, introduction of an additional *meta* or *ortho* substituent to an already existing *para* substituent does not favour mesophase formation. Liquid crystals can also form when two benzene rings are linked directly. These biphenyls have substituents at 4, 4' positions for extending linearity and rigidity. For example, propyl (4-*n*-butyloxybiphenyl)-4'-carboxylate.



These are thermally stable. The most common rigid cores, bridging groups and terminal groups found in rod-like mesogens are given below.



From the molecular structure it is also possible to predict whether a liquid crystal can be formed (i) Salts of carboxylic acids, rings with OR, $-\text{COOR}$, $-\text{NHCOR}$ substituents form smectic mesophase. (ii) Rings with terminal $-\text{NO}_2$, $-\text{CN}$, and $-\text{OMe}$ substituents form preferentially nematic mesophases.

ELECTRO-OPTIC EFFECT OF LIQUID CRYSTALS:

Nematic liquid crystals have rod like molecular structure and align themselves spontaneously along the director. Nematic materials have two dielectric constants- one in the direction parallel to the director and the other perpendicular to the director. Dielectric anisotropy ($\Delta\epsilon$) is defined as the difference between the dielectric constants parallel and perpendicular to the director. Similarly, the **optical anisotropy** (Δn) is defined as the refractive index parallel to the director minus the refractive index perpendicular to the director. These two properties are important for the electro-optic effects in liquid crystals.

Effect of electric field: The director in a liquid crystal is free to point in any direction. But when a film of liquid crystal is placed between two plates of certain materials, director is forced to point along a particular direction when an electric field is applied. For example, when a film of liquid is placed between two specially treated glass sheets (such as rubbing with a velvet cloth, or applying a thin coat of a polyamide followed by unidirectional rubbing with a roller), the molecules close to the glass surfaces are forced to orient themselves parallel to the surfaces of the glass sheets.

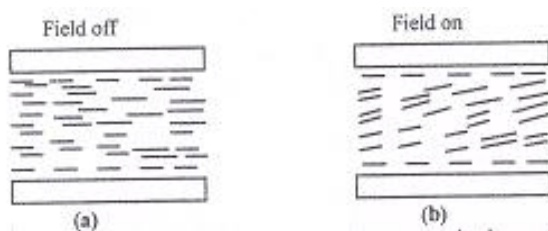


Fig.8 Liquid crystal film kept between two treated glass plates (a) in the field off state all molecules and the director orient parallel to the surface (b) in the field on state the molecules near the surface orient parallel to the surface whereas in others it is deformed

In the absence of an electric field, (below a threshold value) the molecules at other layers are also aligned parallel to the surfaces giving a homogeneous arrangement. But when an electric field is applied perpendicular to the glass surface, molecules near the surface are aligned parallel to the surface (perpendicular to the applied field). The molecules near the centre of the liquid crystal layer (away from the surface) are free to orient themselves along the

applied field. The crystal undergoes deformity (Fig. 8). The deformity begins at a threshold value of the applied field and increases with increase in the strength of the field. This transition (deformity) is important in the operation of liquid crystal displays (LCD) because the transition brings about a significant change in the optical characteristics of the liquid crystal.

Effect of light: When light is incident on two crossed polarizers, no light emerges because the light emerging from the first polarizer is completely absorbed by the second polarizer and hence appears dark. When a film of a liquid crystal is placed between two polarizers, only a part of the light from first polarizer is absorbed by the second polarizer some light emerges giving bright appearance. A cell is assembled such that the direction of alignment at the top surface is perpendicular to that at the lower surface of the cell. Then it filled with a twisted nematic liquid crystal (TNLC) having a positive dielectric anisotropy (dielectric constant parallel to the director is higher). Twisted structure acts like a wave-guide and gradually rotates the plane of polarization of light by 90° . Hence a linearly polarized light incident on the cell emerges linearly polarized but in an orthogonal direction resulting in a bright appearance (Fig. 9).

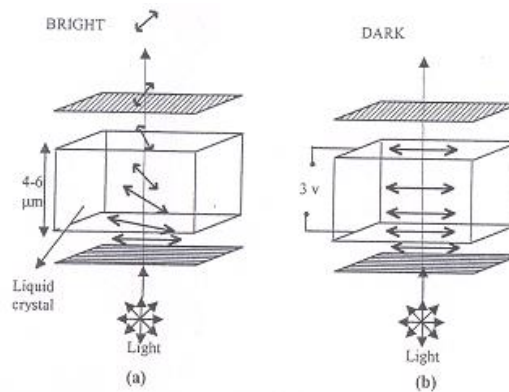


Fig.9 Bright and dark appearance when light is passed through twisted nematic liquid crystal placed between two crossed polarizers (a) appearance is bright in the absence of electric field (b) appearance is dark in the presence of electric field.

The 90° twist in the cell is lost when a sufficiently strong electric field (2-5V) is applied to the cell. Hence the cell appears dark between two crossed polarizers (Fig. 8b). The following conditions, however should be met to see the electro-optic effect.

- (i) The plane of polarization of incident light should be parallel or perpendicular at the surface of the cell.
- (ii) The product of optical anisotropy, Δn , (the difference in refractive indices parallel and perpendicular to the director) and pitch P should be greater the wavelength of the incident light. $\Delta n \times P > \lambda$.

APPLICATIONS OF LIQUID CRYSTALS IN DISPLAY SYSTEMS:

The electro-optic effect of liquid crystals controls brightness/darkness of the light emerging from its elements and is used in information displays. Information is passed into the user using the liquid crystals which control the brightness/darkness of the parts of the display. Numeric display has seven segments whereas alphabets are displayed using fourteen-segments. More complex graphic images are formed using pixels (picture elements) which are closely packed array of dots in two dimensions.

A numeric display consists of seven segments for each digit. Light from the area of each of the seven segments of pixels is controlled independently and is used to create any one of the ten digits. When an electric field is applied to a segment, the liquid crystal in that segment undergoes deformation (is activated) and when polarized light is incident, the light is

modulated depending on the deformation in that segment. A typical liquid display cell (reflection mode) is shown in Fig.9.

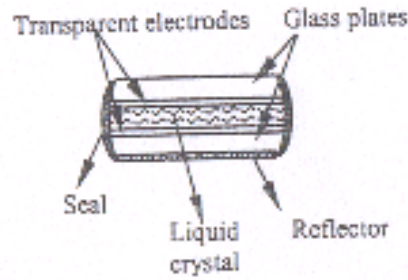


Fig.9. Schematic representation of a liquid crystal display (reflection mode pixel) where the liquid crystal is embedded between two glass plates.

The seven-segment display shown in Fig.10 is used to display numbers in calculators and watches. The top and bottom glass plates of a display have electrode patterns formed by etching a layer of indium tin oxide using standard photolithographic process. All the seven segments in the bottom glass plate are interconnected as shown in Fig. 10a to form a back plane. Connections to the segments *a* to *g* are brought out separately on the other glass plate as shown in Fig. 10b. Liquid crystal mixture is filled in the cell formed by sealing the edges of the top and bottom glass plates. Area of intersection between the electrode patterns on the top and bottom glass plates decides the shape of the segments in the display. The distance between the top and bottom glass plate is called cell thickness. It is usually in the range 4 to 8 μm to ensure that display can be switched in milliseconds. The quantity of liquid crystal mixture used in a display is small.

Figure 10c shows a 3 digit numeric display. Application of a voltage between the back plane and the corresponding electrode on the top plate turns ON a segment. For example the segment *b* is turned ON by applying a voltage about 3 volts between the back plane and the electrode *b* on the top plate. The ac waveforms applied to the back plane, an ON segment and an OFF segment are as shown in Fig.10d.

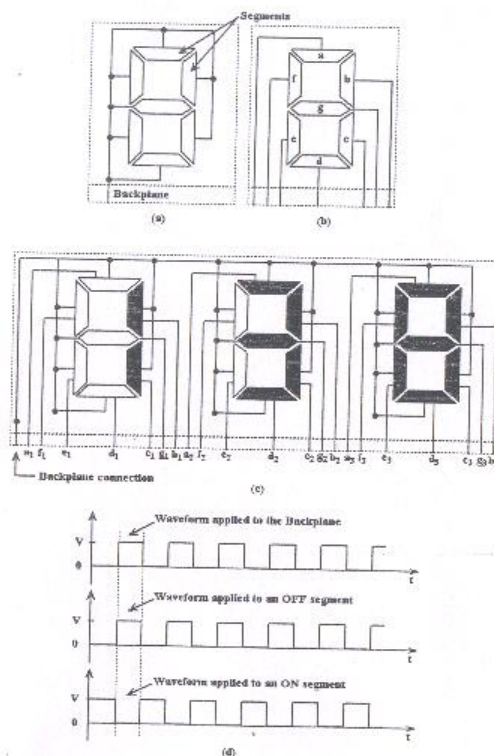


Fig.10. Seven segment liquid crystal display used to display numbers in calculators

Dyes used in liquid crystal displays are called dichroic dyes and give desired colours to the displays with a good contrast. Liquid crystal displays operate at low voltages (a few volts) and consume less power as compared to other display.

Applications:

- i) Watches, calculators, mobile telephones, laptop computer and related electronic gadgets.
- ii) Indicators used in automobile dashboards, airplane cockpits, traffic signals, advertisement boards and petrol pump indicators.
- iii) Blood pressure instruments, digital thermometers and TV channel indicators.
pH meters, conductometers, colorimeters, potentiometers and other analytical instruments.
