# Green Chemistry

The design of processes that reduce or eliminate the use and production of toxic products is known as green chemistry. Green Chemistry implies:

- Prevention of pollution rather than treatment of pollution
- Environmentally Benign Chemistry
- Sustainable Chemistry

Green chemistry should not be confused with environmental chemistry as environmental chemistry deals with various facets of pollution, degree of pollution and treatment of pollution, while as green chemistry does not lead to pollution at all, hence we say it prevents pollution. Thus green chemistry approach is a prevention approach, while as environmental chemistry approach is a treatment approach.

**Objectives of green chemistry**

1) To minimize the environmental pollution caused due to chemical processes.

2) To design harmless chemical processes w.r.t. chemicals used, products formed, byproducts generated, waste generated from the process and energy requirement.

3) Sustainable development of chemical industry

4) To reduce or eliminates the use or generation of hazardous substances in the manufacture.

To achieve these objectives the green chemistry utilizes a set of principles, known as Twelve Principles of Green Chemistry, suggested by Paul Anastas and John Warner.

**Twelve Principles of Green chemistry**

1. Prevention of waste
2. Maximize % Atom economy
3. Non-hazardous chemical synthesis
4. Design safer chemicals and products
5. Auxiliary substances (Use safer solvents and reaction conditions)
6. Energy efficiency
7. Use of renewable feedstock
8. Avoid chemical derivatives
9. Use of catalysts, not stoichiometric reagents
10. Design chemicals and products to degrade after use (Design for degradation)
11. Use of new analytical methods (Real time monitoring)
12. Minimize the potential for accidents

**1. Prevention of waste**

In designing a process/synthesis, the acronym, "Prevention is better than cure" must be obeyed. Waste prevention is necessary because of the following reasons:-

(a) If a process produces waste, it invokes the need for its treatment/disposal, which in turn amounts to additional expenditure.

(b) Secondly if the waste is toxic or hazardous, the release of waste in to the environment leads to its pollution, which further invokes the need of treatment, causing additional expenses.

So we must try to devise processes/reactions that minimize the production of wastes to the best possible extent. Since majority of the reactions produce the byproducts in addition to the normal desired product, we may say the byproducts of reactions are wastes. It has been a common practice to dump waste on land or in water, which resulted in soil, water and air pollution. This made the legislation to be very stringent on industries and hence there was compulsion to have waste treatment and disposal units attached to the manufacturing plants. This increases the cost of process.

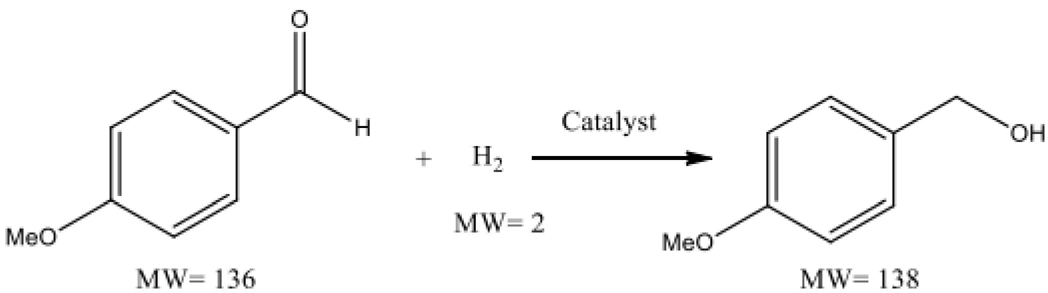
Thus green chemistry involved to design chemical syntheses in such a way that the process involve pathway to give only products, leaving no byproducts to treat or clean up. i.e. Prevention is better than cure.

**2. Maximize % atom economy**

- Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
- Atom economy (atom efficiency) is the conversion efficiency of a chemical process in terms of all atoms involved and the desired products produced. Atom economy is an important concept of green chemistry philosophy.
- It is common observation that most of organic reactions release undesired products along with useful products of the reaction.
- Green chemistry requires that new processes should be designed such that the most of the starting material gets converted into product. This is called as Maximizing atom economy.
- It is one of the fundamental and most important principle of green chemistry. The concept of atom economy has been developed by B.M. Trost. Atom economy is defined as the measure of the amount of reactants that ends up directly into the desired product. It is often referred to as percent atom utilization

$$\%\ Atom\ Economy = \frac{Formula\ weight\ of\ atoms\ utilised\ in\ the\ desired\ products}{Formula\ weight\ of\ reactants\ used\ in\ the\ reaction} \text{ x } 100$$

$$\%\ Atom\ Economy = \frac{Relative\ molecular\ mass\ of\ desired\ product}{Relative\ molecular\ mass\ of\ all\ reactants} \text{ x } 100$$




$$\% \, \textbf{Atom Economy} = \frac{138}{136+2} \times 100 = 100 \text{ percent}$$

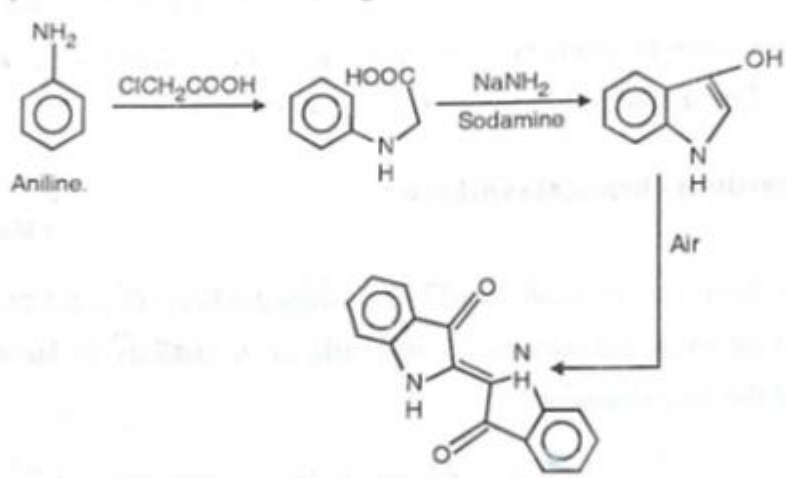
**3. Non-hazardous chemical synthesis**

- The synthetic method should be designed to generate substances having little or no toxicity to human health and the environment.
- The starting material selected should be least toxic. E.g. pyridine or α-napthylamine being carcinogenic should be avoided as starting materials.
- The reactions in which intermediates or reagents or products are toxic should be avoided, instead alternative pathways should be developed.
- E.g. Bhopal gas tragedy was caused due to leakage of Methyl isocyante (MIC) gas, an intermediate in the manufacture of pesticides and was known to be highly poisonous.
- Hence green chemistry recommends the design of synthesis to use and generate the substances with little or no toxicity to humans and the environment.

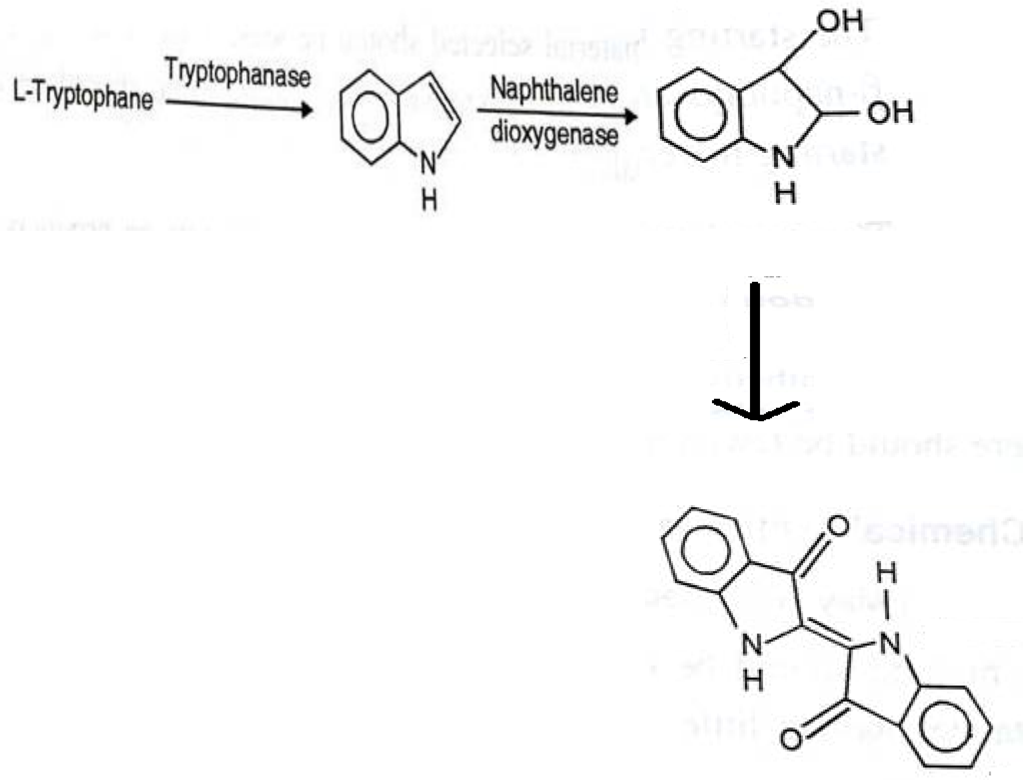
**Synthesis of indigo**

**Synthesis of Indigo**

**(A) Conventional Route using hazardous Aniline**



Green synthesis route:




**4. Design safer chemicals and products**

- The chemical products should be designed to preserve the efficiency of desired function while reducing toxicity.
- When any new drug formulations are to be put in market, they are put first on clinical trials to check their toxic effects on humans.
- If found toxic then alternatives are prepared keeping in consideration of medicinal properties but only toxicity reduced.
- Many insecticides like DDT, gamaxane, aldrin etc. are found to be toxic to humans, use of these should be avoided and alternatively biological pesticides should be used.
- A well-known example of retrometabolic design is that of ethylene glycol, which is used as antifreeze and has been replaced by propylene glycol which is less hazardous. Ethylene glycol once ingested in to body gets converted in to glyceraldehyde, glyoxylic acid and oxalic acid which are toxic to body, as against propylene glycol which gets metabolized into normal body metabolites like lactic and pyruvic acid.

**5. Auxiliary substances (Use of safe solvents)**

- Chemists generally use any organic solvent of their choice in synthetic reactions. Most often these solvents are the volatile organic solvents (VOCs) and have a major environmental concern.
- Most commonly used solvents are CHCl3, CCL4, acetonitrile, benzene and other organic solvents are toxic and they are carcinogenic in nature.
- They are able to form smog and free-radicals which is responsible for ozone depletion. They are also highly flammable and cause adverse effects like eye-irritation, headaches and allergic skin reactions in human biengs.
- These facts have made it necessary to use green alternative solvents. However if possible the use of solvents should be avoided. If however there is no choice and use of solvent becomes imperative, it is recommended to use such solvents which are inert, have low toxicity, easy to recycle without contaminating the products. The solvent selected should not have any negative impact on the environment or human health. Green alternatives like water, ionic liquids, liquid CO2 have been used to avoid the problems associated with the conventional VOCs, immobilized solvents have been harnessed. Such solvents maintain the solvency, are non-volatile and do not pose any environmental problem.
- For dry-cleaning of the fabrics, the toxic solvents like perchloroethylene was used, which is replaced during recent years by liquid CO2.

**6. Energy Efficiency (Energy efficient chemical processes)**

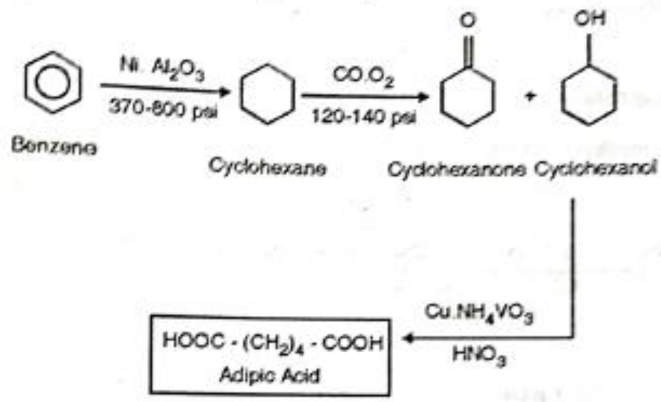
- The energy requirements of chemical processes should be minimized considering their environmental and economic impacts.
- This can be achieved by use of catalysts and by stopping use of fossil gaseous fuels which cause pollution.
- Most commonly used conventional energy source in reactions is the thermal energy. Thermal energy is non-specific, as it is not targeted directly at a bond or the molecules undergoing the reaction. Much of the thermal energy is wasted in heating up the reactors, solvents and even general environment.
- To avoid these things associated with thermal energy, alternate and more specific forms of energy are used. These sources are green energy sources include photochemical, microwave and ultrasonic sources of energy.
- The energy efficiency of the process can be increased by proper heat transfer and minimal wastage of energy during the process.
- Use fermentation process for chemical synthesis where energy requirement is low and products are less harmful.

**7. Use of renewable feedstock**

- The raw materials used should be renewable rather than depleting, wherever feasible economically and experimentally.
- Renewable feedstock is often made from agricultural products or of waste products of other processes.
- Example, Adipic acid was earlier synthesized from benzene, which is carcinogenic. A new method is developed to prepare adipic acid from glucose obtained from corn starch or cellulose. This is a green process.

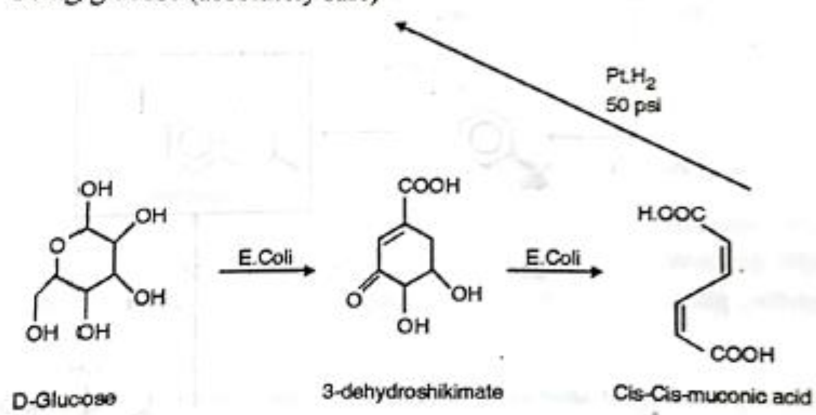
**Synthesis of Adipic Acid**

**(A) Traditional pathway :** Using Benzene (Carcinogenic solvent)




**(B) Greener pathway**

Using glucose (absolutely safe)

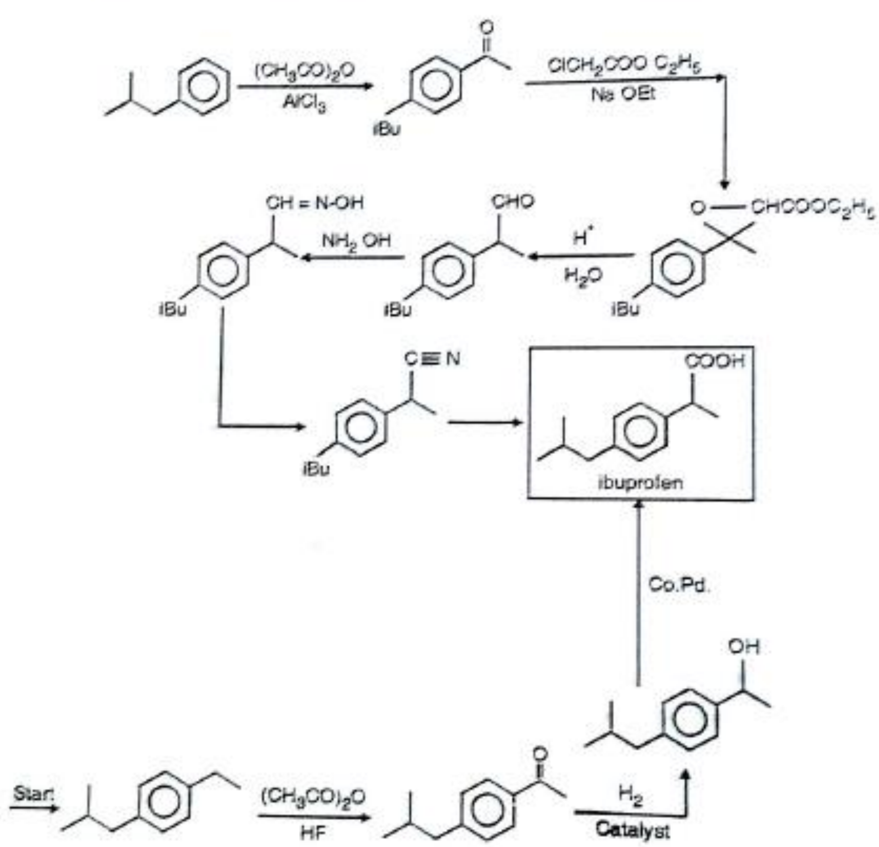


**8. Avoid chemical derivatives**

- During the synthesis unnecessary derivatisation such as protecting groups or any temporary modifications should be avoided if possible.
- The use of derivatives increases the steps of the process.
- The additional reagent required and it also generates more waste products.
- To avoid these effects alternative reagents are to be used which are more selective.
- Example, synthesis of ibuprofen is as given below. A traditional synthesis involves large number of steps and atom economy is low (40%). An alternative method increases the atom economy to 77%.

**Synthesis of Ibuprofen**

(A) **Traditional method** : With larger number of steps (Atom economy = 40 %)




**9. Use of catalysts**

- This principle advocates the use of catalytic reagents rather than the stoichiometric reagents. Being unchanged the catalytic reagent can be recovered completely as the reaction comes to an end. All catalysts including enzymes lower the activation energy of reaction, accelerating the reaction several million time, without being changed.

- Catalysts are selective in their action in that the degree of reaction that takes place is controlled, e.g. mono addition v/s multiple addition.
- A typical example is that reduction of triple bond to a double bond or single bond.
- In addition to the benefits of yield and atom economy, the catalysts are helpful in reducing consumption of energy.
- Catalysts carry out thousands of transformation before being exhausted.
- Catalytic reactions are faster and hence require less energy. They are preferable to stoichiometric reagents, which are used in excess and work only once.
- In recent years many processes are been developed which use non-toxic recoverable catalysts and also biocatalysts.

**10. Design chemicals and products to degrade after use**

- Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.
- It is extremely important that the products designed to be synthesized should be biodegradable.
- They should not be persistent chemicals or persistent bio accumulators.
- It is now possible to place functional groups in a molecule that will facilitate its biodegradation.
- Functional groups which are susceptible to hydrolysis, photolysis or other cleavage have been used to ensure that products will be biodegradable.
- It is also important that degradation products do not possess any toxicity and detrimental effects to the environment. Plastic, Pesticides (organic halogen based) are examples which pose to environment.
- Example, DDT when used as pesticide, its residues remains in soil for many years causing pollution. The alternative to this is biological insecticides.

**11. New Analytical methods**

- Analytical methodologies need to be further developed to allow for real time, in process monitoring and control prior to the formation of hazardous substances.
- Methods and technologies should be developed so that the prevention or minimization of generation of hazardous waste is achieved.
- Analytical technologies need to be developed that will allow the prevention and minimization of generation of hazardous wastes.
- One need to have accurate and reliable sensors, monitors, and techniques to assess the hazards that are present in the process stream. Using various techniques a process can be monitored for generation of hazardous byproducts and side reactions.

- It is necessary to have accurate and reliable results, monitors and other analytical methodologies to assess the hazardous that may be present in the process stream.
- These can prevent any accidents which may occur in chemical plants.
- Example, preparation of ethylene glycol, in which if reaction conditions are not monitored perfectly, toxic substances are produced at higher temperature.

**12. Minimize the potential for accidents**

- Substances and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions and fires.
- The occurrence of accidents in chemical industry must be avoided.
- It is well known that the incidents in Bhopal (India) and Seveso (Italy) and many others have resulted in the loss of thousands of life.
- It is possible sometimes to increase accidents potential inadvertently with a view to minimize the generation of waste in order to prevent pollution.
- It has been found that in an attempt to recycle solvents from a process (for economic reasons) increases the potential for a chemical accident or fire.
- The use of safer chemicals, minimizing temperature, pressure and using catalysts help in minimizing the potential of accidents which is desirable.

Green solvents:

The solvent selected should not have any negative impact on the environment or human health. e.g. halogenated solvents like $CHCl_3$, $CCl_4$ are suspected carcinogens and to avoid their use, green alternatives like water, ionic liquids, liquid $CO_2$ have been used.

To avoid the problems associated with the conventional VOCs, immobilized solvents have been harnessed. Such solvents maintain the solvency, are non-volatile and do not pose any environmental problem.

1. Supercritical $CO_2$:

Supercritical carbon dioxide is an attractive alternative in place of traditional organic solvents. CO2 is not considered a VOC. Although CO2 is a greenhouse gas, if it is withdrawn from the environment, used in a process, and then returned to the environment, it does not contribute to the greenhouse effect. There have been an increasing number of commercialized and potential applications for supercritical fluids. This article summarizes the fundamentals of supercritical CO2 properties and processing, and presents a number of current and potential applications. Supercritical fluids Above its critical values, a compound's liquid-vapor phase boundary no longer exists and its fluid properties can be tuned by adjusting the pressure or temperature. $CO_2$ becomes supercritical when its temperature and pressure are higher than 31.1 °C (critical temperature, $T_c$) and pressure 7.38 MPa (critical pressure, $P_c$). SCFs have many unique properties, such as strong solvation power for different solutes.

Supercritical $CO_2$ has the ability to diffuse into solid particles and dissolve many valuable non polar molecules. Examples of existing $CO_2$ extractions include:

- Decaffeination of coffee and tea
- Defatting of cacao
- Production of extracts from hops
- Oil from sesame seeds
- Extraction of pesticides from rice

2. $H_2O$ as Green Solvent: Water is regarded as the best solvent for the reactions to be carried out. Water however has a number of advantages but at the same time so many disadvantages as well. Water is naturally occurring, non-toxic, non-explosive solvent as against the voc's. However at the same time water is difficult to heat or cool rapidly, its distillation is energy expensive, the contaminated waste streams are difficult to treat. Although chemical reactions in human systems occurs within the water, but in lab synthetic reactions hardly occur in it. However at higher temperatures the density decreases while the ionic product of water increases. At temperatures of more than 200 0C water becomes as good as an organic solvent. It is believed that water behaves like acetone at a temperature of 300 °C. This is possibly because higher temperature removes hydrogen bonding in the water. In some reactions a significant amount of rate enhancement has been observed when the reaction is carried out using water. A typical example of this is the Diel's alder reaction between cyclopentadiene and butanone. It has been found that this reaction occurs 700 times faster in water compared to the isooctane.

3. Ionic Liquids An ionic liquid comprises of a large nitrogen containing organic cation and a small inorganic anion. Since one part is large and other is small, it creates asymmetry in the compound which makes it a low melting solid. Simple ionic liquids when mixed with the other inorganic salts result in the production of a multicomponent ionic liquid. Since the components of an ionic liquid are held by strong forces of attraction, it is found that they possess no or low vapour pressure rendering them non-volatile in nature. Further they are non-flammable and non-explosive which is an additional feature rendering them safe to use. They can also be used both as solvent as well as catalysts.

Thus the properties of ionic liquids which make them ideal green solvents include:

a) Lack of vapour pressure.

b) Non flammability and non-explosiveness.

c) Stable at high temperature which makes them better for carrying out reactions at high temperatures.

d) The property of these ionic liquids can be changed by just changing their concentrations of cations/anions, varying the side chain length in cations.