UNIT-V: ENGINEERING CHEMISTRY AND GREEN CHEMISTY

COMPOSITES:

Composite: *A Composite is defined as 'any multiphase material which consists of two or more physically and / or chemically distinct phases with an interface separating them.*

Examples:

1. Wood (a composite of cellulose fibres & lignin)
2. Bone (a composite of strong protein Callogen, and hard material apatite)
3. The earliest man-made composite materials were straw and mud combined to form bricks for building construction
4. Concrete is the most common artificial composite material of all and typically consists gravel (aggregate) held with a matrix of cement.

Constituents of composites:

The two essential constituents of composites are, 1.**Matrix phase** 2.**Dispersed phase**

1. **Matrix phase:**
   It is a continuous body constituent of composite, enclose the composite and gives it its bulk form. The Matrix phase may be a **metal, ceramic or polymer**.
2. **Dispersed phase or Reinforcement:**
   It is a structural constituent of composite, which determines the internal structure of composite.
   Dispersed phase may be a fiber, particle, flakes and whiskers.
   What are fibers?
   Fibers: *Any polymer, metal or ceramic that has been drawn into long and thin filament, is termed as fiber.* It is characterized by high aspect ratio (length to diameter ratio) and near crystal sized diameter. They have high strength and stiffness.
   - Fibers may be, glass **fibers,** carbon fibers, **aramide fibers**, boron fibers and ceramic fibers.

   What are particulates?
   Particulates (Particle): *Particulates are small pieces of hard solid material (Metallic and non-metallic).*The distribution of particles in a given matrix is usually, random thereby the resulting isotropic composite.
   What are flakes?
   Flakes: *Flakes are thin solids having a two-dimensional geometry*. Examples: mica flakes
   What are Whiskers?
   Whiskers: *These are thin strong filaments or fibres made by growing crystals*
   Examples: Graphite, Silicon carbide, Silicon nitride and aluminium oxide.

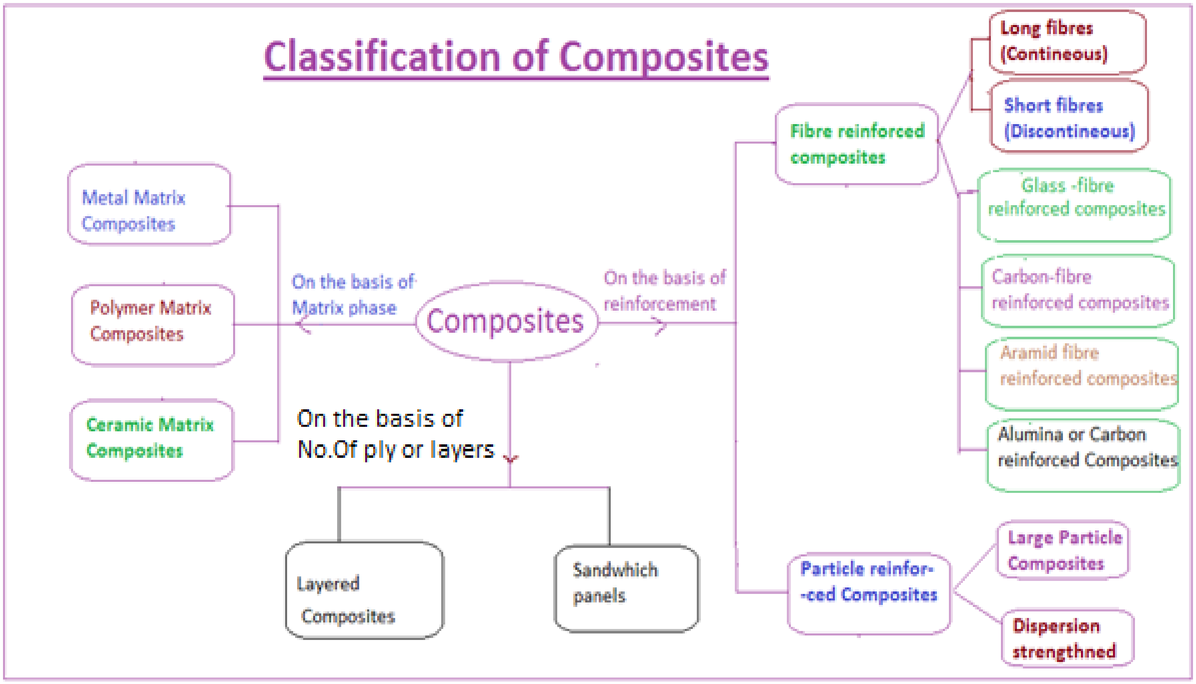
Characteristic properties of Composite Materials:

The composite materials show properties distinctively different from those of the individual materials of the composite.

The composites show extraordinary combination of properties like **toughness and strength** with **low weights & high temperature resistance**. Compared to steel and aluminum, composites are **lighter, have low coefficient of thermal expansion and have superior strength, stiffness & fatigue resistance**. They have lower electrical conductivity and have **better corrosion & oxidation-resistances**.

The properties of the composites depend on: The properties composites depends on properties, relative amounts (i.e.concentration) , distribution and orientation of the constituent materials and geometry of the dispersed phase namely the shape, size and size distribution.

Types of composites:



Fiber reinforced composites:

One of the most common types of composites is fiber-reinforced composites. **Fiber-reinforced composites** are a composite material made of a polymer matrix reinforced with fibers. The polymer matrix is usually poly ester, epoxy resins, phonolic resins, silicone resins and melamine resins. The fibers are usually glass, carbon and graphite, aramide, alumina fiber, boron fiber, poly crystalline metal oxide fiber, silicon carbide fiber.

Thus ,based on type of fiber used for reinforcement, fiber reinforced composites are further sub classified as,

1. **Glass-fiber reinforced composites: Glass-reinforced composites**, are fiber reinforced polymers made of a Polymer matrix reinforced with fine fibers of glass. Fiberglass is a light weight, extremely strong, material. Its bulk strength and weight properties are also very favourable when compared to metals, and it can be easily formed using molding processes. The polymer matrix may be epoxy, a thermosetting plastic.

   Glass-fiber reinforced composites (GFRC) are strong, corrosion resistant and lightweight, but not very stiff and cannot be used at high temperatures.

   Applications include auto and boat bodies, aircraft components. Applications: Automotive parts, storage tanks, industrial floorings, plastic pipes and in transportation industries to reduce vehicle weight & boost fuel efficiency.

2. **Carbon fiber reinforced composites: Carbon Fiber Reinforced Composite**, is a Polymer Matrix Composite material reinforced with carbon fibers. Carbon fibers are very expensive but they possess the highest specific mechanical properties: modulus of elasticity and strength.

   Carbon-fiber reinforced composites (CFRC) use carbon fibers, which have the highest specific module (module divided by weight). CFRC are strong, inert, allow high temperature use.
   Applications: i) Military and commercial aircraft structural components such as wing, ii) Wing, body and stabilizer components of helicopters, iii) Sports and recreational equipments like fishing rods, golf clubs etc.
   Applications include fishing rods, golf clubs and aircraft components.

3. **Aramid fiber-reinforced polymer composites :**
   They are basically aromatic polyamides like Nomex and Kevlar. Kevlar is spun from a nematic liquid crystalline solution using a dry jet wet spinning technique using sulphuric acid as a solvent and cold water as coagulant. These are commonly used in PMC's along with polyesters and epoxides. Kevlar, and aramid-fiber composite can be used as textile fibers.

   Applications: Automobile brakes and clutches {short fibre}, Structural material of commercial aircraft, helicopter parts like rotor blades, motor housing and protective apparel (thermal & ballistic) etc-{Long fibre}.
4. **Alumina and /or carbon fibre-reinforced metal composites:**
   These possess good specific strength, stiffness, abrasion resistance, creep resistance and dimensional stability. The two important composites of this class are

(a) Composition: Matrix- Al alloy ; Reinforcement – Al_2O_3 or C fibers Properties: Low density, wear resistant, resistant to thermal distortion.
   Application : Components of engine in automobile industry

(b) Composition: Matrix- Ni & Co alloy ; Reinforcement – Al_2O_3 or W.

Properties: Excellent resistance to impact strength,creep and rupture and high temperature

Application : Components of turbine engines.

Based on length of fiber, fiber reinforced composites are classified as,

Long Fiber (Continuous) reinforced composites:

The high mechanical performance characteristics of long fiber composites is the reason they are often chosen as substitutes for metals, as a replacements for under-performing plastics, or as alternatives to higher cost engineering polymers through up-engineering of lower cost plastics.

Applications:

These composites are excellent structural and advanced engineering materials and find applications in commercial aircrafts, helicopter parts(rotor blades, motor housing),small business aircrafts, protection apparel(thermal an ballistic).

Short fiber (discontinuous) reinforced composites:

Short fiber reinforced composites give effective reinforcement due to their better aspect ratio, high surface area, inherent toughness, strength, heat stability and high wears resistance.

Applications:

Automobile brakes and clutches.

Particle-reinforced composites:

These composites are made by dispersing particles of varying size and shape of one material in a matrix of another material. These composites are the cheapest and most widely used. These may be sub classified into two types depending on the size of the particles:

i. Large-particle composites
ii. Dispersion-strengthened composites

(i) Large-Particle Composites:

Large particle composites may involve metals, polymers and ceramics as matrices.

Concrete: The most common large-particle composite is concrete, made of a cement (a fine mixture of lime, alumina, silica, and water) matrix that bonds particles of different size (gravel and sand)

Cermets are composites of ceramic particles (strong, brittle) in a metal matrix (soft, ductile) that enhances toughness. A typical example of cermet is, tungsten carbide or titanium carbide ceramics in matrix of ductile metal such as Co or Ni. **They are used for cutting tools for hardened steels.**

Reinforced rubber is an example of *large particle composites* which is obtained by adding reinforcement, carbon particles, to a polymer matrix. **They are used in automobile tires.**

(ii) Dispersion-Strengthened Composites:

These type of composites contain extremely small particles, in the range of 10-100 nm, dispersed the matrix at low concentrations. The small particles hinder the migration of dislocations within the matrix thereby restricting the plastic deformation.An important group of dispersion-strengthened composites is thoria-dispersed (TD) metals.

A common example of this kind of composite is TD-nickel.

Layered composites (or) Laminar Composites

Laminar composites consist of number of two dimensional sheets that are stacked and subsequently cemented together such that the orientation of reinforcement varies with each successive layer.

These layers possess relatively high strength in the direction of reinforcement and hence the resulting laminar composite has high strength in number of directions in the two dimensional plane.

Examples:

1. Plywood- the adjacent wood sheets in plywood are aligned with the grain direction at right angles to each other.
2. Stainless steel cooling vessel with a copper clad bottom etc.

Sandwich panels:

These are another type of layered composites which consists of two strong outer sheets (called faces) and an intervening layer of less dense core material. These three layers are joined by using an adhesive. Most popular core material is of ‘honeycomb’ structure consisting of thin foils forming interlocked hexagonal cells with their axes oriented at right angles to the direction of face sheets.

These kind of composites find application in fabrication of wings of aircrafts, boat hulls, ship structure parts, building structures (roofs, floors, walls, etc).

Advantages of composites

1. The greatest advantage of composite materials is strength and stiffness combined with light weight.
2. Composites are less likely than metals to break up completely under stress. A small crack in a piece of metal can spread very rapidly with very serious consequences. The fibers in a composite act to block the widening of any small crack and to share the stress around.
3. The right mix of constituent materials often results in composites which are heat and corrosion resistant.
4. Composite materials are also very durable.
5. They provide design flexibility, as they can be molded into complex shapes.
6. The manufacturing processes are often more efficient when composites are used.

Applications of composites:

1. **Transportation:** Composites are used in the manufacturing of automobile parts, racing vehicle components and engine parts.
2. **Marine:** They are used as propeller shafts, hulls, spars (for racing boats) etc.
3. **Aerospace:** They are used in military aircrafts, helicopters, missiles and rocket components etc.
4. **Consumer product:** They are used in sporting goods like tennis rackets, and in musical instruments etc.
5. **Composite Applications in Building & Construction**
   Components made of composite materials find extensive applications in shuttering supports, special architectural structures imparting aesthetic appearance, with the advantages like corrosion resistance, longer life, low maintenance, ease in workability, fire retardancy etc
6. Composites are frequently used in industrial and scientific equipments like high speed machinery, electronic circuit boards (PCB) , communication antenna etc.
7. Safety equipments like ballistic protection and air bags of cars etc.

LIQUID CRYSTALS

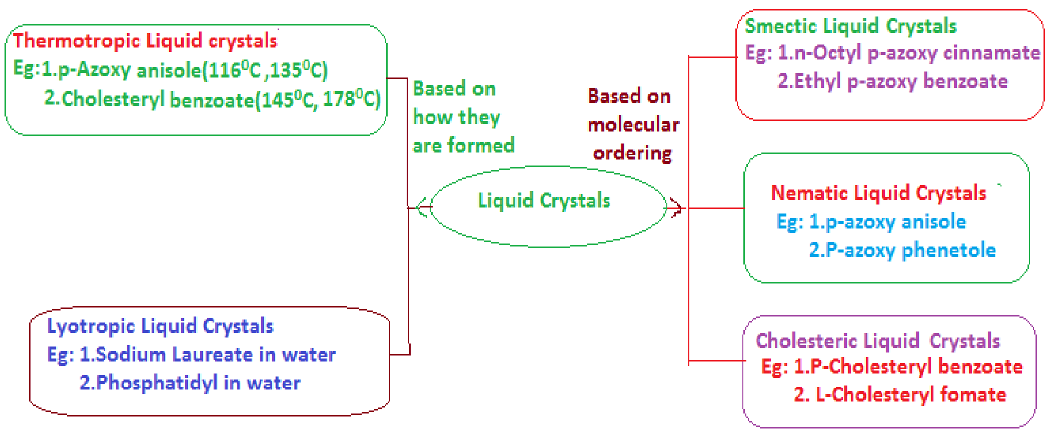
Liquid Crystal: A state of matter that is intermediate between the solid crystalline phase (anisotropic) and true liquid phase (isotropic) is known as **Mesomorphic state (intermediate form ,in Greek) or Liquid crystals.**

P-cholesteryl benzoate (crystalline form) $\xrightarrow{145^0C}$ P-cholesteryl benzoate (Liquid crystal) $\xrightarrow{175^0C}$ P-cholesteryl benzoate (true liquid)

The first temperature at which solid changes into turbid liquid is known **as "*transition point*"** and the second temperature at which turbid liquid changes into a clear liquid is known as ***"melting point"*.**

Examples: 1.Cholesteryl benzoate(145^0C,178^0C)
2.P-Azoxy anisole (116^0C,135^0C)

Classification of liquid crystals:



Based on how they are formed they are classified as follows:

Thermo tropic liquid crystals:

The class of compounds which exhibits liquid crystalline phase as the temperature changes is called Thermo tropic liquid crystals.

Thermo tropic liquid crystals are formed from organic molecules with rod like shape , having planar and rigid benzene rings as the characteristics structural feature.

Examples: 1. Cholesteryl benzoate (145^0C ,178^0C)

2. P-azoxy anisole (116^0C ,135^0C)

Lyotropic liquid crystals:

The compounds which exhibit liquid crystalline behaviour when mixed with solvent and with change of concentration in solution are called ‘Lyotropic Liquid Crystals. Class of compounds which exhibit lyotropic liquid crystals are amphiphilic as they have both lyophilic (solvent loving) and lyophobic (solvent hating) parts in the same molecule.

Examples: 1. Sodium laureate in water ,

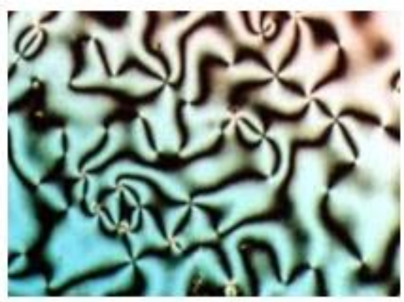
2. Phosphatidyl choline in water .

Based on molecular ordering liquid crystals are classified as,

a) **Smectic Liquid Crystals : (Smectic means Soap like)**

i. This type of crystals are formed by certain molecules with chemically dissimilar parts .The chemically similar parts attract each other and there is tendency to form layers as well to have the molecules aligned in one direction
ii. The smectic liquid crystals do not flow as normal liquids. They have limited mobility and flow in layers. The layers can slide over one another because of weak attractive forces.
iii. The flow of smectic liquid crystals is non –Newtonian while that of true liquids is Newtonian.
iv. Smectic liquid crystals form a series of terraces or strata, when they are spread over a clean glass plate.
v. They are always uniaxial and are not affected by magnetic field.
vi. Smectic liquid crystal also gives X-ray diffraction pattern like solid crystals but is only in one direction.
vii. Smectic liquid crystals appear to have fan like structure when they are viewed in polarized light.
viii. Eg ; n-Octyl p- azoxy cinnamate (94^0C , 175^0C); Ethyl p- azoxy benzoate (114^0C , 121^0C) ; Ethyl p-azoxy cinnamate (94^0C , 249^0C)





b) **Nematic Liquid Crystals : (Nematic means thread like)**

i. Molecules are parallel to each other like soda straws but they are free to slide or roll individually .However, the molecules are not arranged in layers like the smectic crystals.

ii. Nematic liquid crystals have a translucent appearance.

iii. Nematic liquid crystals show near normal flow behaviour of liquids .Their flow is also Newtonian and concept of viscosity is applicable to their flow.

iv. They are uniaxial but affected by a strong magnetic field .

v. Eg: p- azoxy anisole ; p- azoxy cinnamic acid ; p-azoxy phenetole.

c) **Cholesteric Liquid Crystals :**

i. The name Cholesteric comes from the fact that many derivatives of cholesterol from this type of liquid crystal.

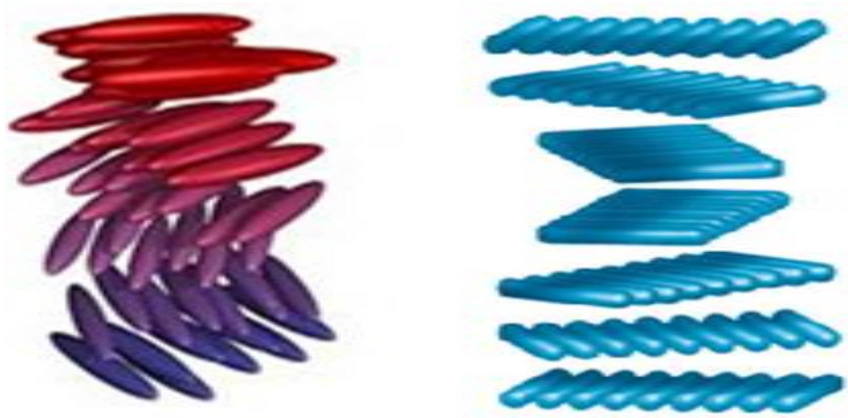
ii. These types of liquid crystals have some characteristics of Nematic and some characteristics of Smectic liquid crystals.

iii. In this type of liquid crystals, the molecules are parallel but are arranged in layers .The molecules in successive layers are slightly rotated with respect to the layers above and below so as to form a helical structure .They are also called as twisted Nematic liquid crystals. Or Chiral LC.

iv. There is some colour effect under polarized light.

v. These types of liquid crystals have appreciable rotator power.

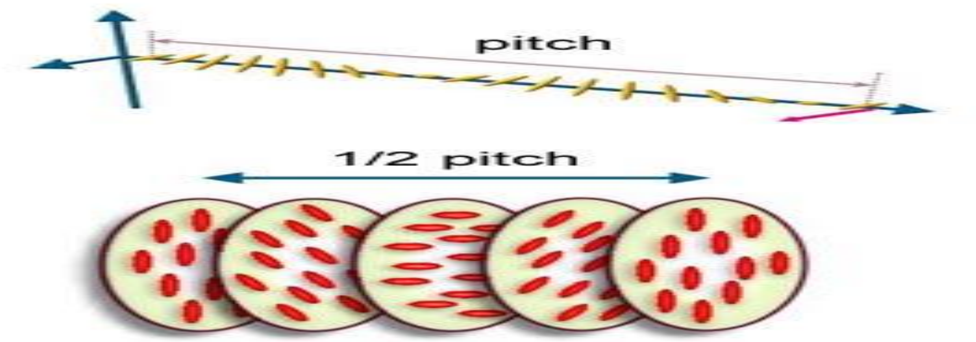
vi. Eg; p-Cholesteryl benzoate; L-cholesteryl formate.



Cholesteric phase

Pitch:

It is defined as the distance taken by the director to rotate one full turn (360^0) in the helix. The pitch varies sensitively with temperature. When pitch corresponds to the wave length of visible light, the scattered light is highly coloured.



Applications of Liquid Crystals;

Liquid crystals have the following applications;

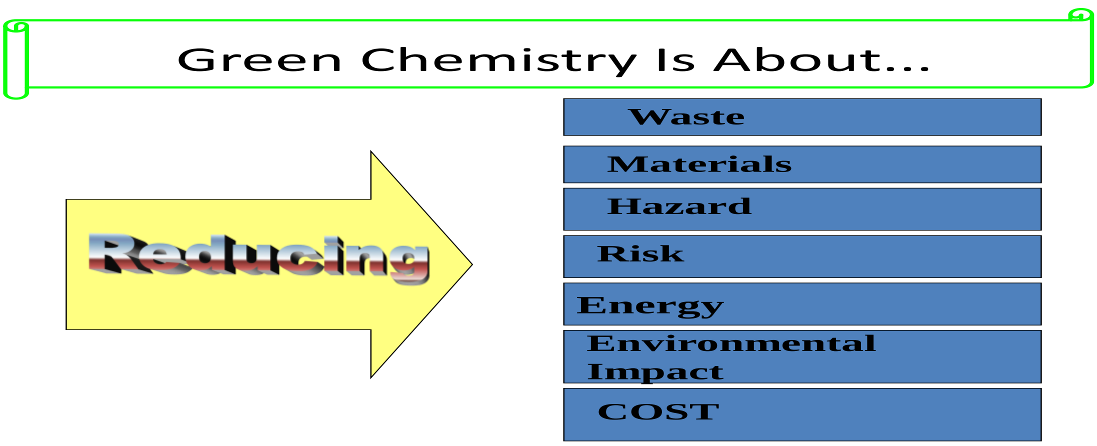
1. LCD Displays
2. Liquid crystal thermometers
3. In Optical imaging
4. In Helmets and bullet proof vests
5. For Battery testing strips or Charge indicators for batteries
6. They are used as commercial lubricants

Green Chemistry:

Definition:

Green Chemistry is the science which utilizes a set of chemistry principles in the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances".

The concept of Green chemistry was proposed by Paul Anestas in 1994.



Principles of Green Chemistry:

1. **Atom Economy:**

   The Atom Economy is a measure of efficiency of particular reaction. It is an assessment which tells that the extent to which the atoms of reactants are incorporated into the desired final product.

$$\%\ \text{Atom Economy} = \frac{\text{Mass of atoms in desired products}}{\text{Total mass of atoms in reactants}}$$

   A reaction to be considered as green synthesis, the atom economy must be very high, approaching or equal to 100 %. Then most of the reactant atoms are incorporated in to the final product, thereby reducing the waste or the by-products.

2. **Improved Process:** The process should use renewable feed stock rather than depleting material or feedstock whenever technically and economically practicable.
3. **Minimize:** Minimize energy consumption and material use.
4. **Environment friendly: The products produced or t he processes developed should not show negative impact on environment.**
5. **Less hazardous chemical synthesis:** Synthetic methods should be designed to use and generate substances that possess no or little toxicity to human health and the environment.
6. **Prevent Waste:** It is better to prevent waste than to treat or clean up waste after it has been created.
7. **Real–time analysis for pollution prevention**: Use suitable analytical methodologies need to be further developed to allow for real-time analysis, in-process monitoring and control prior to the formation of hazardous substances.
8. **Omit/Reduce derivatives:** Unnecessary derivatization (blocking group, protection or deprotection, and temporary modification of physical or chemical process) should be avoided whenever possible.
9. **Design safer chemicals and degradable products** :

   Chemical products should be designed to perform their desired function even after minimizing their toxicity. Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.
10. **Use safer chemicals and methods:**

Substances and the form of substances used in chemical process should be chosen **to** minimize the potential for chemical for chemical accidents including releases, explosions and fires.

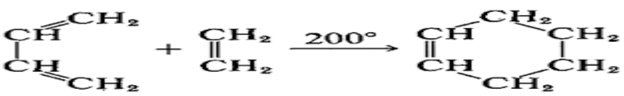
11. Catalysis: Catalytic Reagents (as selective as possible) are superior to stoichiometric reagents.

12. Technology: A technology where ambient temperature and pressure conditions are used to minimize the potential for chemical accidents, including releases, explosions, and fires

"AIM Environment friendly Less Hazardous PRODUCT"

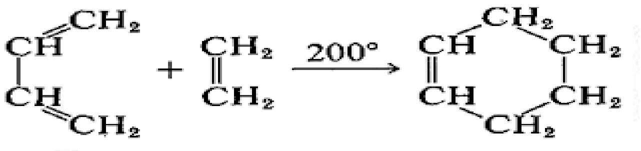
Examples of clean technology:

1. Examples of **Atom Economic** reactions:



Calculate % atom economy for cyclo addition reaction of ethene and butadiene to form cyclohexene .

Sol.

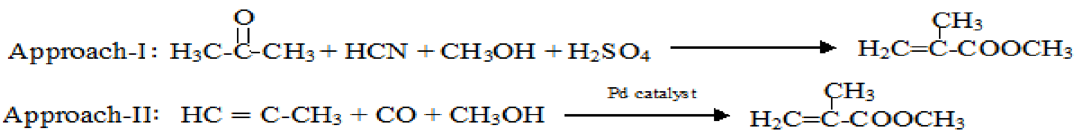


1,3-Butadiene(54) Ethene(28) Cyclo hexane(82)

$$\% \text{ Atom Economy} = \frac{\text{Mass of atoms in desired products}}{\text{Total mass of atoms in reactants}}$$

$$= \frac{82}{82} x\ 100 \quad = 100\%$$

2. Methylmethacrylate is industrially important monomer for the synthesis of PMMA polymer. It can be synthesized by one of the following two approaches : **{Example for Atom Economy & Catalysis }**



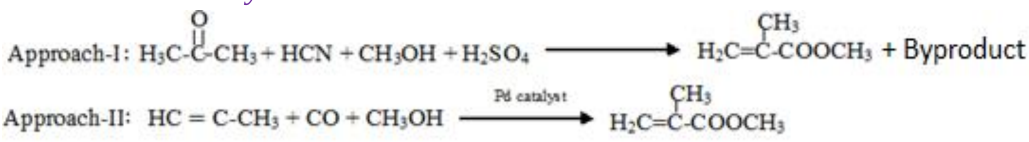
Predict which one approach is qualifying as Green synthesis.
(Hint: Calculate the mass of atoms of all the reactants in both approach and Moecular weight of desired product)

$$\% \text{ Atom Economy} = \frac{\text{Mass of atoms in desired products}}{\text{Total mass of atoms in reactants}}$$

Now, make use of above formula and find out atom economy for both the approaches. The approach with the higher atom economy is qualified as green synthesis.
Ans: Approach-II is qualified as green synthesis.

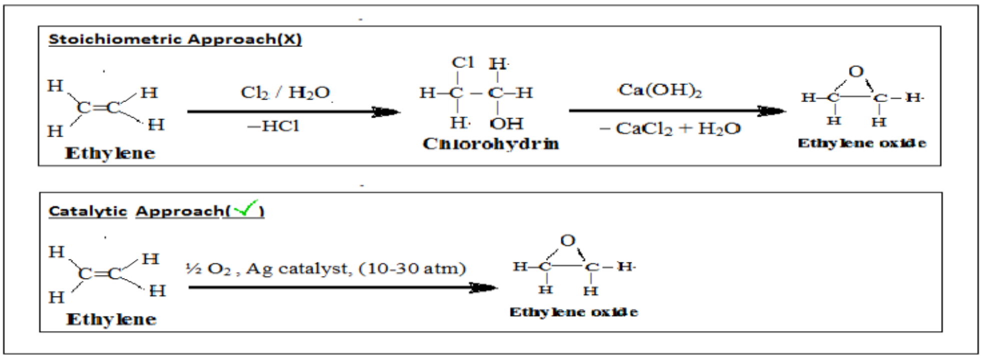
Examples of Green Catalysis:

1. *Preparation of MMA is done in two approaches as shown below Approach –II is qualified as green synthesis since catalyst used and minimization of use of reactants and atom economy is 100%.*



2. **Ethylene oxide is widely used in the synthesis of ethylene glycol (anti- freeze), polyesters, ethanolamine etc.**

Consider the synthesis of ethylene oxide via stoichiometric chlorohydrins route. It requires expensive & hazardous chlorine gas as a reagent. It also produces 3.5 kg of waste $CaCl_2$ per kg of ethylene oxide product**.** However, the catalytic route gives an approximately 80% product yield without generating by products. The unreacted reagents can simply be recycled through the synthesis.



3. Toluene can be converted into p-xylene by shape selective Zeolite catalyst avoiding o-xylene & m-Xylene.
4. **Preparation of Hydrazine:**

Hydrazine is traditionally produced by the Olin Raschig process from sodium hypochlorite and ammonia. The net reaction produces one equivalent of sodium chloride for every equivalent of the targeted product hydrazine

$NaOCl + 2\ NH_3 \rightarrow H_2N\text{-}NH_2 + NaCl + H_2O$

In the greener **peroxide** process , hydrogen peroxide is employed as the oxidant, the by product is water. The net conversion follows:

$2\ NH_3 + H_2O_2 \rightarrow H_2N\text{-}NH_2 + 2\ H_2O$ (clean reaction)