

UNIT

8

Green Technology and Green Chemistry

"Green Chemistry represents the pillars that hold up our sustainable future. It is imperative to teach the value of green chemistry to tomorrow's chemists".

Daryle Busch

Objectives

- Introduction
- Green Technology
- Green Chemistry and its Basic Principles
- Concept of Atom Economy
- Tools of Green Chemistry
- Zero waste technology

8.1 INTRODUCTION

Chemical Manufacturing has brought revolution in the life on earth. It is the source of many useful products like drugs, antibiotics, plastics, fuels (like gasoline), agricultural chemicals (like pesticides and insecticides, fertilisers; synthetic fabrics (like nylon, rayon, polyesters) and many others. The ill effects of the chemical industries are also not less in magnitude. The recipient of the ill effects is not only man but environment also. The alarming increase in the level of pollution forced the governments all over the world to make laws to minimize it. This gave rise to the birth of **Green Technology** and **Green Chemistry** by the middle of 20th century.

Green chemistry is environment friendly chemical synthesis in which schemes are designed in such a way that environment pollution is minimized. It is based on this age old principle "**Prevention is better than cure**". In this field, attempts are made to prevent wastes during chemical synthesis so that later cleaning up the environment does not become a problem. Here the starting materials, solvents, catalysts etc. are so chosen that they have no or minimum toxic effects on the environment. For instance the use of Benzene, Toluene etc. are discouraged as solvents since they are carcinogenic in nature. If possible, the reactions are carried out in the aqueous phase. Thus, alternate methods of chemical synthesis developed in Green Chemistry should be applied to the maximum to minimize the ill effects of pollution.

8.2 GREEN TECHNOLOGY

Whenever the term "Green" is used, it refers to the environment friendly objects and "Technology" means the application of knowledge for practical purposes. Since Green Chemistry involves new methodologies hence Green Chemistry or Technology means the same in the broader sense. The concepts of Green Technology is described in details in Chapter 1 under the topic 'Introduction of the concept of Green Technology'.

8.3 GREEN CHEMISTRY AND ITS BASIC PRINCIPLES

As defined by Paul T. Anastas and J.C. Warner "Green chemistry or environmentally benign chemistry is the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances". This emerging field has gained importance not only in the areas of research and development but in the world of both academics and industry.

Basic Principles of Green Chemistry

Green Chemistry (defined in the previous section) basically aims at reducing the environmental pollution by involving various innovations in the chemical synthesis. Paul Anastas and John Warner in their publication (1998) titled, Green Chemistry: "Theory and Practice" have developed 12 principles (given in the box) to give guidelines for chemists for developing Green Chemistry.

The Twelve Basic Principles are Explained below:

8.3.1 Prevention of Waste

The by-products formed in a chemical reaction constitute the waste. The unreacted starting materials (which may or may not be hazardous) also forms part of the waste. Chemical synthesis should be designed in such a way that the waste products are minimized. This is because sometimes the cleaning and disposal of waste becomes so expensive that it adds tremendously to the overall production cost. By prevention of waste generation, the associated problems such as hazards associated with waste storage, transportation and treatment is minimized.

8.3.2 Atom Economy

Chemical Synthesis should be designed to maximize the incorporation of the starting materials and reagents in the final products. This concept developed by B.M. Trost is described in detail in a separate section of 'Concept of Atom Economy'.

8.3.3 Minimization/Prevention of Hazardous Chemical Synthesis

Wherever practicable, synthesis should be designed to use and generate substances imposing minimum or no toxicity to human health and environment. For instance if for a particular reaction, a range of reagents

are available, then the reagents are such chosen that they not only pose less risk but also generate only benign by products. For example, synthesis of adipic acid explained in section 8.5.1)

Twelve Principles of Green Chemistry¹

1. It is better to prevent waste than to treat or clean up waste after it is formed.
2. Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. Chemical products should be designed to preserve efficiency of function while reducing toxicity.
5. The use of auxiliary substances (e.g., solvents, separation agents) should be made unnecessary wherever possible and innocuous when used.
6. 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. A raw material or feedstock should be renewable rather than depleting wherever technically and economically practicable.
8. Unnecessary derivitization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible.
9. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. Chemical products should be designed so that at the end of their function they do not persist in the environment and breakdown into innocuous degradation products.
11. Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
12. 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.

¹Anastas and Warner, *Green Chemistry*, 1998.

8.3.4 Design Safer Chemicals

The reaction products should be designed in such a way that they should be fully effective without having any toxic effects. For example, 'thalidomide' a drug used for lessening the effects of vomiting during pregnancy by expecting mothers resulted in the birth defects of the children born to these mothers (having missing or deformed limbs). The medicine has now been banned totally. With the advancing technologies, now it has become possible to manipulate the chemical structure to produce safer chemicals. Using this principle, new products can be designed which are not only safer but also highly effective for target applications.

8.3.5 Use of Safer Solvents and Auxiliaries

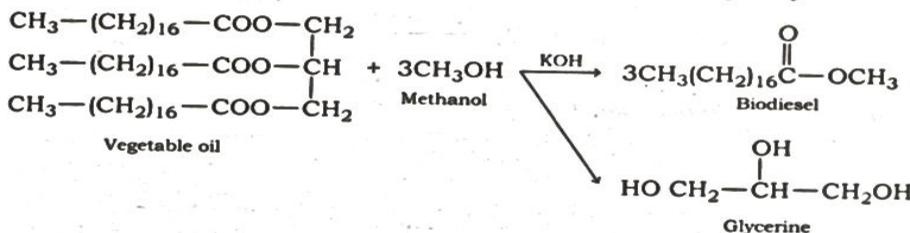
The use of auxiliary substance (e.g. solvents, separating agents etc.) should be avoided. If these chemicals are necessary safer chemicals should be used. Many solvents like carbon tetrachloride, chloroform, perchloroethylene etc. which are used in large quantities in industry are not only harmful to human health and environment but can also create other dangers like explosion or fire hazards. Sometimes it is possible to substitute safer solvents like water or liquid carbondioxide. For example in the new dry-cleaning processes for clothing, liquid carbondioxide instead of perchloroethylene is used for dissolving grease. Efforts should also be made to reduce the volume of the solvent. A large number of synthesis, also involves purification hence, wherever possible the use of auxiliary supports like chromatographic supports etc. for such purifications be avoided.

8.3.6 Design for Increase in Energy Efficiency

The chemical reactions should be carried at ambient temperatures and pressure whenever possible, to minimize the environmental economic impacts. In the exothermic reactions, sometimes extensive cooling is required, which adds to the overall cost. If the final product obtained in any reaction is impure again energy is required for purification by distillation, recrystallization, ultrapurification etc. Thus the process should be designed such that there is no need for separation or purification. Energy to a reaction can also be supplied by photochemical means, microwave and incineration.

8.3.7 Selection of Renewable Feedstocks as Starting Material

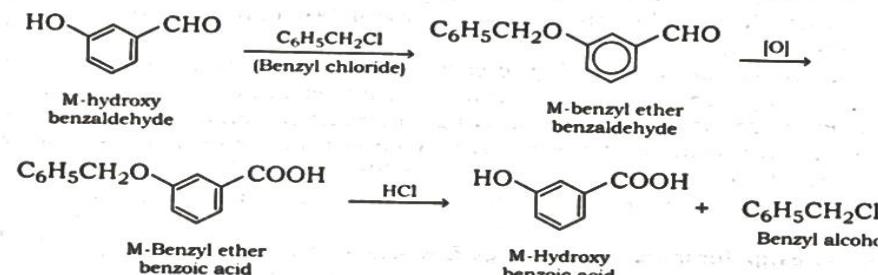
Raw materials and feedstocks that are renewable should be preferred over that of depleting ones. Biodiesel which is Methyl or Ethyl ester of fatty acid is made from virgin or used vegetable oils (both edible and non-edible) and animal fats. It can be either used in its pure form as a fuel or it can be blended at any level with petroleum diesel to create a biodiesel blend. It is also considered as a clean fuel because it has no sulfur, no aromatics and has 10% built in oxygen, which helps it to burn completely.



8.3.8 Avoid of Chemical Derivatives

In a chemical reaction, the blocking groups, protection/deprotection or any temporary modification of physical/chemical process should be avoided (if possible). Derivates use additional reagents and generate waste. For

example in the synthesis of M-hydroxy benzoic acid from M-hydroxy benzaldehyde by the conventional method, Benzyl chloride (a known hazard) is used as the protecting group for "OH" group. The waste generated after the deprotection should be handled properly. This reaction is also less atom economical since a lot of waste is generated.

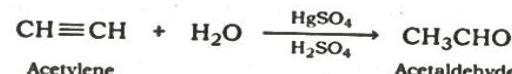


8.3.9 Use of Catalysts and Non-Stoichiometric Reagents

The waste is minimized if the catalytic reagents are used since the catalytic reactions are highly specific and are needed in very small amounts. The reactions are also energy efficient (take place at lower temperature). The stoichiometric reagents are used in excess and work only once and hence should be avoided (if possible).

Few advantages of catalytic reactions are as follows:

- Reaction is feasible with a catalyst which is otherwise not possible under ordinary conditions.



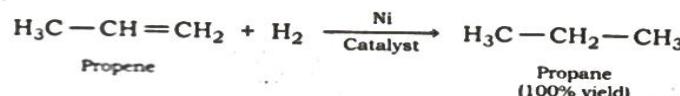
- Selectivity is increased*

Hydrogenation of propynes to propenes



- Better yield is obtained*

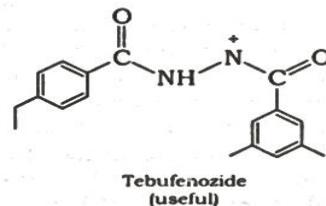
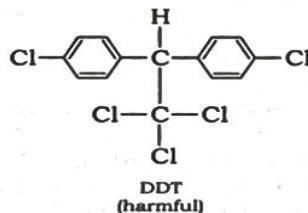
Reduction of olefins in the presence of Nickel Catalyst gives excellent yield.



8.3.10 Products Designed should be Biodegradable After Use

The chemical products should be such designed so that they breakdown into safer substance after use and not accumulate in the environment.

Pesticides and insecticides like aldrin, dieldrin and DDT remain in the environment for a longer period as they are non-biodegradable and hence have a detrimental effect on human health and environment. Whereas, some of the diacylhydrazines (Tebufenozide, Halofenozone etc.) developed by Rohm and Hass company are useful insecticides.



8.3.11 Strengthening of Analytical Techniques for Pollution Prevention

The in-process real-time monitoring and control should be designed during synthesis (that is monitoring the progress of the reaction to know whether the reaction is complete or incomplete) and that the formation of by-products is minimized and detected. For instance placement of accurate sensors to monitor the generation of hazardous by-products is very important so that it can be controlled. Also, for the minimum usage of chemicals in a reaction, the unreacted reagents (chemicals) should be recycled.

8.3.12 Design of Manufacturing Plants to Minimize the Potential for Accidents

The chemicals and their forms (solid, liquid, or gas) should be chosen to minimize the potential for not only the chemical accidents but also explosions, fires and release of toxic substances to the atmosphere. A number of accidents have been found to occur in industrial units for example the infamous Bhopal Gas Tragedy (December 1984)*, resulted not only in loss of thousands of human lives but also left many people in the next generation disabled.

8.3.13 Case Study

CASE STUDY

The Bhopal Gas Leak Disaster

On December 3, 1984, disaster struck Bhopal, the capital city of the state of Madhya Pradesh located in Central India.

The Union Carbide Factory involved in the manufacture of carbamate type of pesticide used Methyl iso-cyanate (MIC) as a intermediate product. Due to the alleged functional failure of "vent scrubber" outlet, 30 tonnes of a potentially toxic, methylisocyanate

gas escaped from the underground storage tanks of the pesticide manufacturing plant. As a consequence there were nearly 2500 deaths and severe disability of more than 1,00,000 survivors.

Inhalation of MIC causes vomiting, violent coughing, suffocation, removal of oxygen from the lungs, pulmonary disorders, cardiac failure, and death due to choking. Burning sensation in the eyes caused eye infections (conjunctivitis) and eventual blindness in the survivors. The survivors were disabled not merely for a lifetime but even beyond, because serious genetic effects would pass on the disabilities to the future generations as well.

It is indeed ironical that the disaster occurred towards the end of the Golden Jubilee celebrations of Union Carbide Limited and the simple precaution of breathing through a wet towel could have saved so many lives.

This worst ever disaster in Bhopal is an example of an industrial pollution accident caused due to the failure in handling a toxic material in large-scale chemical processing.

SOME OF THE FINEST EXAMPLES OF GREEN CHEMISTRY/TECHNOLOGY'S ACHIEVEMENTS ARE AS FOLLOWS

1. Barry Trost's concept of Atom Economy for expressing the efficiency of a reaction (discussed in section 8.4)
2. New Synthesis of Ibuprofen.
3. Use of waste carbon dioxide as a blowing agent instead of CFC's for foam polystyrene synthesis.
4. Development of CO₂ as a solvent for dry cleaning.
5. Development of oxidant activators for hydrogen peroxide in the manufacture of paper.
6. Development of new insecticides.

8.4 CONCEPT OF ATOM ECONOMY

The concept of atom economy was developed by Barry Trost in 1991 which is a method of expressing the efficiency of a particular reaction in which reactant atoms are incorporated into the desired final product. The main objective of this concept is to develop a new methodology or design a new synthesis in which most of the reactant atoms become incorporated into the final desired product thus reducing the waste or the by products.

The percentage yield of any reaction is calculated by:

$$\% \text{ yield} = \frac{\text{Actual yield of the product}}{\text{Theoretical yield of the product}} \times 100$$

A reaction may have a percentage in yield of 100% but may not be considered as green synthesis if large amounts of by-products are obtained. Typical examples are Grignard and Wittig reactions which give a yield of 100% along with large amount of by-products. For a reaction to be considered

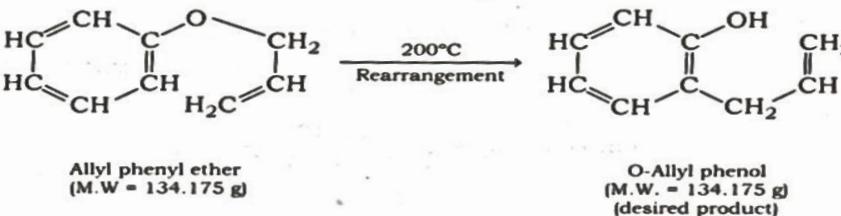
as green synthesis, the percentage of atom economy is calculated by the following equation.

$$\% \text{ atom economy} = \frac{\text{Mass of atom in desired products}}{\text{Mass of atoms in reactants}} \times 100$$

Let us consider some common reactions and find which has more percentage of atom economy.

8.4.1 Rearrangement Reactions

Allyl phenyl ether gives O-Allyl phenol by heating at 200°C.



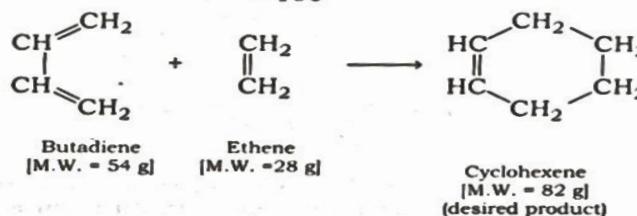
$$\begin{aligned} \% \text{ Atom economy} &= \frac{134.175}{134.175} \times 100 \\ &= 100. \end{aligned}$$

This is a 100% atom economical reaction.

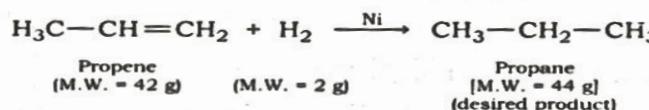
8.4.2 Addition Reactions

(a) Cycloaddition reactions of Butadiene to Cyclohexene

$$\begin{aligned} \% \text{ Atom economy} &= \frac{82}{82} \times 100 \\ &= 100 \end{aligned}$$



(b) Catalytic addition reaction

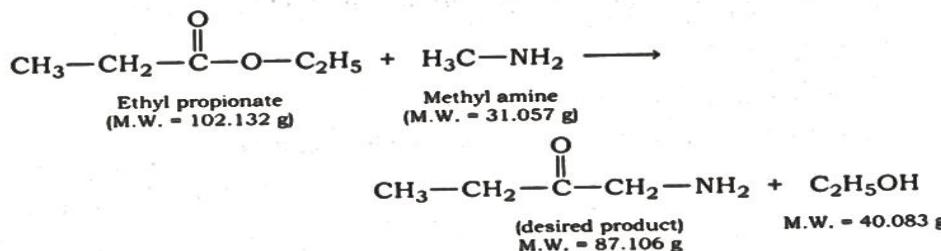


$$\% \text{ Atom economy} = \frac{44}{44} \times 100 = 100$$

Since Ni is used as a catalyst, it can be recovered fully after the reaction. Thus both type of addition reactions give an atom economy of 100%.

8.4.3 Substitution Reaction

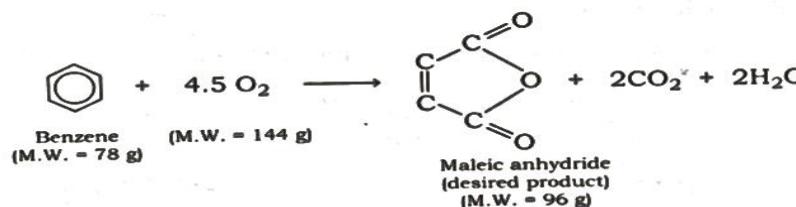
Let us consider a substitution reaction of Ethyl propionate with Methyl amine



$$\begin{aligned}
 \% \text{ Atom economy} &= \frac{87.106}{102.132 + 31.057} \times 100 \\
 &= \frac{87.106}{133.189} \times 100 \\
 &= 65.40
 \end{aligned}$$

8.4.4 Oxidation Reaction

Conversion of Benzene to maleic anhydride

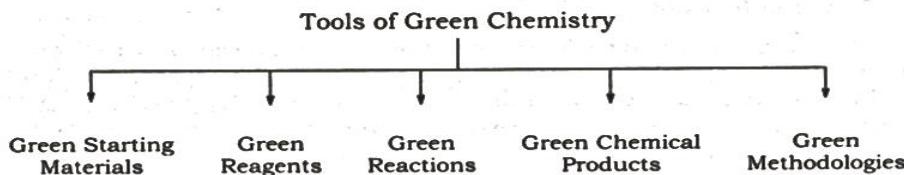


$$\begin{aligned}
 \% \text{ Atom economy} &= \frac{96}{78 + 144} \times 100 \\
 &= 43.
 \end{aligned}$$

A very important example of atom economy is the synthesis of Ibuprofen. The conventional method used six steps with an atom economy of just 40.1%. In the 1990s the HCC developed a new three stage process with an atom economy of 77.4%, now a commercial method. This reaction won the Presidential Green Chemistry Challenge Award and in 1996 in U.S.A.

8.5 TOOLS OF GREEN CHEMISTRY

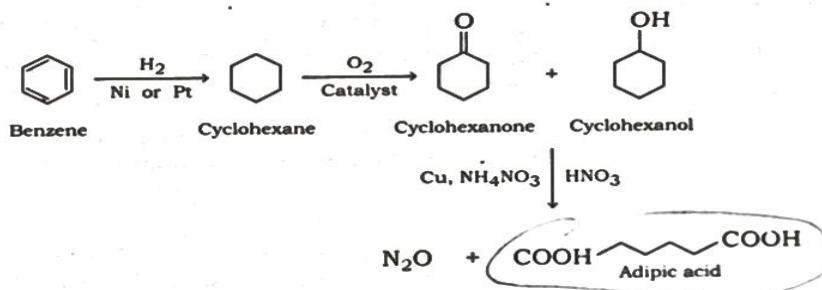
The objectives of green chemistry is to reduce the toxicity in the environment. In order to achieve this, the new areas have to be found where improvements can be made. These areas serve as 'tools' for Green Chemistry. The identified areas (i.e. tools of Green Chemistry) are as follows:



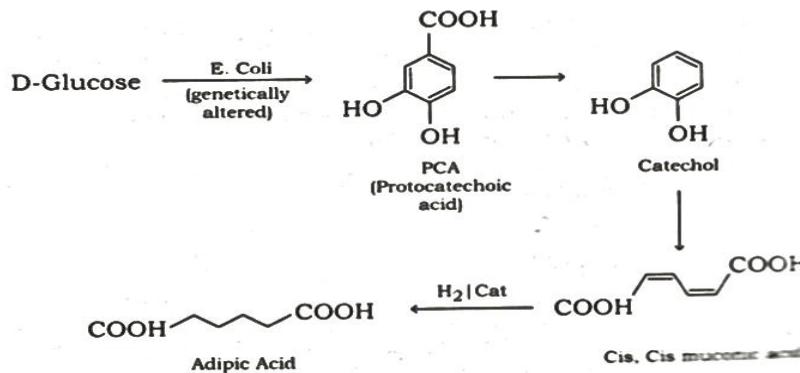
8.5.1 Green Starting Materials

The starting material is said to be green when it is non toxic, preferably renewable and does not degrade the quality of the environment*. Adipic acid which is an important chemical used in the synthesis of nylon, plasticisers and lubricants is conventionally prepared from benzene which is carcinogenic. An environmentally benign synthesis of Adipic acid is from D-glucose (a nontoxic and renewable source) and the solvent used is water instead of organic solvents.

Conventional Synthesis of Adipic Acid



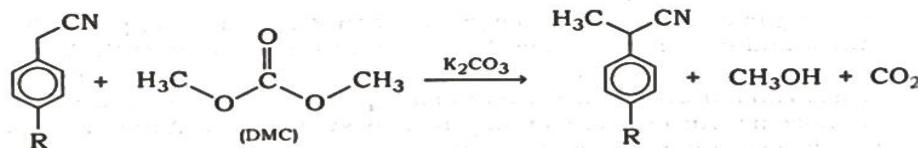
Green Synthesis of Adipic Acid from D-Glucose



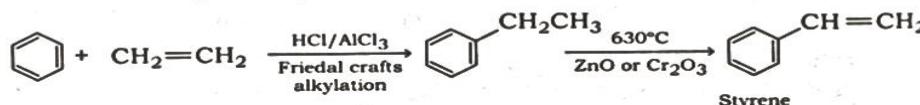
8.5.2 Green Reagent

The reagents are said to be green when they are easily available (preferably from natural renewable sources), non-toxic, give maximum atom economy and the waste products formed (if any) are non-toxic and biodegradable.

Conventionally methylation reactions were carried by using Methyl halides or Methyl Sulphate which are very toxic, hence the synthesis is undesirable. Tundo developed a method to methylate active methylene compounds using Dimethyl Carbonate (DMC) without producing any inorganic salts.



In the conventional method Styrene (the Monomer used for the manufacture of polystyrene) used in large quantities every year is made from Benzene (carcinogenic) by Friedal-Crafts alkylation.



In the green synthesis which is developed by Chapman, a single step is used to convert mixed Xylenes to Styrene. (better atom economy)

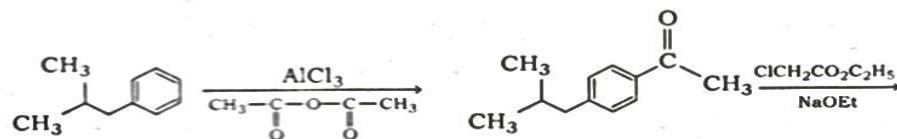
8.5.3 GREEN REACTIONS

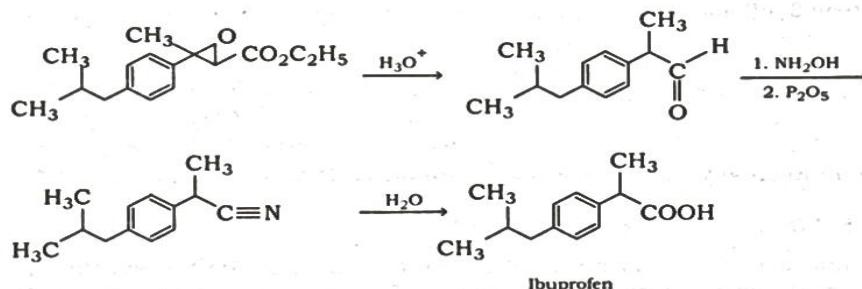
'Green Reactions' is based on the "Concept of Atom Economy". The concept of Atom Economy is described in details in the earlier section. Few examples of Green Reaction are given below:

8.5.3.1 Synthesis of Ibuprofen

The conventional synthesis of Ibuprofen was developed by Boots Company of England in 1960. This is a six step process with an atom economy of 40.1% whereas the green Synthesis developed by BHC company is a three step process with atom economy of 77.4%.

Conventional Synthesis of Ibuprofen

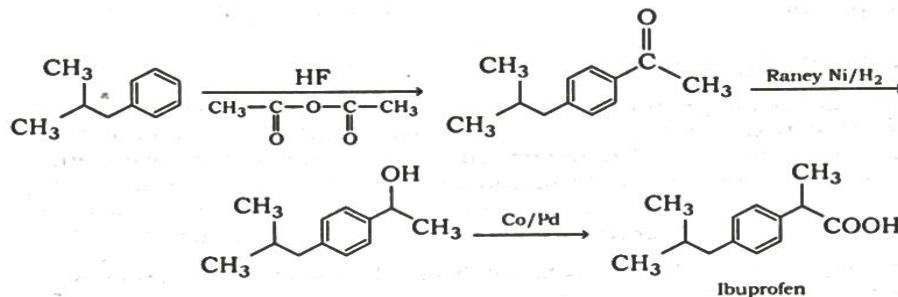




Atom economy by this process is only 40.1%.

Green Synthesis

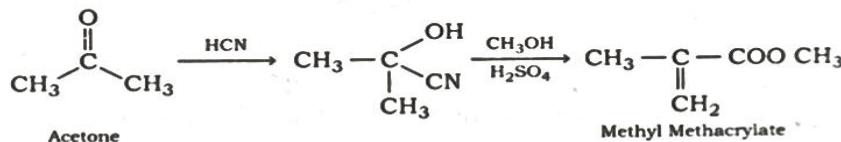
Atom Economy by this process is 77.4%.



8.5.3.2 Synthesis of Methyl Methacrylate

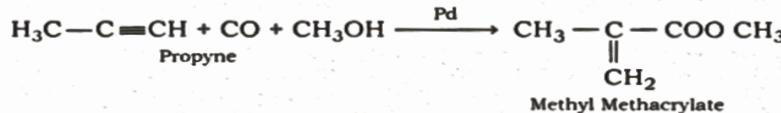
Methyl methacrylate is used in large quantities for the manufacture of polymers. The conventional method uses HCN (highly poisonous) with an atom economy of only 47% whereas the green synthesis developed by Shell corporation uses Pd catalyst with an atom economy of 100%.

Conventional Method



Atom economy is only 47%.

Green Synthesis



Atom Economy by this method is 100%.

8.5.3.3 Synthesis of Adipic Acid

Adipic acid which is required in large quantities for the synthesis of polymers was conventionally prepared from Benzene (carcinogenic). The by product formed by this method is N₂O which contributes to greenhouse effect as well as results in the destruction of Ozone layer. The green synthesis of Adipic acid is environmentally benign and is synthesized from D-Glucose using biocatalyst. This was developed by J.W. Frost and K.M. Draths (Reaction is described in details in the section of green starting material).

8.5.4 Green Methodologies

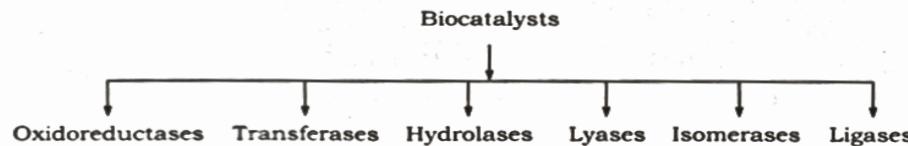
New methodologies are designed as an alternative to the existing methods, so that toxic starting materials, reagents, catalysts, by products or intermediates are either minimized or totally eliminated. Few methods for the environmentally benign synthesis are:

8.5.4.1 Use of Biocatalysts

Enzymes are also known as biocatalysts. The use of biocatalysts have the following advantages.

- The reactions are performed at ambient temperatures and pressures.
- Most of the reactions are carried out in aqueous medium.
- The conversions are normally single step conversions.
- Atom economy is maximized.
- Conversion are stereospecific.

The Biocatalysts are classified into six major classes.



1. **Oxidoreductases:** These enzyme catalyze oxidation reduction reaction.
2. **Transferases:** They catalyze the transfer of various functional groups.
3. **Hydrolases:** These enzymes catalyse hydrolytic reactions.

4. **Lyases:** Carry out the addition and eliminations of small molecules on sp^3 hybridized carbon atom.
5. **Isomerase:** Responsible for the isomerisation reactions.
6. **Ligases:** They catalyse the formation or cleavage of sp^3 hybridized carbon.

8.5.4.2 Use of Aqueous Medium as Solvents

The advantage of using water as a solvent instead of organic solvents is it is cheaply available, safe (non-inflammable), non-carcinogenic and simple in operation. It has the highest value of specific heat. The few reaction carried out in as medium are.

1. **Diels Alder reaction:** Heterocyclic compounds with Nitrogen or Oxygen containing dienophiles are synthesised using this reaction.
2. **Claisen Rearrangement:** The thermal rearrangement of Allyl vinyl ether to give aldehyde in pure water.
3. **Michael Reactions:** 2-Methyl-cyclopentane-1, 3-dione when reacted with vinyl ketone in water gave a 5-6 fused ring system without using a basic catalyst (as in conventional method).
4. **Aldol Condensation:** Vinyl ketones can be obtained by the reaction of 2-alkyl-1, 3, diketones with aqueous formaldehyde using 6 – 10 M aqueous potassium carbonate as base.

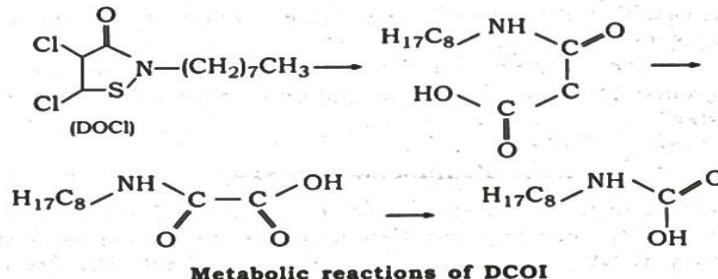
Attempts are also being made to carry out the reactions in the solid state. Some of the solid phase reactions which are already carried out successfully are halogenation, hydrohalogenation (addition of HBr), Michael Addition, Dehydration of Alcohols to Alkenes, Aldol condensation, Grignard reactions and may others.

8.5.5 Green Chemical Products

The green products are those which serve the same function without themselves being toxic or breaking down into toxic subs. For examples many insecticides use organochlorines, organophosphates, or carbonates. Organochlorine compounds (like aldrin, dieldrin) are readily incorporated into the food chain. Where as organophosphates and carbonates although are less persistent in the environment (DDT), but they readily decompose in the environment and tend to be toxic to human beings and other non-target organism. A new class of insecticides (diacetyl hydrazine) developed by Rohm and Hass is non-toxic.

The conventional antifouling agent used on boats is Tributyltin (TBT) compounds. Antifouling agents are used on boat hulls to reduce the build up marine organisms, such as algae, plants, diatoms etc). TBT compounds are persistent in the environment and result in bioaccumulation in various microorganism.

Rohm and Hass developed DCOI {4, 5 dichloro-2-n-octyl-4-iso thiazole-3-one} as antifouling agent which is less persistent in marine as well as the product of metabolism are also non toxic.



8.6 ZERO WASTE TECHNOLOGY

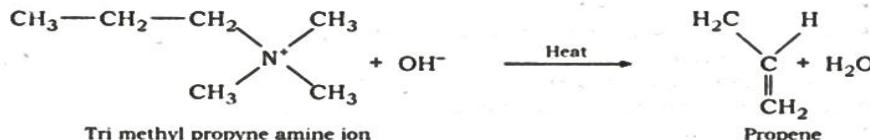
Zero waste technology is the essence of green chemistry. In this concept methodlogives are devised for the synthesis in such a manner that there are no by products formed during a reaction, or if any waste by products are formed they can be used as raw materials or starting materials of other units. **Thus zero waste is the recycling of all materials back into the nature or the market place is a manner that protects human health and environment.**

This can be explained by the following examples.

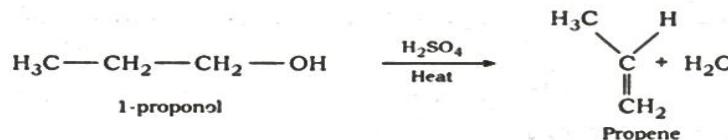
1. The glass milk bottle which is used for distributing milk to the consumers is made of silica. In the normal waste methods, the bottles can be disposed to a landfill by the municipality. But in the zero waste method, the bottle can be recycled, reduced to its constituent part and formed into a new milk bottle or any other glass product.
2. Carbon dioxide which is formed is a by product from ammonia manufacturing and natural gas units is used as a blowing agent for making extruded polystyrene form sheet. Earlier chlorofluoro carbons and hydrofluoric carbons were used instead of liquid and supercritical carbon dioxide. When CFC's are released into the atmosphere, they rise though the troposphere into the statoscope where they are decomposed by UV radiations. The photo chemical decomposition of CFC's results in the formation of atomic chlorine which results in the depletion of the ozone layers from the atmosphere which is responsible for causing skin cancer and cataract among many other diseases. The use of supercritical CO_2 as a blowing agent in making polystyrene foam sheet (green Synthesis) has the following advantages.
 - (i) From the ammonia manufacturing units, the by product formed i.e. CO_2 is removed hence it does not contribute to green house effect.
 - (ii) It replaces CFCs (which results in ozone depiction) thus reducing the adverse impact on the environment.
 - (iii) Apart from other advantages, CO_2 is economical, easy to handle, and neither forms smog or depletes the ozone layer.

EXERCISES

1. What is Green Technology?
2. What are the basic principles of green Chemistry?
3. Which principle of green chemistry refers to 'Atom Economy'?
4. Benzene is oxidized to maleic anhydride. Calculate the 'Atom Economy' for this reaction.
5. It is said "Prevention is better than cure" Justify this statement in context to 'Green Chemistry'.
6. What are the various tools of Green Chemistry?
7. Write Short notes on:
 - (a) Zero waste Technology.
 - (b) Green Reagents.
 - (c) Atom Economy.
 - (d) Green Starting Materials.
8. Chemists sometimes refer to "by-products" rather than "waste". List one advantage and one disadvantage of using this term.
9. Consider the following two reactions:



Reaction 1



Reaction 2

- Which of the two reactions have a better Atom Economy?
10. What do you understand by the term 'sustainability'?
 11. Illustrate with examples 'Green Reactions'.
 12. How do the green starting materials help to improve the environmental conditions.
 13. What is "Waste" product? How does the law of Conservation of Matter justify this word.
 14. How is the new synthesis of Ibuprofen better than the conventional synthesis.
 15. Why unnecessary derivitization in a reaction should be avoided?

