Bachelor of Science
(B.Sc.- CBZ)

GREEN METHODS IN CHEMISTRY
(DBSZSE301T24)

Self-Learning Material
(SEM-III)

Jaipur National University
Centre for Distance and Online Education

Established by Government of Rajasthan
Approved by UGC under Sec 2(f) of UGC ACT 1956
&
NAAC A+ Accredited

TABLE OF CONTENT

EXPERT COMMITTEE

Prof. R. S. Lokhende
Department of Life Sciences
Jaipur National University, Jaipur

Prof. Purnima Nag
Department of Basic Sciences
Jaipur National University, Jaipur

COURSE COORDINATOR

Dr. Urvija Garg
Department of Life Sciences
Jaipur National University, Jaipur

UNIT PREPARATION

Unit Writers
Dr. Azhar Ullah Khan
Department of Life Sciences
JNU, Jaipur
Unit: 1-3

Ms Annu Yadav
Department of Life Sciences
JNU, Jaipur
Unit: 4-6

Assisting & Proof Reading
Dr. Sunil K Sharma
Department of Life Sciences
JNU, Jaipur

Editor
Prof. Ruby Singh
Department of Life Sciences
JNU, Jaipur

COURSE INTRODUCTION

This course provides a comprehensive introduction to Green Chemistry, exploring its principles, applications, and emerging trends. Students will gain a thorough understanding of the fundamental concepts of Green Chemistry and how they are applied to real-world scenarios. The course emphasizes the importance of sustainable practices in chemistry and introduces innovative methods for minimizing environmental impact.

The content is divided in six chapters including Introduction to the concept of Green Chemistry, including its definition, importance, and goals. Explore how Green Chemistry integrates into broader environmental and sustainability frameworks.

Exploration of cutting-edge technologies and research in Green Chemistry, including nanotechnology, biocatalysis, and renewable energy sources.

Course Outcomes: After the completion of the course, the students will be able to:

1. Understand and apply the principles of Green Chemistry to reduce environmental impacts in chemical processes.
2. Analyze and evaluate real-world case studies to identify successful Green Chemistry practices and their benefits.
3. Utilize advanced techniques such as microwave and ultrasound-assisted reactions to improve process efficiency and sustainability.
4. Implement strategies for pollution prevention and apply green solvents and reagents in practical scenarios.
5. Apply advanced techniques such as microwave and ultrasound-assisted reactions to enhance process efficiency and sustainability.
6. Anticipate and prepare for future trends and challenges in Green Chemistry, contributing to ongoing innovation in the field.

Acknowledgements:

The content we have utilized is solely educational in nature. The copyright proprietors of the materials reproduced in this book have been tracked down as much as possible. The editors apologize for any violation that may have happened, and they will be happy to rectify any such material in later versions of this book.

Chapter: 1
Introduction of Green Chemistry

Objective

- Develop chemical processes that reduce or eliminate hazardous substances and waste.
- Design chemicals and processes that prioritize human health and safety.

1.1 Introduction

The concept of "green chemistry," coined by Paul Anastas in 1991, underscores a pivotal shift in chemical science. Historically and presently, chemistry has often been associated with the release of pollutants, the production of non-biodegradable materials, and environmental harm, affecting both ecosystems and human health. Recognizing these challenges, there is now a pressing need to redirect chemical science away from exploiting finite resources and generating excessive waste.

Instead, there is a growing imperative to harness chemistry in ways that meet human needs sustainably, without compromising the Earth's delicate support systems upon which all life depends. Fortunately, both the practice of chemical science and industry are steadily pivoting towards environmental stewardship and resource efficiency. This transformation aims to maximize the benefits of chemistry while significantly reducing or eliminating its detrimental impacts.

This progressive approach, known as green chemistry, champions the design and implementation of chemical processes and products that prioritize safety, minimize waste, and utilize renewable resources. By embracing these principles, the field of chemistry can contribute positively to a sustainable future, safeguarding the environment for current and future generations.

There is a misconception that green chemistry implies chemicals are entirely benign, which isn't entirely accurate because no chemical can be perfectly harmless. Green chemistry, instead, focuses on shifting chemical usage from more harmful (malign) to less harmful (benign) pathways.

For instance, common salt is essential for life but excessive consumption can lead to hypertension. Similarly, carbohydrates provide vital energy for daily life, yet overconsumption can pose health risks. Therefore, green chemistry aims to adopt processes and use chemicals in ways that minimize their negative impacts.

As the saying goes, "The dose makes the poison." This principle is central to homeopathy, where extremely small amounts of potentially toxic substances are used, and paradoxically, they can treat various serious illnesses. Interestingly, the efficacy of these homeopathic remedies often increases with dilution.

In essence, green chemistry promotes the transformation of chemical practices towards methods that are less harmful and more sustainable, acknowledging that all chemicals, even in small quantities, can have significant effects.

Definition of Green Chemistry: Green chemistry is the design, development, and implementation of chemical products and processes that reduce or eliminate the use and generation of hazardous substances.

It aims to promote sustainability by minimizing the environmental impact of chemical practices, enhancing safety for humans and ecosystems, and conserving resources throughout the lifecycle of products. Key principles of green chemistry include the use of renewable feedstock's, the design of less toxic chemicals and processes, the maximization of atom efficiency, and the reduction of energy consumption and waste generation. Overall, green chemistry strives to integrate economic viability with environmental and social responsibility, ensuring that chemical innovations contribute positively to a sustainable future.

Green chemistry, also known as **sustainable or circular chemistry**, is a specialized field within chemistry and chemical engineering. It centers on designing products and processes with the primary goal of reducing or eliminating the use and creation of harmful substances. Where **environmental chemistry** examines the impacts of pollutants on the natural world, green chemistry directs its focus towards mitigating the environmental footprint of chemical activities. This encompasses strategies to minimize the depletion of nonrenewable resources and innovative technologies aimed at pollution prevention.

1.2. Need of Green Chemistry

Green chemistry is essential for several compelling reasons:

Environmental Impact: Traditional chemical processes often generate hazardous waste, consume large amounts of energy, and release harmful pollutants into the environment. Green chemistry aims to minimize these impacts by designing processes that are inherently safer and more sustainable.

Resource Conservation: Many chemical processes rely on finite resources, such as fossil fuels and rare earth metals. Green chemistry promotes the efficient use of resources, including renewable feedstock's and recyclable materials, reducing dependence on scarce resources.

Health and Safety: Chemical substances used in industry and consumer products can pose risks to human health and the environment. Green chemistry emphasizes the design of chemicals and processes that are less toxic and safer throughout their lifecycle.

Regulatory Compliance: Increasingly stringent regulations and public awareness regarding environmental and health impacts require industries to adopt cleaner and more sustainable practices. Green chemistry provides solutions to meet these regulatory requirements while maintaining competitiveness.

Innovation and Economic Benefits: Developing greener technologies often leads to innovation and new opportunities for economic growth. Companies that embrace green chemistry principles can reduce costs through improved efficiency, waste reduction, and enhanced product quality.

Global Sustainability: As global populations and industrial activities grow, the demand for chemicals and materials increases. Green chemistry offers pathways to meet these demands without compromising the ability of future generations to meet their own needs, aligning economic growth with environmental and social responsibility.

1.3 Goal of Green Chemistry

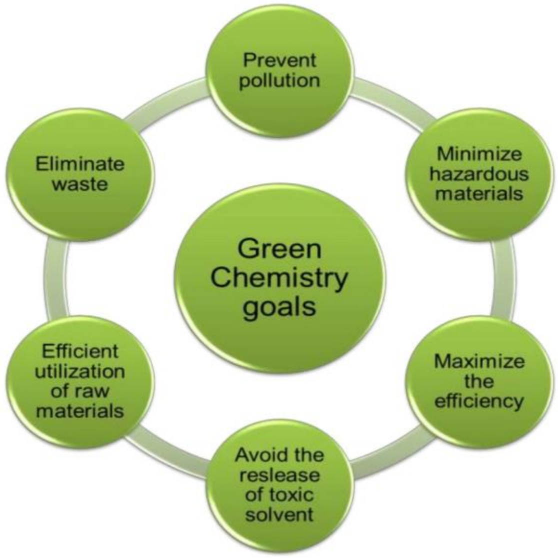
The primary goal of green chemistry is to design and develop chemical processes and products that minimize the use and generation of hazardous substances. This discipline aims to achieve sustainable outcomes by:

1. **Reducing Environmental Impact**: Green chemistry seeks to prevent pollution at the source by minimizing waste and eliminating the use of toxic substances. By designing processes that produce fewer hazardous by-products and emissions, it aims to mitigate environmental harm.
2. **Conserving Resources**: It promotes the efficient use of raw materials, energy, and water throughout the lifecycle of chemical products. This includes using renewable resources,

optimizing reaction conditions to reduce energy consumption, and enhancing resource efficiency.

3. **Enhancing Safety**: Green chemistry prioritizes the safety of chemical processes and products for humans and the environment. By minimizing the use of hazardous chemicals and designing inherently safer chemicals and processes, it aims to reduce risks to health and ecosystems.
4. **Promoting Innovation**: It fosters innovation in chemical design and manufacturing processes to achieve sustainable solutions. By integrating principles such as atom economy, catalysis, and renewable feedstocks, green chemistry encourages the development of new technologies and products that are both economically viable and environmentally benign.
5. **Supporting Sustainability**: Ultimately, green chemistry aligns chemical practices with broader sustainability goals. It aims to ensure that chemical industries contribute positively to global sustainability efforts, including reducing greenhouse gas emissions, conserving biodiversity, and promoting circular economy principles.

Hence, the goal of green chemistry is to transform the field of chemistry towards practices that meet current societal needs without compromising the ability of future generations to meet their own needs. It strives to harmonize economic growth with environmental stewardship and social responsibility, paving the way for a sustainable and equitable future.

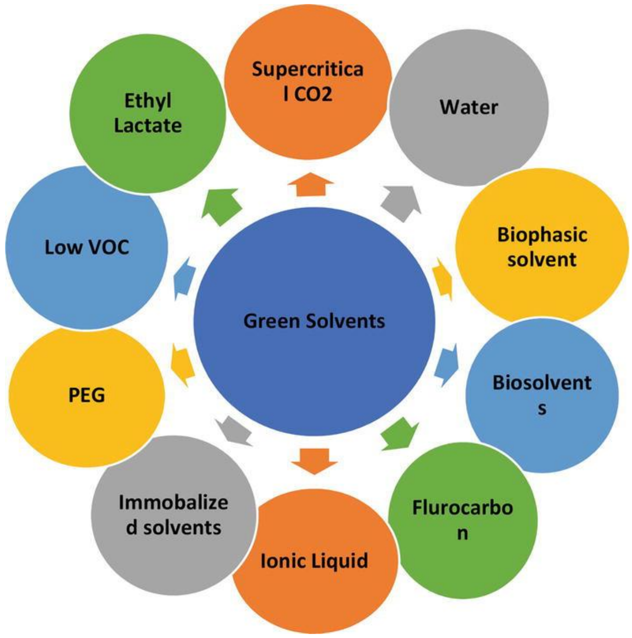


1.3 Tools of Green Chemistry

Chemists and innovators face a formidable challenge: to create new products, processes, and services in organic synthesis that meet the demands of society, affordability, and environmental sustainability. Meeting these goals requires a fresh approach focused on minimizing the materials and energy needed for chemical processes and products, reducing or eliminating the release of hazardous chemicals into the environment, maximizing the use of renewable resources, and enhancing the durability and recyclability of products. Organic chemists encounter specific challenges in this endeavor, such as pioneering novel synthetic pathways using green chemistry methodologies. These include the adoption of green solvents, catalysis in organic synthesis that is environmentally benign, synthesis in dry media conditions, catalyst-free reactions, and promoting energy-efficient synthesis techniques.

This proactive approach aims to revolutionize organic synthesis by integrating principles that not only advance scientific discovery but also prioritize sustainability and environmental stewardship.

- **Green solvents** are recognized for their favorable attributes, including low toxicity, limited water solubility, easy biodegradability in environmental settings, high boiling points, minimal volatility, mild odor, reduced health risks to workers, and recyclability post-use. Chemists employ various green solvents such as water, ionic liquids, supercritical fluids, and polyethylene glycols. The adoption of these green solvents has significantly advanced the development of environmentally sustainable reactions.

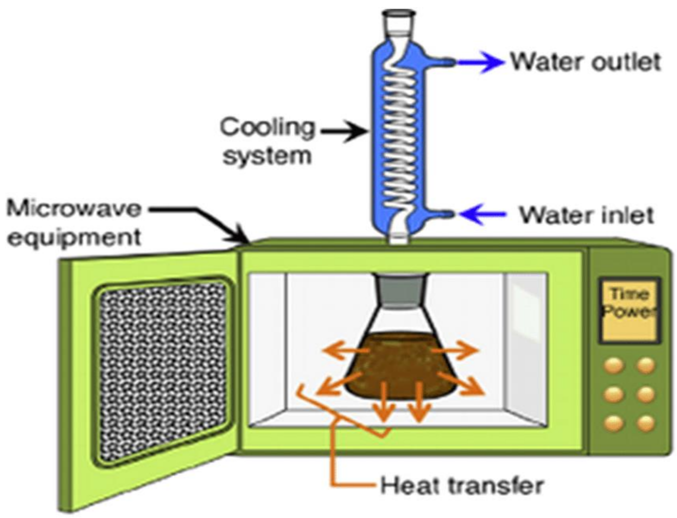


- **Green catalysis** in organic synthesis is a cornerstone of green chemistry, focusing on designing and deploying new catalysts and catalytic systems that simultaneously achieve environmental protection and economic benefits. Catalysis offers numerous advantages in green chemistry, including reduced energy requirements, catalytic efficiency compared to stoichiometric methods, enhanced selectivity, minimized use of processing and separation agents, and the ability to utilize less hazardous materials.

Catalysis is broadly classified into two branches: homogeneous catalysis, where the catalyst and the reaction mixture are in the same phase (typically liquid phase), and heterogeneous catalysis, where the catalyst is in a different phase (solid/liquid or solid/gas/liquid/gas). Homogeneous molecular catalysts offer distinct advantages when operating under optimal conditions, as their active sites are well-separated spatially, akin to enzymatic catalysis.

- **Heterogeneous catalysis**, on the other hand, addresses green chemistry goals by facilitating easy phase separation of products and catalysts. It involves bi-functional phenomena where reactants are activated between support and active phases, thereby obviating the need for separation via distillation or extraction. Environmentally beneficial catalysts like clays and zeolites have the potential to replace more hazardous catalysts currently in use, further advancing the principles of green chemistry.

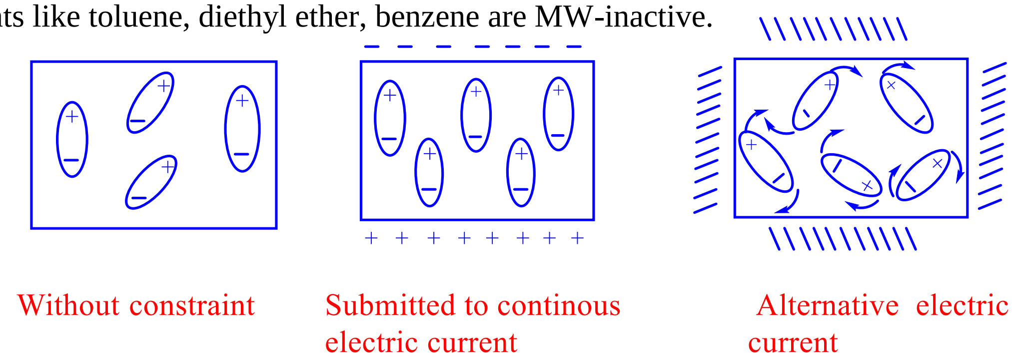
- **A dry media reaction**, also known as a solid-state or solventless reaction, occurs in a chemical system where no solvent is present. In these reactions, the reactants are used either alone or incorporated into materials like clays, zeolites, silica, alumina, or other catalytic substances.
- **Solvent-free reactions** offer clear advantages, including reduced pollution and economic benefits due to simplified experimental procedures, streamlined workup processes, and time savings. These methods contribute to more efficient and environmentally friendly chemical synthesis practices.
- **Alternative energy tool in chemical synthesis** Microwave (MW) radiation, a form of electromagnetic radiation, serves as a prevalent heating source in organic synthesis. Its energy is sufficient to energize the reaction mixture, enabling it to surmount energy barriers and expedite reaction completion in a shorter duration.



Scientific microwave oven

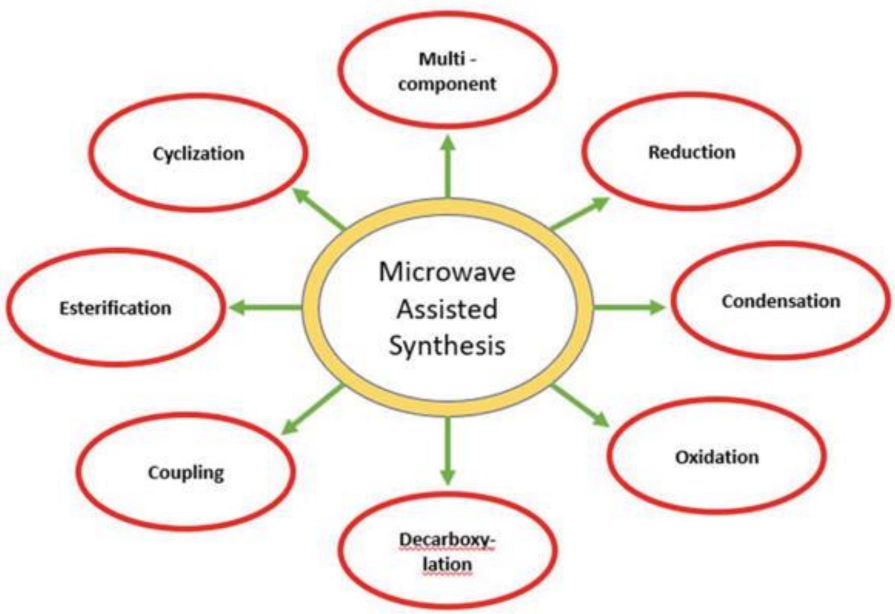
Theory of Microwave Heating- *Dipolar Polarization*

For MW heating to occur the matrix should be dipolar or ionic. Polar solvents e.g. water, DMF, CH_2Cl_2 with a dipole moment, i.e. high dielectric constant are MW-active whereas non-polar solvents like toluene, diethyl ether, benzene are MW-inactive.



In the presence of an electric field - dipole moment tend to align parallel to the applied field by rotation. If the electric field oscillates, the dipole realigns and rotates in respond to the alternate electric field. The molecules are extremely agitated, the molecular friction and collisions give rise to dipolar heating, ~10 ^{0}C per second.

•Note - gases are not microwave active because the rotating molecules are far apart



Various types of Microwave assisted synthesis.

- **Ultrasound irradiations in organic synthesis**

Sonochemistry is recognized as a beneficial approach for conducting organic reactions without the need for solvents. Key advantages of sonochemical techniques include high yields, low energy consumption, minimal waste generation, and the absence of solvent usage. Ultrasound application in chemical reactions within solutions operates on the principle of acoustic cavitation. This phenomenon involves mechanical activation that disrupts the molecular attractive forces in the liquid phase. The study of special effects of ultrasound on chemical synthesisis termed as sonochemistry.

1.4 Limitations of Green Chemistry

While green chemistry offers substantial benefits, it also has its limitations and challenges:

1. **Cost and Economic Viability**: Implementing green chemistry practices and technologies may initially involve higher costs due to the development of new processes, materials, and infrastructure. Companies may hesitate to invest in green alternatives if they perceive them as less economically competitive in the short term.
2. **Technological Barriers**: Developing green chemistry methodologies and replacing conventional processes can pose technical challenges. New catalysts, solvents, and technologies may require extensive research and development to achieve efficiency and scalability comparable to traditional methods.
3. **Education and Training**: Adopting green chemistry requires a shift in mindset and expertise among chemists, engineers, and industry professionals. Training and education in green chemistry principles and practices are crucial but may be lacking or insufficient in some contexts.
4. **Performance and Functionality**: Green alternatives must meet or exceed the performance standards of conventional chemicals and processes. If green products or technologies do not perform as effectively or do not meet regulatory requirements, adoption may be limited.
5. **Regulatory and Policy Frameworks**: Existing regulations and policies may not fully support or incentivize the adoption of green chemistry innovations. Regulatory hurdles,

such as lengthy approval processes for new materials or technologies, can impede progress.

6. **Scale-Up and Integration**: Scaling up green chemistry processes from laboratory to industrial scale can be challenging. Factors such as consistency, reliability, and compatibility with existing infrastructure need to be addressed for widespread adoption.
7. **Consumer Awareness and Demand**: Green chemistry products and processes may not yet be widely recognized or demanded by consumers compared to traditional options. Increasing awareness and understanding of the benefits of green chemistry among consumers can drive market demand.

Addressing these limitations requires collaborative efforts among researchers, industries, policymakers, and consumers to overcome barriers and accelerate the adoption of sustainable and environmentally friendly practices in chemistry.

Summary: Green chemistry focuses on designing chemical processes and products to minimize or eliminate hazardous substances, addressing environmental concerns such as pollution and resource depletion. It is driven by the need to meet regulatory requirements, respond to consumer demand for eco-friendly solutions, and enhance sustainability in chemical practices. The advantages of green chemistry include environmental protection through reduced pollution and resource conservation, improved health and safety by using less toxic substances, and fostering innovation and economic competitiveness in sustainable industries. However, challenges such as higher initial costs, technological complexities in scaling up processes, performance disparities compared to conventional methods, and regulatory and market barriers may hinder its widespread adoption and implementation.

Keywords

Green chemistry: Designing chemical processes and products to minimize hazardous substances and environmental impact while conserving resources.

Need: Addressing environmental concerns, regulatory compliance, and consumer demand for sustainable solutions.

Advantages: Reduced pollution, enhanced resource efficiency, improved health and safety, fostering innovation.

Limitations: Initial costs, technological complexities, performance disparities, regulatory and market barriers.

MCQ

1. **What is the primary goal of green chemistry?**
   - A. Maximizing waste generation
   - B. Minimizing hazardous substances
   - C. Ignoring environmental impact
   - D. Using nonrenewable resources **Answer: B.**
2. **Why is green chemistry necessary?**
   - A. To increase pollution levels
   - B. To comply with regulatory requirements
   - C. To maximize resource depletion
   - D. To use toxic chemicals **Answer: B.**

3. Which of the following is an advantage of green chemistry?

- A. Increased pollution
- B. Reduced resource efficiency
- C. Improved health and safety
- D. Limited innovation **Answer: C.**

4. What is a limitation of green chemistry?

- A. High initial costs
- B. Low regulatory barriers
- C. Simple technological advancements
- D. All of these **Answer D**

Short answer questions

1. Define green chemistry
2. Why we need green chemistry.
3. Write the name of tools of green chemistry
4. Give the limitations of green chemistry

Chapter: 2

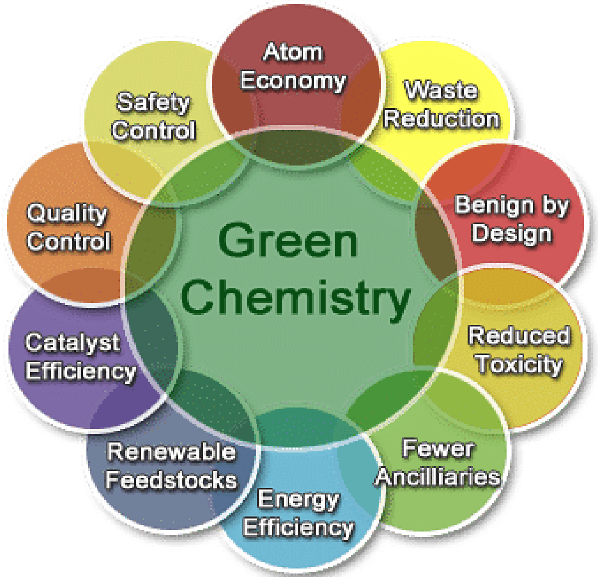
Principles of Green chemistry

Objectives

- Understand how to design chemical processes and products that minimize environmental impact, conserve resources, and support sustainable development goals.
- Learn to develop chemicals and processes that prioritize human health and safety by reducing exposure to hazardous substances.

2.1. Introduction In 1998, Paul Anastas (then leading the Green Chemistry Program at the US EPA) and John C. Warner (formerly of Polaroid Corporation) introduced a set of principles aimed at guiding green chemistry practices. These twelve principles encompass strategies to minimize environmental and health impacts associated with chemical production. They emphasize: Paul Anastas is known as the **Father of green chemistry**

- Optimizing process design to maximize the conversion of raw materials into final products.
- Utilizing renewable feedstocks and energy sources.
- Preferring safe and environmentally benign substances, including solvents.
- Designing processes for energy efficiency.
- Minimizing or eliminating waste production, representing the ideal approach to waste management.



2.2 Twelve Principles of Green Chemistry

Principle 1: Waste prevention

The principle emphasizes that preventing waste is preferable to treating or cleaning it up after it has formed. Therefore, chemical processes should be optimized to minimize waste generation. The environmental factor (E factor) serves as a metric for quantifying the amount of waste generated during a production process, calculated by dividing the mass of waste by the mass of the product obtained. A lower E factor indicates more efficient results. Other methods for assessing waste include comparing the mass of raw materials used to that of the final product.

The Environmental (Mass) Efficiency Factor, or E-factor, is computed as follows:

E-Factor = Total Waste (kg) / Product (kg) equals the E-factor.

Principle 2: Atom Economy

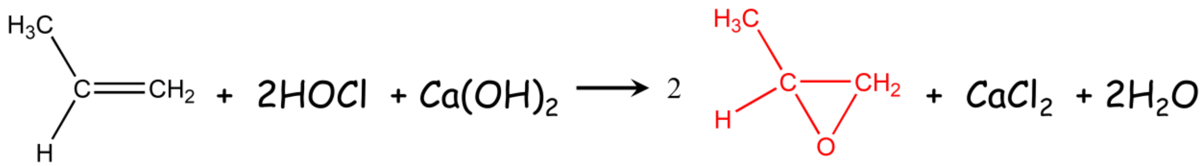
It is among the cornerstones and most significant concepts of green chemistry. The theory behind the atom economy was formulated by B.M. Trost. The quantity of reactants that go straight into the intended result is known as the "atom economy."
It is commonly known as the percentage of atoms utilized. The identical idea, as follows, has also been developed by R. A. Sheldon.

"Synthetic methods should be formulated to maximize the incorporation of all materials used in the process into the final product, minimizing waste generation"

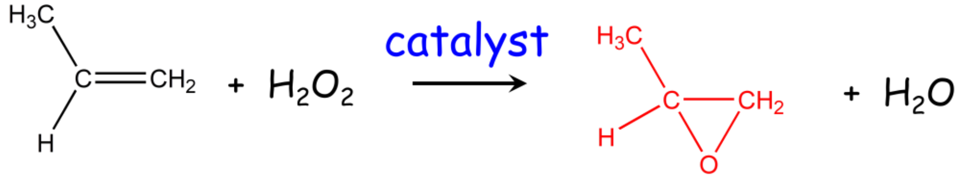
$$\text{Atom economy} = \frac{\text{Mass of desired product}}{\text{Total mass of all products (or reactants)}} \times 100\%$$

The greater the value of the atom economy, the <u>better</u> is the reaction to <u>convert all the reactant</u> atoms to the desired product $\Rightarrow$ Less waste

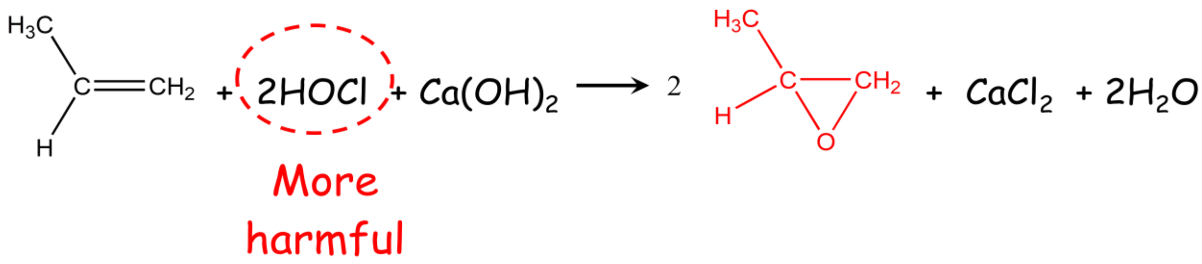
Examples of reactions with their atom economy

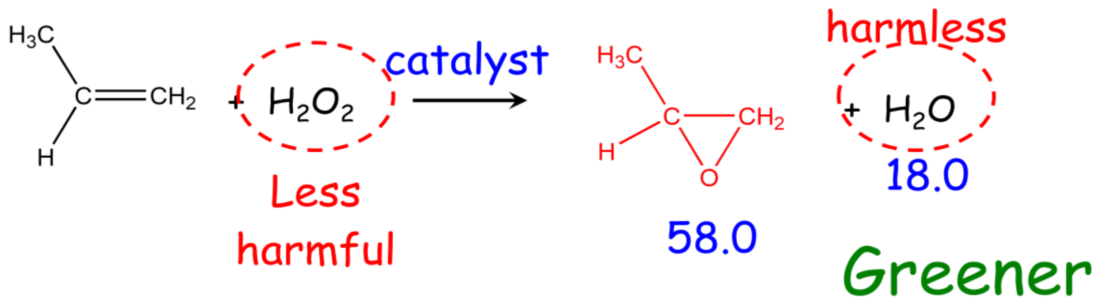


$$AE = \frac{2 \times 58.0}{2 \times 58.0 + 111.0 + 2 \times 18.0} \times 100\% \quad = 44.1\%$$



$$AE = \frac{58.0}{58.0 + 18.0} \times 100\% \quad = 76.3\%$$





Principle 3: Safer syntheses (Synthetic processes should be developed to employ and produce less toxic or non-toxic compounds whenever possible).

Chemists earlier used the chemicals entity as necessary. The green method eliminates the need for everything and favors safer chemicals or reagents. When there are safer substitutes, it is preferable to avoid using and producing harmful substances. It may be problematic to produce harmful wastes in synthesis going forward, which emphasizes the need for safe disposal. If these wastes or primary products are poisonous, workers may be harmed and must be protected, which raises the expense of pollution. The production of polystyrene foam sheet packaging material is a notable example of the employment of safe chemicals; in this case, CO_2 is used as the blooming agent instead of dangerous chlorofluorocarbons, which deplete the ozone layer and contribute to global warming.

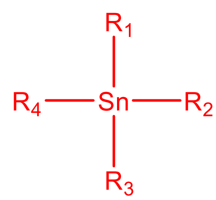
Principle 4: Safer Products

The principle states: "Chemical products should be designed to maintain their efficacy while minimizing toxicity." Achieving this requires deeper understanding of toxicity, knowledge that is often not covered in standard chemistry courses for students.

Advances in chemistry and related sciences have improved our understanding of how chemical structures influence product properties. For instance, this knowledge informs the color of dyes and paints, the amphiphilicity crucial for detergent action, the tensile strength of different fibers, and the non-flammability properties of various fabrics.

To design non-toxic chemicals, it is crucial to understand why certain chemicals exhibit toxicity while others do not, and why some organisms are more susceptible to specific toxic substances than others. Predicting the potential toxicity of a chemical beforehand is essential. Additionally, the dosage of chemicals significantly influences their toxic effects; substances may be harmless in small amounts but toxic above a certain threshold, similar to drug overdoses. Some chemicals accumulate in body fat, necessitating knowledge of their partition coefficient (distribution between lipid and water). Sorting through these factors, among others, is challenging but achievable through gradual progress.

Example; For example, chemicals called organotin compounds (Anti-biofouling agent) were used in large ships to prevent accumulation of barnacles and marine plants traditionally.



The accumulation of barnacles on the ship may increase the resistance to its movement. ‘However, organotin compounds are highly toxic to the surrounding marine life. Then, Rohm and Haas Company developed a non-toxic alternative called Sea-NineTM. It degrades quickly in the marine environment and is not toxic to the surrounding marine life’.

Principle 5: Safer solvents/ auxiliaries

Auxillary chemicals (solvents, separation agents) should be avoided or used sparingly be harmless. In synthetic processes, chemists typically utilize any organic solvent of their choice. These solvents are typically volatile organic solvents (VOCs), which pose a serious threat to the environment since they can cause smog and low-level ozone to form through the oxidation of free radicals in the air. Additionally, they are extremely combustible and have negative effects on humans, such as allergic skin reactions, headaches, and eye irritation. The usage of green alternative solvents has become required as a result of these realities. However, using solvents should be avoided if at all possible. It is essential, advised to use solvents of this type that are inert, have low toxicity, simple to recycle without tainting subsequent goods. The chosen solvent shouldn't be harmful to people's health or the environment. Examples of halogenated solvents that have been linked to cancer include $CHCl_3$ and CCl_4, which can be avoided by using greener alternatives like liquid CO_2, ionic liquids, or water. Immobilized solvents have been used in place of conventional volatile organic compounds to circumvent their issues. These solvents don't harm the environment, retain their solvency, and are non-volatile.

Principle 6: Energy efficiency

Reaction energy requirements should be as low as feasible to avoid negative effects on the environment and the economy. Synthetic procedures ought to be used at room temperature and pressure wherever feasible. The least amount of energy needed for the chemical reactions must be utilized. Since thermal energy is not directed directly at a bond or the molecules undergoing the reaction, it is non-specific and is instead utilized in conjunction with other, more targeted energy sources. Thermal energy is the most widely employed conventional energy source in reactions. These green energy sources include ultrasonic, microwave, and photochemical energy sources.According to this idea, the reactions' energy consumption must be kept to a minimum. There are several approaches to increase the energy efficiency of processes:

(a) Reduce heat and energy losses using well-maintained equipment and good insulation.

(b) Reactants of this type should typically be used for lower temperatures and/or less energy requirement.

(c) It promotes the development of catalysts of this kind that allow processes to operate at lower pressures and temperatures, thereby consuming less energy.

Principle 7: Renewable Feed-stocks

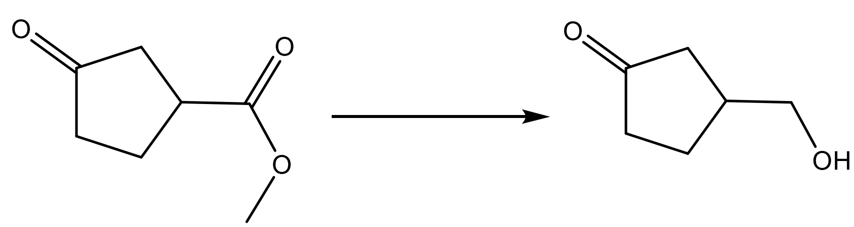
The principle states: "Raw materials or feedstocks should be renewable rather than depleting, whenever technically and economically feasible." Fossil fuels are depletable resources, whereas renewable feedstocks primarily consist of biological materials like plant-based resources.

This principle is closely linked to sustainability, emphasizing the need to ensure resources are available for future generations as we utilize them. Transitioning from petroleum hydrocarbons, which pose environmental challenges, is imperative. For instance, converting petroleum hydrocarbons often involves oxidation catalyzed by toxic metals such as chromium. This illustrates how green chemistry principles are interconnected and cannot be viewed in isolation. Utilizing biological feedstocks holds promise and must meet the requirement of renewability.

Principle 8: Derivative Reduction

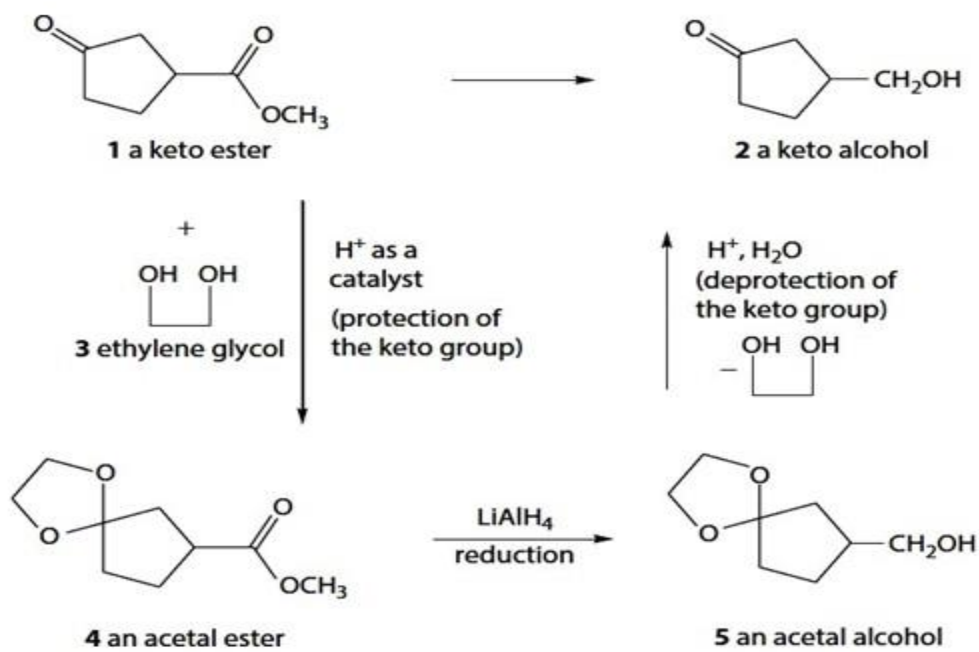
The principle states: "Avoid unnecessary derivatization, such as blocking groups, protection/deprotection, and temporary modifications of physical/chemical processes, whenever feasible."

The derivatization principle is demonstrated with an example from early organic chemistry. Starting with compound 1 containing keto and ester groups, the goal is to produce compound 2 where the ester group is transformed into an alcohol while retaining the keto group.



1 A keto ester **1 a keto alcohol**

Chemists illustrate the derivatization principle with an example from organic chemistry. Starting with compound 1 containing keto and ester groups, the objective is to produce compound 2 where the ester group is converted to an alcohol while preserving the keto group.To achieve this, compound 1 is reacted with ethylene glycol (3) under acidic conditions to form compound 4, where the keto group is protected as an acetal (5), while the ester group remains unchanged. Subsequently, the ester group in compound 5 is reduced to yield alcohol 6 using lithium aluminum hydride ($LiAlH_4$), leaving the acetal group intact. Finally, the acetal group is removed through acid hydrolysis, resulting in the desired product 2.



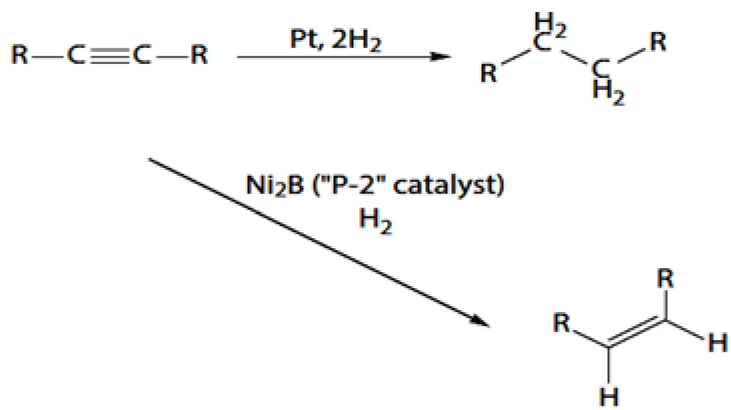
This process demonstrates the sequence of protection, reduction, and deprotection, where the keto group is initially protected to prevent undesired reduction, and later deprotected to expose the ketone functionality.

In this example, for a novice organic chemistry student, the process of protection and deprotection was deemed necessary. However, upon closer examination of the reaction sequence, it becomes evident that there is a poor atom economy due to the waste of ethylene glycol. Alternatively, recycling ethylene glycol would involve extracting it from the aqueous waste and purifying it for reuse, which might not be economically feasible.

Principle 9: Catalysis (Selective catalytic reagents are preferable than stoichiometric reagents.)

The catalytic reagent can be fully recovered because it remains unchanged. All catalysts, including enzymes, reduce the reaction's activation energy, accelerating it millions of times without causing any changes to the reaction. Nonetheless, the specificity of biocatalysts' stereochemistry and chemical selectivity set them apart from all other catalysts. Given the rate of reaction, catalytic specificity, reduced cost, and other advantages over non-biological catalysts, biocatalysts are superior; nonetheless, they have poor stability and lack heat sensitivity. Because they are biodegradable, biocatalysts require less energy. Catachol is a traditional example use as catalytic reagents, catechol synthesis starts with benzene, takes several steps, and has extreme reaction conditions that result in undesirable byproducts. Nevertheless, the biocatalytic approach uses Escherchia coli to synthesize catechol from glucose in a single step, is commercially feasible, and produces no byproducts.

Catalytic selectivity is valuable in numerous fundamental chemical reactions familiar to students. An example is depicted in the figure below.



Selectivity in hydrogenation of unsaturated hydrocarbons

Principle 10: Degradability

Chemical products synthesized their useful to environment and decompose into harmless degradation products. The synthesized moieties must be able to transform into final products that are not harmful. In general, a lot of synthetic products are created that do not break down when they are finished using them. Therefore, it is necessary to create a product that degrades naturally; otherwise, it would linger in the environment, be ingested by plants or animals, and build up inside their biosystems, which would be harmful to the affected species. For instance, the organochlorine class of insecticides, which includes DDT, is not biodegradable and poses serious health risks. As a result, a product should be made so that it breaks down in the environment into harmless materials. Groups and other characteristics can now be included into molecules to speed up their breakdown. The biodegradable, functional groups that are vulnerable to hydrolysis, photolysis, or other potential modifications have been employed.

Principle 11. Real time analysis for pollution control

It is necessary to create analytical technologies that will enable the reduction and prevention of hazardous waste formation. In order to evaluate the risks that are present in the process stream, one needs precise and trustworthy sensors, monitors, and procedures. It is possible to monitor a process for the production of dangerous byproducts and side reactions using a variety of ways.

Principle 12. Inherently safer chemistry to control accidents: When selecting substances for a chemical process, care should be taken to reduce the risk of chemical accidents such as leaks, explosions, and fires. According to this theory, less of these chemicals should be used in chemical reactions that have the potential to go wrong (explosion, fire, and hazardous vapor). As far as possible, accidents, fires, and explosions should be prevented. Because solvents are used so frequently in organic chemistry labs, it is thought that these volatile organic compounds (VOCs) can catch fire easily. It is important to remember that accidents like the Bhopal gas tragedy shouldn't occur when studying chemistry.

Summary: The 12 principles of green chemistry provide a comprehensive framework for developing sustainable chemical practices. These principles advocate for minimizing environmental impact, reducing waste, and enhancing safety throughout the lifecycle of chemical products and processes. They emphasize prevention of waste generation, maximizing atom economy by efficiently using raw materials, and selecting safer chemicals and solvents. Energy efficiency is promoted through optimized processes, while renewable feedstocks are preferred to diminish reliance on finite resources. Reduction of unnecessary derivatization steps and utilization of catalysis further minimize waste and enhance efficiency. Chemical products should be designed for degradation after use to prevent persistent environmental harm. Real-time pollution monitoring and safer design strategies mitigate risks of accidents and hazardous conditions. Collectively, these principles guide the chemical industry towards sustainable practices that support environmental stewardship and ensure the well-being of current and future generations.

Keywords

Green Chemistry: safe and environmental friendly chemistry.

Atom Economy: Maximize the incorporation of all materials used in a chemical process into the final product.

Prevention: Design processes to prevent waste generation by using efficient methods and minimizing by-products.

Catalysis: Use catalytic processes to increase efficiency, reduce waste, and minimize energy requirements.

MCQ

1. Which principle of green chemistry emphasizes designing processes to prevent waste generation?

A. Atom Economy

B. Prevention

C. Renewable Feedstocks

D. Design for Degradation **Answer:** B.

2. The principle of maximizing atom economy aims to:

A. Minimize waste generation

B. Use renewable feedstocks

C. Design safer chemicals

D. Enhance energy efficiency **Answer:** A.

3. Which principle advocates for using safer chemicals and solvents whenever possible?

A. Safer Solvents and Auxiliaries

B. Design Safer Chemicals

C. Use of Renewable Feedstocks

D. Real-time Analysis for Pollution Prevention **Answer:** B.

4. Catalysis in green chemistry primarily aims to:

A. Maximize atom economy

B. Reduce derivatives

C. Design for degradation

D. Increase efficiency and reduce waste **Answer:** D.

5. Which principle encourages the use of renewable resources as raw materials?

A. Use of Renewable Feedstocks

B. Real-time Analysis for Pollution Prevention

C. Safer Chemistry for Accident Prevention

D. Design for Energy Efficiency **Answer:** A.

Short Answer Questions

1. Explain the principle of "Prevention" in green chemistry.
2. What does "Atom Economy" mean in the context of green chemistry?
3. How does green chemistry promote the use of "Renewable Feedstocks"?
4. What is meant by "Design for Degradation"?
5. Discuss the principle of "Safer Chemistry for Accident Prevention".

Chapter: 3

Green Chemistry in Real World Cases

Objectives:

- Green chemistry seeks to minimize pollution by preventing waste generation rather than treating it after it's formed.
- Green chemistry prioritizes the safety of chemical products and processes for workers, consumers, and the environment.
- Fosters innovation in chemical design and manufacturing methods and Developing plastics from renewable resources like corn
- Development of Fully Recyclable Carpet and catalytic processes that require less energy and produce fewer by-products

3.1 Introduction:

Green chemistry, also known as sustainable chemistry, is increasingly important in addressing environmental and health concerns associated with traditional chemical processes. Here are some notable real-world cases where green chemistry principles have been successfully applied:

1. **Benign Solvents in Pharmaceutical Manufacturing**: Pharmaceutical companies have adopted green chemistry by replacing traditional solvents with safer, less toxic alternatives. For example, Pfizer developed a more environmentally friendly synthesis of the drug Zoloft by using water as a solvent instead of hazardous organic solvents.
2. **Catalytic Converters in Automobiles**: Catalytic converters use precious metals like platinum, palladium, and rhodium to convert harmful pollutants in exhaust gases into less harmful ones. This technology has significantly reduced air pollution from vehicles worldwide.
3. **Biofuels Production**: Green chemistry plays a crucial role in the production of biofuels such as biodiesel and bioethanol. These fuels are derived from renewable resources like agricultural crops and algae, offering a more sustainable alternative to fossil fuels.
4. **Water Purification Technologies**: Green chemistry principles are employed in developing water purification technologies that remove pollutants without generating

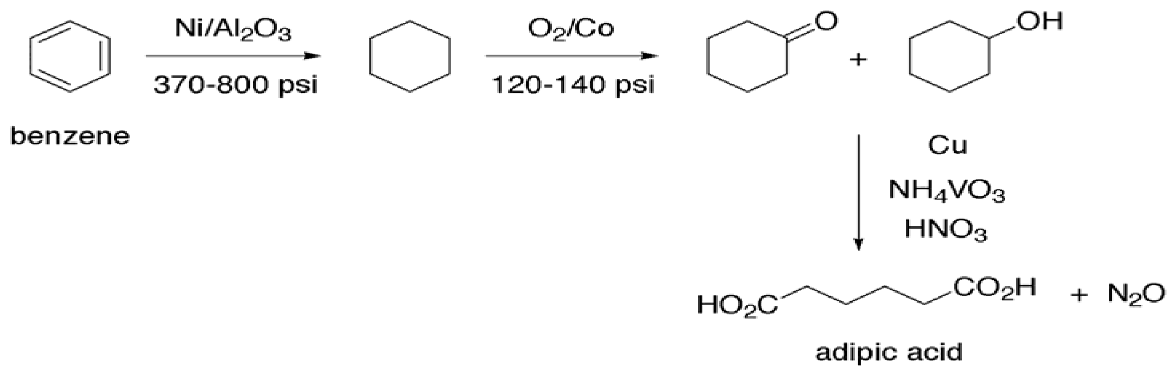
additional harmful by-products. For instance, advanced oxidation processes (AOPs) use hydrogen peroxide and UV light to break down contaminants in water.

5. **Green Nanotechnology**: Nanotechnology applications are being developed with green chemistry in mind to minimize environmental impacts. For example, researchers are working on nanomaterials for efficient water filtration and remediation of contaminated sites.
6. **Detergents and Cleaning Products**: Companies have reformulated detergents and cleaning products to use more biodegradable and environmentally friendly ingredients. This reduces the environmental impact of these products throughout their lifecycle.
7. **Renewable Energy Technologies**: Green chemistry is integral to the development of renewable energy technologies such as solar cells and wind turbines. For example, researchers are exploring greener methods to synthesize materials used in photovoltaic cells.
8. **Green Packaging Solutions**: Innovations in packaging materials focus on using biodegradable and recyclable materials. Companies are also reducing packaging waste through efficient design and recycling programs.
9. **Agrochemicals and Pesticides**: Green chemistry principles are applied to develop safer and more selective pesticides and fertilizers that minimize environmental impact and reduce exposure risks to non-target organisms.
10. **Textile Industry**: Sustainable practices in the textile industry include using natural dyes, reducing water and energy consumption in manufacturing processes, and developing biodegradable fibers.

3.2 Green Synthesis of the Compounds:

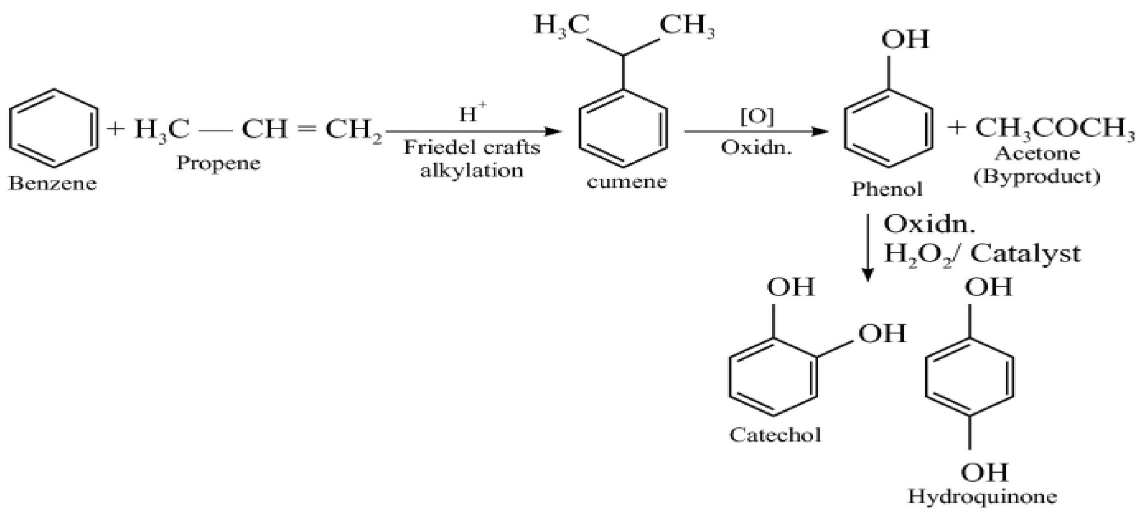
3.2.1 Green Synthesis of adipic Acid:

Green synthesis of adipic acid typically involves methods that minimize waste, reduce energy consumption, and use environmentally benign starting materials and reagents. Adipic acid is traditionally synthesized from petrochemical-derived precursors like benzene, butadiene, or cyclohexane through multi-step processes involving harsh conditions and generating significant waste. Green chemistry aims to address these issues.



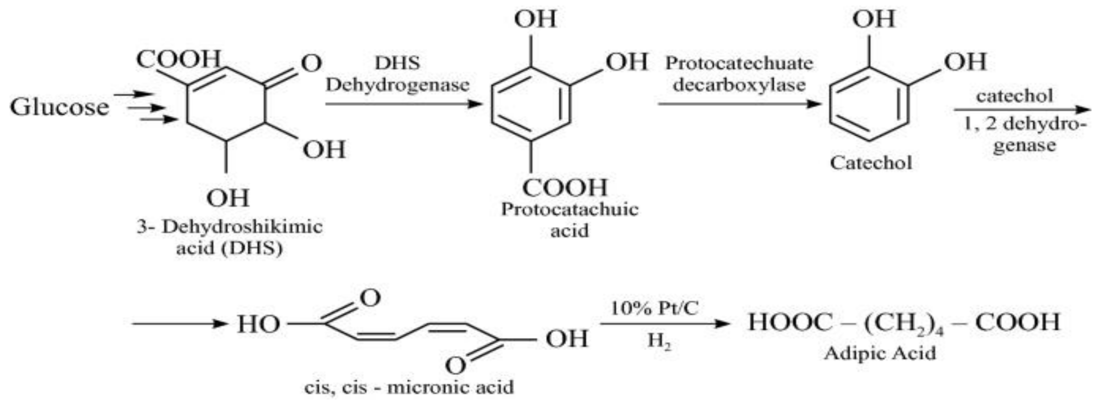
3.2.2 Green Synthesis of catechol:

Green synthesis of catechol involves methods that prioritize sustainability, minimize waste, and use environmentally friendly reagents and conditions. Catechol (1,2-dihydroxybenzene) is a compound of interest due to its applications in various fields including pharmaceuticals, cosmetics, and materials science. Here are some approaches to achieve green synthesis of catechol:



3.2.3 Green Synthesis of disodium iminodiacetate (alternative to Strecker synthesis):

Disodium iminodiacetate (IDA) is a compound used in various applications including as a chelating agent and in pharmaceuticals. The traditional Strecker synthesis of IDA involves the reaction of glycine with formaldehyde and ammonia, followed by oxidation and hydrolysis steps. Green synthesis of disodium iminodiacetate aims to achieve similar results using environmentally benign starting materials, mild conditions, and minimizing waste. Here are some approaches to consider:



3.3 Surfactants for carbon dioxide:

Using surfactants with carbon dioxide (CO2) as a solvent represents an innovative approach in the field of precision cleaning and dry cleaning of garments. This method replaces traditional solvents that contribute to smog formation and ozone depletion with a more environmentally friendly alternative. Here's an overview of how surfactants can be utilized in CO2-based cleaning processes:

3.3.1 CO_2 as a Solvent:

Carbon dioxide in its supercritical state (scCO_2) or as a near-critical fluid is an attractive solvent due to several key properties:

- **Environmental Benefits**: CO_2 is non-toxic, non-flammable, and readily available as a byproduct of various industrial processes. Its use as a solvent reduces the emission of volatile organic compounds (VOCs) and greenhouse gases compared to traditional solvents.
- **Efficiency**: CO_2 has tunable solvent properties depending on pressure and temperature, making it suitable for a wide range of applications from cleaning to extraction and beyond.

3.3.2 Surfactants in CO_2 Cleaning:

Surfactants play a crucial role in enhancing the solubility of non-polar substances in CO2, thereby improving the cleaning efficacy. Here's how surfactants are integrated into CO2 cleaning processes:

1. **Cleaning Mechanism**:

   Surfactants are amphiphilic molecules that have both hydrophobic (non-polar) and hydrophilic (polar) regions. In CO_2 cleaning, they can adsorb onto the surfaces of non-polar contaminants (such as oils and greases on garments) and facilitate their solubilization in CO_2.

2. **Enhanced Removal Efficiency**:

   Surfactants help to reduce the surface tension of CO_2, allowing it to penetrate and dissolve contaminants more effectively. This improves the cleaning efficiency and ensures thorough removal of soils from garments.

3. **Types of Surfactants**:

   Surfactants used in CO_2 cleaning include fluorinated surfactants, silicone-based surfactants, and other specialty formulations designed to optimize cleaning performance without compromising environmental safety.

Precision Cleaning Applications:

- **Industrial Cleaning**: CO2-based cleaning with surfactants is widely used in precision cleaning of delicate components in electronics, aerospace, and medical device manufacturing where residue-free cleaning is critical.
- **Garment Dry Cleaning**: CO2-based dry cleaning offers a greener alternative to traditional solvent-based methods (e.g., perchloroethylene). Surfactants enable effective removal of oils, dirt, and stains from fabrics while maintaining fabric integrity and color vibrancy.

Benefits:

- **Environmental Sustainability**: Reduced emissions of VOCs and greenhouse gases compared to traditional solvents contribute to sustainable practices in cleaning processes.
- **Safety**: CO2 is non-toxic and non-flammable, providing a safer working environment for operators compared to flammable and hazardous solvents.
- **Quality of Cleaning**: Surfactants enhance cleaning efficacy and ensure that garments and components are cleaned thoroughly without leaving residues or compromising material integrity.

3.4 Designing of Environmentally safe marine antifoulant:

Designing environmentally safe marine antifoulants involves creating coatings or treatments that prevent the attachment of marine organisms to ship hulls and marine structures without causing harm to the marine environment. Traditional antifoulants often contain toxic biocides that can leach into the water, posing risks to marine life and ecosystems. Here are key considerations and strategies for designing environmentally safe marine antifoulants:

Principles for Environmentally Safe Marine Antifoulants:

1. **Non-Toxicity to Marine Life**:
   - Use of non-toxic or low-toxicity materials that do not harm marine organisms, including fish, mollusks, crustaceans, and algae.
2. **Biodegradability**:
   - Materials should be biodegradable, breaking down into harmless components in the marine environment over time.
3. **Minimal Environmental Impact**:
   - Antifoulants should not contribute to bioaccumulation or persist in the marine food chain.
4. **Efficient Fouling Prevention**:
   - Effective prevention of biofouling to reduce drag and fuel consumption without relying on toxic biocides.

Strategies for Designing Environmentally Safe Marine Antifoulants:

1. **Physical Barrier Coatings**:
   - Develop non-toxic coatings with smooth surfaces or micro-textures that discourage attachment of marine organisms. Examples include silicone-based or fluoropolymer coatings.
2. **Natural Products and Bio-Based Materials**:
   - Utilize natural products or bio-based polymers that have inherent antifouling properties. For example, compounds derived from marine organisms or natural oils.
3. **Surface Modification**:

    - Modify surfaces with anti-adhesive coatings or incorporate nanostructured materials that inhibit fouling attachment.
4. **Photocatalytic Materials**:
    - Use photocatalytic materials such as titanium dioxide (TiO_2) that, when exposed to sunlight, produce reactive oxygen species that deter fouling organisms.
5. **Release of Repellent Agents**:
    - Develop coatings that release non-toxic repellent agents or compounds that interfere with the settlement of fouling organisms.
6. **Controlled Release Systems**:
    - Implement controlled release mechanisms for antifouling agents, ensuring they are effective over extended periods while minimizing environmental impact.
7. **Testing and Regulation**:
    - Conduct rigorous testing to evaluate the effectiveness and environmental safety of antifoulants before commercial use. Adhere to regulatory guidelines and standards governing marine coatings and antifouling products.

Environmental and Economic Benefits:

- **Reduced Environmental Footprint**: Environmentally safe antifoulants contribute to cleaner marine ecosystems and protect biodiversity.
- **Cost Savings**: By reducing the need for frequent hull cleaning and repainting, these antifoulants can lower maintenance costs for ship owners and operators.

Challenges:

- **Durability**: Ensuring that environmentally safe antifoulants maintain their effectiveness over extended periods under various marine conditions.
- **Regulatory Compliance**: Meeting stringent regulatory requirements for marine coatings and antifoulants in different regions and jurisdictions.

In conclusion, designing environmentally safe marine antifoulants involves leveraging innovative materials and strategies to achieve effective fouling prevention while safeguarding marine ecosystems. By prioritizing non-toxicity, biodegradability, and efficiency, these antifoulants can contribute to sustainable maritime practices and ocean conservation efforts.

3.5 Rightfit pigment:

Developing "Rightfit Pigment," which are synthetic azo pigments aimed at replacing toxic organic and inorganic pigments, involves creating colorants that are safe, environmentally friendly, and perform comparably or better than traditional pigments. Here’s how the development and characteristics of such pigments can be approached:

2.5.1 Characteristics of Rightfit Pigment:

1. **Non-Toxicity**:
   - Rightfit Pigments should be free from heavy metals such as lead, cadmium, and chromium, which are common in many inorganic pigments and pose environmental and health risks.
2. **Environmental Safety**:
   - These pigments should not contribute to pollution or harmful effects on ecosystems during production, use, or disposal.
3. **Color Stability**:
   - They should exhibit good color stability, resistance to fading, and compatibility with various applications such as paints, coatings, plastics, and textiles.
4. **Performance**:
   - Rightfit Pigments should offer comparable or superior performance characteristics to the pigments they are intended to replace, including color strength, opacity, dispersion properties, and durability.
5. **Regulatory Compliance**:
   - Adherence to regulatory standards and certifications (such as REACH in Europe or EPA guidelines in the US) for safety and environmental impact is crucial.

3.5.2 Strategies for Developing Rightfit Pigment:

1. **Synthesis of Azo Pigments**:
   - Azo pigments are synthesized from diazonium salts and coupling components. Focus on developing azo dyes that are structurally stable, economically viable, and environmentally benign.
2. **Substitution of Toxic Components**:

- Replace toxic metal components (like lead and chromium) with safer alternatives without compromising color intensity or performance.

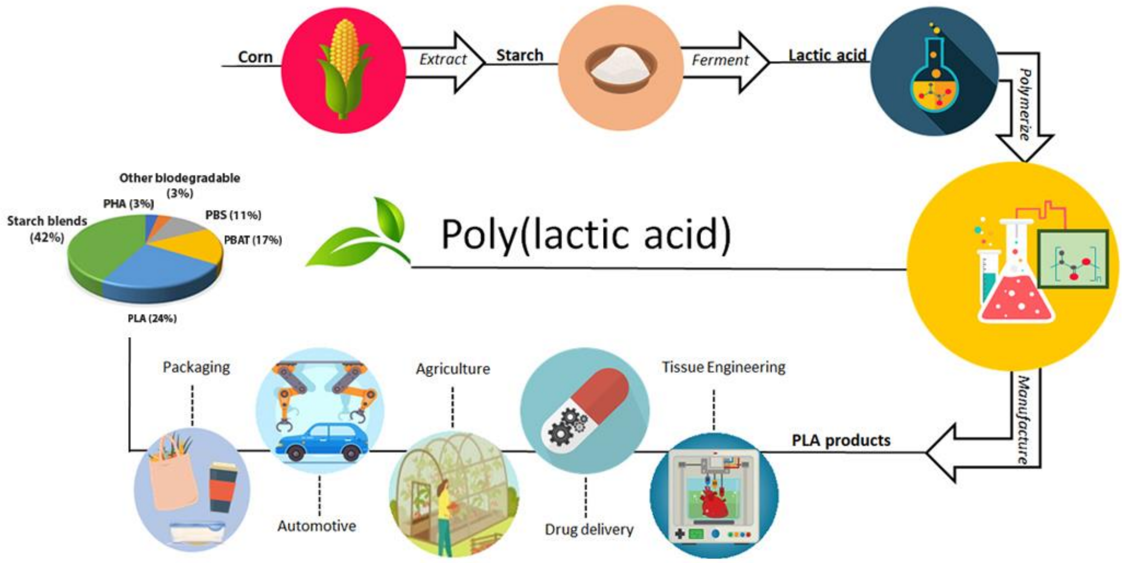
3. **Biodegradability**:
    - Design pigments that are biodegradable under natural environmental conditions, reducing persistence in the environment.
4. **Surface Modification**:
    - Incorporate surface modifications or coatings to enhance pigment dispersion, stability, and compatibility with different media.
5. **Testing and Validation**:
    - Conduct thorough testing for color fastness, chemical stability, lightfastness, and toxicity to ensure the pigments meet industry standards and customer expectations.

3.5.3 Benefits of Rightfit Pigment:

- **Environmental Sustainability**: By eliminating toxic elements, Rightfit Pigments contribute to reducing environmental impact and improving eco-friendliness in various industries.
- **Health Safety**: Workers and consumers are protected from exposure to harmful substances, enhancing safety in production, application, and use.
- **Market Acceptance**: Increasing demand for eco-friendly and sustainable products drives market acceptance and adoption of Rightfit Pigments.

3.6 An Efficient, Green Synthesis of a Compostable and Widely Applicable Plastic (Poly Lactic Acid) Made from Corn:

Poly lactic acid (PLA) is a biodegradable and compostable plastic derived from renewable resources such as corn starch or sugarcane. Developing an efficient and green synthesis of PLA involves several key steps and considerations to ensure sustainability and environmental friendliness throughout the manufacturing process:



3.7 Healthier Fats and oil by Green Chemistry:

Green chemistry principles can be applied to the production and processing of fats and oils to enhance their health benefits, reduce environmental impact, and improve overall sustainability. Here's how green chemistry can contribute to creating healthier fats and oils:

1. Sustainable Sourcing of Raw Materials:

- **Renewable Resources**: Utilize oils and fats derived from sustainable and renewable sources such as plant-based oils (e.g., soybean, sunflower, olive) and animal fats (from responsibly managed livestock).
- **Non-GMO and Organic**: Opt for non-genetically modified (non-GMO) and organic sources to ensure minimal environmental impact and support sustainable agricultural practices.

2. Green Extraction and Refining Processes:

- **Supercritical Fluid Extraction**: Use supercritical CO2 or other green solvents for extracting oils from seeds and nuts. This method avoids the use of toxic solvents and minimizes environmental footprint.
- **Cold Pressing**: Implement cold pressing techniques to extract oils from seeds at low temperatures, preserving natural antioxidants and nutrients.

- **Green Refining Methods**: Develop or adopt refining processes that minimize energy consumption, waste generation, and the use of chemicals. Techniques such as enzymatic refining and membrane filtration are examples of green alternatives.

3. Modification for Healthier Profiles:

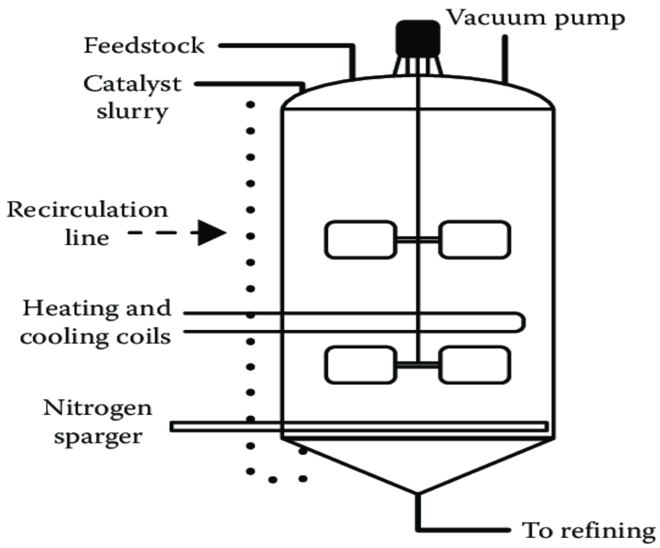
- **Trans-Fat Elimination**: Employ hydrogenation processes that eliminate trans-fats, using safer hydrogenation catalysts and optimizing reaction conditions to reduce or eliminate formation of trans-fatty acids.
- **Omega-3 Enrichment**: Incorporate sustainable sources of omega-3 fatty acids (e.g., algae-based oils) into edible oils through environmentally friendly extraction and enrichment processes.
- **Low-Saturated Fat Content**: Modify oils to reduce saturated fat content while maintaining stability and functionality through enzymatic interesterification or fractionation processes.

4. Waste Minimization and Valorization:

- **By-Product Utilization**: Explore opportunities to utilize by-products from oil refining processes for biofuel production, animal feed, or other value-added applications to minimize waste.
- **Recycling and Circular Economy**: Design processes that promote recycling of used cooking oils and fats into biodiesel or other renewable products, contributing to a circular economy approach.

5. Environmental and Health Benefits:

- **Reduced Environmental Footprint**: Green chemistry practices reduce energy consumption, greenhouse gas emissions, and hazardous waste generation associated with traditional oil processing methods.
- **Improved Nutritional Profiles**: Healthier fats and oils contribute to improved dietary choices, supporting public health initiatives aimed at reducing cardiovascular disease and obesity rates.



3.8 Development of Fully Recyclable Carpet:

Developing a fully recyclable carpet involves integrating sustainable materials, innovative design, and recyclable technologies to minimize environmental impact and promote circular economy principles. Here's a structured approach to the development of such a product.

1. Material Selection:

- **Recyclable Fibers**: Choose synthetic or natural fibers that are easily recyclable at end-of-life. Examples include polyethylene terephthalate (PET) from recycled plastic bottles, nylon, or wool sourced from sustainable practices.
- **Backing Materials**: Select eco-friendly backing materials that enhance recyclability, such as thermoplastic polyolefins (TPO) or other recyclable polymers.

2. Design for Disassembly:

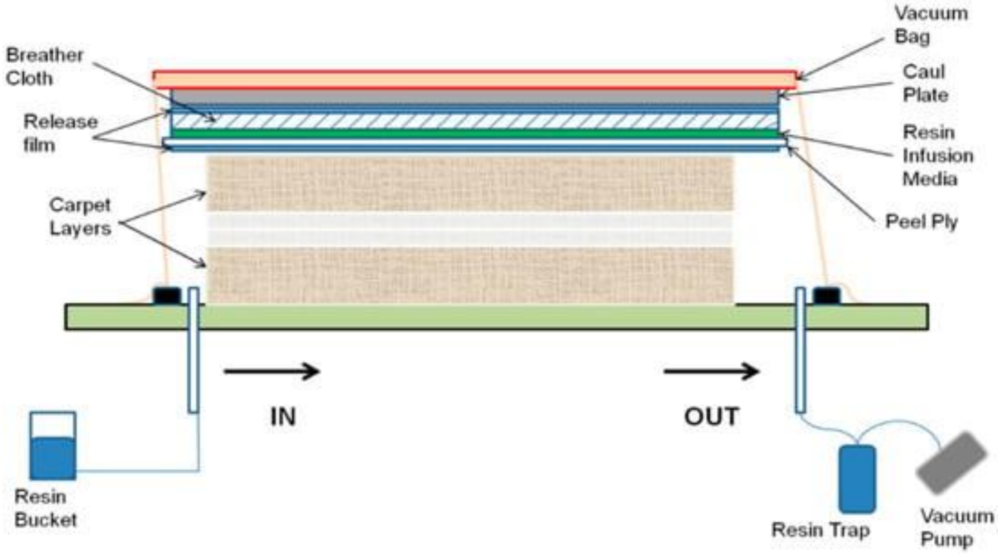
- **Modular Design**: Implement modular carpet tiles rather than broadloom carpets. Modular tiles are easier to replace, repair, and recycle individually, reducing waste.
- **Separable Components**: Ensure that carpet layers (fibers, backing, adhesives) can be easily separated and recycled at the end of their lifecycle.

3. Manufacturing Processes:

- **Low-Energy Production**: Optimize manufacturing processes to minimize energy consumption and greenhouse gas emissions.
- **Water Conservation**: Implement water-efficient practices during dyeing and finishing processes.

4. Recycling Technologies:

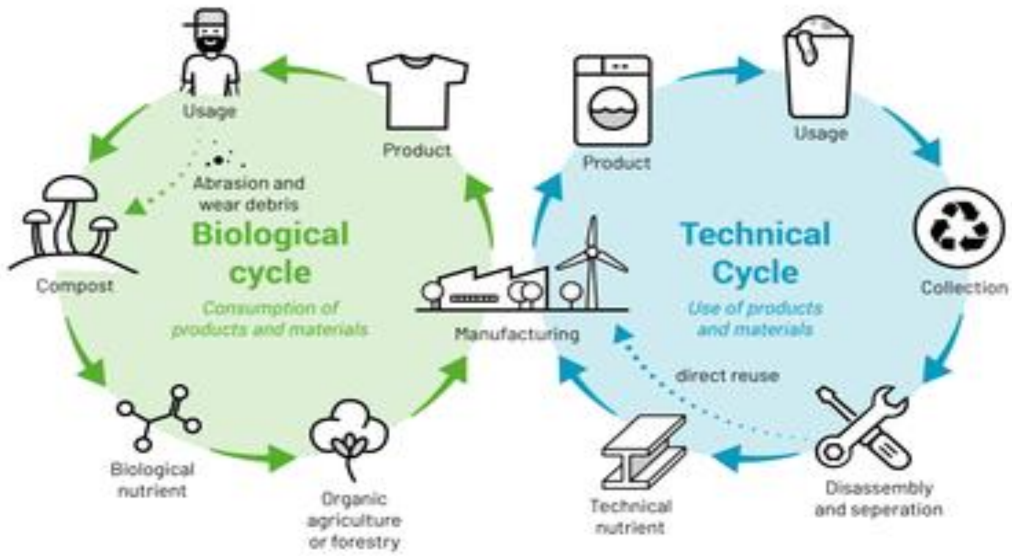
- **Closed-Loop Recycling**: Partner with recyclers equipped with advanced technologies to recycle materials into new carpet or other products.
- **Upcycling Initiatives**: Explore opportunities for upcycling carpet materials into other products, such as insulation, automotive parts, or new fibers.



By focusing on these strategies, manufacturers can develop fully recyclable carpets that minimize environmental impact, conserve resources, and contribute to a circular economy. This approach aligns with the principles of green chemistry by prioritizing sustainability and reducing the environmental footprint of carpet production and disposal.

Cradle to Cradle (C2C):

Cradle to Cradle (C2C) carpeting represents a holistic approach to carpet design and manufacturing that emphasizes sustainability, recyclability, and environmental responsibility throughout the product lifecycle. Here's an overview of what Cradle to Cradle carpeting entails and how it differs from traditional carpeting:



Principles of Cradle to Cradle Design:

1. **Material Health**:
   - **Safe Materials**: Select materials that are safe and non-toxic for humans and the environment. This includes avoiding substances of concern such as heavy metals, formaldehyde, and phthalates.
   - **Biodegradability**: Use materials that can safely biodegrade or be perpetually recycled without loss of quality.
2. **Material Reutilization**:
   - **Recyclable Materials**: Design carpets using materials that can be easily disassembled and recycled into new products at the end of their use.
   - **Closed-Loop Systems**: Aim for a closed-loop system where materials are continuously recycled and reintegrated into the manufacturing process.
3. **Renewable Energy and Carbon Management**:
   - **Energy Efficiency**: Optimize manufacturing processes to minimize energy consumption and utilize renewable energy sources wherever possible.
   - **Carbon Footprint Reduction**: Reduce greenhouse gas emissions associated with carpet production and transportation.
4. **Water Stewardship**:

- Implement water-efficient practices during manufacturing, such as recycling and reusing water, and ensuring wastewater is treated effectively.

5. **Social Fairness**:
    - Ensure fair labour practices throughout the supply chain, promoting worker safety, fair wages, and community engagement.

Cradle to Cradle process represents a paradigm shift towards sustainable and regenerative design, aiming to create products that contribute positively to human health, environmental quality, and economic prosperity throughout their lifecycle.

Summary:

This chapter replaces conventional solvents with CO_2-based surfactants for precision cleaning and dry cleaning, reducing smog and ozone-depleting emissions, and promoting environmental and worker safety. Develops coatings using green chemistry principles to prevent marine organism attachment without harmful environmental impacts, maintaining marine ecosystem health.Synthetic azopigments replace toxic organic and inorganic pigments, ensuring minimal environmental impact throughout their lifecycle, from production to disposal. Uses corn-based feedstocks and green catalysts to produce PLA, a compostable plastic, reducing reliance on fossil fuels and promoting biodegradability. Enzymatic interesterification creates fats and oils without trans-fats, using enzymes as catalysts to improve health benefits and reduce environmental impact compared to traditional hydrogenation methods. Designs carpets using Cradle to Cradle principles, ensuring materials are recyclable at the end of their lifecycle, minimizing waste and promoting resource conservation in the carpet industry.

Keywords:

Green Synthesis: Green synthesis refers to the development of chemical processes and methods that prioritize sustainability, efficiency, and environmental stewardship.

Safe marine antifoulant: Marine antifoulants are coatings or treatments applied to the hulls of ships and marine structures to prevent the attachment and growth of organisms

Healthier Fats and oil by Green Chemistry: Green chemistry principles can be applied to the production and modification of fats and oils to enhance their health profile.

MCQ

Q.1 Which of the following methods is typically used in green synthesis of adipic acid?
A. Nitric acid oxidation
B. Hydrogen peroxide oxidation
C. Chlorosulfonic acid oxidation
D. Sulfuric acid oxidation **Answer: B**

Q.2 Azo pigments are synthesized through a reaction between:

A. An amine and an alcohol
B. An amine and a carboxylic acid
C. A diazonium salt and a phenol
D. A diazonium salt and an aromatic amine **Answer:** D

Q.3 Green chemistry principles aim to improve the health profile of fats and oils by:

A. Increasing trans fats content
B. Minimizing the use of renewable feedstocks
C. Reducing the use of synthetic antioxidants
D. Enhancing the use of toxic solvents **Answer:** C

Q.4 What is the primary goal of developing fully recyclable carpet?

A. To increase manufacturing costs
B. To enhance carpet durability
C. To reduce environmental impact
D. To improve carpet aesthetics **Answer:** C.

Q.5 Enzymatic interesterification is used in the food industry to produce:
A. Hydrogenated fats
B. Trans-fats
C. Saturated fats
D. No trans-fats and oils **Answer: D**

Short Answer Question:

1. How do surfactants used with carbon dioxide (CO_2) contribute to green chemistry practices in precision cleaning and dry cleaning of garments?
2. Discuss the environmental and health benefits of using synthetic azopigments like Rightfit to replace toxic organic and inorganic pigments in various industries.
3. Discuss the environmental advantages and challenges associated with the efficient, green synthesis of poly lactic acid (PLA) made from corn.
4. Explain Cradle to Cradle Carpeting.
5. Discuss Inter esterification for production of no Trans-Fats and Oils.

Chapter: 4
Microwave and Ultrasound Assisted Reactions

OBJECTIVES:

- Accelerate reaction rates
- Enhance yield and selectivity
- Reduce energy consumption and solvent usage
- Explore new reaction pathways
- Facilitate scale-up to industrial applications

4.1 Introduction

Microwave-assisted reactions in water have gained significant attention in recent years due to several advantages over conventional methods.Microwave irradiation selectively heats polar molecules like water and certain reactants, promoting rapid and uniform heating of the reaction mixture. This accelerates reaction rates and can lead to higher yields compared to conventional heating methods.

Overall, microwave-assisted reactions in water combine the advantages of green chemistry with the rapid heating capabilities of microwave irradiation, making them a promising approach for sustainable and efficient synthetic chemistry applications.

4.2Microwave assisted reactions in water:

Microwave-assisted reactions in water offer several advantages in synthetic chemistry, particularly in the context of green and sustainable chemistry practices. Here's an overview of the benefits and considerations when employing microwave-assisted reactions in aqueous environments

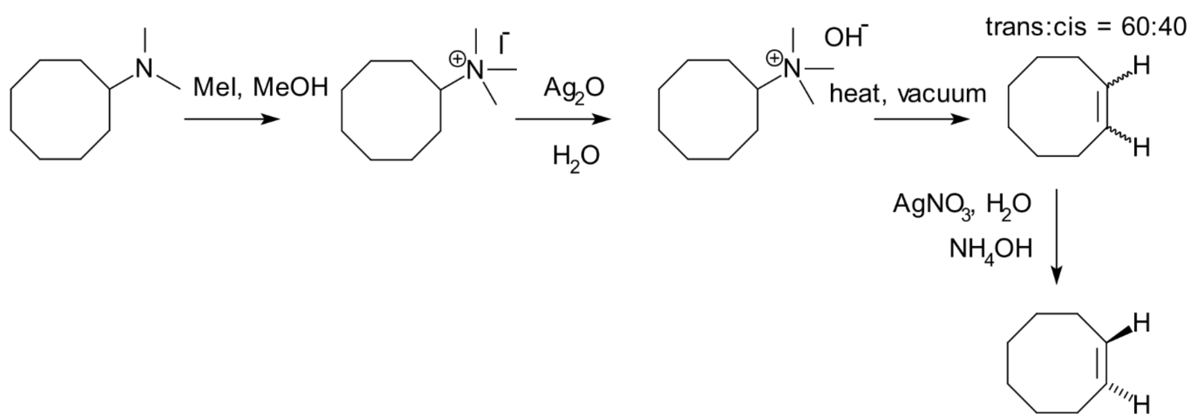
1. **Energy Efficiency**:
    - **Rapid Heating**: Microwaves penetrate the reaction mixture and directly heat the molecules, leading to faster reaction rates compared to conventional heating methods.

- **Reduced Reaction Time**: Reactions that typically take hours or days can often be completed in minutes under microwave irradiation, saving energy and increasing productivity.

2. **Improved Yield and Selectivity**:
    - The controlled and uniform heating provided by microwaves can improve the yield and selectivity of reactions by minimizing side reactions and enhancing reaction pathways.
3. **Reduced Solvent Use**:
    - Aqueous environments are inherently greener than organic solvents due to their lower environmental impact and reduced toxicity. Microwaves can facilitate reactions even in water, reducing or eliminating the need for organic solvents altogether.

4.2.1 Hofmann Elimination:

Hofmann elimination is a classic organic chemistry reaction that involves the removal of an amine group (–NR2) from a quaternary ammonium salt to form an alkene. Here's a detailed overview of Hofmann elimination:

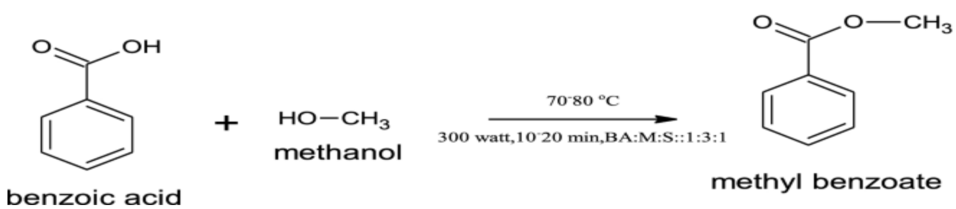


4.2.2 Methyl benzoate to benzoic acid:

Microwave-assisted reactions in water can be effectively used to convert methyl benzoate to benzoic acid. This reaction can be achieved under mild conditions with good efficiency, making it suitable for green and sustainable chemistry practices. Here’s a general outline of how microwave-assisted synthesis in water can be applied to this transformation:

Hydrolysis of Methyl Benzoate:

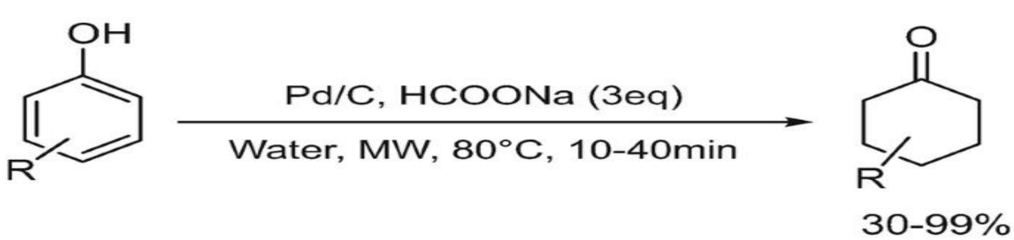
- Methyl benzoate undergoes hydrolysis in the presence of water and a suitable catalyst under microwave irradiation.
- **Microwave Irradiation**: Microwaves rapidly heat the reaction mixture, accelerating the hydrolysis process.
- **Water as Solvent**: Water serves as a green and environmentally benign solvent, facilitating the reaction under milder conditions compared to traditional methods.



4.3.3 Microwave-Assisted Oxidation of Toluene to Benzoic Acid

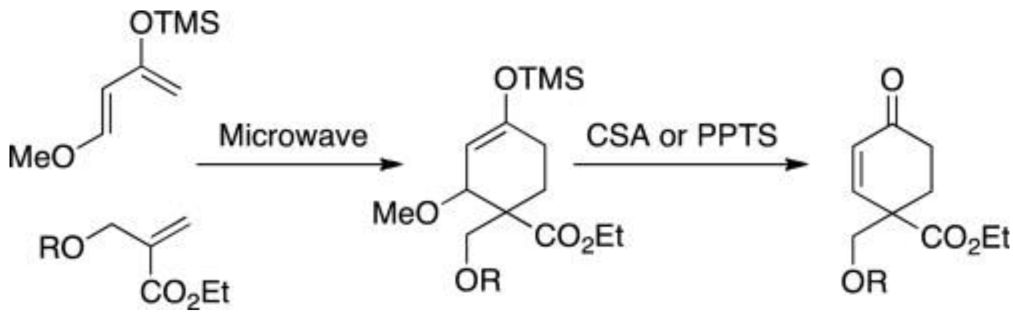
Microwave-assisted reactions in water can be utilized for the oxidation of toluene and alcohols, offering advantages such as improved reaction rates, selectivity, and environmental sustainability. Here’s how these reactions can be approached:

Toluene + Oxidant→ Benzoic Acid



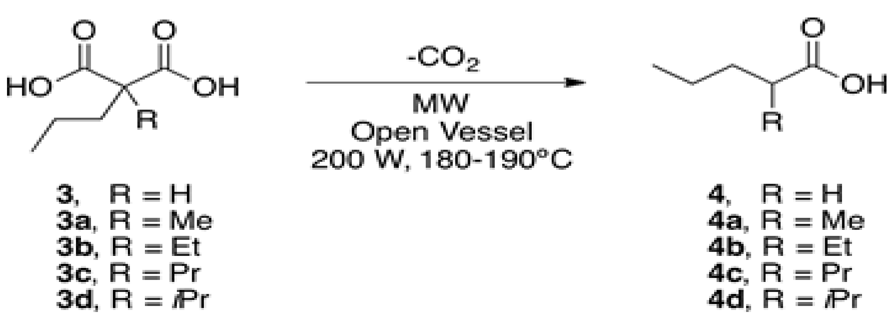
4.3.4 Microwave assisted reactions in organic solvents Diels-Alder reaction:

Microwave-assisted Diels-Alder reactions in organic solvents offer significant advantages in terms of reaction efficiency, yield improvement, and shortened reaction times compared to conventional thermal methods. Here's how microwave irradiation can be applied to enhance the Diels-Alder reaction. The Diels-Alder reaction is a powerful method for the construction of six-membered rings (cyclohexenes) from a conjugated diene (4π-electron system) and a dienophile (2π-electron system).



Decarboxylation reaction

Microwave-assisted decarboxylation reactions in organic solvents leverage the rapid and efficient heating capabilities of microwaves to accelerate the removal of carboxyl groups from organic compounds. Decarboxylation is a fundamental organic transformation where a carboxylic acid group (–COOH) is removed as carbon dioxide (CO2), resulting in the formation of a new carbon-carbon double bond or other products. Here's how microwave irradiation can be applied to enhance decarboxylation reactions. Decarboxylation reactions typically involve the thermal or catalytic decomposition of carboxylic acids or their derivatives to form carbon dioxide and a reactive intermediate or product.

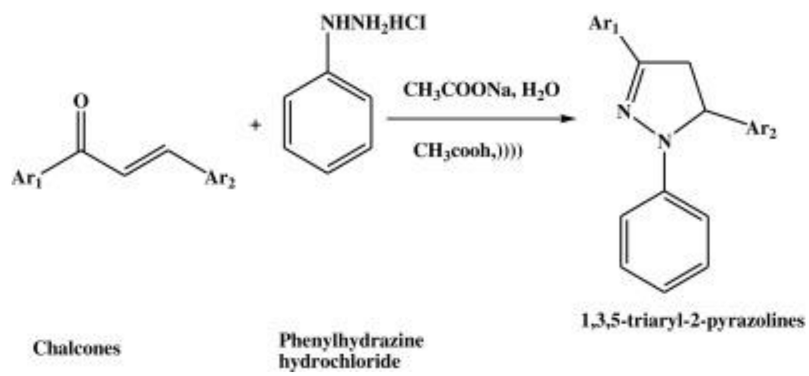


4.4 Ultrasound assisted reactions:

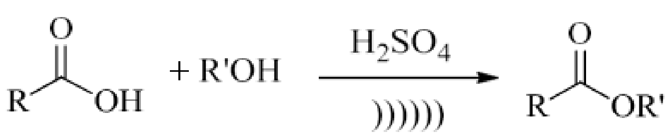
Ultrasound-assisted reactions, also known as sonochemical reactions, provide a unique approach to accelerate chemical reactions through the application of high-frequency sound waves (ultrasound) in a solvent medium. The sonochemical Simmons-Smith reaction is a notable example where ultrasound is used to enhance the efficiency of the Simmons-Smith cyclopropanation reaction. Here's an overview of how ultrasound can be applied in this context:

Simmons-Smith Reaction Overview:

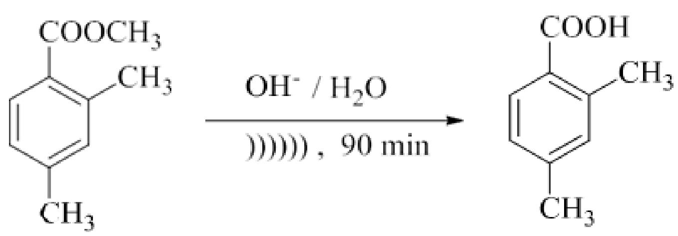
The Simmons-Smith reaction involves the formation of a cyclopropane ring by reacting an alkene with a zinc-carbenoid intermediate generated from diiodomethane (CH_2I_2) and zinc (Zn)



Esterification reaction; A straightforward method for esterification involving various carboxylic acids and different alcohols at room temperature using ultrasound has been documented.



Saponification, when assisted by ultrasound, allows for the process to occur under milder conditions. For instance, methyl-2,4-dimethylbenzoate undergoes saponification at 20 KHz, resulting in the corresponding acid with a yield of 94%. In contrast, the conventional method involving heating with aqueous alkali for 90 minutes yields only 15%.



Summary:

This unit covers the Green Synthesis of Compounds Developed using greener oxidation methods like hydrogen peroxide or ozone, reducing reliance on nitric acid and minimizing emissions. Microwave-Assisted Reactions in Water and Organic Solvents, accelerated in water under microwave irradiation, reducing reaction times and energy consumption. Efficient conversion achieved using mild conditions in water under microwave assistance, minimizing solvent use and waste generation. Utilizes ultrasound as a safer alternative to iodine-based reactions, enhancing reaction kinetics and reducing environmental hazards.

Keywords:

Green Synthesis: Green synthesis refers to the development of chemical processes and methods that prioritize sustainability, efficiency, and environmental stewardship.

Microwave assisted reactions: Microwave-assisted reactions refer to chemical reactions where microwave irradiation is used as a source of energy to accelerate the reaction rate and improve yields.

Ultrasound assisted reactions: Ultrasound-assisted reactions, also known as sonochemical reactions, utilize ultrasound waves to enhance chemical reactions.

MCQ

Q.1 Which reaction can be accelerated using microwave irradiation in water?

A. Grignard reaction

B. Hofmann elimination

C. Friedel-Crafts acylation

D. Wittig reaction **Answer: B**

Q.2 The sonochemical Simmons-Smith reaction utilizes ultrasound waves to:

A. Replace toxic catalysts with benign alternatives

B. Enhance the formation of carbon-carbon bonds

C. Accelerate the addition of a carbene to double bonds

D. Reduce the need for high temperatures in reactions **Answer: C**

Q.3 Ultrasound-assisted reactions are particularly advantageous because they:

A. Utilize toxic heavy metal catalysts

B. Operate at high pressures and temperatures

C. Enhance mass transfer and mixing in the reaction medium

D. Require large amounts of organic solvents **Answer: C**

Q.4 Which of the following is a characteristic of water that makes it suitable for microwave-assisted reactions?

A. Non-polar nature

B. High viscosity

C. Low dielectric constant

D. Polar nature and high dielectric constant **Answer:** D.

Q.5 Microwave-assisted reactions in water are particularly beneficial for:

A. Reactions that require prolonged heating

B. Reactions sensitive to high temperatures

C. Reactions that need high pressure

D. Reactions involving toxic solvents **Answer:** B.

Short answer Question:

1. How does microwave irradiation in water enhance chemical reactions compared to conventional heating methods?
2. What is a key advantage of ultrasound-assisted reactions in green chemistry?
3. Explain Diels-Alder reaction and Decarboxylation reaction

Chapter: 5

Pollution Prevention

Objective

- Decreasing health risk
- Reducing the liability
- Cutting cost
- Enhancing the public perception
- Social advantages

5.1 Introduction

Environmental pollution considerable matter and continuously effect the human being for last few decades. In this study the Mellon Institute of Pittsburgh PA USA reported about smoke abatement proceed in legislation to frame to reduce the influence of smoke. This was earlier described that environmental pollutant developed the adverse effect on health. The report of WHO described that every year 2.4 million people die due to air pollution, rapidly enhanced to control this need to develop some strategies to decrease it and provide considerable benefits for human health. Here in our study mainly focus and obtained the information related to the impact on pollution on respiratory health main issue and examine in a number of clinical data such as ozon (O_3) and particulate matter (PM) pollution are serious problem in the society.

According to US environmental Protection Agency, the mitigation policy like change in diesel engine technology shown a less premature mortalities.

- Matter of air pollution on respiratory disease
- Supportive information decreases the air pollution and gave a positive influence to curbing the disease.
- Express the impact particularly on concentrated polices connected with health that governments plan to decrease air pollution.

Air pollution generally influences a huge range of peoples suffered with constraint in their respiratory efficiency, for instance PM and O_3 trigger asthma indication and shown a premature death. In another case study revealed that pollutants increase liberate allergenic pollen grains that enhanced pollen-induced asthma. We can control the air pollution level generated from heavy traffic decreased and the diseases related to respiratory and asthma can be decreased. On the other side effectively effort performs to decrease air pollution that stop the change in environment. The earlier studies described that low anti-oxidant level and dietary supplement utilized promising way to decrease the air pollution, gave an another plan for neutralizing attempt on pollutants on health.

5.2 New green and sustainable synthetic methods

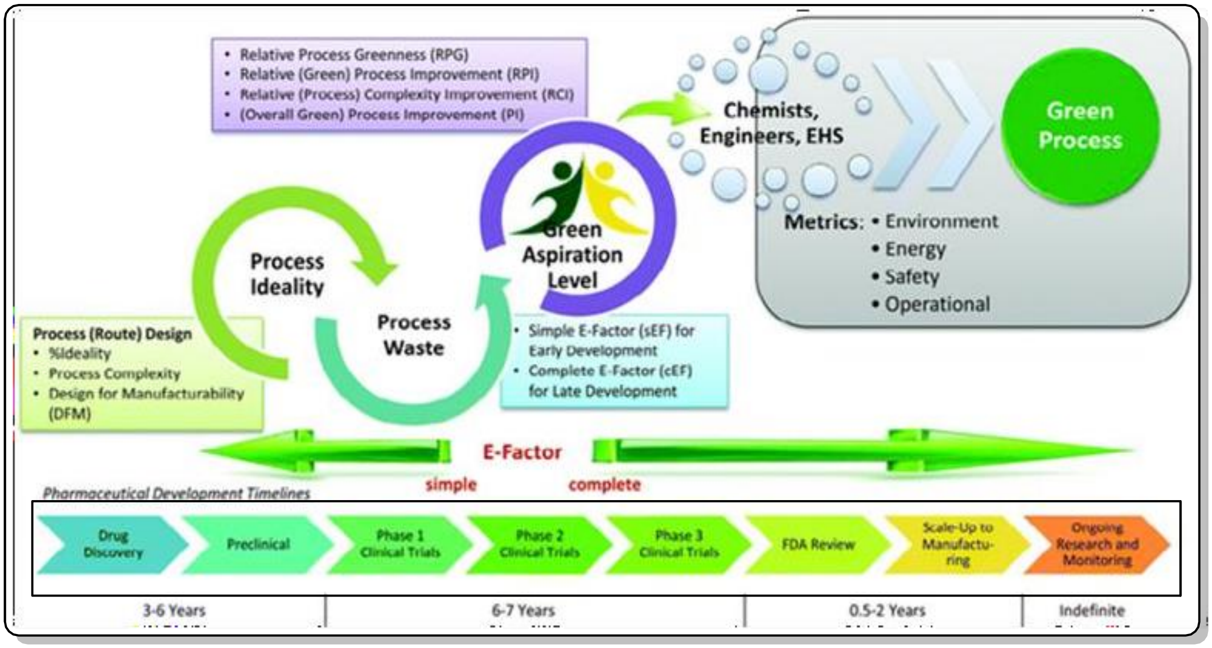
Green and sustainable chemistry methods that utilized synthesis of organic compounds and other chemical moieties that remove the hazardous chemicals. The term ‘Green” synthesis divided in three parts

- Solvent
- Reagent/catalyst
- Energy consumption
- Creation of environmentally favorable substances and materials
- Using solvent systems that are safe for the environment.
- To create industrial processes that shield against risk issues
- Examining how processing biomass affects the environment and ecotoxicology.

Green chemistry methods applied in decreasing the possibilities of danger and control of pollution, handling the toxic compounds. For instance Benzene a solvent has the characteristic as carcinogenic instead of this use a greener solvent ethanol.

5.3 Green chemistry and environmental sustainability

Sustainability and environmental matter a burning topic increasing expeditiously utilized to design product and their development. Additionally upcoming task connected with resource economic that environment and sustainability need organized techniques, accomplished the chemical and their production, GC control these task enhanced the favorable substance and reduced the byproducts. The appliances used to synthesis the chemical inherently, ecologically and environs.



The concept of sustainability is the process of designing industrial and human systems so that the use of natural resources and the human cycle does not diminish the worth of life or the environment's disparity. Reducing solid and liquid waste, emissions, resource consumption, and the usage of harmful chemicals are some examples of how environmental sustainability is practiced.

5.5 Green synthetic methods: Microwave irradiation MWI

MWI, dipolar polarization an environmentally friendly method of heating both organic and inorganic chemistry. Numerous organic compounds have been reported to have been produced in this quick, easy, cost-effective, and clean manner; it is currently acknowledged as a standard tool in synthetic chemistry and has greatly advanced organic synthesis. Non-ionizing radiation, or MW energy, has no effect on a compound's molecular structure. In contrast to CCl_4, toluene, or aliphatic hydrocarbons, N,N-dimethyl-formamide (DMF), acetone, methanol and water are rapidly heated under radiations of microwave. This is because a substance's MW coupling is dependent on its dielectric constant. The electromagnetic energy drives the interactions between molecules by converting into heat. Because of the direct contact between the reaction components and MW irradiation, heating them requires the least amount of energy possible without extending the process to the furnace material.

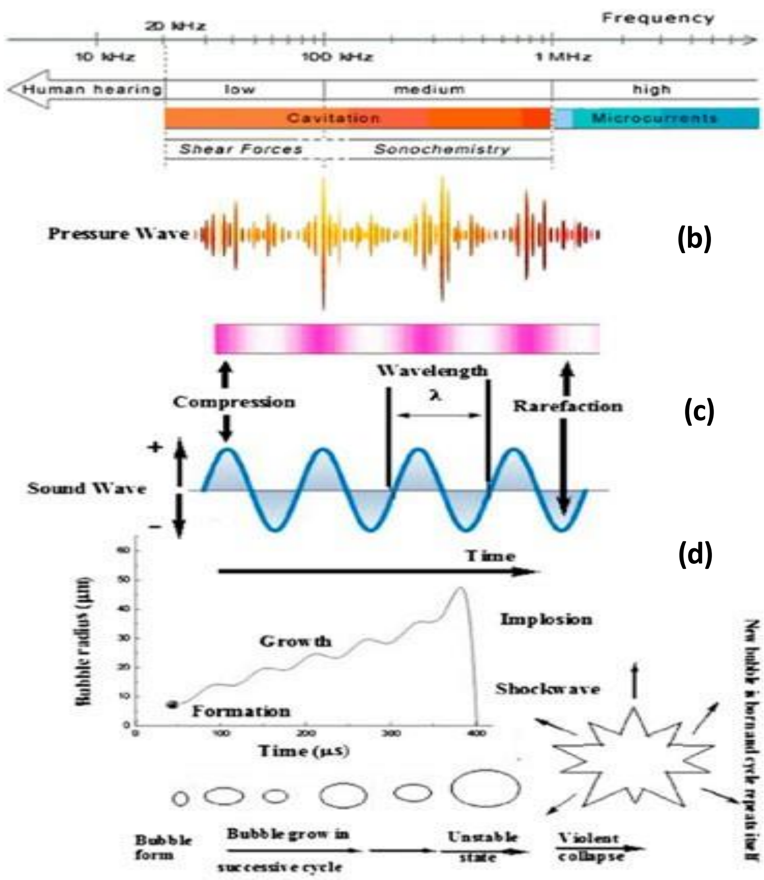
When compared to traditional heating, MW heating offers the following benefits, among others: quick process speeds, pure products, reduced heat loss, high heating efficiency, less waste, low operating costs, and fewer potential side products. For MW-assisted reactions, solvent-free (dry media) conditions are preferred in order to prevent explosive explosions and rapid, uncontrollable solvent heating. It is possible for precursors to be adsorbed on inorganic substrates that are transparent to microwave radiation (such as montmorillonite clays, zeolites, ceramics, Al_2O_3, and SiO_2) or, conversely, have a substantial microwave absorbance (such as graphite). These supports may also include extra catalysts or reagents. In the routes of oxidation /reduction deprotection / protection, rearrangement, condensation, heterocyclic synthesis, etc., MW-prompted solvent-free reactions on inorganic supports at relatively low bulk temperature have demonstrated definite advantages. These reactions can result in significant products like HCN, imines, nitro-alkenes, and enamines, among others.

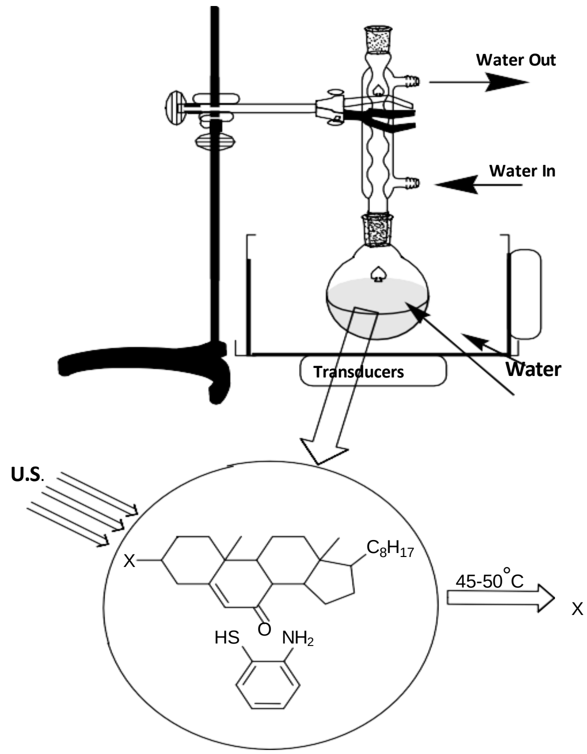
5.6 Catalysis

Under UV light, photochemical processes are synthesised and regarded as green chemistry interactions. The generation of singlet oxygen act in photo-oxygenation (the incorporation of molecular oxygen into molecules), Also treated with photochemical processes with enzyme catalysis and the use of constant flows or micro-reactors for their optimization. Asymmetric oxidations facilitated by enzymes, the synthesis of N-containing heterocycles via photo-oxidation of furan derivatives, and the production of multiple F-organic compounds via photocatalyzed trifluoro-methylation of aromatics, utilizing the photocatalysis booth and reactors respectively.

5.7 Ultrasound-assisted (sonochemical) synthesis

This phenomenon takes place within a liquid environment and does not directly affect the vibrational energy of bonds. Alongside generating free radicals and hydrogen peroxide (H_2O_2), these conditions can trigger or enhance chemical reactions. Such collisions can profoundly modify the chemical composition, reactivity, and surface structure of a substance, frequently leading to an augmentation in surface area. Sonochemical processes, such as the degradation of halogenated aromatics, are commonly conducted in liquid systems, involving interfaces between solids and liquids or between different liquids (sonocatalysis included). These reactions offer environmental benefits due to their minimal energy requirements and the avoidance of hazardous chemicals. Ultrasound-assisted organic synthesis and the fabrication of functional materials represent significant contributions to green chemistry. Moreover, equipment costs are generally affordable, especially for basic ultrasonic cleaning baths operating at frequencies of 20–40 kHz, except for high-power ultrasonic horns.





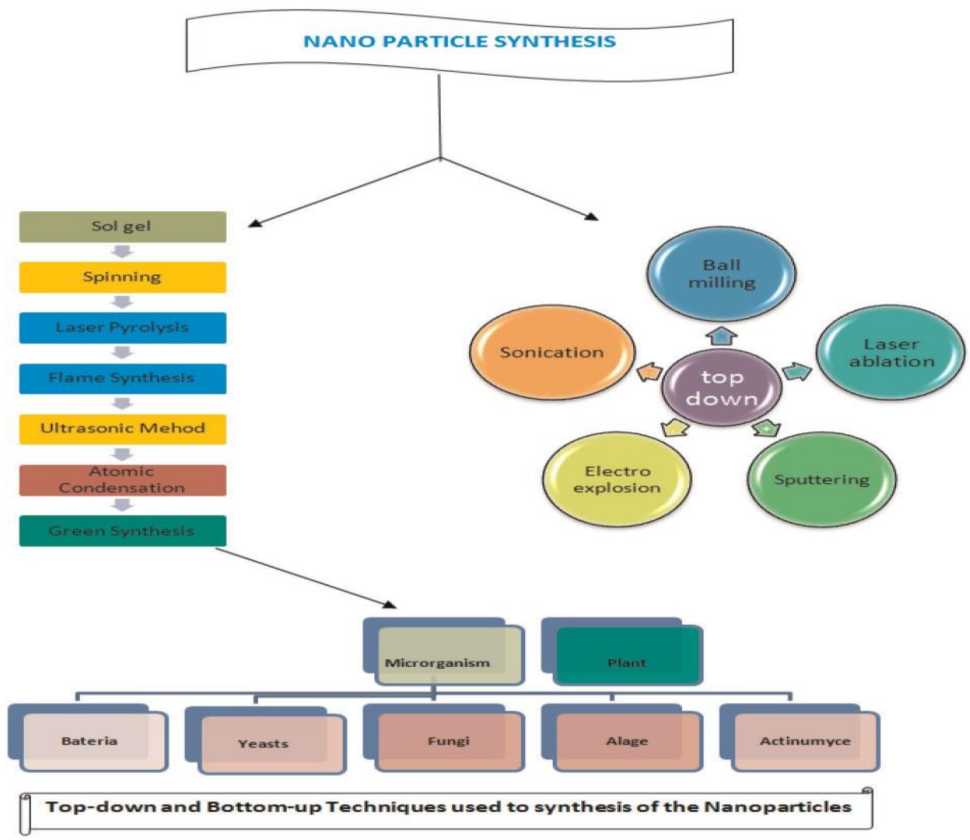
5.8 Green synthesis of organic, labeled and hybrid compounds

Many chemical synthesis reactions under green processes have lately been examined. Thus, among heterocycles containing nitrogen, benzimidazole derivatives—and specifically, benzimidazole–diindolylmethane hybrid compounds—have received some attention. By combining a number of green chemistry concepts, hybrid regioisomers of 2-(3,3'-diindolylmethylphenyl)-1Hbenzimidazole were produced under microwave treatment in a short amount of time (3–8 min) and with good yields.

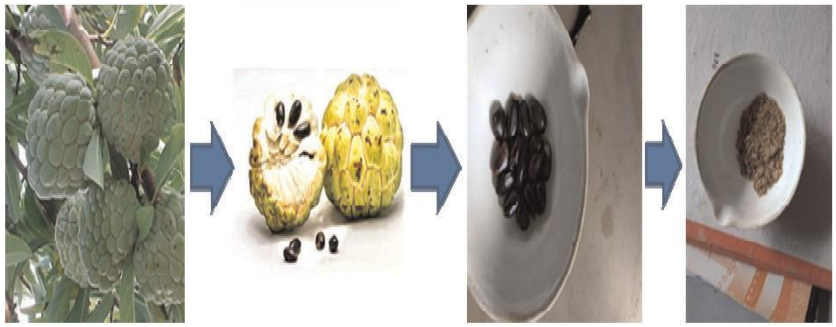
5.9 Metal nanoparticles : Greener approach

The following substances are regarded as greener in the synthesis processes for the creation of nanoparticles for the objectives of green chemistry: (i) Biomolecules (proteins and peptides) with high biocompatibility; (ii) small molecules (like CO) combined with organic capping agents; (iii) polysaccharides (like starch or dextran) with mild capping ability and water solubility (sometimes reduction properties), avoiding toxic solvents and facilitating easy separation of nanoparticles from reaction media. The surfaces of nanoparticles can be stabilized, prevented from aggregating, and have their chemical characteristics altered by the application of ligands by passivation and coating. Phosphines, thiols, amines, selenols, carbenes, and alkynyls are common ligands used in the synthesis of nanoparticles; these are categorized based on their chemical structures and "head group."

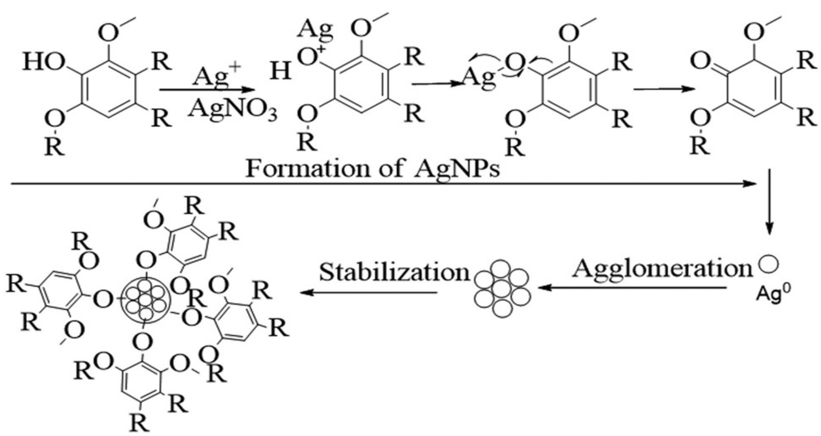
The utilization of plant waste products with various names, seed coat, such as shell, fruit peel, skin, hull, etc., having bioactive chemicals is one of these areas where scientists are particularly focused. These waste products serve as an excellent illustration of an underappreciated and underutilized energy source that can be employed in the synthesis of nanoparticles as a reducing agent. Since non-toxic (green) reductants are not as powerful to generate metal nanoparticles of adequate high quality, where a considerably faster kinetics is required, their employment is either directly or indirectly related to toxicity. Strong reductants, however, are often costly and hazardous. Thus, finding or producing green (non-toxic) and potent reductants at the same time is one of the primary goals of green synthesis of high-quality nanoparticles.



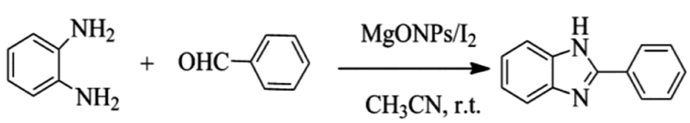
General methods of preparation of nanoparticles and their techniques



Schematic depiction of powder made from custard apple seeds for preparation of nanoparticles



: Tentative mechanism and stabilization of biogenic AgNPs.

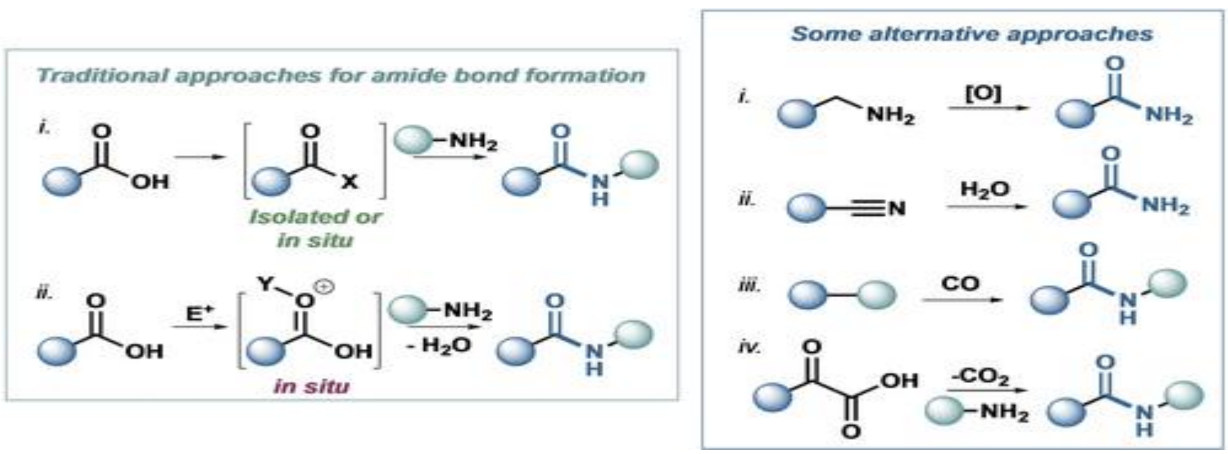


Synthesis of 2-phenylbenzimidazole in the presence of nanocrystalline MgO/I_2

Synthetic procedure of water-soluble CQDs by hydrothermal treatment of lemon peel waste precursor

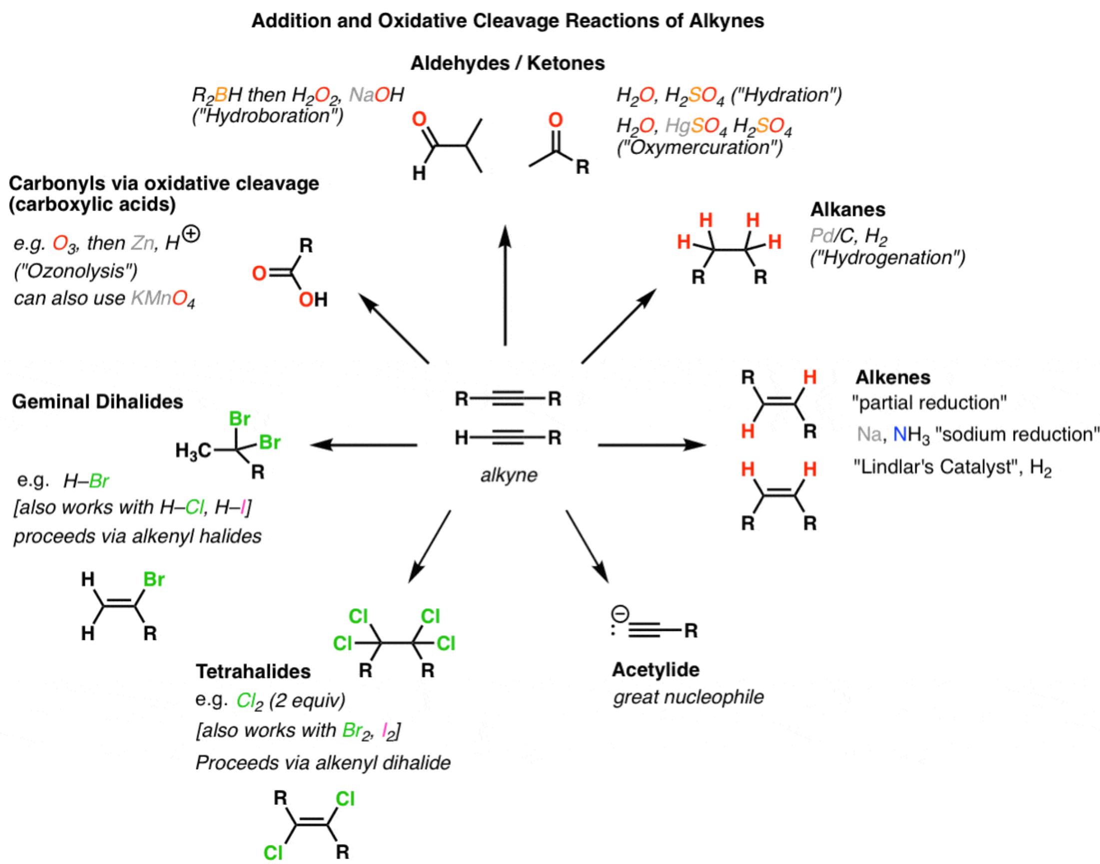
5.10 Amide bond formation

As one of the most common functional groups in bioactive compounds, amides have attracted a lot of attention to the creation of amide bonds in recent years. Since it's important to distinguish between amide synthesis and amide bond production, this article will concentrate on outlining particular techniques for creating new C(O)−N bonds. By using this method, all of the most frequent chemical reactions that result in the production of new amide bonds are covered.



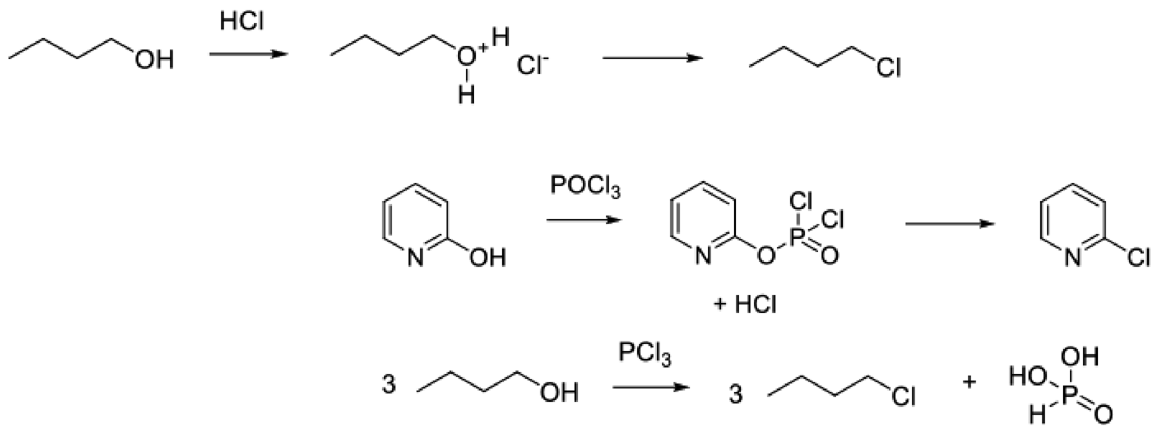
5.11 Alkene reduction

In contrast to homogeneous reactions performed in a single phase (such as a gas) while heterogeneous chemical reactions involve with reactants having at least two distinct phases (such as a gas with a solid). The description of the catalyst utilized in the reaction between hydrogen and alkenes may cause some confusion. Although palladium, platinum, and nickel are the three metals that are most frequently utilized, these metals to a combination of hydrogen and alkene and expect a reaction. Metal like nickel known as "Raney nickel," reacting with NaOH and Ni-Al alloy. Commercial palladium is "supported" on an inert material, like charcoal (Pd/C). Typically, ethanol dissolves the alkene when Pd/C is utilized as the catalyst. Although platinum metal acts as the catalyst, used as Adams' PtO2 catalyst. Finely divided platinum metal is produced by reducing platinum(IV) oxide with hydrogen added to the carbon-carbon double bond.



5.12 Deoxychlorination

It is far more usual to create carbon-chlorine bonds via activating oxygen and then SN^2 or SN^1, as opposed to just moving leaving groups' chloride anion. For deoxychlorination, common reagents include $SOCl_2$, PCl_3, PCl_5, $POCl_3$, $PhPO(Cl)_2$, and HCl. These chemicals are used to change C-OH or C=O bonds into chlorides, which are typically classified as acid, heteroaromatic, or alkyl.



Summary

Green approach synthesis a ecofriendly approach, time saving, yield improver and beneficial for human being.

Keywords:

Sustainability: Sustainability is the practice of ensuring current societal needs are met without compromising the ability of future generations to meet their own needs.

Waste: Waste is any material or substance that is discarded or no longer useful, typically requiring disposal.

Biogenic synthesis of nanomaterials: Biogenic synthesis of nanomaterials refers to the process of producing nanoscale materials using biological organisms or their components.

MCQ

1. The green chemistry based on treatments.
   A) Harmful
   B) Costly
   C) Easy
   D) Hard   Answer: B

2. The green chemistry to produce the
   A) Harmful
   B) Safer
   C) Commercial
   D) Most used   Answer : C

3. After the use of chemicals, we can...
   A) Use
   B) Reuse
   C) Dispose
   D) Store — Answer : B

4. Green approach benifts are
   A) Yield improver
   B) No yield
   C) Lesser in time
   D) None of these — Answer : A

Short answer Question:

1. What are sustainable synthetic methods?
2. Explain the based reduction methods?
3. Write a note on amide bond formation.
4. Define the deoxychlorination.

Chapter: 6

Green Solvents and Reliance Chemicals

Objectives

- Solvents produced from biomass that are currently of interest for pretreatment were found.
- The theory of solubility parameters is a useful tool for solvent screening prior to treatment.
- A summary of biomass pretreatment with biosolvents was provided.
- Future research on biosolvents is encouraged due to the obstacles and opportunities that already exist.

6.1 Introduction

In synthetic processes, chemists typically utilize any organic solvent of their choice. These solvents are typically volatile organic solvents (VOCs), which pose a serious threat to the environment since they can cause smog and low-level ozone to form through the oxidation of free radicals in the air. Additionally, they are extremely combustible and have negative effects on humans, such as allergic skin reactions, headaches, and eye irritation. The usage of green alternative solvents has become required as a result of these realities. However, using solvents should be avoided if at all possible. However, if there is no other option and using a solvent becomes necessary, it is advised to utilize inert, low-toxicity, easily recyclable solvents that won't contaminate the products. The greener solvents do not show the harmful effect, beneficial to health as well as environment. Examples of halogenated solvents that have been linked to cancer include $CHCl_3$ and CCl_4, which can be avoided by using greener alternatives like liquid CO_2, ionic liquids, or water. Immobilized solvents have been used in place of conventional volatile organic compounds to circumvent their issues. These solvents don't harm the environment, retain their solvency, and are non-volatile.

- **Water as a Green Solvent**

Water is a greener solvent, play a significantly role in organic synthesis. water is a naturally occurring, non-toxic, and non-explosive solvent. Water, however, is difficult to quickly heat or chill, requires a lot of energy to distill, and its contaminated waste streams are challenging to handle. Chemical reaction interacted with water in human system unable perform in laboratory.

Over 200 0C is the temperature at which water becomes as effective as an organic solvent. At 300 °C, it is thought that water behaves similarly to acetone. This could be as a result of water's hydrogen bonds being broken by greater temperatures. The use of water in certain reactions has been shown to significantly increase the rate of reaction. The Diel's Alder reaction between butanone and cyclopentadiene is a common illustration of this. It has been discovered that in water, this reaction happens 700 times more quickly than it does in isooctane.

- **Ionic liquids**

A solution having ions knows as ionic liquids found in the form inorganic ions such as cations and anions. The compound exhibits asymmetry due to the large and tiny parts, resulting in a low melting solid. A multicomponent ionic liquid is created when simple ionic liquids are combined with various inorganic salts. An ionic liquid's constituent parts are held together by strong forces of attraction, which results in their low or nonexistent vapour pressure and non-volatile nature. They are additionally safe to use due to their non-flammable and non-explosive properties. They can also be employed as catalysts and solvents.

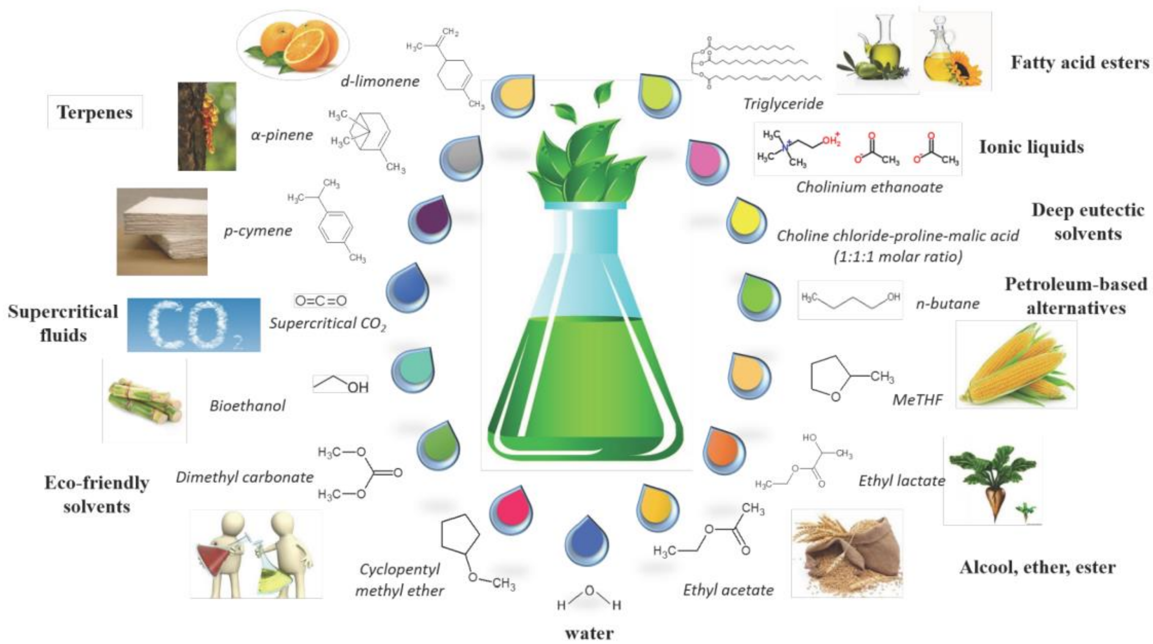
Ionic liquids exhibited the property and made good green solvents, including

No vapour pressure.

The absence of flammability and explosion.

They are more suitable for conducting reactions at high temperatures since they are stable at such temperatures.

By simply altering the cation/anon concentrations and side chain length in the cations, the properties of these ionic liquids can be modified. There is a list of following diffent liquids



- **Supercritical carbon dioxide (sc CO_2)**

One of the most significant advancements in green chemistry for the chemical industries' pursuit of sustainability is the supercritical carbon dioxide. This is a green medium that shows promise as an alternative to conventional volatile organic compounds and toxic organic solvents, both of which pose serious environmental risks.

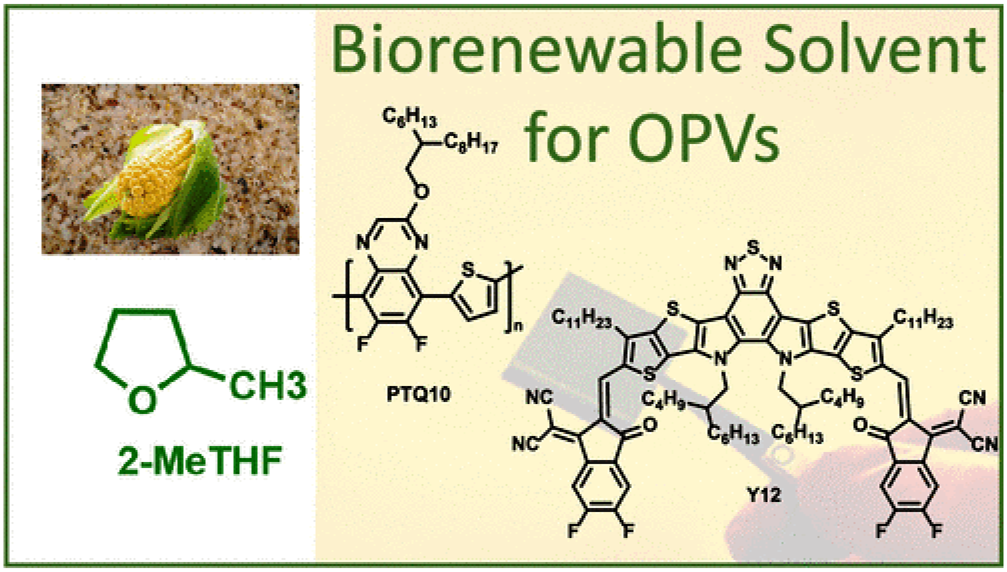
Supercritical carbon dioxide and binary a mixtures including CO2 (theory and experiment) and their diverse scientific and technological uses in a range of industrial and natural processes. A thorough assessment is conducted of the knowledge regarding the enhancement (anomaly) and thermodynamic and transport features (experiment and theory) of supercritical carbon dioxide and SC CO2 + solute mixtures.

- **Biorenewable solvents**

Herein we shown the two biorenewable solvents in following such as

(a) 2-methyltetrahydrofurane (2MeTHF),

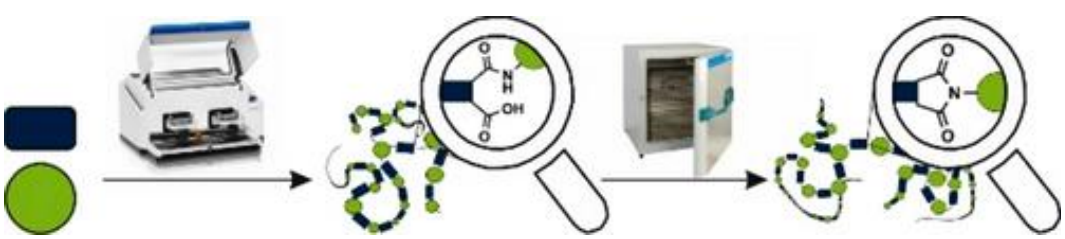
(b) Cyclopentyl methyl ether (CPME)



Hence to decrease the carbon footprint to design cycle of OPVs

- **Mechanochemistry**

Polyimides were obtained in 99 % yield in under 1 h through the "beat and heat" approach, involving solvent-free vibrational ball milling and a thermal treatment step. The influence of a plethora of additives was explored, such as Lewis acids, Lewis bases, and dehydrating agents, and the mechanochemical reaction was identified to run via a polyamic acid intermediate. The protocol was adopted to a range of substrates inaccessible through solution-based processes, including perylene tetracarboxylic acid dianhydride and melamine. Furthermore, quantum chemical calculations were conducted to identify the water removal as the crucial step in the reaction mechanism.



- **Solvents selection guides**

  It is advised—or preferred—that solvents be tested in a screening exercise first,

  provided that the process conditions do not exhibit any chemical incompatibility.

Example Water and ethanol

Problematic: while these solvents are suitable for use in the lab or Kilolab, their application in a pilot plant or on a large scale will necessitate special precautions or high energy usage.

Perilous: severe limitations prevent scale-up from occurring. Priority one during process development is the substitution of these solvents.

Extremely dangerous: even in the lab, solvents should be avoided.

6.2 Society Relient Chemicals-Commodity & Fine chemicals

The fine chemicals essential in laboratory to perform the research activity and overcome several hindrance to maintain innovation and growth in production processes. For example Quality control and regulatory compliance.

Every step in the production of fine chemicals requires process quality control. SEMI Standards must be met by materials used in the electronics and semiconductor industries, and good manufacturing practices for pharmaceuticals, regulatory compliance for active pesticide ingredients, and other end-use industry or regulatory standards are just a few examples of the strict customer requirements that apply to fine chemicals.

QC considerations for production:

Content and Focus

stability and purity

characteristics, both chemical and physical

Operational

yield, throughput, and efficiency

Necessities for regulatory compliance may include:

Permits, including those hazardous materials

Materials management includes managing, storing, and transporting materials as well as preventing spills and storm water contamination.

Waste management includes transportation and disposal of hazardous waste, control of process wastewater, and disposal of solid waste connected to processes.

Bio-based Substances

Products made from biomass, or living matter, or through processes utilizing biomass are known as biobased materials. Innovation in biobased chemicals is being pushed by consumer demand for more sustainable materials and product maker desire for higher-performing chemicals, even in an environment where petroleum prices are low. Forward-thinking biotechnology firms are creating biobased compounds that can be utilized to create more environmentally friendly materials. The chemicals industry will probably witness increased sustainability in their operations as innovation progresses, which could result in increased productivity and cost savings.

Pharmaceuticals

Along with novel drug therapies, they anticipate focusing their efforts on non-pharmacological therapy, early identification, and prevention. The fine chemicals sector will have to keep coming up with incredibly focused, cutting-edge solutions for diagnostics, prophylactic therapies, and active components. The chemicals sector will be counted on to supply cutting-edge fine chemicals to support the ongoing expansion of biosimilar development, availability, and efficacy.

A chemical route to recycling the plastics

Products that aren't suitable for conventional mechanical recycling, like multi-layer plastics, highly contaminated plastics, or unsorted plastic garbage, can be recycled chemically. It is common to refer to advanced recycling, transformational technology, and chemical recycling interchangeably. In order to create one or more of the original monomer building blocks that are utilized as feedstocks for the synthesis of other chemicals, it involves breaking down used plastics. Solvents or heat are used in the procedure to degrade the plastics so they can be reused.

When paired with mechanical recycling accomplishments, chemical recycling practices significantly reduce the quantity of plastic trash that needs to be disposed of by burning or landfilling, which in turn reduces the usage of non-renewable resources like petroleum.

Material science

The goal of nanotechnology developers is to create catalysts with extended lifetimes, minimal energy requirements, and great selectivity and activity. For many medicinal treatments, nanoparticles are also employed as drug delivery vehicles. Currently, materials for drug delivery nanoparticles include carbon, polymers, metals, and lipids. Comparing nanoparticle systems to conventional distribution techniques (such pills and capsules), there are a number of benefits, including:

A greater emphasis on targeted advertising

Reduced cytotoxicity

Enhanced metabolism and biodistribution

Consistent and regulated release

distribution of poorly soluble medications

6.2 Reliance on their production from fossil fuels

Growing extreme weather events brought on by climate change make us wonder how they will affect the electricity generation system and what that means for the supply of fossil fuels vs renewable energy. Here, we systematically quantify the effects of extreme climate events.

We discover that extreme weather condition in which energy production's related to carbon intensity, enhance dependency on fossil fuels and lowers the potential of renewable energy sources. Extreme weather also had a greater impact on the states that generated more electricity from renewable sources. Our findings highlight the degree to which the current American electrical system is dependent on fossil fuels for dependability and resilience during extreme weather events, and they point to the necessity of taking adaptation steps as the nation moves toward a greater proportion of renewable energy sources as extreme weather events increase in frequency.

6.3 Biorenewable lignocellulosic biomass

Lignocellulosic biomass (LCB) is a renewable resource obtained using a wide range of plants a viable source of energy, different bioproducts. Fossil fuels are mostly used in the production of chemical and synthetic polymers, despite the fact that these materials have finite resources and concerning environmental effects. By using renewable natural resources to produce chemicals and polymers, we can lessen our existing reliance on fossil fuels and the environmental effects they cause. LCB is a reasonably priced and abundant natural resource. LCB provides an energy along with environmental solution. Biofuels are produced from the organic biomass of renewable resources, which also includes waste lignocellulosic biomass. Many techniques have been employed to achieve bioconversion, including chemical, biological, and physical techniques. To ensure the survival of the human species, alternative fuels generated from LCB must be created. The process's cost-effectiveness and the capabilities of the technology employed to create ethanol continue to raise questions.

6.4 Use of biorenewable platform chemicals in chemical synthesis with care studies.

Growing the process to developed fossil fuels chemical obtained from biomass an exciting possibility to achieve a sustainable supply from renewable sources. Technologies that simply use chemical catalysis have demonstrated limits in terms of reaching the target yield of a product molecule. Technologies that simply use chemical catalysis have demonstrated their inability to produce product molecules at the required yield. In order to manufacture commodity chemicals with high conversion and selectivity, it is crucial to integrate a biocatalytic method with a chemo-catalytic pathway, as recent research discoveries have highlighted. Because of their adaptability, microorganisms such as bacteria, fungi, and algae can synthesize platform molecules that can be refined to create their petrochemical equivalents. The platform molecule can be purified further and then utilized as a reactant in chemo-catalytic processing to provide a variety of high-value compounds. This will pave the way for the development of new combined fermentation and catalytic processing strategies, which will facilitate the production of chemicals from renewable resources. The chapter summarizes the methods for creating a platform molecule by biocatalytic reactions, covering the advancements made in this direction.

6.5 Lignin and its potential

Lignin is a naturally occurring phenolic polymer with a high molecular weight, intricate structure, and complicated chemistry that makes up a significant portion of plant cell walls. Plant growth, tissue/organ development, lodging resistance, and responses to a range of biotic and abiotic stressors are significantly influenced by lignin production. Lignin giving plants structure and their stiffness, lignin acts as a naturally occurring, very powerful barrier against microbial invasion and facilitates the passage of water and nutrients through plant tissues. The components of lignin can differ significantly among plant species, resulting in a great deal of variation in the chemistry and structure of lignin.

Summary

In integrated biorefineries, biomass-derived solvents have proven for special benefits in terms of sustainability, selectivity, stability, and reusability. They could be adjusted to maintain lignin structure during organosolv pretreatment or make lignin more vulnerable to depolymerization. In addition to demonstrating adaptability with a variety of feedstocks, biomass-derived ILs and DESs have demonstrated the prospective capacity to solubilize biomass components and facilitate their conversion to fuels/chemicals as both catalysts and solvents. Despite significant advancements, air pretreatment or moderate temperature methods that can extract high-quality lignin without compromising the sugar platform through the use of adjustable solvents produced from biomass are still required.

Keywords : Biomass, lignin, biorenewable, lignocellulosic biomass

Biomass; Biomass refers to organic material, such as wood, agricultural crops, or waste, that can be used as a renewable energy source.

Lignin; Lignin is a complex organic polymer that provides structural support to plant cell walls and is a byproduct of biomass processing.

Bio renewable: refers to resources derived from biological sources, such as plants and microbes, that can be replenished naturally or through sustainable practices.

Lignocellulosic biomass: refers to plant material composed of cellulose, hemicellulose, and lignin, used for biofuel production and other sustainable applications.

MCQ

1. What is the principle of atom economy in green chemistry?
   - A) Maximizing the use of renewable feedstocks
   - B) Minimizing the use of energy in chemical reactions
   - C) Minimizing the use of catalyst
   - D) Minimizing the use of energy in chemical reactions **Answer : C)**

2. What is the term for the efficient use of all reactants ina chemical reaction, minimizing waste generation?
   - A) Atom Economy
   - B) Rebewable Feedbacks
   - C) Biodegrdability
   - **D)** Photodegrdation **Answer: (A)**
3. Which of the following is a renewable feedback used in green chemistry?
   - A) Fossil fuels
   - B) Petroleum
   - C) Coal
   - **D)** Plant-based biomass **Answer: (D)**
4. Which environmental impact does green chemistry seek to minimize during a chemical product's entire life cycle?
   - A) Energy consumption
   - B) Water usage
   - C) Air pollution
   - D) Environmental toxicity **Answer: D)**

Short Answer Questions

1. What are the green solvents give their characteristics.
2. Define the ionic liquids and write their characteristics.
3. Write a note on Bio-renewable.
4. Explain the fossil fuels

Chapter 7

Future Trends in Green Chemistry

Objectives:

- Develop efficient, sustainable oxidizing agents and catalysts to reduce environmental impact and improve reaction selectivity.
- Mimic biological processes to create versatile reagents that enhance efficiency and specificity in chemical reactions.
- Advance methods for rapid synthesis and screening of diverse compounds under environmentally friendly conditions, accelerating discoveries in various fields.
- Expand solvent-free techniques to minimize environmental footprint, lower costs, and simplify reaction procedures.

7.1 Introduction

Green chemistry continues to evolve with advancements in technology and increasing awareness of environmental sustainability. Here are some future trends that are expected to shape the field:

a) **Bio-based Feedstocks**: There is a growing emphasis on using renewable, bio-based feedstocks as alternatives to fossil fuels. This trend aims to reduce dependency on non-renewable resources and decrease the environmental footprint of chemical production.

b) **Catalysis and Greener Reaction Conditions**: Development of efficient catalytic processes and milder reaction conditions is a key focus. This includes the use of enzymes, organocatalysts, and other innovative catalytic systems that enhance reaction selectivity and reduce energy consumption.

c) **Circular Economy Principles**: Integration of circular economy principles into chemical manufacturing involves designing products and processes that minimize waste generation, maximize resource efficiency, and promote recycling and reuse of materials.

d) **Safer Chemicals and Materials**: There is a shift towards designing chemicals and materials that are inherently safer, reducing hazards to human health and the environment throughout their lifecycle. This includes the reduction or elimination of toxic substances.

e) **Energy Efficiency and Sustainable Energy Sources**: Continued efforts to improve energy efficiency in chemical processes, as well as increasing the use of sustainable energy sources such as solar and wind power to power chemical manufacturing.

f) **Digitalization and Data-driven Approaches**: Adoption of digital tools, machine learning, and computational modeling to optimize chemical processes, predict environmental impacts, and design greener chemicals and materials.

g) **Green Chemistry Metrics and Standards**: Development of standardized metrics and criteria to assess the environmental impact of chemical processes and products, facilitating comparisons and driving continuous improvement in sustainability.

h) **Public Policy and Regulatory Drivers**: Increasing regulatory pressures and consumer demand for sustainable products are likely to drive companies towards adopting greener chemistry practices and technologies.

i) **Collaboration and Interdisciplinary Approaches**: Collaboration across disciplines (chemistry, biology, engineering, etc.) and sectors (academia, industry, government) to foster innovation and develop holistic solutions to environmental challenges.

j) **Education and Awareness**: Enhanced education and awareness among scientists, engineers, policymakers, and the public about the principles and benefits of green chemistry, promoting its widespread adoption and implementation.

7.2 Oxidizing Reagent and Catalysts

Numerous oxidizing agents have historically been employed in organic chemistry to selectively oxidize various functional groups. While transition metals are effective in this role, they often necessitate stoichiometric quantities and can generate substantial amounts of hazardous metallic waste. Moreover, some metals are costly or toxic. Thus, there is a growing demand for alternative, cost-effective oxidizing reagents. Non-metallic catalysts have garnered attention recently as potential solutions. However, many traditional non-metallic oxidants suffer from issues such as excessive consumption (beyond stoichiometry), hazardous properties, and difficulties in recovery or regeneration, often requiring external additives.

a) **Metal oxidant:** Metal-based oxidants offer significant potential to enhance oxidation reactions in a cleaner and more efficient manner. They provide benefits such as easier product isolation and purification, as well as increased reaction selectivity. In many instances, these reagents or catalysts can be recovered and recycled, further improving their economic and environmental impact.

b) **Potassium permanganate** is a widely recognized oxidizing agent in organic chemistry, extensively employed for converting alcohols into carbonyl compounds and alkylbenzenes into benzoic acids. Its oxidation activity is notably slow under neutral conditions but accelerates in acidic or basic environments. In alkaline conditions, potassium permanganate is renowned for its ability to synthesize cis-diols from alkenes and convert tertiary amines into nitro compounds.

c) **Jones reagent;**The oxidation of alcohols using chromium trioxide in acetic acid with sulfuric acid is commonly referred to as the Jones oxidation. This reagent is highly selective as it specifically targets alcohols in the presence of alkenes, alkynes, benzylic, and allylic functional groups.

d) **Collins reagent**, also known as pyridinium chlorochromate (PCC), is a popular and versatile oxidizing agent used in organic chemistry. It is particularly valued for its ability to selectively oxidize primary alcohols to aldehydes without further oxidizing them to carboxylic acids. This makes it a valuable tool in synthetic organic chemistry where the preservation of aldehyde functionality is desired. Compared to other oxidizing agents like chromium-based reagents (e.g., chromium trioxide), Collins reagent offers several advantages. It operates under mild conditions, typically at room temperature, which helps to avoid over-oxidation and degradation of sensitive functional groups. Additionally, it produces less hazardous waste and is relatively easy to handle in the laboratory.

e) **Non-metal oxidants** are compounds or reagents that are used in organic chemistry to facilitate oxidation reactions without relying on transition metals. These oxidants are valuable alternatives to metal-based oxidants due to various reasons such as cost-effectiveness, lower toxicity, and reduced environmental impact. They are particularly useful in cases where metal-based oxidants might introduce unwanted metal contaminants or hazardous waste.

- **Dess-Martin Periodinane**: This reagent is commonly used for the oxidation of primary and secondary alcohols to aldehydes and ketones, respectively. It operates under mild conditions and avoids the use of transition metals.

- **IBX (o-Iodoxybenzoic acid)**: IBX is a versatile oxidizing agent that can selectively oxidize primary alcohols to aldehydes and secondary alcohols to ketones. It is stable and effective under various reaction conditions.
- **TEMPO (2,2,6,6-Tetramethylpiperidine-1-oxyl)**: TEMPO is a stable nitroxyl radical that is often used as a catalyst in combination with co-oxidants such as sodium hypochlorite (NaClO) for selective oxidation of primary alcohols to aldehydes.
- **Pyridinium Chlorochromate (PCC)**: While containing chromium, PCC is classified as a non-metal oxidant due to its unique properties and selective oxidation capabilities. It is used for converting primary alcohols to aldehydes without further oxidation.
- **Swern Oxidation Reagent**: A combination of oxalyl chloride, dimethyl sulfoxide (DMSO), and a base, this reagent is used for the oxidation of primary and secondary alcohols to aldehydes and ketones, respectively.

7.3 Green Oxidants

Green oxidants refer to environmentally benign oxidizing agents used in organic chemistry that minimize or eliminate the generation of hazardous wastes and reduce environmental impact compared to traditional oxidants. These oxidants play a significant role in promoting sustainable chemistry practices. Here are some examples and characteristics of green oxidants:

a) **Hydrogen Peroxide (H_2O_2)**: Hydrogen peroxide is a versatile and environmentally friendly oxidant that can be used in various oxidation reactions. It decomposes into water and oxygen, leaving no harmful residues. It is often used in combination with catalysts such as transition metals or enzymes to enhance its efficacy.

b) **Ozone (O_3)**: Ozone is a powerful oxidizing agent that can be used in organic synthesis for selective oxidations. It decomposes into oxygen, making it environmentally benign. Ozone reactions often require careful control of conditions to prevent over-oxidation.

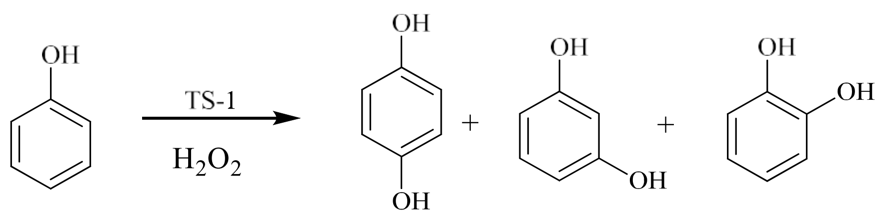
c) **Organic Peroxides**: Certain organic peroxides, such as tert-butyl hydroperoxide (TBHP), can serve as green oxidants. They are relatively stable and can selectively oxidize alcohols to carbonyl compounds under mild conditions.

d) **Sodium Hypochlorite (NaClO)**: Sodium hypochlorite, commonly known as bleach, is used as a mild oxidant in some organic transformations. It can be effective for oxidizing alcohols to carbonyl compounds and is generally less toxic compared to other chlorinated oxidants.

e) **Hydrogen Peroxide-Based Oxidants**: Modified forms of hydrogen peroxide, such as peroxy acids (e.g., performic acid, peracetic acid), can offer selective oxidation capabilities while degrading into harmless by-products.

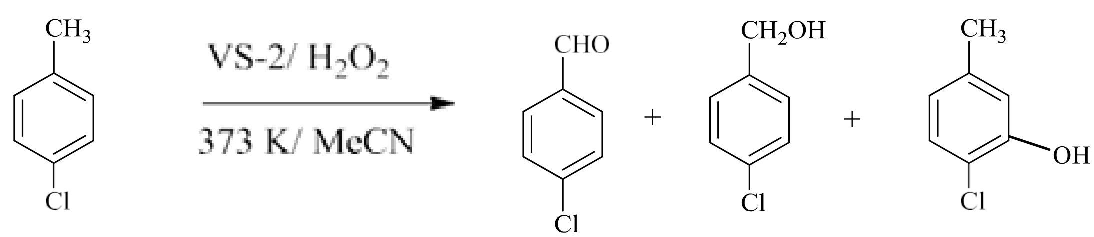
f) **Enzymes**: Certain enzymes, such as laccases or peroxidases, can catalyze oxidation reactions under mild conditions and with high selectivity. They are biodegradable and can be regenerated, making them environmentally friendly options for oxidation reactions.

7.4 Oxidation catalysts play a crucial role in the liquid-phase partial oxidation of organic substrates. Supported reagents, particularly molecular sieves containing titanium and vanadium, have demonstrated significant success in industrial applications. Titanium silicates (TS-I) are notably employed in the hydroxylation of phenol, yielding mixtures of hydroquinone and catechol, highlighting their pivotal role in these processes.



The process is environmentally friendly, achieving high product conversion with minimal waste generation.

Vanadium silicate molecular sieves selectively oxidize 4-chlorotoluene to 4-chlorobenzaldehyde using hydrogen peroxide as the oxygen source in acetonitrile solvent.



7.5 Biomimetic, Multifunctional Reagents

Scientists are working to understand the underlying mechanisms behind the various reactions that keep life in the human body. The goal of chemists is to simulate these processes in the lab.

Biological processes use the same reagent to execute various manipulations, unlike synthetic chemistry, which frequently uses catalysts for transformations including oxidation, reduction, and methylation. These procedures consist of various transformations, conformational shifts, and activation. Enzyme-catalyzed hydrolysis, biological oxidations, and reductions are now possible in laboratories. Many different kinds of proteins, including ligases, transferases, oxidoreductases, hydrolases, lyases, isomerases, and ligases, are essential to these activities.

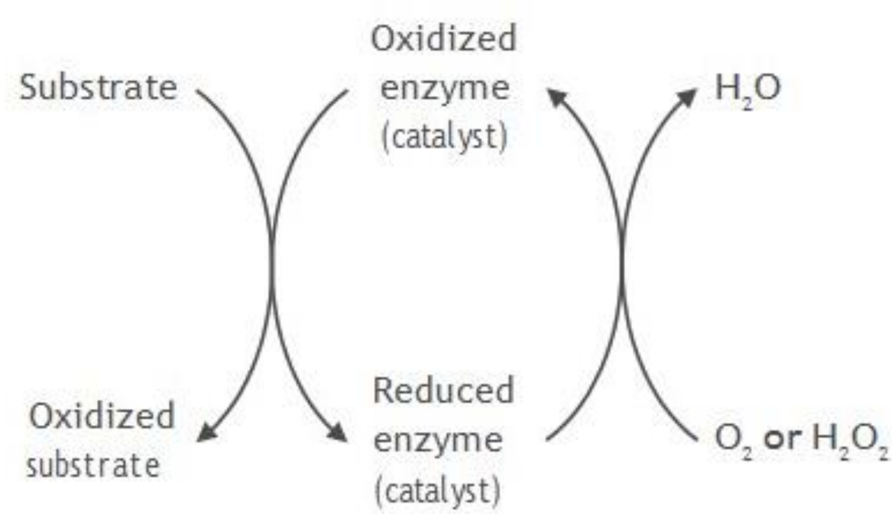
Biocatalytic conversions offer several advantages in the context of green chemistry:

a) **High Selectivity**: Enzymes are highly selective catalysts, often producing desired products without generating undesired by-products. This reduces the need for purification steps and minimizes waste.
b) **Mild Reaction Conditions**: Enzymes operate under mild conditions of temperature and pH, reducing energy consumption and potentially hazardous conditions compared to traditional chemical catalysts.
c) **Renewable and Sustainable**: Biocatalysts are derived from renewable resources (microorganisms, enzymes from plants or animals), making them environmentally sustainable.
d) **Reduced Chemical Waste**: The selectivity of biocatalysts means fewer side reactions and less chemical waste generated during the process, contributing to cleaner production methods.
e) **Biodegradability**: Enzymes are typically biodegradable and pose minimal risk to the environment after use, aligning with principles of sustainability and environmental safety.
f) **Versatility**: Enzymes can catalyze a wide range of reactions, including complex transformations, offering versatility in synthetic applications.
g) **Lower Energy Requirements**: Enzymes often require lower activation energies compared to traditional chemical catalysts, resulting in energy-efficient processes.
h) **Facilitates Use of Renewable Feedstocks**: Biocatalysts enable the use of renewable feedstocks and bio-based materials, further reducing reliance on fossil fuels and petrochemicals.

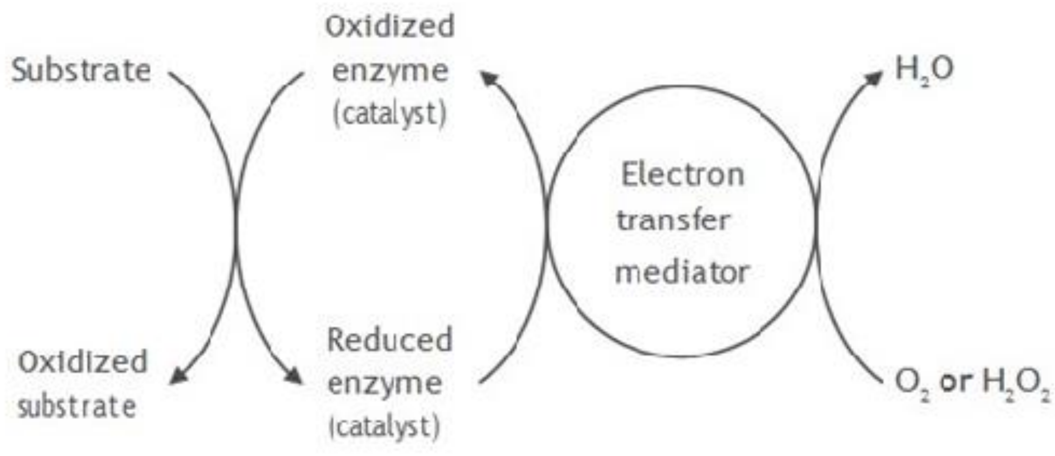
i) **Potential for Process Integration**: Biocatalytic processes can be integrated into existing industrial processes or combined with other green chemistry principles, such as solvent-free or aqueous reactions, to enhance sustainability.

j) **Regio- and Stereo-selectivity**: Enzymes can often control regio- and stereochemistry in complex molecules, enabling precise synthesis of chiral compounds, which is challenging with traditional chemical methods

A biomimetic catalyst operates in a manner similar to natural enzymes, mimicking their mode of action.



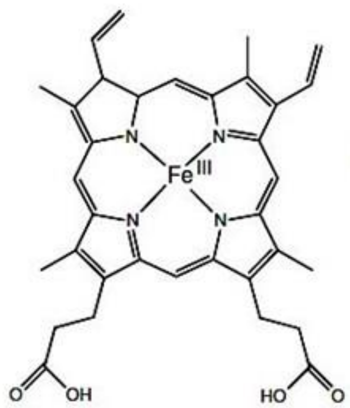
Biomimetic catalysis based on direct reocidation of enzyme(catalyst) by O_2 or H_2O_2

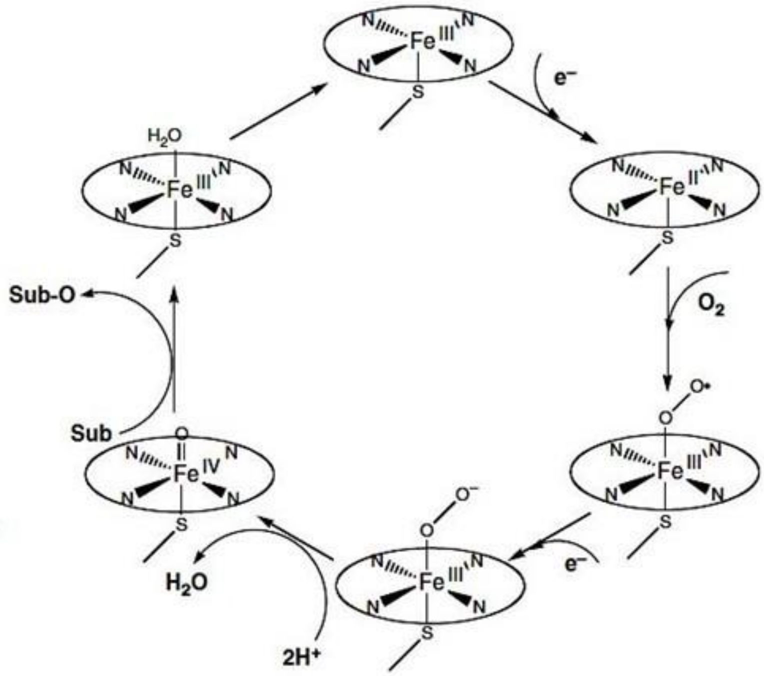


Biomometic catalysis based on electron-transfer mediator reoxidation of the enzyme

Biomimetic oxidation reactions, particularly those catalyzed by transition metal complexes, have significantly advanced scientific knowledge across various domains including structure, function, thermodynamics, kinetics, mechanism, synthesis, and improved analytical and spectroscopic techniques. Biomimetic chemists benefit from designing environmentally friendly catalysts, inspired by nature's preference for using non-toxic and abundantly available metals from the Earth's crust. Metals like manganese, iron, and copper are prominently involved in biological oxidation processes, with additional roles played by metals such as vanadium. These metals facilitate efficient electron transfer cycles essential for oxidation processes.

In natural oxidations, transition metals are typically coordinated by organic ligands. However, the challenge of ligand oxidation has often impeded the widespread adoption of highly effective commercial biomimetic oxidation catalysts. Nonetheless, even these imperfect catalysts can be classified as green catalysts due to their use of natural elements. They remain valuable in specific applications and contexts.





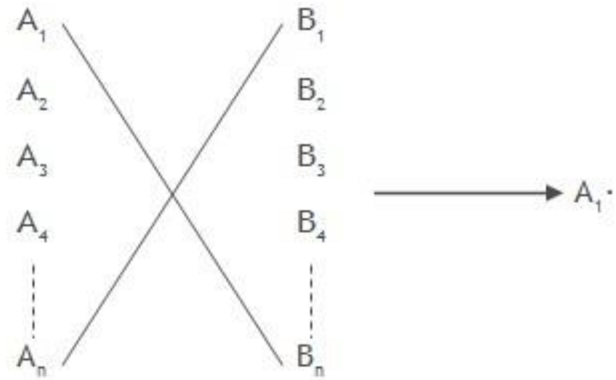
7.6 Combinatorial Chemistry

Combinatorial chemistry is a powerful approach in modern chemistry that revolutionizes the way new compounds are discovered and developed. It involves systematically creating large libraries of diverse compounds and rapidly screening them to identify those with specific desired properties. This method accelerates the process of drug discovery, materials science, catalysis, and other areas of chemical research.

Traditionally, chemists produced compounds one at a time. For instance, they would react compound A with compound B to obtain product AB. This product would then be isolated following reaction workup and purified using methods such as crystallization, distillation, or chromatography.

A+B → AB

In contrast to this traditional approach, combinatorial chemistry enables the synthesis of every possible combination of compound A_1 to An with compound B_1 to Bn.



Combinatorial Synthesis

Combinatorial techniques encompass a broad range, allowing for the synthesis of products either individually in parallel or as mixtures, utilizing both solution and solid-phase methods. Regardless of the technique employed, the key factor is the significant increase in productivity compared to traditional methods used over the past century.

7.6.1 Key Concepts and Techniques:

a) **Parallel Synthesis**: Combinatorial chemistry allows for the simultaneous synthesis of numerous compounds in a single experiment. This is achieved through automated systems or by utilizing solid-phase synthesis techniques where reactions occur on a solid support.

b) **Diversity-Oriented Synthesis**: The goal is to generate libraries of compounds that cover a wide range of chemical structures and properties. This diversity increases the likelihood of finding compounds with novel and useful characteristics.

c) **High-Throughput Screening (HTS)**: Once a library of compounds is synthesized, high-throughput screening methods are employed to quickly test each compound for specific activities or properties. This screening can involve biological assays, spectroscopic techniques, or other analytical methods.

d) **Rapid Optimization:** Combinatorial chemistry facilitates the optimization of lead compounds by systematically varying chemical structures and analyzing their effects on activity or properties. This iterative process accelerates the development of improved compounds.

e) **Computational Tools**: Computational methods play a crucial role in designing combinatorial libraries, predicting properties of compounds, and analyzing screening data. This integration of experimental and computational approaches enhances efficiency and effectiveness.

f) **Green Chemistry**: There is increasing emphasis on applying combinatorial chemistry principles to promote sustainability and reduce environmental impact. This includes using greener solvents, minimizing waste, and optimizing synthetic routes.

7.6.2 Applications:

- **Drug Discovery**: Combinatorial chemistry has significantly impacted pharmaceutical research by enabling the discovery of potential drug candidates with enhanced efficacy and reduced side effects.
- **Materials Science**: It has contributed to the development of new materials with tailored properties such as polymers, catalysts, and sensors.
- **Catalysis**: Rapid screening of catalyst libraries has led to the discovery of more efficient catalysts for various chemical transformations.

7.7 Proliferation of solvent-less reactions

Solvent-free reactions have gained widespread adoption in recent years due to their numerous advantages and contributions to green chemistry principles. Traditionally, chemical reactions have relied heavily on solvents to facilitate the mixing of reactants, control reaction conditions, and aid in product isolation. However, the use of solvents poses environmental and safety concerns, including waste generation, toxicity, and energy-intensive solvent recovery processes.

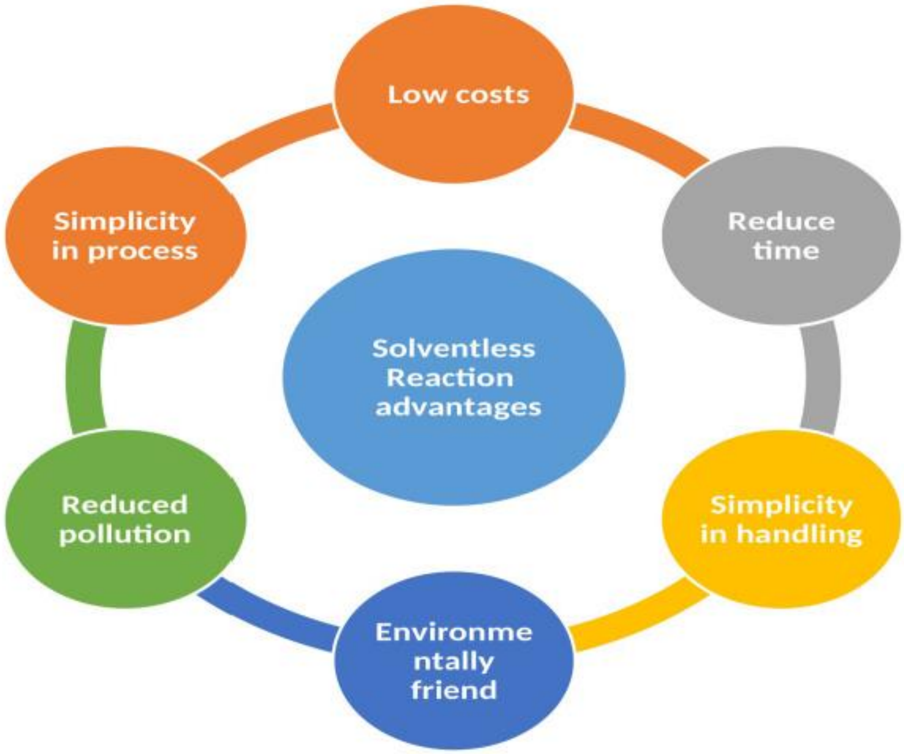
Solvent-free reactions have garnered significant attention among synthetic organic chemists. Many reactions have been discovered to proceed cleanly and efficiently in the solid state or without the use of solvents. Reduced chemical pollution, lower costs, and simplified procedures are key factors driving the recent surge in popularity of solvent-free reactions.

From the perspective of Green Chemistry, an ideal reaction should be conducted under solvent-free conditions, minimizing or eliminating side-product formation and maximizing atom economy. Solvent-free techniques are strategically important because solvents are often toxic, expensive, and pose challenges in terms of usage and disposal. This necessity has driven the development of modern technologies in this area.

Furthermore, these approaches facilitate experiments without the need for strong mineral acids (e.g., HCl, H_2SO_4), which can contribute to corrosion, safety hazards, handling difficulties, and environmental pollution through waste generation. Solid and recyclable acids such as clays offer advantageous replacements for these mineral acids.

7.7.1 Advantages of Solvent-Free Reactions:

a) **Environmental Sustainability**: Solvent-free reactions significantly reduce or eliminate the need for organic solvents, leading to reduced environmental impact and lower carbon footprint. This aligns with the goals of sustainable chemistry and resource conservation.
b) **Improved Safety**: Solvent-free conditions reduce the risk of solvent-related hazards such as flammability, toxicity, and exposure risks to workers. This enhances laboratory safety and minimizes health risks associated with chemical handling.
c) **Energy Efficiency**: Without the need for solvent evaporation or recovery, solvent-free reactions often require less energy input compared to traditional solvent-based processes. This contributes to overall energy efficiency and cost savings.
d) **Increased Reaction Concentration**: Solvent-free conditions allow for higher reactant concentrations, which can promote reaction efficiency and yield. This is particularly advantageous for reactions that are equilibrium-limited or require high concentrations of reactants.
e) **Simplified Product Isolation**: Products of solvent-free reactions are often easier to isolate and purify. They may require fewer purification steps, such as simple filtration or extraction, compared to solvent-based reactions involving solvent removal and recovery.
f) **Compatibility with Green Chemistry Principles**: Solvent-free reactions support several principles of green chemistry, including waste prevention, atom economy, and the use of safer chemicals and processes.



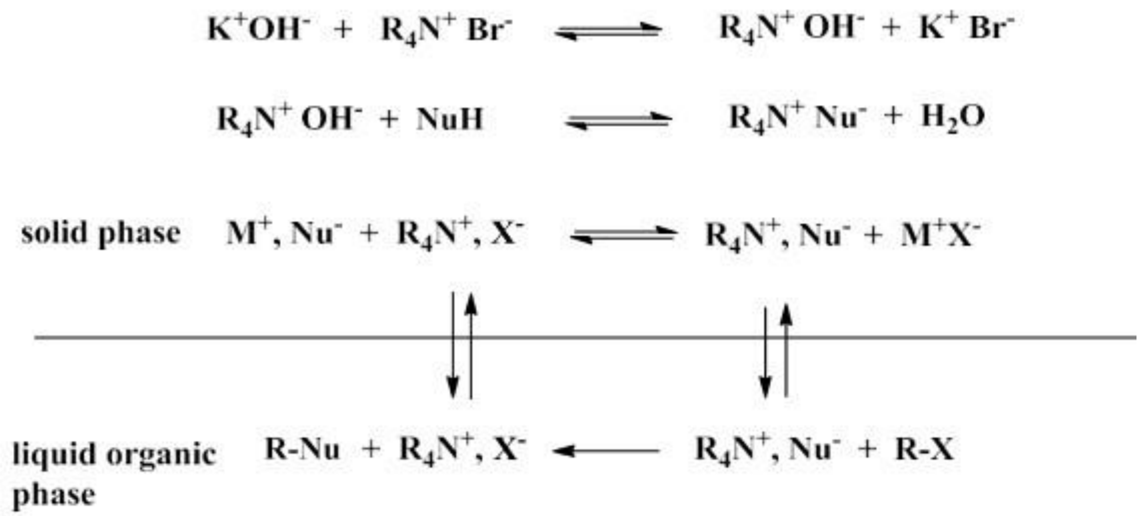
Some common advantages of solvent-free reactions

7.8 Solvent-free Techniques

Reactants are initially applied either as neat liquids onto solid supports like aluminas, silicas, and clays, or via solutions in suitable organic solvents, with subsequent solvent removal in the case of solid supports. Reactions in "dry media" proceed with individually impregnated reactants, often followed by heating. Upon completion of the reaction, organic products are easily extracted by elution with diethyl ether or dichloromethane.

Solvent-free and catalyst-free reactions: These heterogeneous reactions occur between neat reactants in approximately equivalent amounts without any additional substances. In solid-liquid mixtures, the reaction involves either dissolution of solids into the liquid phase or adsorption of liquids onto the solid surface, facilitating interfacial reactions.

Solid-liquid phase transfer catalysis (PTC) involves reactions where neat reactants are used in approximately equivalent amounts, facilitated by a catalytic quantity of tetraalkylammonium salts or cation-complexing agents. When conducted without solvents, the liquid organic phase contains the electrophilic reagent and potentially the reaction product.



Nucleophilic anionic species can be generated in situ by reacting their conjugate acids with strong solid bases, facilitated by ion-pair exchange involving $R_4N^+X^-$.

7.9 co crystal controlled solid state synthesis

Cocrystals are crystalline solids composed of two or more different molecular or ionic compounds in a specific stoichiometric ratio. They are distinct from solvates and simple salts. A broader definition describes cocrystals as having a unique crystalline structure and unique properties due to their composition of multiple components. Cocrystals can include hydrates, solvates, and clathrates, exemplifying the principles of host-guest chemistry. Numerous instances of cocrystallization are reported annually, demonstrating their versatility and wide-ranging applications.

Cocrystal-controlled solid-state synthesis utilizes cocrystals to align reactive components, enhancing reaction speed and yield compared to traditional solution methods. Cocrystallization of drug substances presents a significant opportunity for developing new drugs with improved physical and pharmacological properties, including solubility, stability, hygroscopicity, dissolution rates, and bioavailability.

Advancements in green chemistry have enabled the engineering and development of cocrystals through environmentally friendly approaches such as solvent-free solid-state synthesis. Moreover, there has been considerable focus on computational screening, continuous manufacturing of cocrystals, and real-time quality monitoring using various analytical tools.

7.9.1 Application of Co crystals

- Cocrystals have demonstrated diverse applications, including altering electrical properties and serving as organic semiconductors.
- In another notable application, hydroquinones were synthesized with diamine coformers and utilized in instant photograph development.
- Cocrystal reagents present intriguing opportunities as well. By forming cocrystals from olefins, solid-state reactions were conducted with high yields.
- Diarylethene exhibited unique photochemical reactions facilitated by the conformation induced by cocrystals.
- Furthermore, cocrystals have been employed to influence chiral resolution. For instance, co crystals prepared from the racemic mixture DL-arginine demonstrated differential solubility, leading to enantiomeric separation of D- and L-based cocrystals.

7.10 Green chemistry in sustainable development

Green chemistry is poised to become one of the most crucial fields in the future. Despite rapid advancements over the past two decades, it remains in its nascent stages. Promoting green chemistry is a long-term endeavor, requiring resolution of numerous challenging scientific and technological issues spanning chemistry, materials science, engineering, environmental science, physics, and biology. Collaboration among scientists, engineers, and industrialists is essential to advance this field. The development and adoption of green chemistry undoubtedly promise significant contributions to achieving sustainable societal development.

In the future, the expansion of green chemistry must accelerate significantly to meet the sustainability challenges posed by molecular science. Collaboration among relevant scientific, engineering, educational, and other communities is essential for fostering a sustainable future through green chemistry. Indeed, the principles of green chemistry are closely intertwined with a new ethical approach, suggesting that revolutionary practices today will become tomorrow's norms. Once the twelve principles of green chemistry are fully integrated into everyday chemical practices, the need to emphasize and rename green chemistry will diminish. At that point, chemistry will face unimaginable new challenges.

Moreover, the success of green chemistry hinges on educating and training a new generation of chemists. Students at all educational levels must be introduced to the philosophy and practical application of green chemistry. Education plays a pivotal role in overcoming the challenges of implementing green chemistry principles into practice. As Albert Einstein famously remarked, "The significant problems we face today cannot be solved at the same level of thinking we were at when we created them." This underscores the need for innovative approaches and transformative thinking in advancing green chemistry towards a sustainable future.

Summary:

The chapter explores several innovative approaches within green chemistry, beginning with oxidation reagents and catalysts that aim to minimize environmental impact while enhancing efficiency in chemical reactions. Biomimetic and multifunctional reagents draw inspiration from natural systems to develop synthetic methods that mimic biological processes. Combinatorial green chemistry methodologies focus on optimizing chemical processes through systematic exploration of reaction conditions and parameters. Green chemistry's role in sustainable development is underscored throughout these advancements, emphasizing the integration of environmentally friendly practices with economic viability

Keywords

Biomimetic, multifunctional reagents: Synthetic substances that mimic biological processes and perform multiple functions in chemical reactions.

Combinatorial chemistry: Methodologies for optimizing chemical processes by exploring various reaction conditions simultaneously.

Solvent-less reactions: Increasing use of techniques that eliminate the need for solvents in chemical reactions, reducing environmental footprint.

MCQ

1. Which type of chemistry focuses on minimizing environmental impact in oxidation processes?

    A) Reductive chemistry

    B) Green chemistry

    C) Biochemistry

    D) Inorganic chemistry **Answer: B)**

2. What is a primary objective of biomimetic, multifunctional reagents in green chemistry?

A) Enhancing toxicity

B) Mimicking biological processes

C) Increasing waste generation

D) Using traditional reagents **Answer: B)**

3. Combinatorial green chemistry aims to optimize processes by:

A) Increasing waste

B) Using toxic chemicals

C) Systematically exploring conditions

D) Minimizing resource use **Answer: C)**

3. Advancements in solventless reactions contribute to:

A) Increased pollution

B) Lower safety standards

C) Enhanced production efficiency

D) Greater solvent use **Answer: C)**

4. Co-crystal controlled solid-state synthesis focuses on:

A) Maximizing solvent use

B) Minimizing purity

C) Using hazardous chemicals

D) Minimizing solvent use **Answer: D)**

5. Green chemistry in sustainable development integrates practices such as:

A) Increasing waste production

B) Avoiding renewable resources

C) Energy efficiency and waste reduction

D) Toxic material use **Answer: C)**

Short Answer Questions

1. What are biomimetic, multifunctional reagents in green chemistry? How do they differ from traditional reagents?
2. Describe the concept of combinatorial green chemistry.
3. Explain the co-crystal controlled solid state synthesis (C2S3)
4. How does green chemistry contribute to sustainable development

REFERENCES

1) Green Chemistry: Theory and Practice. P.T. Anastas and J.C. Warner. Oxford University Press, 2000.

2) Green Chemistry: Introductory Text. M. Lancaster, Royal Society of Chemistry (London), 2010.

3) Introduction to Green Chemistry. M. A. Ryan and M. Tinnes and, American Chemical Society (Washington), 2002.

4) Real World Cases in Green Chemistry. M.C. Cann and M.E. Connelly. American Chemical Society, 2008.

5) A Textbook of Green Chemistry, Dey, Sankar and Sepay, Nayim., 2021.