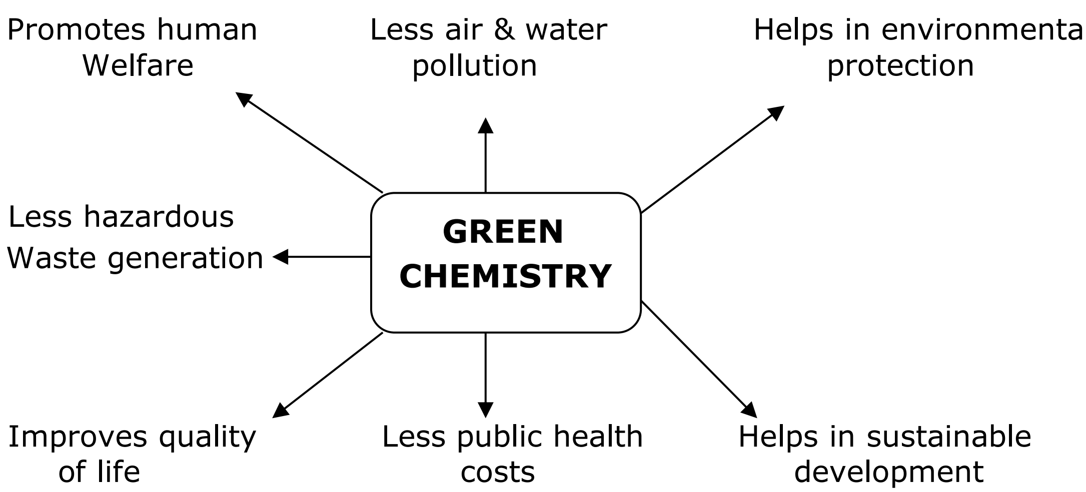
GREEN CHEMISTRY

Green Chemistry : Green Chemistry is '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.

Green Chemistry is about

Waste
Materials
Hazards
Risks
Energy
Cost

Benefits of Green Chemistry :



Principles of Green Chemistry : The 12 Principles of Green Chemistry are:

1) *Prevention :* It is better to prevent waste than to treat or clean up waste after it is formed.
2) Atom Economy : Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3) Less Hazardous chemical synthesis : Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4) Design Safer Chemicals : Chemical products should be designed to preserve efficacy of function while reducing toxicity.

5) Safer solvents and Auxiliaries : The use of auxiliaries substances (eg: solvents, separation agents etc) should be made unnecessary wherever possible and innocuous when used.
6) Design for energy efficiency : Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.
7) Use of Renewable Feed stocks : A raw material feed stock should be renewable rather than depleting whenever technically and economically practicable.
8) Reduce Derivatives : Unnecessary derivatization (use of blocking groups, protection/deprotection, temporary modification of physical/chemical process) should be avoided whenever possible.
9) Catalysis : Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10) Design for Degradation : Chemical products should be designed so that at the end of their function they do not persist in the environment and break down in to innocuous degradation products.
11) Real-time analysis for pollution prevention : Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substance.
12) Inherently safer chemistry for Accident Prevention : Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions and fires.

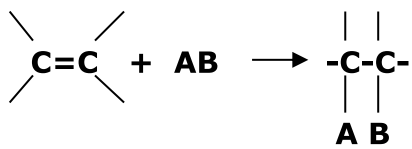
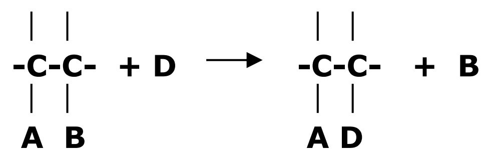
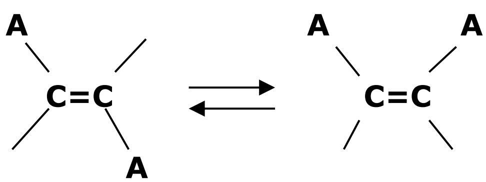
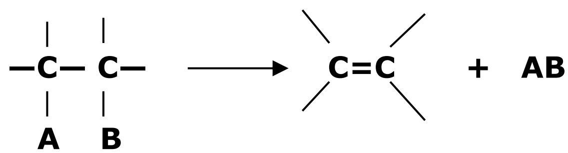
EXAMPLES OF CLEAN TECHNOLOGY :

1)Atom Economy : Atom Economy is defined as the ratio of the formula weight of the target molecule to the formula weight of all the starting materials and the reagents.

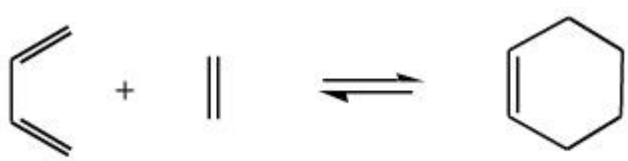
$$\% \text{ Atom Economy} = \frac{\text{Mass of atoms in desired products}}{\text{Total mass of atoms in reactants}} \times 100\ \%.$$

For 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.

Examples of **Atom Economic** and **Atom Un-economic** reactions.

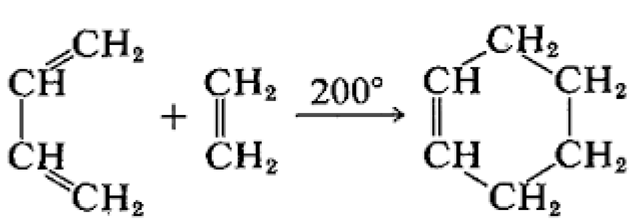
Atom Economic Reactions	Atom Un-economic Reactions
Addition : 	***Substitution :*** 
Rearrangement :  Trans cis	***Elimination :*** 

Eg :1. calculate % atom economy for cyclo addition reaction of ethene and butadiene to form cyclohexene .



1,3-Butadiene Ethene Cyclo hexene

<u>Sol.</u>



1,3-Butadiene Ethene Cyclo hexene

<u>Butadiene</u> **<u>Ethene</u>** **<u>Cyclo hexene</u>**

Molecular mass of butadiene

= 4 x atomic mass of C
+ 6 x atomic mass of H

= (4 x 12) + (6 x 1)
= 48 + 6
= 54 gms

Molecular mass of ethene

= 2 x atomic mass of C
+ 4 x atomic mass of H

= (2 x 12) + (4 x 1)
= 24 + 4
= 28 gms

Molecular mass of Cyclohexene

= 6 x atomic mass of C
+ 10 x atomic mass of H

= (6 x 12) + (10 x 1)
= 72 + 10
= 82 gms

$$\% \text{ Atom Economy} = \frac{\text{Mass of Atoms in desired product}}{\text{Total mass of atoms in reactants}} \times 100 \%$$

$$= \frac{82}{54 + 28} \times 100 = \frac{82}{82} \times 100 = \mathbf{\underline{100 \%}} .$$

<u>Eg: 2.</u> Methyl methacrylate 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 }**

<u>Approach-I.</u>

$$H_3C-\overset{\overset{O}{||}}{C}-CH_3 + HCN + CH_3OH + H_2SO_4 \longrightarrow H_2C=\overset{\overset{CH_3}{|}}{C}-COOCH_3$$

<u>Approach-II.</u>

$$HC \equiv C-CH_3 + CO + CH_3OH \xrightarrow{\text{Pd catalyst}} H_2C=\overset{\overset{CH_3}{|}}{C}-COOCH_3$$

Predict which one approach is qualifying as Green synthesis .

<u>Sol:</u> <u>Step-1</u> <u>Calculation of molecular masses :</u>

a) Molecular mass of $H_3C-\overset{\overset{O}{||}}{C}-CH_3$ = (3x12)+(6x1)+(1x16) = 58 gm
b) Molecular mass of HCN = (1x12)+(1x1)+(1x14) = 27 gm
c) Molecular mass of CH_3OH = (1x12)+(4x1)+(1x16) = 32 gm
d) Molecular mass of H_2SO_4 = (2x1)+(1x32)+(4x16) = 98 gm

e) Molecular mass of $H_2C=\overset{\overset{CH_3}{|}}{C}-COOCH_3$ = (5x12)+(8x1)+(2x16) = 100 gm
f) Molecular mass of $HC \equiv C-CH_3$ = (3x12)+(4x1) = 40 gm
g) Molecular mass of CO = (1x12)+(1x16) = 28 gm
h) Molecular mass of CH_3OH = (1x12)+(4x1)+(1x16) = 32 gm

<u>Step-2 :</u> calculation of Atom economies

$$\% \text{ Atom Economy} = \frac{\text{Mass of Atoms in desired product}}{\text{Total mass of atoms in reactants}} \times 100 \%$$

For Approach-I.

$$\% \text{ Atom Economy} = \frac{e}{a+b+c+d} \times 100 \%$$

$$= \frac{100}{58+27+32+98} \times 100 \%$$

$$= \frac{100}{215} \times 100 = \mathbf{46.5 \%} \longrightarrow (1)$$

For Approach-II.

$$\% \text{ Atom Economy} = \frac{e}{f+g+h} \times 100 \%$$

$$= \frac{100}{40+28+32} \times 100 \%$$

$$= \frac{100}{100} \times 100 = \mathbf{100 \%} \longrightarrow (2)$$

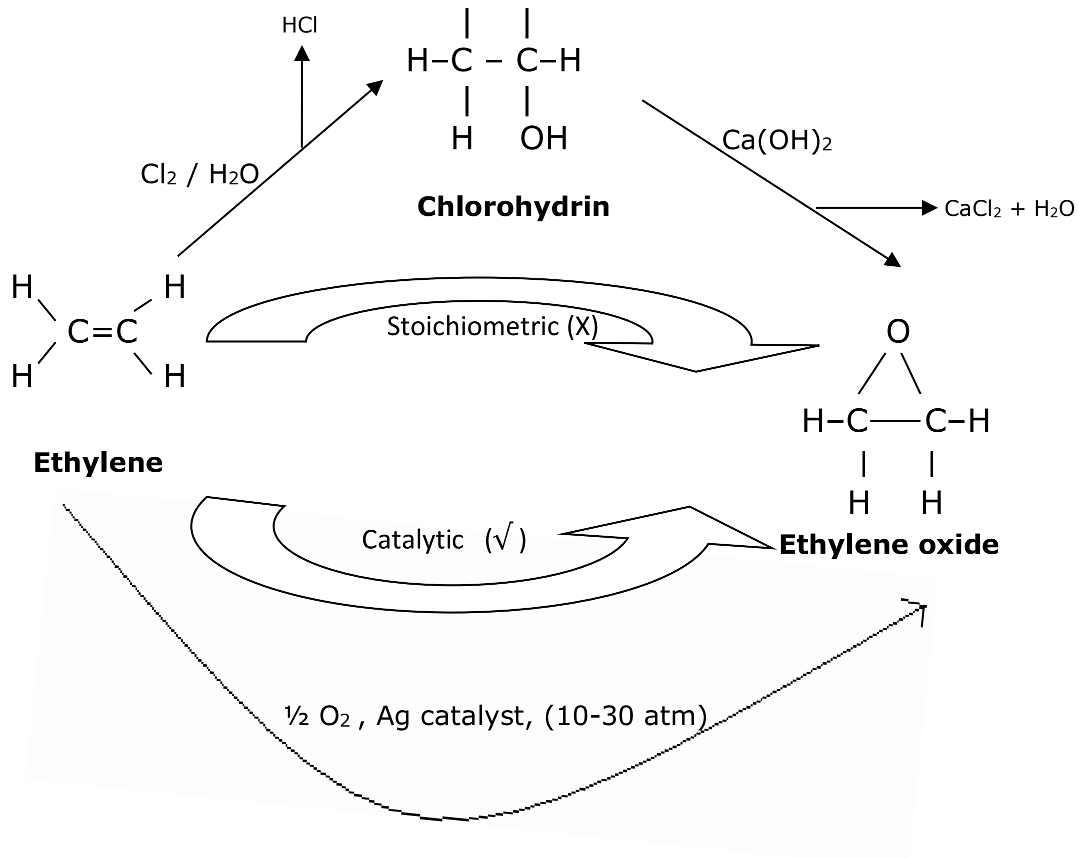
From results (1) & (2), Approach-II is qualifying as Green Synthesis .

Examples of **GREEN CATALYSIS :**

i) 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.

Cl H

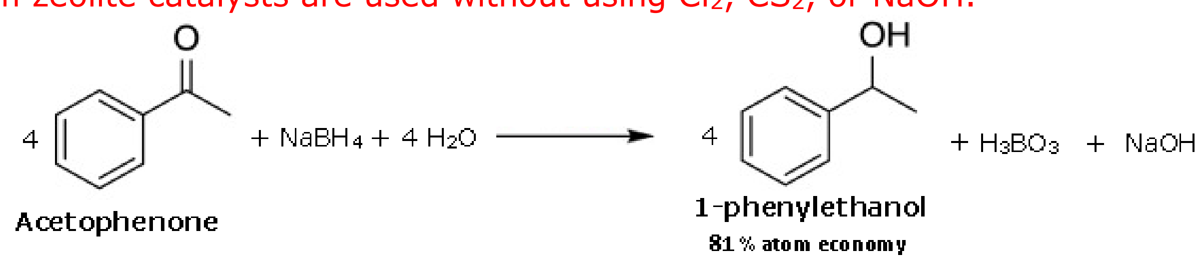


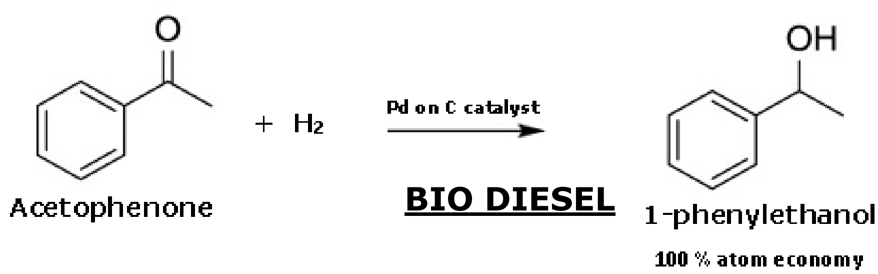
ii) Toluene can be converted into p-xylene by shape selective Zeolite catalyst avoiding o-xylene & m-Xylene.

iii) In the alkylation of butene, large amounts of corrosive acids like HF and H_2SO_4 are used conventionally, but in greener process, solid acid catalysts such as zeolites are used in place of acids.

In the synthesis of 4-methyl thiazole (a fungicide), the basic sites of cesium zeolite catalysts are used without using Cl_2, CS_2, or NaOH.

iV)



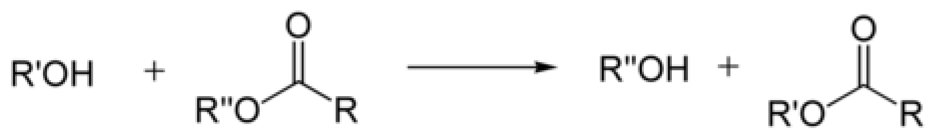


BIO DIESEL

Bio diesel is a natural and renewable domestic fuel alternative for diesel engines made from vegetable oils such as soya bean oil, palm oil, peanut oil & Sunflower seed oil. It is a green fuel and does not produce CO_2. It is non-toxic, bio degradable and free from sulphur compounds.

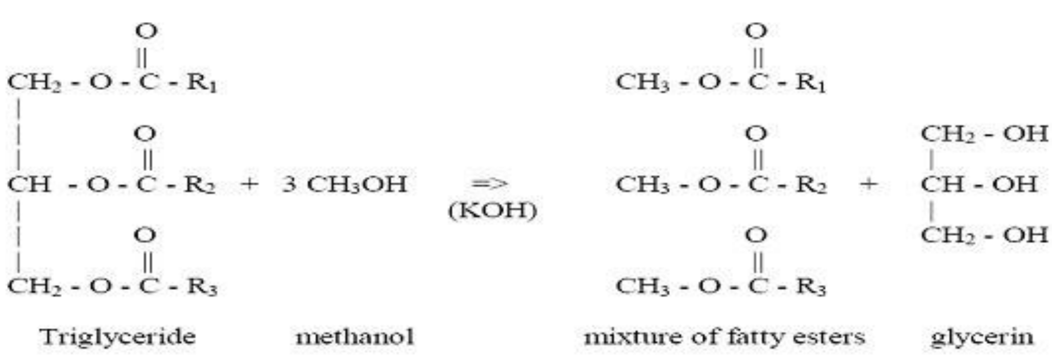
Vegetable oils contain 90-98% triglycerides along with small quantities of mono and diglycerides, free fatty acids, phospholipids, phosphotides, carotenes etc. Triglycerides are esters of long chain fatty acids such as stearic acid, palmitic acid, linoleic acid, oleic acid. Bio diesel is produced from the seeds of Jetropa and Rape seed vegetable oils and these are not used directly as diesel fuel due to their high viscosities & high flash point. Therefore Trans – esterification of Vegetable oils is done to reduce the viscosity.

Trans – esterification is the process of exchanging the organic group R″ of an ester with the organic group R′ of an alcohol.



Trans – esterification of triglyceride present in vegetable oils using methanol may be represented as:

Transesterification



Biodiesel is defined as 'Mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats which conform to ASTM D6751 specifications for use in diesel engines'.

Advantages /Significance of Bio diesel:

1) It can be produced from renewable domestic resources

2) Bio diesel is carbon neutral. Plants use the same amount of CO_2 to make the oil that is released when the fuel is burned.

3) Bio diesel is rapidly bio degradable & completely non-toxic (i.e., spillages are less risk than petroleum diesel spillages)

4) Bio diesel has a high cetane number of above 50, compared to only 40 for petroleum diesel fuel.

5) Bio diesel can be made from recycled vegetable & animal oils or fats.

6) It burns more efficiently than petroleum diesel.

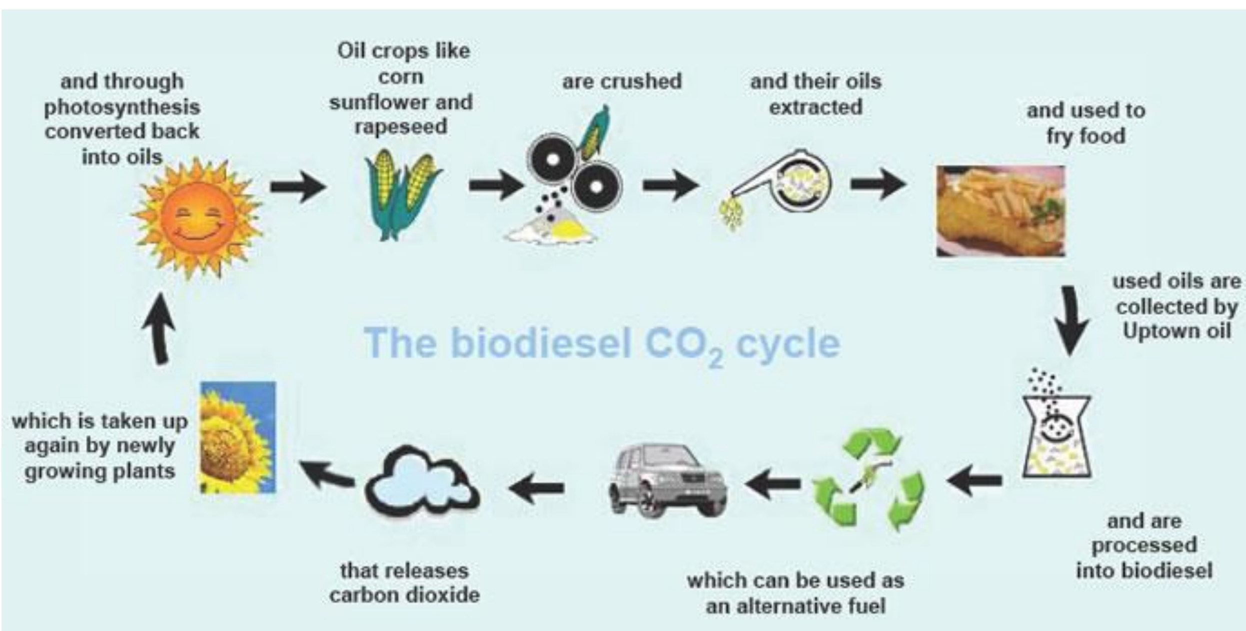
Limitations:

1) It has higher cloud and pour point, so it will freeze at higher temperature than conventional diesel.

2) It is not compatible with some metals and plastics.

Bio diesel is a Carbon neutral :

Biodiesel is said to be **carbon-neutral** because the carbon dioxide that is absorbed by the plants for photosynthesis process is equal to the carbon dioxide that is released when the fuel is burnt. So, there will be no net increase of CO_2 emission to the atmosphere .



COMPOSITE MATERIALS

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.'
Eg: Wood (a composite of cellulose fibres & lignin), bone (a composite of strong protein Collagen, and hard material apatite),reinforced concrete, insulating tape etc

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. These are easily fabric able, have lower electrical conductivity and have better corrosion & oxidation-resistances.

Constituents of composites:

Composites consist of body constituents and structural constituents. The body constituent encloses the composite and gives it its bulk form. The continuous matrix phase is the body constituent. The structural constituent determines the internal structure of the composite, and is known as 'dispersed phase'.
The Matrix phase may be metal, ceramics or polymers.
The dispersed phase can be fiber, particle, flake, whisker etc

The properties of the composites depend upon:
i) The properties of the constituent materials
ii) Their relative amounts (i.e., concentration of constituents)
iii) Their distribution and orientation and
iv) The geometry of the dispersed phase namely the shape, size and size distribution.

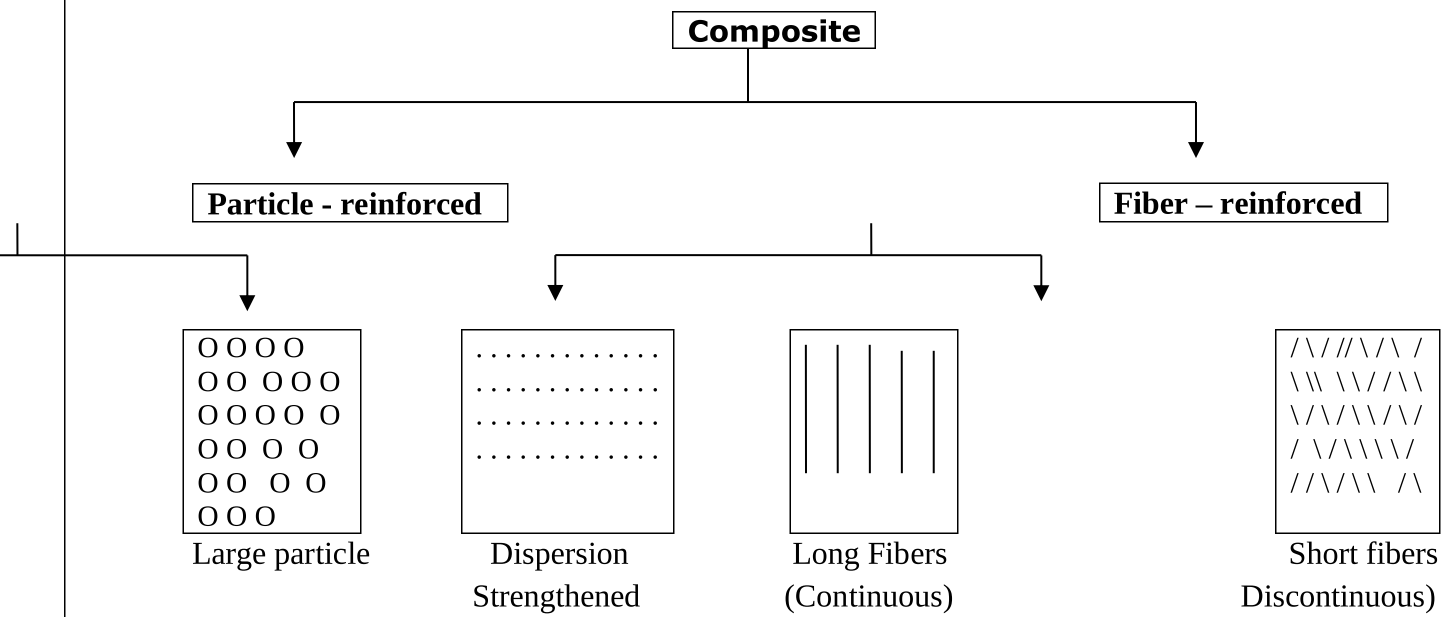
Functions of Matrix phase :

a) It binds the fibers
b) It acts as medium by transmitting & distributing the externally applied load to the dispersed phase.
c) It protects the individual fibers from chemical reaction and mechanical abrasion.
d) It keeps the reinforcing fibers in the proper position & orientation.
e) It prevents the propagation of brittle cracks.

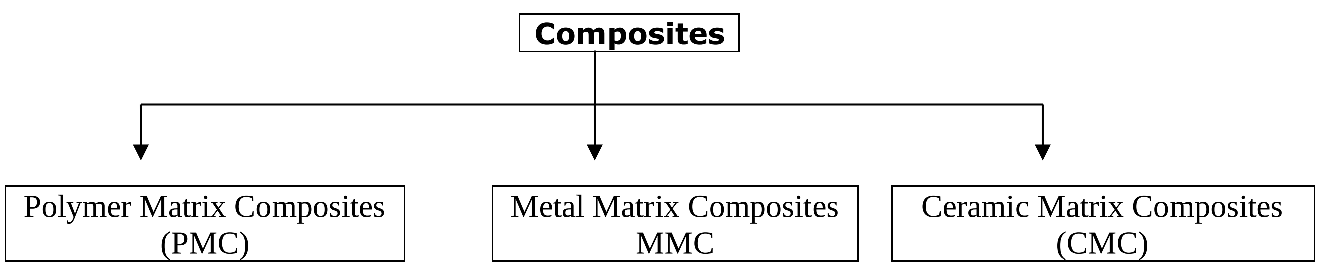
CLASSIFICATION OF COMPOSITE MATERIALS:

Composite materials can be broadly classified into the following types:

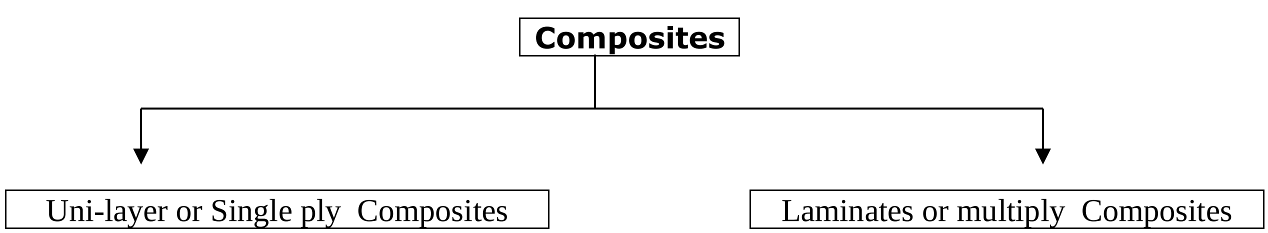
(1) On the basis of type of reinforcement used in the Matrix:



(2) On the basis of type of Matrix:



(3) On the basis of number of ply or lamina's or layers:



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) Composites are frequently used in industrial and scientific equipments like high speed machinery, electronic circuit boards (PCB), communication antenna etc.
6) Safety equipments like ballistic protection and air bags of cars etc.

Advantages of composite materials:

1) Composites are more economical than metals and ceramics.

2) Weight of the composite articles are approximately 25% to 50% of the weight of the conventional metallic design and hence fuel consumption is also minimized.

3) Composites show excellent mechanical properties & chemical properties.

4) Composite materials can be tailored to comply with thermal expansion design requirements & to minimize thermal stresses.

5) Better heat loss control is possible with composite structures

6) Composites have the selection flexibilities, changing of styling according to market needs and product aesthetic considerations.

7) Better corrosion and oxidation resistances

8) Better creep and fatigue strength