GREEN CHEMISTRY

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Green Chemistry

DEFINITION

- ***Green Chemistry is the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products.***

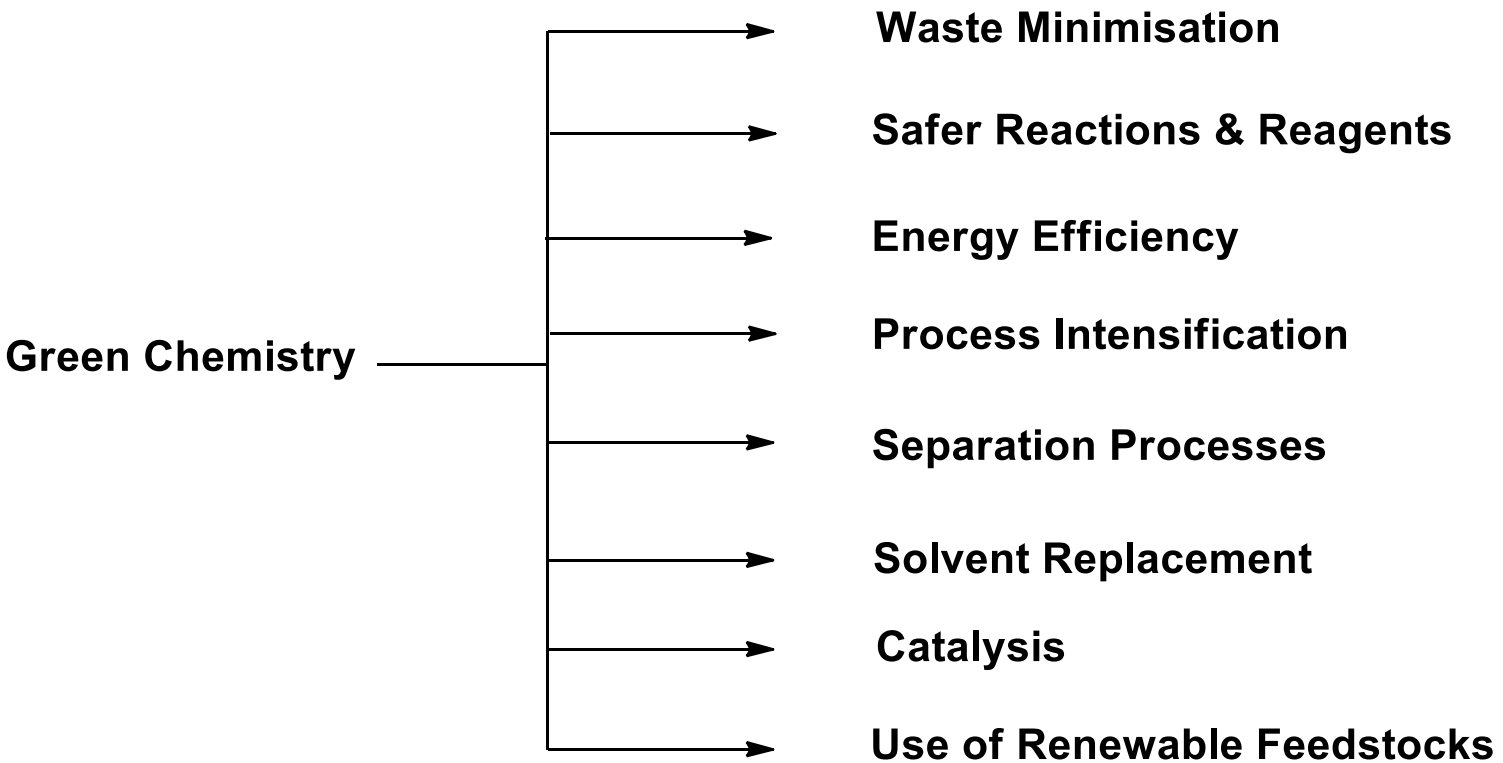
Green Chemistry Is About

- **Waste Minimization at Source**
- **Use of Catalysts in place of Reagents**
- **Using Non-Toxic Reagents**
- **Use of Renewable Resources**
- **Improved Atom Efficiency**
- **Use of Solvent Free or Recyclable Environmentally Benign Solvent systems**

Green Chemistry Is About

- **Waste**
- **Materials**
- **Hazard**
- **Environmental Impact**
- **Cost**
- **Risk**
- **Energy**

Aspects of Green Chemistry



Twelve Principles of Green Chemistry

1. Prevent waste
2. Maximize atom economy
3. Design less hazardous chemical syntheses
4. Design safer chemicals and products
5. Use safer solvents and reaction conditions
6. Increase energy efficiency
7. Use renewable feedstocks
8. Avoid chemical derivatives
9. Use catalysts, not stoichiometric reagents
10. Design chemicals and products to degrade after use
11. Analyze in real time to prevent pollution
12. Minimize the potential for accidents

Preventing Waste

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

- Any synthesis should be carried out in such a way that the waste or by-product formation is minimum or wastes are not generated.
- The overall cost of production is much more if the cost of treatment and disposal of waste is added to the overall cost.
- The waste or the byproducts, if formed are discharged into the environment and are responsible for pollution.

- **Basic Principle: Prevention is better than cure.**

Atom Economy

Atom Economy: Synthetic methods should be designed to maximize the incorporation of all the starting materials in the process into the final product.

$$\% \text{ Atom economy} = \frac{\text{F.W. of atoms utilised}}{\text{F.W. of the reactants used in the reaction}}$$

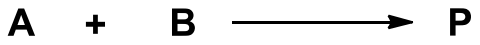
- **When calculating atom economy, stoichiometry of reactants and products are included.**

- **The calculation considers only the reactants used and ignores the intermediates that are made in one stage and consumed in the next.**

Atom Economy

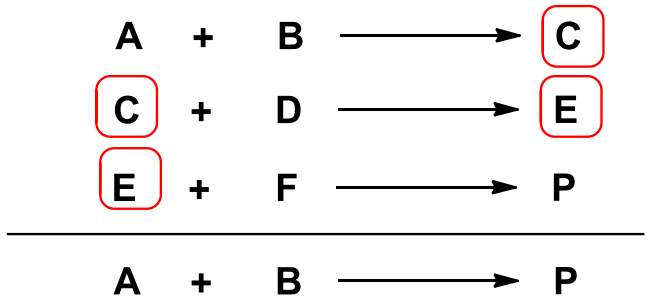
Atom Economy: Synthetic methods should be designed to maximize the incorporation of all the starting materials in the process into the final product.

Single step reaction



$$\% \text{ Atom economy} = \frac{\text{F.W. of Product P}}{\text{F.W. of A + F.W. of B}}$$

Multi-step reaction



$$\% \text{ Atom economy} = \frac{\text{F.W. of Product P}}{\text{F.W. of A + F.W. of B + F.W. of D + F.W. of F}}$$

Design less hazardous chemical syntheses

Whenever possible, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and environment

- No hazardous starting materials should be used.
- No hazardous by-products should be generated in any synthetic procedure
- The chemicals used should not be toxic to the workers and it should not have harmful effects in the environment.
- The disposal of hazardous chemicals increase the overall cost of production.

Design safer chemicals and products

Chemical products should be designed to preserve efficacy of function while reducing toxicity.

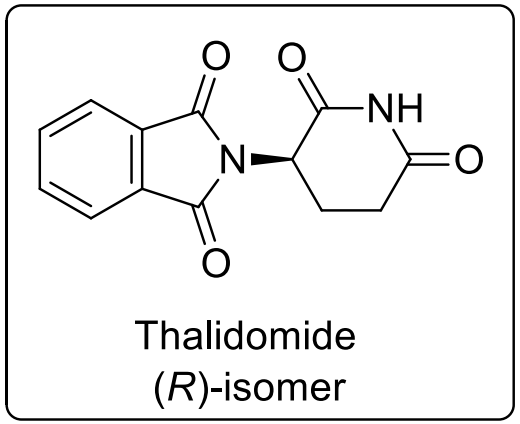
- The chemicals synthesized should be safe to handle
- It should not have toxic effects.

Example: Thalidomide was used in 1960s to reduce morning sickness for the pregnant ladies.

A chiral drug with two enantiomeric forms.

(*R*)-isomers have therapeutic activity.

(*S*)-isomers cause abnormalities of the embryos causing birth defects.



Thalidomide
(*R*)-isomer

Use safer solvents and reaction conditions

Chemical products should be designed to preserve efficacy of function while reducing toxicity. The use of auxiliary substances (solvents, separation agents, etc.) should be made unnecessary wherever possible and when used innocuous.

- Chlorinated solvents such as $CHCl_3$, CH_2Cl_2, CCl_4, etc. and aromatic hydrocarbons, such as , benzene have excellent solvent properties. However, they are believed to be suspected human carcinogens.
- Solvents should not have hazardous effect on the environment.
- Chlorofluorocarbons were used as cloning solvents, blowing agents and as refrigerants. CFCs are responsible for depletion of the ozone layer. This has serious health effects on humans.
- It is necessary to use green solvents.
  Some of the green solvents: water, super critical CO_2, ionic liquids, polyethylene glycol (PEG) and fluorus solvents.

Increase energy efficiency

Energy requirements should be recognized for their environmental and economic impacts and should be minimized.

- Energy is required for all chemical reactions. However, this should be kept to a minimum.
- The reactants are dissolved in a suitable solvent and the reaction mixture is heated for completion
- The reaction time should be made small for energy minimization.

- The energy requirement can be reduced:
  (1) By using a suitable catalyst.
  (2) Carrying out the reaction in MW heating.
  (3) Photochemical activation can be used.

Use renewable feedstocks

A raw material or feedstock should be renewable rather than depleting whenever technically and economically practical.

- The starting material can be obtained from:

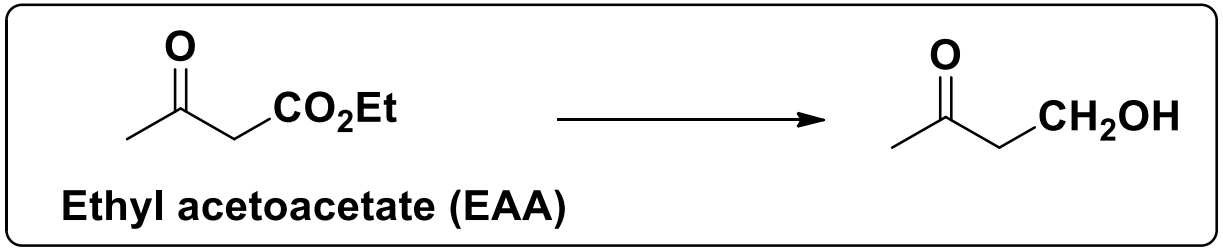
  (1) Renewable sources, e.g., agricultural products. However, this cannot be obtained in continuous supply due to harsh environmental condition, such as, short rainfall, etc. Other renewable sources are CO_2 (obtained from natural sources or synthetic process) and methane (obtained from natural sources such as natural gas, marsh gas, etc.)

  (2) Non-renewable sources, such as petroleum oil, source of petrochemicals. Petroleum oil formation take millions of years from animal and vegetable remains.

Avoid chemical derivatives

Unnecessary derivatization (protecting group, protection and deprotection, temporary modification of physical/chemical processes) should be avoided wherever possible.

- In organic synthesis it is sometimes necessary to protect a particular group, usually the more reactive functional group, so that the desired product is obtained.



Advantages: (1) The reaction proceeds in the desired direction.
(2) It solves the problem of chemoselectivity.

Avoid chemical derivatives

Disadvantages:

(1) The reagent for protection and deprotection of a particular group must be added in stoichiometric amount.

(2) After the completion of the reaction, the protecting group is deprotected to get the desired product.

(3) Protection and deprotection of groups increase the number of steps in organic synthesis.

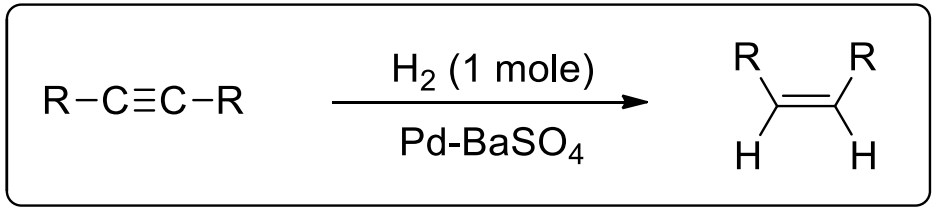
(4) Reagents used for protection and deprotection ultimately form wastes.

Use catalysts, not stoichiometric reagents

Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

In most reactions, all starting materials are not consumed and the reaction does not go to completion.

- The unreacted starting materials form wastes.
- Catalysts (wherever available) facilitate the transformation without being consumed.
- The catalysts are selective in their action.



- **Different catalysts:**
  (1) Phase transfer catalyst
  (2) Biocatalysts

Design chemicals and products to degrade after use

Chemical products should be so designed that at the end of their function they do not persist in the environment and instead break down into innocuous degradation products.

- An aspect of green chemistry is that the synthetic product or product of a reaction should not be persistent chemicals but should be biodegradable.

- The persistent chemicals are not biodegradable and remain in the environment in the same form for the long periods of time.

- These chemicals are bioaccumulates in animal systems as these are taken up by plants and various animal species.

  This is very harmful not only for the concerned species but also harmful to the humans indirectly.

Design chemicals and products to degrade after use

- Some pesticides, e.g., DDT, are known to be non-biodegradable. These are bioaccumulates and transfers into the human beings resulting in serious health issues.
- Groups which are susceptible to hydrolysis, photolysis, or other cleavage make the product biodegradable.
- Introduction of certain groups and other features in a molecule makes it biodegradable. However, the product of biodegradation should not be toxic to the environment.
- Plastics are known to be non-biodegradable. However, it is now possible to make few biodegradable plastics with the advancement of science and technology.

Analyze in real time to prevent pollution

Analytical methodologies need to be further developed to allow real-time, in process monitoring and control prior to the formation of hazardous substances.

- Development of methodologies as a result of the advancement of knowledge minimizes / prevent the generation of hazardous substances in any chemical process.
- It is necessary to have reliable sensors, monitors and analytical techniques to assess the hazards that may be present in a process stream
- It is possible to monitor a chemical process for the generation of hazardous by-products and also prevent any accident which may occur.

Minimize the potential for accidents

Substances and the form of a substance used in a chemical process should be chosen so as the minimize the potential for chemical accidents, including releases, explosion and fires.

- Adequate precautions must be taken to avoid the occurrence of accidents including releases, explosions and fires in chemical industries.
- The disasters happed in Bhopal (India, 1984), Seveso (Italy) and many other places are responsible for the deaths and disability of thousands of people.
- In some cases, people are disabled for the rest of their lives as happened in the episode of Bhopal.

Minimize the potential for accidents

A mnemonic ‘PRODUCTIVELY’ was given by S. L. Y. Tang, R. L. Smith and M. Poliakoff in 2005 to remember and express twelve principles of green chemistry.

PRODUCTIVELY

P Prevent wastes

R Renewable materials

O Omit derivatisation steps

D Degradable chemical products

U Use of safe synthetic methods

C Catalytic reagents

T Temperature, pressure, abient

I In-process monitoring

V Very few auxiliary substances

E E-factor; maximise feed in the product

L Low toxicity of chemical products

Y Yes, it is safe.