Green Chemistry

Introduction:

Green chemistry is the design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances. Green chemistry applies across the life cycle of a chemical product, including its design, manufacture, use, and ultimate disposal. Green chemistry is also known as sustainable chemistry.

Green chemistry:

- Prevents pollution at the molecular level
- 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

Twelve Principles of Green Chemistry

Basics of green chemistry include any chemical process or technology which improves the environment and our quality of life. It is a special contribution of the chemists to the condition for sustainable development. These principles are given below.

1. Prevention: It is better to prevent waste than to treat or clean up waste after it has been created. The first principle aims to develop the zero-waste technology (ZWT). In terms of ZWT, in a chemical synthesis, waste product should be zero or minimum.
2. Atom Economy: Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. Less Hazardous Chemical Syntheses: Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment. This principle aims to develop the methodologies that will minimize the use and formation of toxic and hazardous.
4. Designing Safer Chemicals: Chemical products should be designed to affect their desired function while minimizing their toxicity. In many chemical industries, not only the waste product but the starting materials are also quite hazardous to the workers and environment.
5. Safer Solvents and Auxiliaries: The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.
6. Design for Energy Efficiency: Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.
7. Use of Renewable Feedstock: A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable. It encourages the use of starting material (i,e. raw material or feedstock) which should be renewable, if technically and economically practicable. Moreover, use of these nonrenewable resources puts a burden on the environment.

8. Reduce Derivatives: Unnecessary derivatization (use of blocking groups, protection/ deprotection, temporary modification of physical/chemical processes) should be minimized or avoided, if possible, because such steps require additional reagents and can generate waste.
9. Catalysis: Catalytic reagents (as selective as possible) are superior to stoichiometric reagents. This principle of green chemistry states that catalytic reagents are superior to stoichiometric reagents. The use of catalysts is preferred because of following advantages.
    - 100% atom economy because the true are fully recovered without any change in their chemical and physical properties.
    - The catalyzed reactions are faster i,e. energy save is possible.
    - Reaction yield are better.
    - Selective reaction product.
    - Maximum utilization of the starting material and minimum production of the waste material.
10. Design for Degradation: Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment. It states that the waste product should degrade automatically to clean the environment.
11. Real-time analysis for Pollution Prevention-Analytical methodologies needs to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances. This is very much important for the chemical industries and nuclear reactors to avoid the accident.
12. Inherently Safer Chemistry for Accident Prevention-Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires. The substance to be used in a chemical industry should be in such forms so that the possibility of accidents can be minimized.

Green Chemicals

In order to carry out the transformation of selected feedstock into the target molecule the criteria of efficiency, availability and effect of the green reagent used is important. These reagents are to target the conversion of a specific functional group without affecting the other, a challenging task, and to give higher yields as far as possible. A good reagent must give least problems while working up the reaction. The qualities of a good reagent suitable for modern organic synthesis are:

- The reagent should be cost effective.
- It should be eco-friendly i.e., poses less risk to the environment and could be recycled whenever required.
- It should be versatile i.e., works under variety of conditions.
- The reagent may require to target specific functional group.
- It should give a good yield of the desired product.
- The workup conditions must be less tedious.

(a) Use of Safer solvents

The replacement of toxic or hazardous organic solvents in industrial processes and systems has been initiated long time ago. Green solvents are environmentally friendly solvents or bio-solvents, which are derived from the processing of agricultural crops. The uses of petrochemical solvents are the key to the majority of chemical processes but not without severe implications on the environment.

Ethyl lactate, an ester of lactic acid is a green solvent derived from processing corn. Lactate esters solvents are commonly used solvents in the paints and coatings industry and have numerous attractive advantages including being 100% biodegradable, easy to recycle, non-corrosive, non-carcinogenic and non-ozone depleting. Ethyl lactate is a particularly attractive solvent for the coatings industry as a result of its high solvency power, high boiling point, low vapour pressure and low surface tension.

(b) Supercritical Fluids

Supercritical fluids comprise the liquid and gases at temperature and pressure higher than their critical temperature and pressure (Fig 1). Above the critical point the liquid-vapour phase boundary disappears and the supercritical fluids exists the unique properties of both its gas and liquid. High compressibility of supercritical fluids in the vicinity of the critical point makes it easy to adjust density and solution ability by a small change of temperature or pressure. Due to this, the supercritical fluids are able to dissolve many compounds with different polarity and molecular mass.

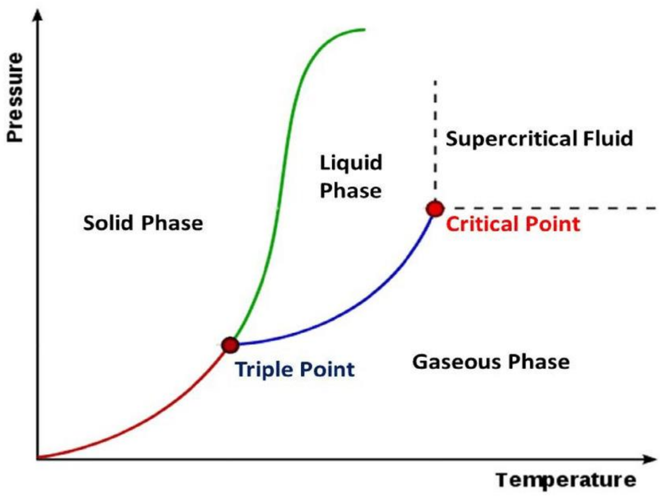


Fig. 1. Phase diagram showing supercritical fluid region

Supercritical carbon dioxide-SCO2

It is a fluid state of carbon dioxide where it is held at or above its critical temperature and pressure. Carbon dioxide usually behaves as a gas in air at standard temperature and pressure, or as a solid called dry ice when cooled and pressurized sufficiently. If the temperature and pressure are both increased from STP to be at or above the critical point for carbon dioxide, it can adopt properties midway between a gas and a liquid. More specifically, it behaves as a supercritical fluid above its critical temperature (304 K) and critical pressure (73 bar), expanding to fill its container like a gas but with a density like that of a liquid.

Applications: Supercritical CO2 is becoming an important commercial and industrial solvent due to its role in chemical extraction in addition to its low toxicity and environmental impact.

The relatively low temperature of the process and the stability of CO_2 also allow most compounds to be extracted with little damage or denaturing. In addition, the solubility of many extracted compounds in CO_2 varies with pressure, permitting selective extractions.

Advantages of supercritical CO_2 as solvents

The advantages of supercritical CO_2 are,

- It can be used under mild process conditions
- It is a harmless solvent and it is generally regarded as safe for food and pharmaceutical products
- It is inexpensive and available at low cost
- It is easily available and it can be obtained in large quantities with high purity.
- It can be easily separated from the product purified and recycled
- In extraction it does not affect the sample mixture and the product formed
- It can be used to extract thermally labile compounds.
- It is the toxic non inflammable eco-friendly and inert to most of the materials

Supercritical water (SCH_2O)

Water has a critical temperature of 647 K and a critical pressure of 220 bar due to its high polarity.

- At this temperature, water loses many peculiar properties it has in its liquid state, such as hydrogen bonding and insolubility of non-polar substances in it. At the critical point, they disappear completely.
- When hydrogen bonds are broken, water molecules can dissolve chemicals that were previously insoluble. Thus, the character of water at supercritical conditions changes from one that dissolves only ionic species at normal conditions to one that dissolves paraffins, aromatics, gases and salts.

  Applications: Due to this unique property, research has been carried out on supercritical water for reaction and separation processes to treat toxic wastewater. Both near-critical and supercritical water (SCH_2O) have increased acidity, reduced density, and lower polarity, greatly extending the possible range of chemistry that could be carried out in water.

*Advantage*s of chemistry with supercritical water is the possibility of varying the properties of the reaction medium over a wide range solely by changing the pressure and temperature and of optimising the reaction in this way without changing solvent. Supercritical fluids such as water and carbon dioxide are substances that are compatible with the earth's environment. However, several other supercritical fluids can be used, but the final choice would depend on the specific application and additional factors such as safety, flammability, phase behaviour and solubility at the operating conditions and the cost of the fluid.

(c) Room-Temperature Ionic Liquids

Most of the common liquids (e.g., water, ethanol, benzene, etc.) are molecular and are basically made up of molecules. However, since the early 1980s an exciting new class of room-temperature liquids has become available. These are the ambient-temperature ionic liquids. Ionic liquids are composed entirely of ions.

- An ionic liquid is a salt in which the ions are poorly coordinated, which results in these solvents being liquid below 100°C, or even at a room temperature. Generally, viewed like common ionic materials such as sodium chloride, the difference being that they are liquid at low temperatures, this being due to poor packing of the respective ions.

- Ionic liquids possess a unique array of physico-chemical properties that make them excellent solvents with high thermal stability and high electrical conductivity.

- These simple liquid salts (single anion and cation) can be mixed with other salts (including inorganic salts) to form multicomponent ionic liquids.

- Some common examples of ionic liquids are shown in Fig. 2.
- The absence of volatility is one of the most important benefits of ionic liquids, offering a much lower toxicity as compared to low-boiling-point solvents.

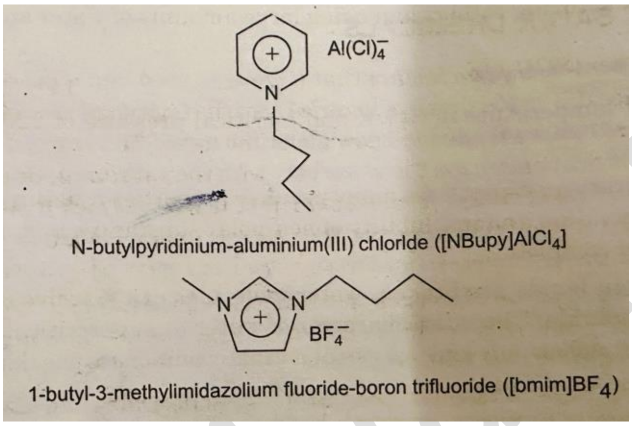
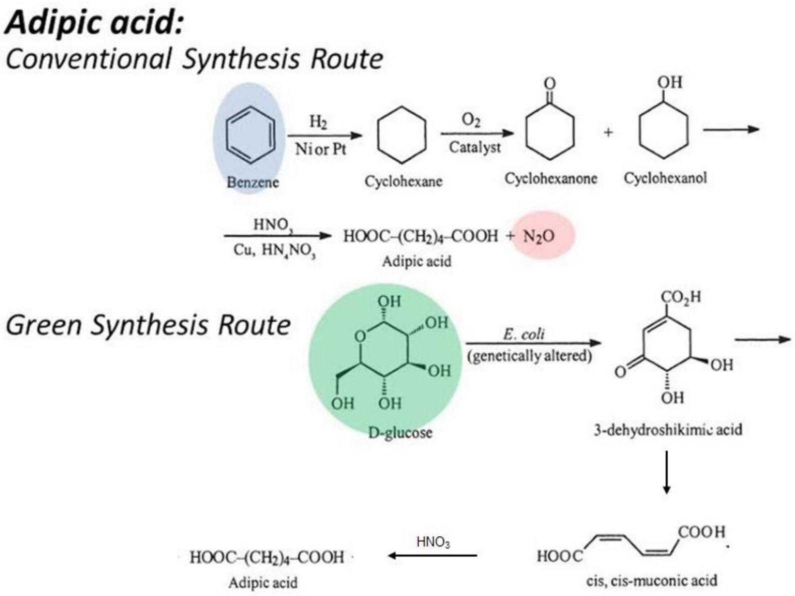


Fig. 2. Some common room temperature ionic liquids

Synthesis of organic compounds by conventional and green route

(A) Adipic acid

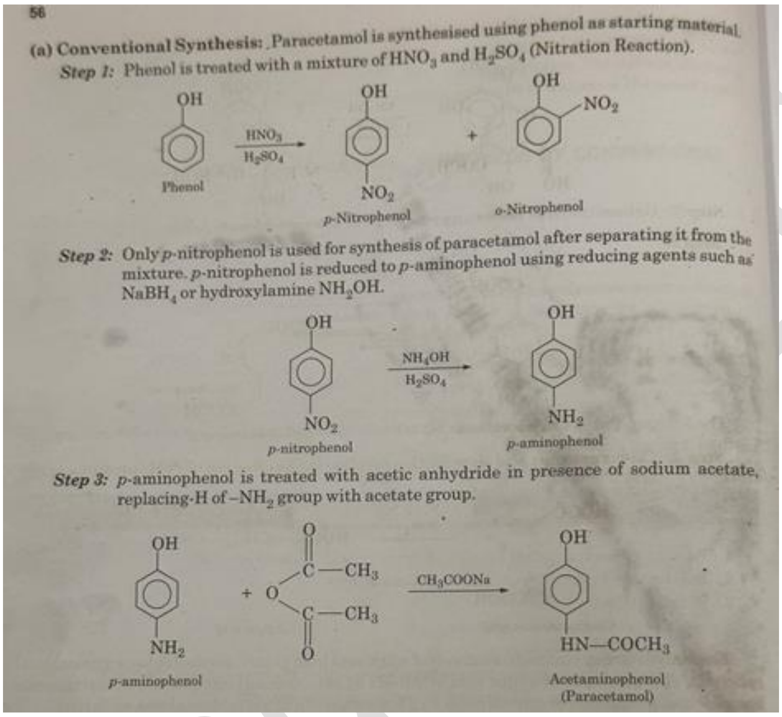
Adipic acid the organic compound which is widely used as a monomer for the production of nylon by the polycondensation reaction with hexamethylene diamine forming nylon 6,6. It is also a monomer of polyurethane. Adipic acid can be synthesized by using both conventional and green route



The conventional method requires high temperature and pressure and the use of benzene which is carcinogenic. By product formation was observed in first step and nitrous oxide is produced in step 3.

(B) Paracetamol

Paracetamol is an effective antipyretic and analgesic drug widely used in the treatment of fever and mild body pain. Paracetamol is synthesized using phenol as starting material. This can be synthesized by both conventional and green routes.



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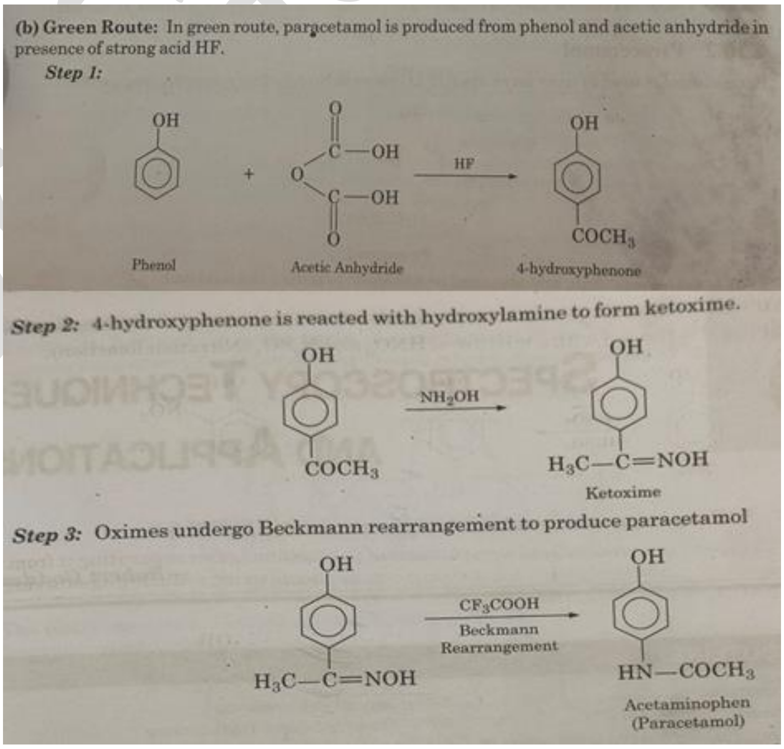
(a) Conventional Synthesis: Paracetamol is synthesised using phenol as starting material.

Step 1: Phenol is treated with a mixture of HNO_3 and H_2SO_4 (Nitration Reaction).

Step 2: Only *p*-nitrophenol is used for synthesis of paracetamol after separating it from the mixture. *p*-nitrophenol is reduced to *p*-aminophenol using reducing agents such as $NaBH_4$ or hydroxylamine NH_2OH.

Step 3: *p*-aminophenol is treated with acetic anhydride in presence of sodium acetate, replacing-H of $-NH_2$ group with acetate group.



(b) Green Route: In green route, paracetamol is produced from phenol and acetic anhydride in presence of strong acid HF.

Step 1:

Step 2: 4-hydroxyphenone is reacted with hydroxylamine to form ketoxime.

Step 3: Oximes undergo Beckmann rearrangement to produce paracetamol

An alternative industrial synthesis uses directly acylation of phenol with acetic anhydride. The resulting ketone is then converted to ketoxime with hydroxylamine, followed by an acid-catalyzed Beckmann rearrangement to give the desired amide product. Which give atom economy of 56% better than conventional 36% atom economy.

Environmental impacts of Green Chemistry on society

The primary goal of green chemistry to minimize the environmental impact of chemistry on society while also providing economic and social benefits. Here are some of the keyways in which green chemistry impacts society and the environment:

Human health:

- Cleaner air: Less release of hazardous chemicals to air leading to less damage to lungs
- Cleaner water: less release of hazardous chemical wastes to water leading to cleaner drinking and recreational water
- Increased safety for workers in the chemical industry; less use of toxic materials; less personal protective equipment required; less potential for accidents (e.g., fires or explosions)
- Safer consumer products of all types: new, safer products will become available for purchase; some products (e.g., drugs) will be made with less waste; some products (i.e., pesticides, cleaning products) will be replacements for less safe products
- Safer food: elimination of persistent toxic chemicals that can enter the food chain; safer pesticides that are toxic only to specific pests and degrade rapidly after use
- Less exposure to such toxic chemicals as endocrine disruptors

Environment:

- Many chemicals end up in the environment by intentional release during use (e.g., pesticides), by unintended releases (including emissions during manufacturing), or by disposal. Green chemicals either degrade 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
- Less chemical disruption of ecosystems
- Less use of landfills, especially hazardous waste landfills

Economy and business:

- 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