1. Green Chemistry

Definition

Green chemistry is defined as invention, design, development, and applications of chemical products and processes to reduce or to eliminate the use and generation of substances hazardous to human health and environment.

Green Chemistry - Introduction

Green chemistry is also known as sustainable chemistry. The main idea of green chemistry is to enhance production efficiency, minimize waste generated during the production. Green synthesis must follow few of the green strategies, such as avoid waste, be atom economic, avoid auxiliary substances, use catalytic amount of catalyst and recycled, reduce energy requirements and be energy efficient, use renewable materials and biodegradable materials.

- Is a philosophy that applies to all areas of chemistry, not a single discipline of chemistry
- Applies innovative scientific solutions to real-world environmental problems.
- Results in source reduction because it prevents the generation of pollution.
- Reduces the negative impacts of chemical products and processes on human health and the environment.
- Lessens and sometimes eliminates hazard from existing products and processes.
- Designs chemical products and processes to reduce their intrinsic hazards

Major Environmental Pollutants

Pollutant is a substance that pollutes something, especially water or the atmosphere. It can enter the environment naturally, such as from volcanic eruptions, or through human activities, such as burning coal and gasoline. The major pollutant, their sources, and their effects on humans and environment are as follows:

1. **Oxides of Carbon (CO_X)**

Types:

- Carbon dioxide (CO_2)
- Carbon monoxide (CO)

Source of Production:

- Combustion of coal, oil and other fuels for energy production, manufacturing, and transport
- Biomass burning

Effects on Humans and Environment:

- CO_2 has a major role in green-house effect
- It produces weak carbonic acid adding to acid rains
- CO affects human health by binding to haemoglobin

2. **Oxides of sulphur (SO_X)**

Types:

- Sulphur dioxide (SO_2)
- Sulphur trioxide (SO_3)
- Sulphate (SO_4^-)

Source of Production:

- Combustion of sulphur containing fuel (e.g., coal)
- Petroleum extraction and refining
- Paper manufacturing
- Municipal incineration, Ore smelting for metal extraction

Effects on Humans and Environment:

- SO_2 cause damage to human and other animal lungs
- It is important precursor to acid rain: adverse effects include corrosion of paint, metals and injury or death to animals and plants.

3. **Oxides of Nitrogen (NOx)**

Types:

- Nitrogen oxide (NO)
- Nitrogen dioxide (NO_2)
- Nitrous oxide (N_2O)
- Nitrate (NO_3^-)

Source of Production:

- Burning of fuels
- Biomass burning
- By product in the manufacturing of fertilizers Effects on

Humans and Environment:

- Form the secondary pollutants: peroxy acetyl nitrate and nitric acid (HNO_3)
- Suppression of plant growth and tissue damage
- Cause irritation to eyes, viral infections like influenza
- Nitrate form in atmosphere impairs the visibility

Basic Principles of Green Chemistry

Green chemistry is generally based on the 12 principles proposed by Anastas andWarner.

Now a days, these 12 principles of green chemistry are considered the fundaments to contribute to sustainable development.

The principles comprise instructions to implement new chemical products, new synthesis, and new processes.

1. **Prevent waste:** Design chemical syntheses to prevent waste. Leave no waste to treat or clean up.
2. **Maximize atom economy:** Design syntheses so that the final product contains the maximum proportion of the starting materials. Waste few or no atoms.
3. **Design less hazardous chemical syntheses:** Design syntheses to use and generate substances with little or no toxicity to either humans or the environment.
4. **Design safer chemicals and products:** Design chemical products that are fully effective yet have little or no toxicity.
5. **Use safer solvents and reaction conditions:** Avoid using solvents, separation agents, or other auxiliary chemicals. If you must use these chemicals, use safer ones.
6. **Increase energy efficiency:** Run chemical reactions at room temperature and pressure whenever possible.
7. **Use renewable feedstocks:** Use starting materials (also known as feedstocks) that are renewable rather than depletable. The source of renewable feedstocks is often agricultural products or the wastes of other processes; the source of depletable feedstocks is often fossil fuels (petroleum, natural gas, or coal) or mining operations.
8. **Avoid chemical derivatives:** Avoid using blocking or protecting groups or any temporary modifications if possible. Derivatives use additional reagents and generate waste.

9. Use catalysts, not stoichiometric reagents: Minimize waste by using catalytic reactions. Catalysts are effective in small amounts and can carry out a single reaction many times. They are preferable to stoichiometric reagents, which are used in excess and carry out a reaction only once.

10. Design chemicals and products to degrade after use: Design chemical products to break down to innocuous substances after use so that they do not accumulate in the environment.

11. Analyze in real time to prevent pollution: Include in-process, real-time monitoring and control during syntheses to minimize or eliminate the formation of byproducts.

12. Minimize the potential for accidents: Design chemicals and their physical forms (solid, liquid, or gas) to minimize the potential for chemical accidents including explosions, fires, and releases to the environment.

Various Green Chemical Approaches

Some of the green chemistry approaches are 1) use of microwave for heating a chemical reaction, 2) use of biocatalysts (i.e., enzymes), 3) Use of phase transfer catalysts, 4) solvent free synthesis, 5) use of super critical conditions (example: supercritical CO_2) of solvents for synthesis, etc.

Microwave Synthesis

A microwave is a form of electromagnetic energy, which falls at the lower end of the electromagnetic spectrum between infrared and radio frequencies.

While fire is now rarely used in synthetic chemistry, the Bunsen burner was also replaced by the mantle, oil bath or hot plate as a source of applying uniform heat to a chemical reaction.

Heating chemicals for their reactions by microwave energy is generally referred to as microwave-assisted organic synthesis. **It is based on the principle of Dipolar polarization and ionic condution mechanism.**

Advantages

Microwave heating include following advantages, over the conventional heating:

- The difference between microwave energy and other forms of radiation is that microwave energy is non-ionizing and therefore does not alter the molecular structure of the compounds being heated – it provides only thermal activation.
- Microwave-assisted synthes is provides clean synthesis with the advantage of
    - Uniform heating
    - enhanced reaction rates,
    - reduce reaction times,
    - higher yields,
    - Purity in final product,
    - greater selectivity,
    - Low operating cost: economic for the synthesis of a large number of organic molecules,
    - Reduction in unwanted side reaction.

Bio Catalysed Reactions

Biocatalyst requires enzymes to promote chemical reactions. Enzymes are very efficient biocatalysts, present in every living organism to carry out a wide range of chemical reactions, and also finds application as an important tools used in greenchemistry.

Features of Biocatalysed Reactions

Biocatalysis has many attractive features in the context of green chemistry and sustainable development:

1. The catalyst (an enzyme) is derived from renewable resources and is biocompatible (sometimes even edible), biodegradable, and essentially nonhazardous, that is, it fulfils the criteria of sustainability remarkably well.
2. Biocatalysis avoids the use of, and contamination of products by, scarce precious metals such as palladium, platinum, and rhodium.
3. Reactions are performed in an environmentally compatible solvent (water) under mild conditions (physiological pH and ambient temperature and pressure).
4. Reactions of multifunctional molecules proceed with high activities and chemo-, regio-, and stereo-selectivity and generally without the need for functional group activation, protection, and de-protection steps required in traditional organic syntheses. Biocatalysed reactions are economic and more efficient in energy and raw material consumption, generate less waste, and are, therefore, both environmentally and economically more attractive than conventional routes.
5. As a direct result of the higher selectivity and milder reaction conditions, biocatalytic processes often afford products in higher purity than traditional chemical or chemo-catalytic processes.
6. Enzymatic processes (but not fermentations) can be conducted in standard multipurpose batch reactors and, hence, do not require any extra investment, for example, for high-pressure equipment.
7. Biocatalytic reactions are conducted under roughly the same conditions of temperature and pressure, and, hence, it is relatively easy to integrate multiple reactions into eco-efficient catalytic processes.

In short, biocatalysis fits very well with the principles of green chemistry and sustainability.

Solvent Free Reactions or Dry Media Reactions

Avoiding organic solvents during the reactions in organic synthesis leads to a clean, efficient, and economical technology (green chemistry).

Use of organic solvents is objectionable from the standpoint of environmental hazard. This is why solvent free reaction conditions are an important object of green chemistry.

Examples for the techniques used are mechano-chemical mixing (i.e., grinding), microwave irradiation, solid/mineral support to the reactants, catalysis by solid surfaces of inexpensive and recyclable minerals (e.g. alumina, silica, clay, doped clay surface, etc.)

Advantages:

A wide variety of industrially important compounds and intermediates such as enones, imines, enamines and nitroalkenes have been prepared by this environmentally friendly solvent-free approach. In these reactions, the organic compounds adsorbed on the surface of inorganic oxides, such as alumina, silica and clay or 'doped' supports absorb microwaves whereas the solid support does not absorb or restrict their transmission. The bulk temperature is relatively low in such solvent free reactions.

Synthesis of Adipic Acid by Conventional and Green Route

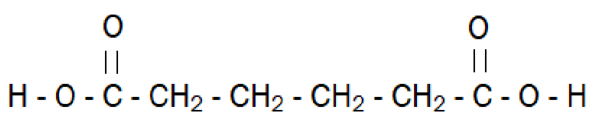
Chemistry and Uses of Adipic Acid

Chemistry of Adipic Acid

Adipic acid or hexanedioic acid is the organic compound with the formula $(CH_2)_4(COOH)_2$.

IUPAC Name: Hexanedioic acid Molecular

Structure:

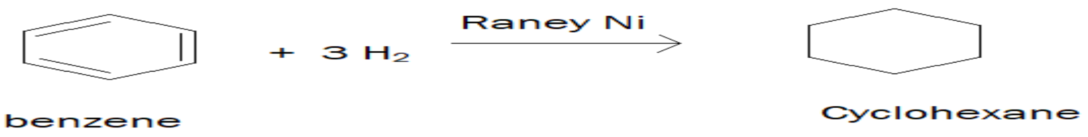


Uses of Adipic Acid

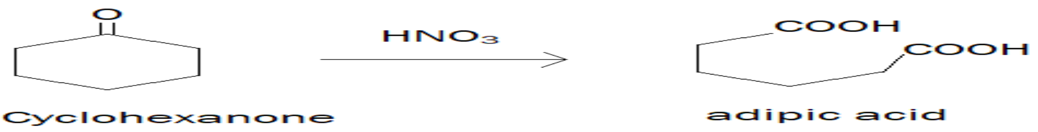
- About 60% of the adipic acid produced is used as monomer for the production of nylon by a polycondensation reaction with hexamethylene diamine forming nylon 66.
- It is a monomer for production of polyurethane
- Its esters are plasticizers, especially in PVC
- It has been incorporated into controlled-release formulation matrix tablets to obtain pH-independent release for both weakly basic and weakly acidic drugs.
- Small but significant amounts of adipic acid are used as a food ingredient as a flavorant and gelling aid.

Conventional Synthesis of Adipic Acid from Benzene

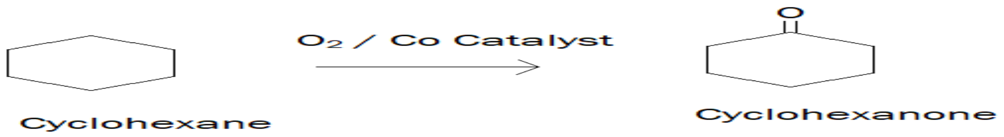
Step 1: Reduction of benzene to cyclohexane using Raney Ni and hydrogen



Step 2: Oxidation of cyclohexane to cyclohexanone: Cyclohexane is treated with oxygen in the presence of Co (cobalt) catalyst to obtain cyclohexanone



Step 3: Oxidation of cyclohexanone to adipic acid: cyclohexanone on oxidation with nitric acid ring opening reaction takes place to produce adipic acid

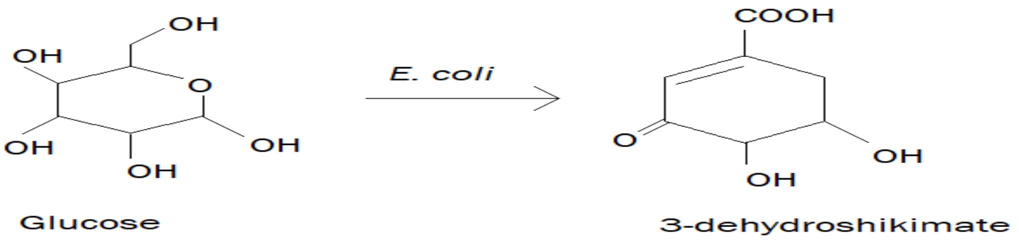


Draw-backs of Conventional Synthesis

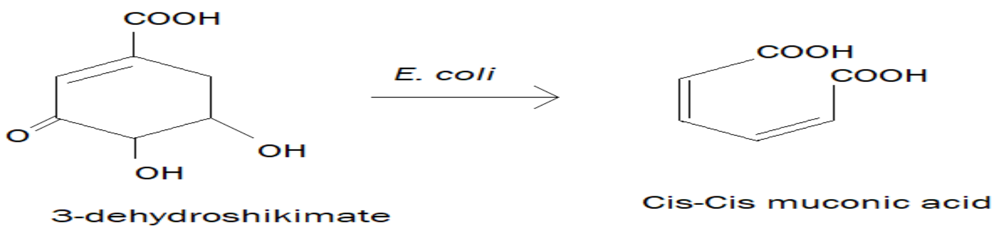
Benzene is the starting material for the synthesis of adipic acid. Benzene is carcinogenic and being VOC (volatile organic compound) it pollutes air. The green chemistry approach now uses glucose as the starting material for the enzyme catalyzed adipic acid synthesis.

1.6.2 Green Synthesis of Adipic Acid from Glucose

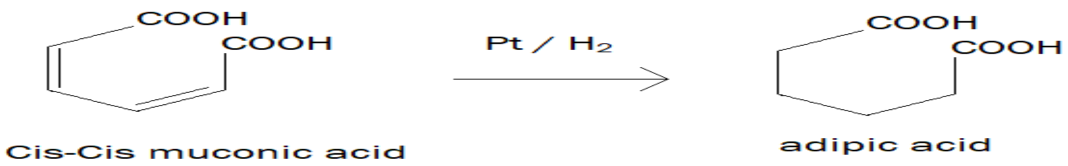
Step 1: Glucose on reaction with *Escherichia coli* (*E.coli*) bacteria produces 3-dehydroshikimate



Step 2: 3-dehydroshikimate on further reaction with *E. coli* produces Cis-Cis muconic acid



Step 3: Cis-Cis muconic acid on reduction reaction in the presence of Pt/H2 produces adipic acid



Synthesis of Paracetamol by Conventional and Green Route

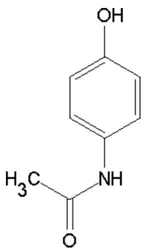
Chemistry and Uses of Paracetamol

Chemistry of Paracetamol

Paracetamol, also known as acetaminophen, is a medication used to treat fever and mild to moderate pain.

IUPAC name: N-(4-hydroxyphenyl)ethanamide

Molecular structure:



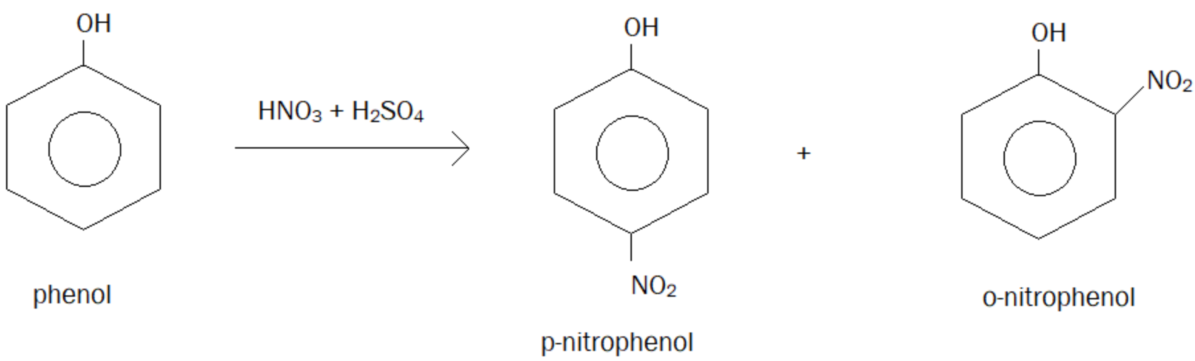
Uses of Paracetamol

- It is used as antipyretic drug to reduce body temperature in case of high fever.
- It is also used as a weak analgesic to reduce the mild to moderate pain (examples: head ache, tooth pain, menstrual pain, etc.)

Conventional Synthesis of Paracetamol from Phenol

Step 1: Nitration reaction of phenol using nitrating mixture (H2SO4 + HNO3), which is an example for electrophilic aromatic substitution reaction.

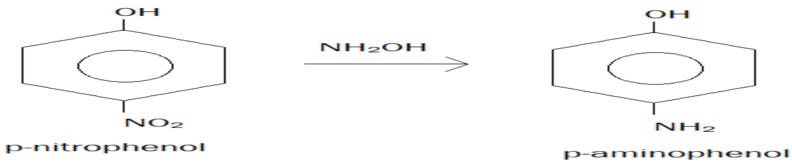
p-nitrophenol is more stable than o-nitrophenol as:



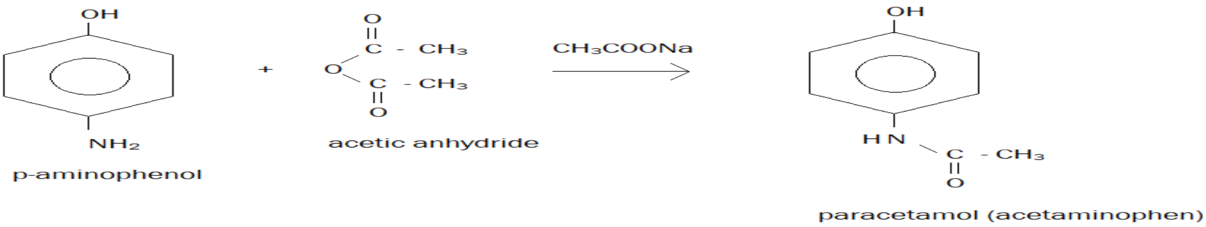
p-nitrophenol can be separated from o-nitrophenol by HPLC (high performance liquid chromatography) or column chromatography. Only p-nitrophenol is further used for the synthesis of paracetamol.

Step 2: Reduction of nitro group (–NO_2 group) to amine group (–NH_2 group)

p-nitrophenol is reduced to p-aminophenol using NH_2OH



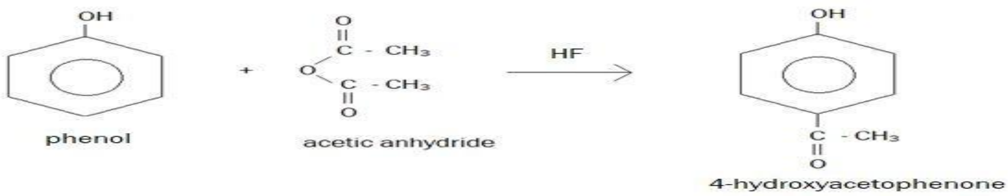
Step 3: Nucleophilic addition reaction of p-aminophenol with acetic anhydride (CH_3CO-O-$OCCH_3$) in the presence of sodium acetate (CH_3COONa).



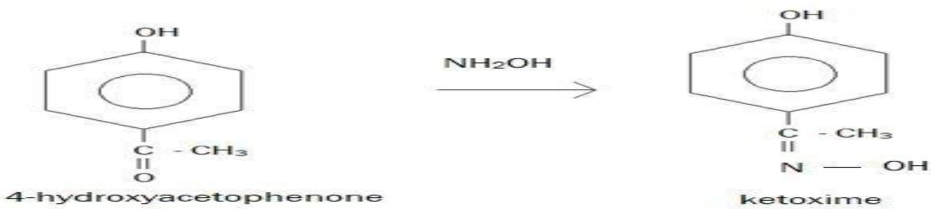
The % atom economy calculated for this synthesis is ≈ 36%

Green Synthesis of Paracetamol from Phenol

Step 1: Phenol reacts with acetic anhydrie in the presence of strong acid like HF to undergo acylation reaction which is an electrophilic substitution reaction, to produce 4-hydroxyacetophenone.



Step 2: Reaction of aldehydes and ketones with hydroxylamine (NH_2OH) gives oximes. 4-hydroxyacetophenone reacts with hydroxylamine to give corresponding ketoxime.



Step 3: Oximes in acidic medium (trifluroacetic acid, CF_3COOH) undergoes Beckmann rearrangement to produce substitute amides. Beckmann rearrangement of the above ketoxime gives paracetamol.

The % atom economy calculated for this green synthesis ≈ 58%

Industrial Applications of Green Chemistry

Chemical industry involves major chemicals, reagents, solvents, catalysts and almost all types of organic reactions for synthesis of active pharmaceutical substances. Therefore, many chemicals and chemical processes involved are hazardous, toxic and may show adverse effects on human health, environment, and on economic growth.

Green chemistry approach is responsible for cleaner air, cleaner water, increased safety for workers in the chemical industry, safer consumer products of all types, saferfood, safer pesticides, etc.

Green chemicals either degrades to innocuous products or are recovered for further use; plants and animals suffer less harm from toxic chemicals in the environment; lower potential for global warming, ozone depletion, and smog formation, etc.

Some of the industrial applications of green chemistry are:

- Higher yields for chemical reactions, consuming smaller amounts of feedstock to obtain the same amount of product
- Fewer synthetic steps, often allowing faster manufacturing of products, increasing plant capacity, and saving energy and water
- Reduced waste, eliminating costly remediation, hazardous waste disposal, and end-of-the-pipe treatments
- Allow replacement of a purchased feedstock by a waste product
- Better performance so that less product is needed to achieve the same function
- Reduced use of petroleum products, slowing their depletion and avoiding their hazards and price fluctuations
- Reduced manufacturing plant size or footprint through increased throughput
- Increased consumer sales by earning and displaying a safer-product label (e.g., Safer Choice labeling)
- Improved competitiveness of chemical manufacturers and their customers