Green Chemistry

Our life depends on many useful chemical products like medicines, fabrics, insecticides, drugs, dyes, rubber, etc. Production of these chemical products causes severe pollution problems. All chemicals are toxic in varying extent. Hence it became necessary to review and modify all the chemical processes used for manufacture.

Thus the design of harmless processes to produce various products has emerged a new branch of chemistry called as Green chemistry or environmentally benign chemistry.

Green chemistry is highly effective approach to pollution prevention because it applies innovative scientific solutions to real world environmental situations.

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
11. Use New analytical methods
12. Minimize the potential for accidents

1. Prevention of waste

· It is better to prevent waste than to treat or clean up waste after it is formed. · 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.

Atom Economy

The theoretical yield for every reaction can be calculated as.

$$\text{Theoretical yield} = \text{Stoichiometric ratio} \times \left[\frac{\text{Molecular weight of the desired product}}{\text{Molecular weight of limiting reagent}}\right] \times \text{weight of limiting reagent}$$

On conducting the reaction the experimental or actual yield of the process is obtained. From this percentage yield is calculated.

$$\text{Percentage yield} = \left[\frac{\text{Actual yield}}{\text{Theoretical yield}}\right] \times 100$$

e.g. Preparation of n-propyl bromide from n-propyl alcohol (0.6 g)

$$CH_3CH_2CH_2\text{-}OH + NaBr + H_2SO_4 \longrightarrow CH_3CH_2CH_2Br + NaHSO_4 + H_2O$$

Mol Wt = 60   103   98   Mol Wt 123   120   18

Thus 1 mole of reactant gives one mole of product

Hence

$$\text{Theoretical yield} = \text{Stoichiometric ratio} \times \left[\frac{\text{Molecular weight of the desired product}}{\text{Molecular weight of limiting reagent}}\right] \times \text{Weight of limiting reagent}$$

$$= \frac{1}{1} \times \left[\frac{123}{60}\right] \times 0.6$$

$$= 1.23 \text{ gms}$$

But actually yield of the above reaction is found to be 0.99 gms

$$\text{Hence percentage yield} = \frac{0.99}{1.23} \times 100$$

$$= 80.49\ \%$$

Atom economy can be calculated by using following formula,

$$\%\ \text{Atom economy} = \frac{\text{Molecular weight of product}}{\text{Total molecular weight of reactants}} \times 100$$

$\therefore$ In above reaction, % atom economy can be calculated as,

$$\%\ \text{Atom economy} = \frac{\text{Molecular weight of n-propyl bromide}}{\text{Molecular weight of (n-propanol + NaBr)}} \times 100$$

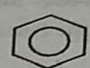
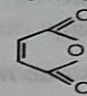
$$= \frac{123}{60 + 103} \times 100$$

$$= \frac{123}{163} \times 100$$

$$= 75.5\%$$

Other examples for understanding the efficiency of reaction is given here.

I)

I)  + $4.5\ O_2$ $\xrightarrow{V_2O_5}$ $[C_4H_2O_3]$  + $2CO_2$ + $2H_2O$

Benzene

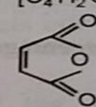
Mol.wt. 78 $\quad 4.5 \times 32 = 144 \quad\quad 98$

$$\%\ \text{Atom economy} = \frac{98}{78 + 144} \times 100$$

$$= \frac{98}{222} \times 100$$

$$\boxed{\therefore \%\ \text{Atom economy} = 44.1\%}$$

II)

C_4H_8 + $3O_2$ $\longrightarrow$ $[C_4H_2O_3]$  + $3H_2O$

Butene

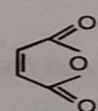
Mol. Wt. = 56 $\quad 3 \times 32 = 96 \quad\quad 98$

$$\%\ \text{Atom economy} = \frac{98}{56 + 96} \times 100$$

$$= \frac{98}{152} \times 100$$

$$\boxed{\therefore \%\ \text{Atom economy} = 64.5\ \%}$$

III)

C_4H_{10} + $2.5\ O_2$ $\longrightarrow$ $[C_4H_2O_3]$  + $4H_2O$

Butane

Mol. wt. = 58 $\quad 2.5 \times 32 = 80 \quad\quad 98$

$$\%\ \text{Atom economy} = \frac{98}{58 + 80} \times 100$$

$$= \frac{98}{138} \times 100$$

$$\boxed{\therefore \%\ \text{Atom economy} = 71.0\ \%}$$

(May 2011, 4 Marks)

Calculate the percent atom economy for the following reactions –

(i) $CH_3CH = CH_2 + H_2 \xrightarrow{Ni} CH_3CH_2CH_3$.

(ii) $C_6H_6 + CH_3Cl \xrightarrow{AlCl_3} C_6H_5CH_3 + HCl$.

3. Non-hazardous chemical synthesis

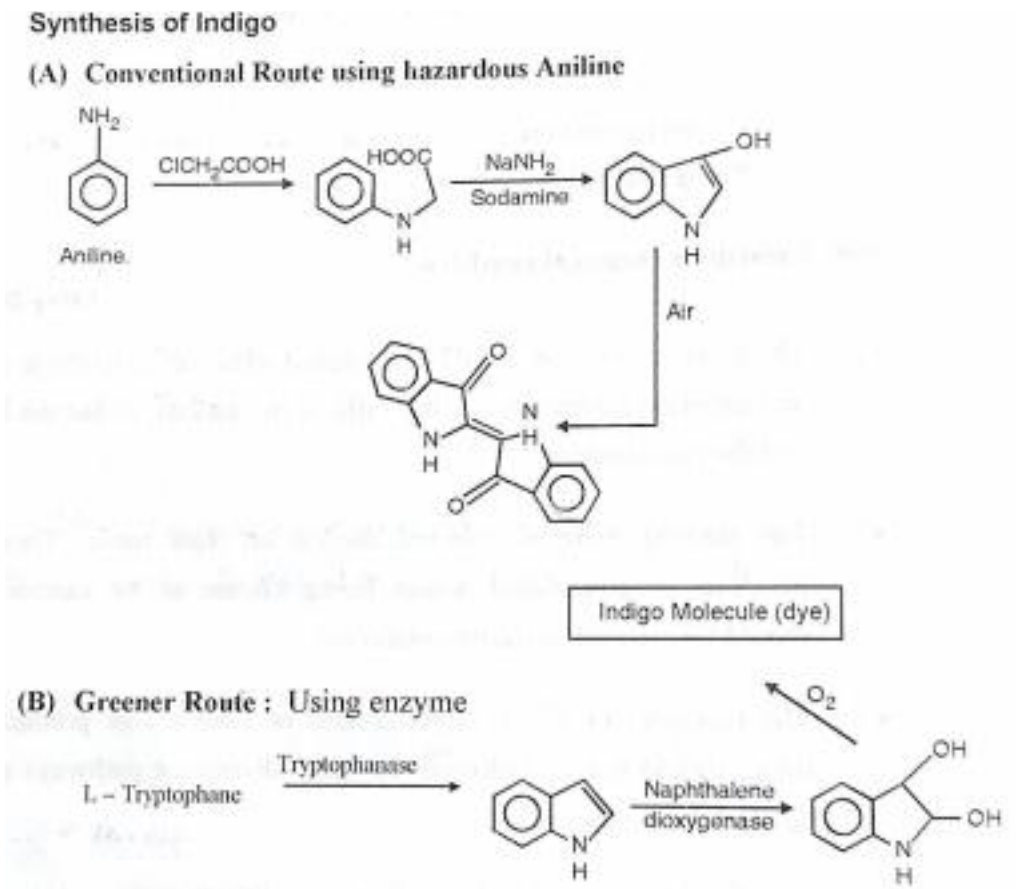
· The synthetic method should be designed to generate substances having little or no toxicity to human health and the environment.

· The starting material selected should be least toxic. E.g. pyridine or β- 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



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.

5. Auxiliary substances

- The use of auxiliary substances like solvents, separating reagents etc should be avoided in the synthesis.
- Avoid using carcinogenic solvents, separating reagents or other auxiliary chemicals, instead use safer chemicals.
- The solvents such as acetone, benzene, ether being highly inflammable should be avoided.

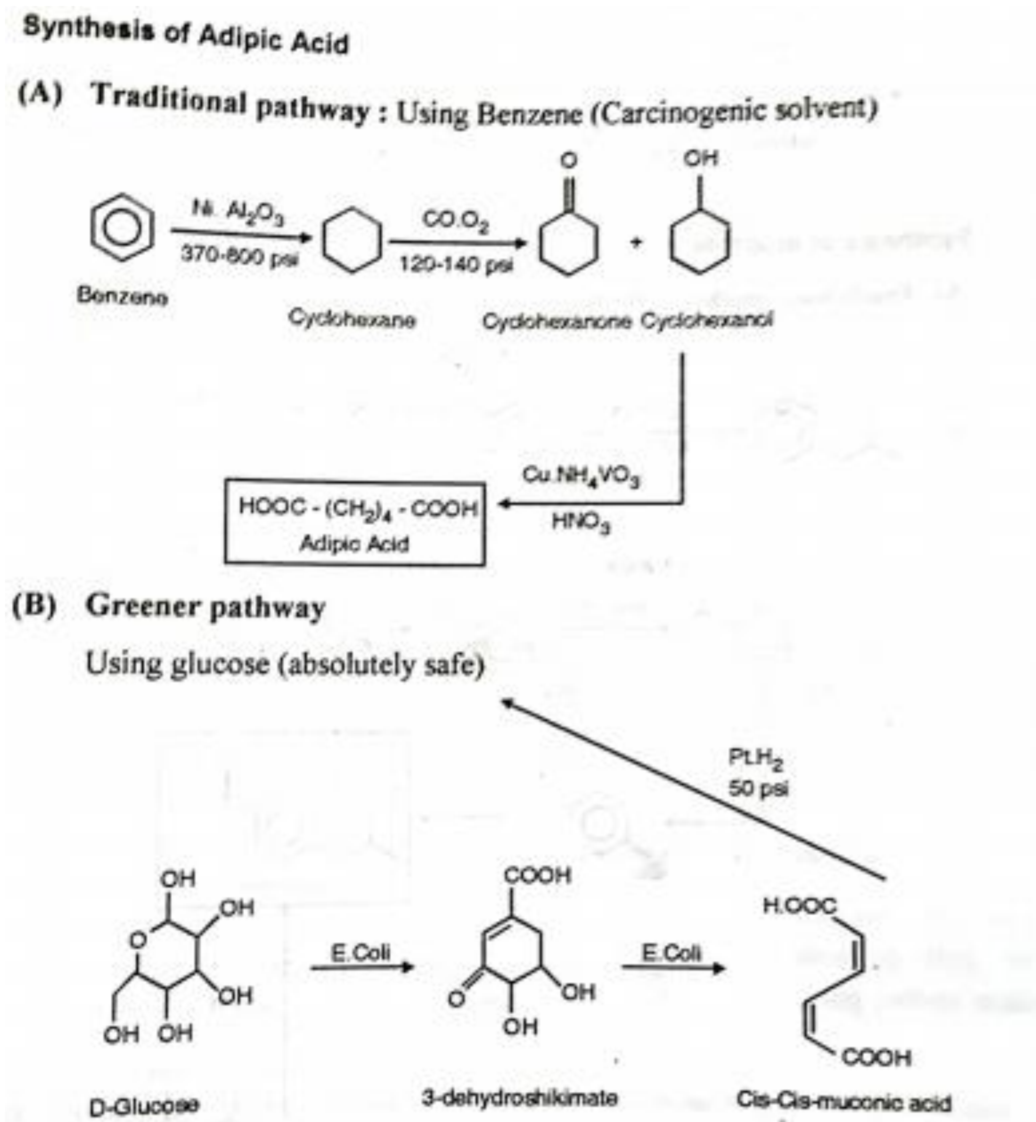
· Other chemicals such CCl_4, $CHCl_3$ causes ozone depletion hence should be avoided.
· If a solvent is necessary, water is a universal solvent which is safer to use. · For drycleaning of the fabrics, the toxic solvents like perchloroethylene was used, which is replaced during recent years by liquid CO_2.

6. Energy Efficiency

· The energy requirements of chemical processes should be minimized considering their environmental and economic impacts. The synthetic methods should be carried at ambient temperature and pressures.
· The main aim of green chemistry is to increase energy efficiency.
· This can be achieved by use of catalysts and by stopping use of fossil gaseous fuels which cause pollution.
· The energy efficiency of the process can be increased by proper heat transfer and minimal wastage of energy during the process.
· Wherever found suitable microwave radiations and ultra sound methods can be used.
· Use fermentation process for chemical synthesis where energy requirement is low and products are less harmful.
·

7. Use renewable feedstock

· The raw materials used should be renewable rather than depleting, wherever feasible economically and experimentally.
· Renewable feedstock are 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.



8. Avoid chemical derivatives

· During the synthesis unnecessary derivatisation such as protecting groups or any temporary modifications should be avoided if possible.

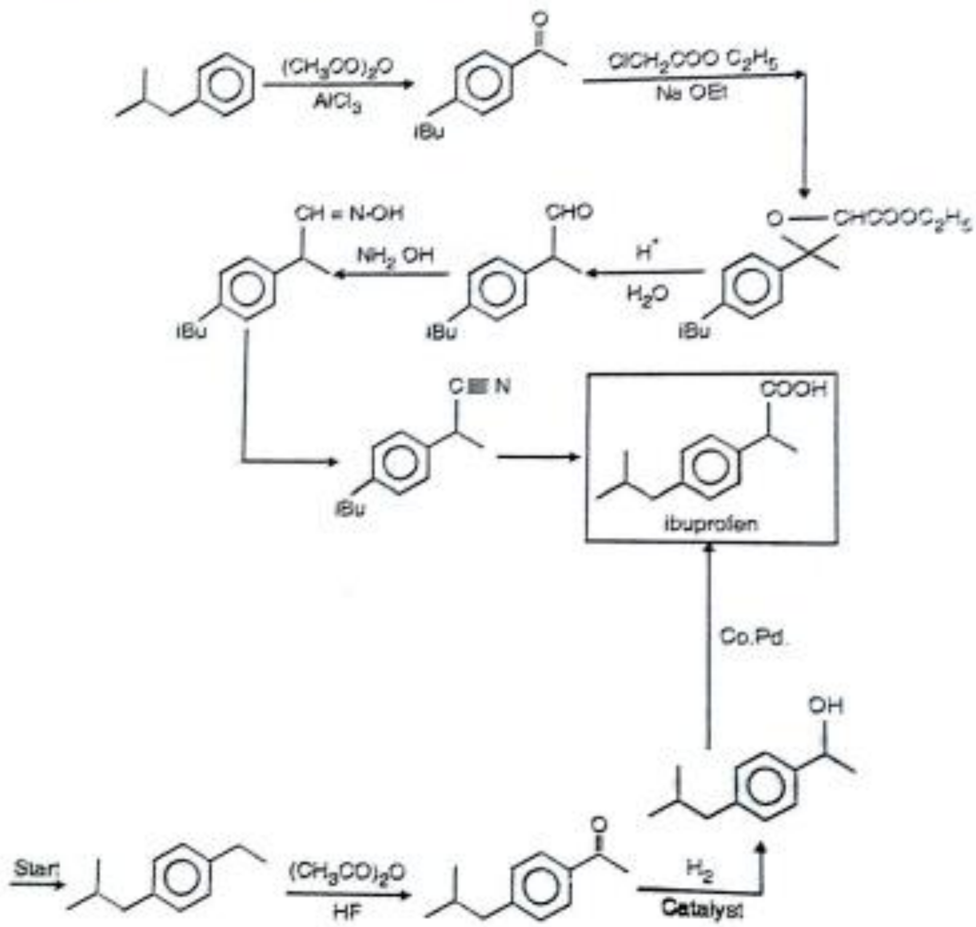
· The use of derivatives increases the steps of the process.

· 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%.

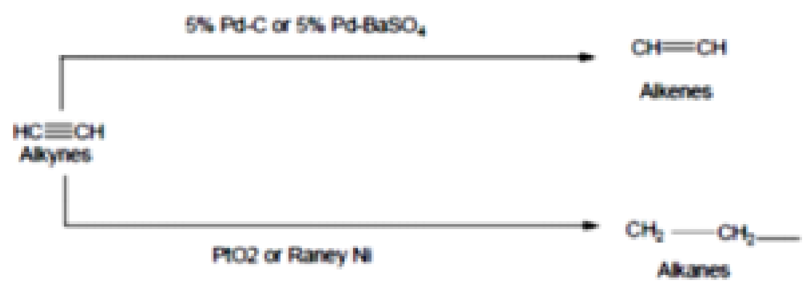
Synthesis of Ibuprofen

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



9. Use of catalysts

- The catalyst as we know facilitates transformation without being consumed or without being incorporated into the final product.
- 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.

· It is necessary to have accurate and reliable reasons, 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.