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,

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

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

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

$$= 75.5\%$$

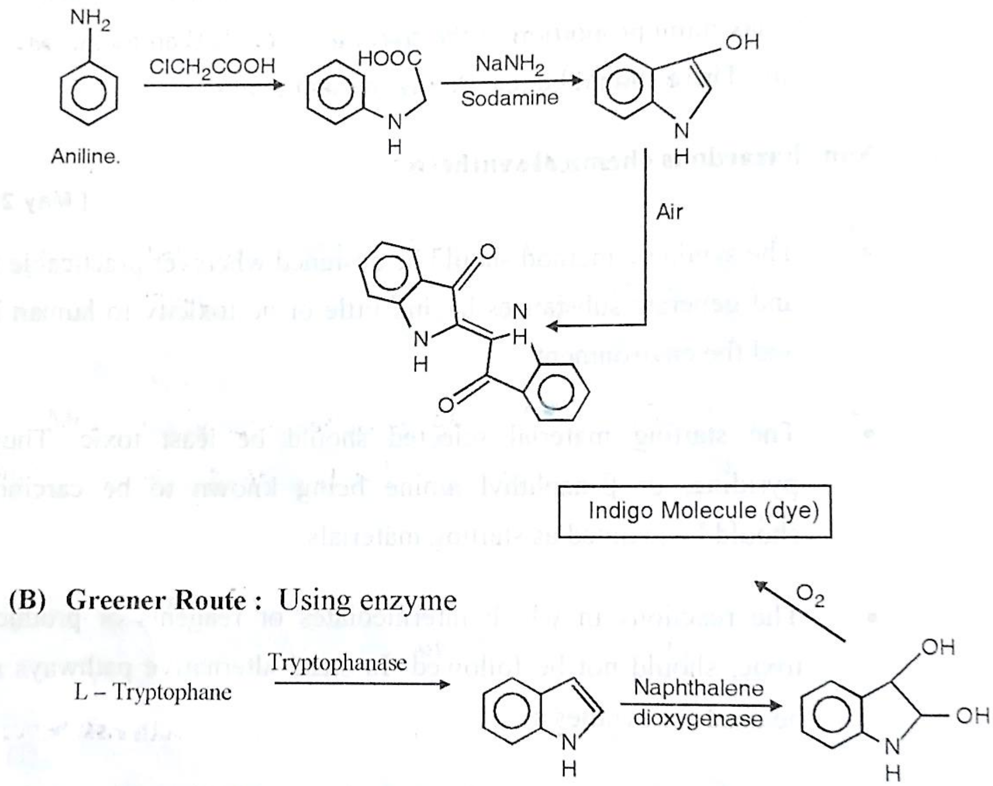
Other examples for understanding the efficiency of reaction is given here.

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

Synthesis of Indigo

(A) Conventional Route using hazardous Aniline



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

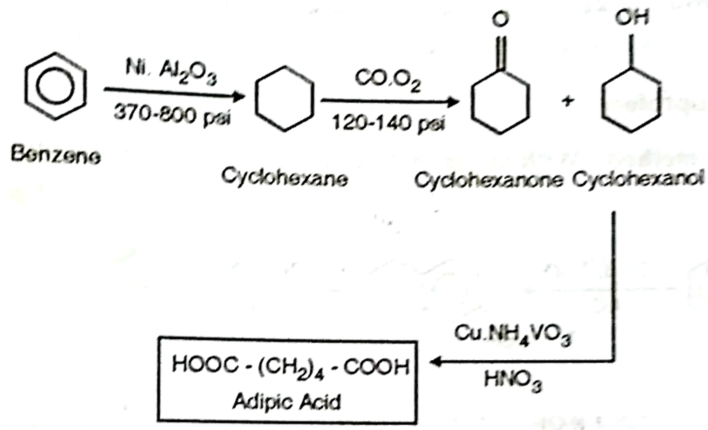
- The energy requirements of chemical processes should be minimized considering their environmental and economic impacts. The synthetic methods should be carried at ambient temperature and pressures.
- The main aim of green chemistry is to increase energy efficiency.
- This can be achieved by use of 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.

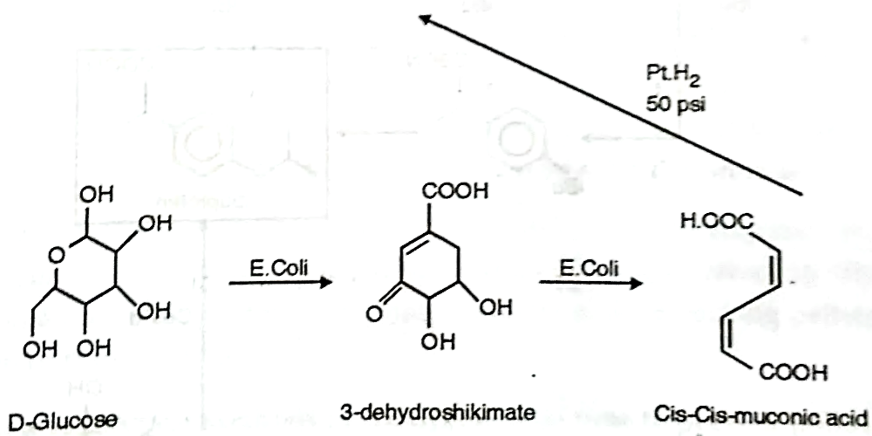
Synthesis of Adipic Acid

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



(B) Greener pathway

Using glucose (absolutely safe)

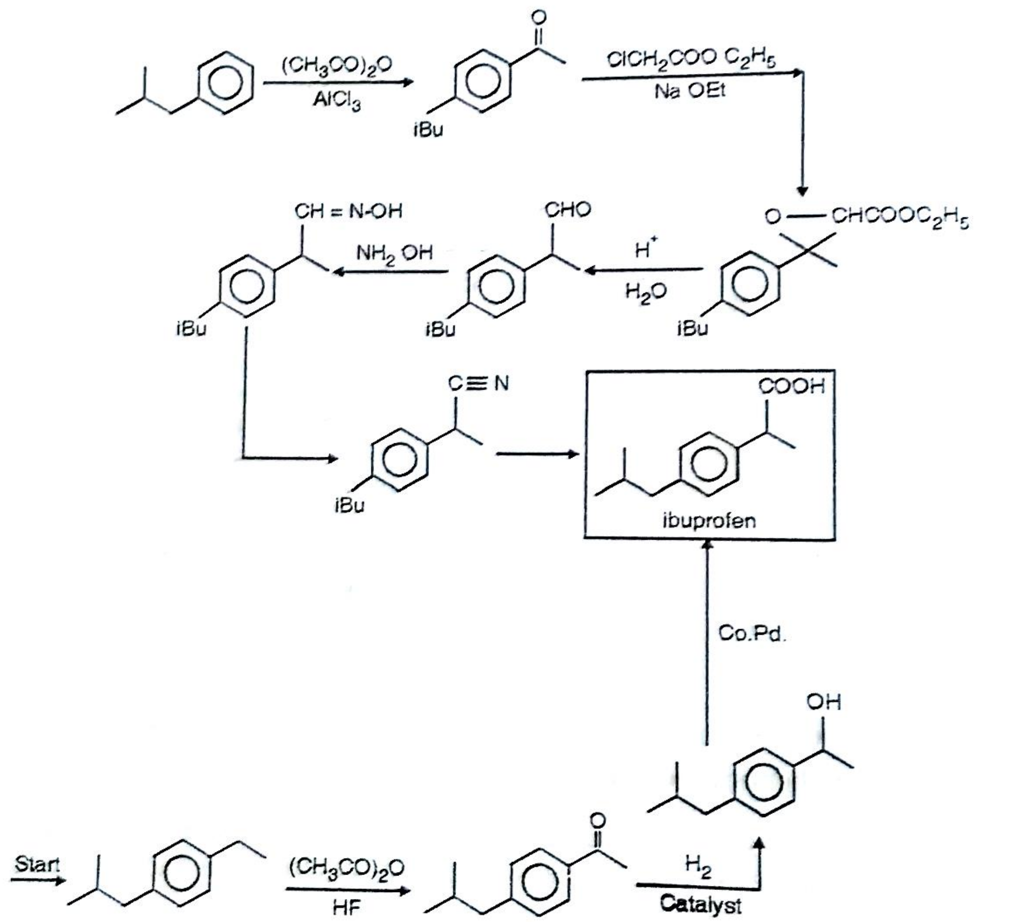


8. Avoid chemical derivatives

- 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%.

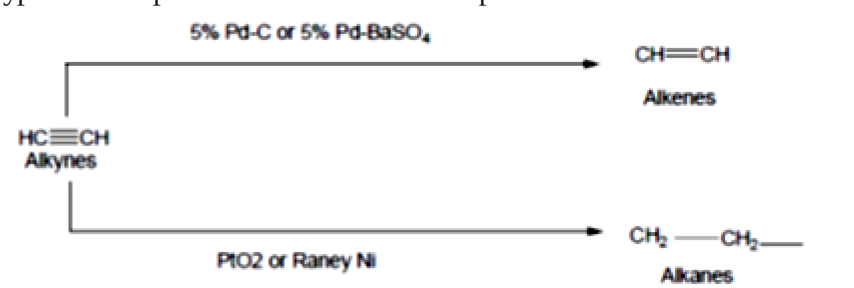
Synthesis of Ibuprofen

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



9. Use of catalysts

- 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.

Green Solvents

- Solvents are substances that are liquid during application and will dissolve other substances, which can be recovered unchanged on removal of solvents.
- Selection of solvent should be based not only on any hazards that it may possess but also on existing environmental problems that its use may cause.
- Solvents define a major part of the environmental performance of processes in chemical industry and also impact on cost, safety and health issues.
- The idea of 'green' solvent expresses the goal to minimize the environmental impact resulting from the use of solvents in chemical production.
- Various Green solvents: Water, Ethanol, DMSO, Supercritical H_2O, Supercritical CO_2, Ionic liquids, Ethyl Lactate, Polylactic acid, DMC (Dimethyl Carbonate)

Water as a solvent:

Water is environmentally benign solvent and abundantly available. It is polar in nature and apparently it is not useful as organic solvent for carrying out organic reactions. Due to the hydrophobic interactions with water, many organic chemicals try to associate themselves when reactions performed in water; this is especially the case for organic liquid interactions. For eg. Chlorination of anisole using cyclodextrin catalyst in water as solvent medium, some cycloaddition reactions in water, surfactant mediated organic reactions in water, bio-catalyzed reactions, enzyme catalyzed organic reactions in water.

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. Although supercritical fluid has liquid-like density, it exhibits gas-like diffusivity, surface tension and viscosity. Its gas-like viscosity results in high mass transfer. Its low surface tension and viscosity lead to greater penetration into porous solids. Because of its liquid-like density, a supercritical fluid's solvent strength is comparable to that of a liquid.

The critical temperatures and pressures of materials vary quite significantly. Generally, substances that are very polar at room temperature will have high critical temperatures since a large amount of energy is needed to overcome the polar attractive energy.

At critical conditions, the molecular attraction in a supercritical fluid is counterbalanced by the kinetic energy. In this region, the fluid density and density-dependent properties are very sensitive to pressure and temperature changes.

The solvent power of a supercritical fluid is approximately proportional to its density. Thus, solvent power can be modified by varying the temperature and pressure. Because their properties are a strong function of temperature and pressure, supercritical fluids are considered tunable solvents.

In contrast, conventional liquid solvents require relatively large pressure changes to affect the density.

Many reactions, extractions, separations and other operations in the chemical process industries (CPI) involve the use of organic solvents. In addition to handling and disposal issues, organic solvents can pose a number of environmental concerns, such as atmospheric and land toxicity. In many cases, conventional organic solvents are regulated as volatile organic compounds (VOCs). In addition, certain organic solvents are under restriction due to their ozone-layer-depletion potential.

Supercritical carbon dioxide is an attractive alternative in place of traditional organic solvents. CO_2 is not considered a VOC. Although CO_2 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 CO_2 properties and processing, and presents a number of current and potential applications.

Unlike many organic solvents, supercritical CO_2 is non-flammable. It is inert, non-toxic, has a relatively low cost and has moderate critical constants. Its solvation strength can be fine-tuned by adjusting the density of the fluid. CO_2 leaves a lower amount of residue in products compared to conventional solvents, and it is available in relatively pure form and in large quantities.

CO_2's critical temperature (T_c: 32.1°C) is near ambient, making it an attractive solvent for temperature-sensitive materials. CO_2's critical pressure is 73.8 bar (P_c: 1,070 psi), as shown in its phase diagram.

Examples of existing supercritical 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