ISSN (Online): 2455-3662
EPRA International Journal of Multidisciplinary Research (IJMR) - Peer Reviewed Journal
Volume: 11| Issue: 4| April 2025|| Journal DOI: 10.36713/epra2013 || SJIF Impact Factor 2025: 8.691 || ISI Value: 1.188

GREEN ANALYTICAL CHEMISTRY

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ABSTRACT

Green chemistry is an approach to the design production and use of chemicals that aims to the intentionally reduce or eliminate the hazardous chemicals. Eat focuses on reducing recycling and eliminating the use of toxic and harmful chemicals in manufacturing processes by minimizing the environment impact and finding creative alternative ways to produce desirable products. The article introduces the basic principles underlying the concept of green chemistry.

KEY WORDS: *Green Chemistry, Eco-Friendly, Sustainability.*

1. INTRODUCTION

Green Chemistry refers to the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances. When this concept is extended to the field of analytical chemistry, we arrive at the idea of **Green Analytical Chemistry (GAC)**.

Green Analytical Chemistry integrates the principles of Green Chemistry into analytical practices, focusing on reducing environmental impact and promoting safer, more sustainable methods. GAC adds a value-based perspective to traditional analytical chemistry by considering environmental and safety factors in the development and implementation of analytical techniques. This approach encourages innovation and drives research toward more sustainable practices in the field.

The principles of Green Analytical Chemistry have been recently outlined and can be remembered using a mnemonic acronym:

SIGNIFICANCE

- **S** – Select direct analytical methods
- **I** – Integrate analytical processes and operations
- **G** – Generate minimal waste and manage it responsibly
- **N** – Never waste energy
- **I** – Implement automated and miniaturized methods
- **F** – Favor materials from renewable sources
- **I** – Increase operator safety
- **C** – Carry out in-situ measurements
- **A** – Avoid derivatization steps
- **N** – Note that sample size and number should be minimized
- **C** – Choose multi-analyte and multi-parameter techniques
- **E** – Eliminate or substitute toxic solvents

Green Analytical Chemistry has established its own role within the broader field of analytical chemistry. Its main objective is to reduce the environmental footprint of laboratories involved in medical, environmental, food, and industrial testing.

Various strategies fall under the umbrella of GAC, with a key focus on selecting analytical approaches that lessen environmental harm. This includes optimizing sample preparation, avoiding unnecessary procedures, replacing hazardous chemicals, and generally minimizing the ecological impact of analytical practices.

2. HISTORY

Between 1994 and 1998, Paul Anastas edited several important texts on Green Chemistry, published as part of the ACS Symposium Series. These works included *Benign by Design: Alternative Synthetic Design for Pollution Prevention*, *Green Chemistry: Designing Chemistry for the Environment*, and two influential books released by Oxford University Press: *Green Chemistry: Theory and Practice* and *Green Chemistry: Frontiers in Benign Chemical Synthesis and Processes*.

The foundation of Green Chemistry in the United States was significantly shaped by the **Pollution Prevention Act of 1990**, which emphasized eliminating pollution through smarter design strategies. This national policy advocated for reducing pollution at its source through improvements in product design, raw material selection, process efficiency, and recycling, rather than relying solely on treatment and disposal. Although the U.S. Environmental Protection Agency (EPA) traditionally focused on end-of-pipe regulation, it gradually moved toward integrating the principles of Green Chemistry into its practices.

In 1994, the **Royal Society of Chemistry** launched the journal *Green Chemistry*, promoting a new vision for the field that emphasized environmentally responsible practices in both research and industry. Around the same time, the Journal of Analytical Chemistry began highlighting key innovations in Green Analytical Chemistry (GAC).

Some important milestones in the development of Green Analytical Chemistry include:

- **1987**: At the EcoAnalysis Conference in Paris, Melissa introduced early concepts relating to environmentally conscious practices in analytical chemistry.
- **1994**: During the Flow Analysis Conference in Toledo, Spain, new methods for real-time waste degradation were presented.

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- **1995**: A special issue of *Analytical Chemistry* focused on environmentally friendly practices in the field, marking a pivotal step in articulating GAC principles.
- **1998**: Paul Anastas and John Warner formulated the **12 Principles of Green Chemistry**, laying the theoretical foundation for the field.
- **1999**: Anastas published work emphasizing the significance of applying these principles to analytical method development.
- **2000**: Green Analytical Chemistry began to formally emerge as a subfield of Green Chemistry.
- **2013**: Researchers Galuszka, Migaszewski, and Namieśnik adapted the 12 Green Chemistry principles specifically for Green Analytical Chemistry, refining them to suit the unique requirements of analytical processes.

These principles, introduced by Anastas and Warner, serve as a practical framework for minimizing the environmental and health impacts associated with chemical practices and synthesis. They provide a guideline for developing safer, more efficient, and sustainable chemical methods.

3. PRINCIPLES OF GREEN CHEMISTRY

What is Green Chemistry, and What Makes Chemistry 'Green'? Green Chemistry refers to the approach of designing chemical products and processes in a way that reduces or completely eliminates the use and generation of hazardous substances. It emerged as a focused scientific movement in the 1990s, when growing concerns over the environmental and health impacts of traditional chemical practices pushed scientists to find more sustainable alternatives. To provide guidance in this area, 12 Principles of Green Chemistry were introduced, outlining key strategies for making chemical processes safer, cleaner, and more efficient.

1. **Waste Prevention**

The first principle emphasizes that it is better to prevent waste than to treat or clean it up after it has been created. Chemical processes should be designed to minimize the amount of waste produced. To measure the efficiency of a process in terms of waste generation, a metric called the Environmental Factor (E-Factor) is used. It is calculated by dividing the mass of waste produced by the mass of the final product. A lower E-Factor indicates a more sustainable and environmentally friendly process.

What is Green Chemistry, and What Makes Chemistry 'Green'? Green Chemistry is an innovative scientific approach focused on designing chemical products and processes that minimize or eliminate the generation of hazardous substances. It aims to address the environmental and health risks traditionally associated with chemical manufacturing. The concept gained prominence in the 1990s, leading to the development of **12 foundational principles** that help guide chemists toward more sustainable practices.

Strategies to Prevent Waste in Green Chemistry

- **Design Efficient Processes**: Consider the full lifecycle of a product—from raw materials to disposal—to reduce environmental impact.
- **Minimize Synthetic Steps**: Fewer reaction steps mean faster production and less waste generation.

1. Atom Economy

Definition: Atom economy refers to the proportion of starting material atoms that are incorporated into the final product. A higher atom economy means less waste.

Benefits: It's a key measure of how sustainable a process is and helps limit pollution at the molecular level.

Development: The concept was introduced by Barry Trost in 1991 and recognized with a Presidential Green Chemistry Challenge Award in 1998.

Calculation

Atom Economy=(Molecular Mass of Desired ProductTotal Mass of All Reactants)
×100\text{Atom Economy} = \left(\frac{\text{Molecular Mass of Desired Product}}{\text{Total Mass of All Reactants}} \right) \times
100Atom Economy=(Total Mass of All ReactantsMolecular Mass of Desired Prod uct)×100

Comparison to Yield: Atom economy focuses on waste reduction, whereas yield only considers the amount of product obtained.

2. Less Hazardous Chemical Syntheses

Chemical processes should aim to be as non-toxic and safe as possible, using less dangerous substances from the start and avoiding the generation of hazardous byproducts.

Methods

- **Use Safer Chemicals**: Substitute harmful substances with benign alternatives (e.g., using CO_2 instead of chlorofluorocarbons).
- **Enzymatic Reactions**: Enzymes can offer precise reactivity and eliminate the need for complex protective steps.
- **Physical Techniques**: Tools like microwave and ultrasound-assisted reactions can minimize solvent use and reduce hazards.
- **Biological Approaches**: While currently more common in labs, biological pathways offer sustainable reaction alternatives.

3. Designing Safer Chemicals

Chemical products should be effective in their intended function while being non- toxic to humans and the environment.

Key Focus

- Understanding molecular toxicity is essential, especially for newly developed compounds.
- Toxicological studies and predictive models guide safer chemical design.

4. Safer Solvents and Auxiliaries

Solvents and other auxiliary agents often contribute to the

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toxicity and energy demands of a process. Safer, less volatile, and recyclable options should be prioritized.

Considerations

- Choose solvents that reduce energy use and environmental impact.
- Auxiliaries, although useful, should be minimized due to potential waste and efficiency issues.

5. Design for Energy Efficiency

Reactions should be carried out under mild conditions (e.g., room temperature and pressure) to lower energy requirements and environmental impact.

Suggestions:

- Recognize the environmental and financial cost of energy usage.
- Opt for synthetic routes that work under ambient conditions.

6. Use of Renewable Feedstocks

Instead of relying on fossil fuel-based inputs, chemical processes should use renewable materials like plant-based compounds.

Applications

- **Raw Materials**: Use in producing plastics, medicines, solvents, and more.
- **Energy**: Feedstocks can replace fossil fuels for powering machinery.
- **Coatings & Polymers**: Enable sustainable manufacturing of surfactants and dispersions.
- **Waste Conversion**: Agricultural and food waste can serve as feedstock.
- **Catalyst Production**: Renewable sources can also contribute to green catalyst development.

7. Reduce Derivatives

Chemical derivatization—such as adding protecting groups—often results in more waste and lower efficiency.

Alternatives

- Enzymatic reactions allow for selective targeting of molecular sites, eliminating unnecessary derivatization.
- Processes like HYDECAT use recyclable catalysts to reduce harmful byproducts.

8. Catalysis

Catalysts increase reaction efficiency and can be reused multiple times, reducing waste and the need for excess reagents.

Examples

- **Laccases**: Natural enzymes used in paper and textile industries.
- **Nano TiO_2**: A recyclable photocatalyst.
- **Nano-Y-Fe_2O_3-SO_3H**: A magnetic catalyst reusable up to five times.
- **Sulfonated Rice Husk Ash**: A low-cost, sustainable acid catalyst.
- **Chlorine Radicals**: Help understand ozone depletion and catalysis in gas- phase reactions.

9. Design for Degradation

Chemical products should be designed to break down into harmless components once they've served their purpose.

Examples

- **Biodegradable Plastics**
- **Eco-friendly Detergents**
- **Sustainable Electronics**: Including degradable battery components

10. Real-Time Pollution Prevention

Monitoring chemical processes as they happen helps detect issues early, avoiding unexpected releases or accidents.

Uses

- Monitor reaction progress, pH, and temperature
- Detect catalyst deactivation or decomposition
- Track pollutants in environmental samples

Industry Role: The FDA encourages real-time monitoring in pharmaceutical manufacturing to ensure safety and compliance.

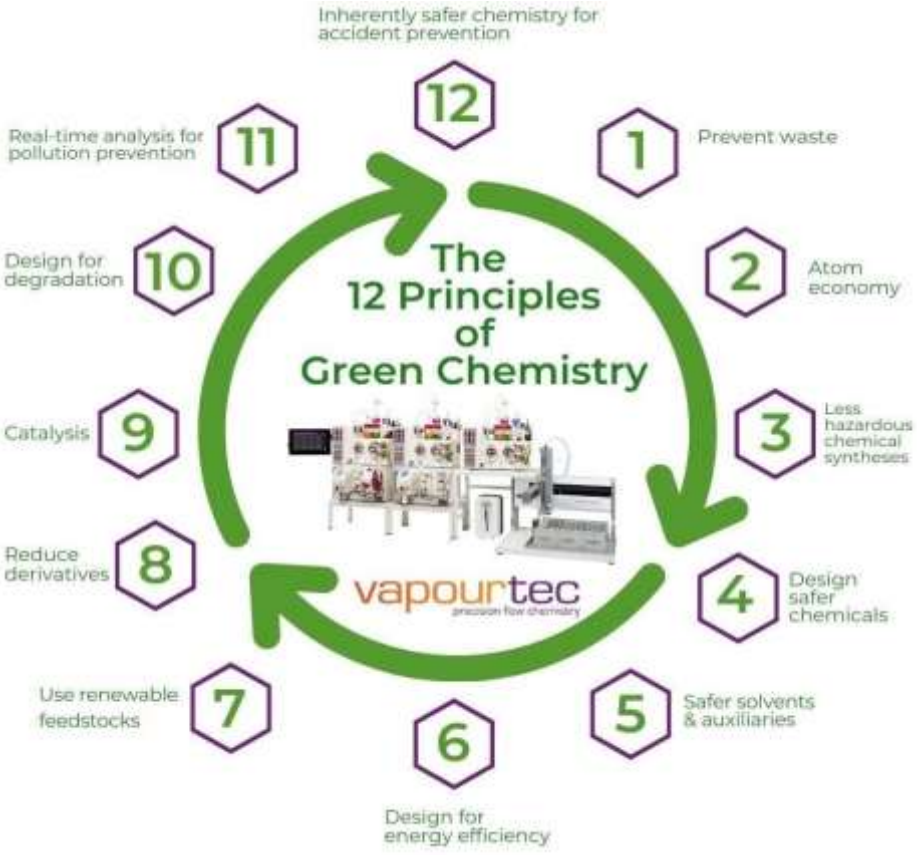
11. Safer Chemistry for Accident Prevention

Reactions and procedures should be designed to reduce the risk of explosions, fires, or exposure to harmful substances.

Best Practices

- Select safer reagents and ingredients
- Avoid highly reactive or unstable compounds
- Clean up spills immediately
- Evaluate hazards using environmental risk indices
- Continuously assess and improve chemical protocol.

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4. GREENING PRE-TREATMENT

Green Pretreatment: A Sustainable Solution for Biomass Processing

Green pretreatment refers to a set of environmentally friendly methods used to separate the main components of **lignocellulosic biomass**. These approaches offer a cleaner and safer alternative to traditional pretreatment techniques, which often involve harmful chemicals, high energy consumption, and potential hazards to human health, equipment, and ecosystems.

Key Benefits of Green Pretreatment

Green pretreatment methods are designed to:

- Reduce the reliance on toxic and hazardous solvents
- Lower the energy needed during the treatment process
- Use chemicals that are safer and more sustainable
- Minimize waste production and environmental impact

Common Green Pretreatment Methods

1. Ionic Liquids

Ionic liquids are specialized solvents capable of breaking down biomass by dissolving its structural components—cellulose, hemicellulose, and lignin— efficiently and with less environmental harm compared to conventional solvents.

2. Organosolv Pretreatment

This technique uses organic solvents in a controlled, eco-friendly manner to disrupt the structure of lignocellulosic materials, making them more accessible for further processing like enzymatic hydrolysis or fermentation.

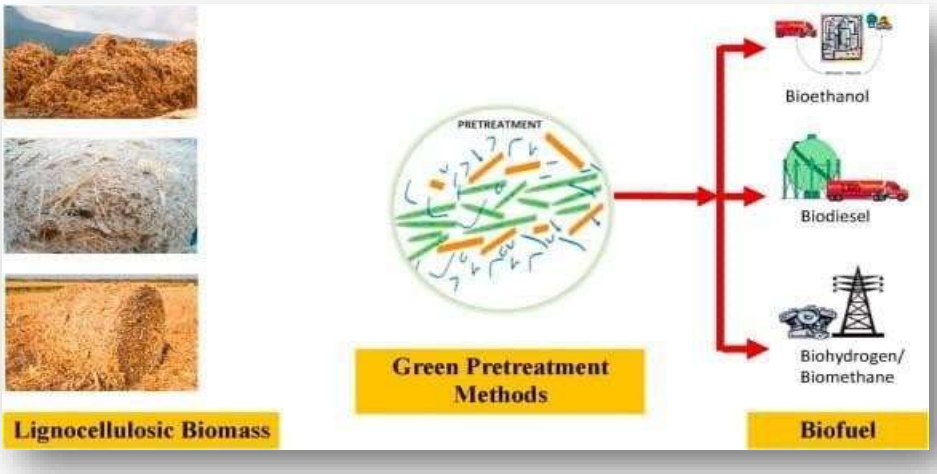
3. Biological Pretreatment

In this method, naturally occurring fungi—such as white rot, brown rot, and soft rot species—are used to degrade lignin in biomass. It is a low-impact, low-energy approach that leverages biological processes for efficient material breakdown.

4. Deep Eutectic Solvents (DESs)

DESs are a new class of green solvents composed of biodegradable and non-toxic compounds.

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These solvents are effective in processing a variety of plant-based feedstocks, including those from forests, broadleaf vegetation, and plants like **Hibiscus**, making them an adaptable and sustainable option.

4.1 SOLVENT REDUCTION AND REPLACEMENT

Solvent Reduction and Replacement in Green Chemistry
Significant advancements have been made in Green Chemistry, particularly in the effort to replace hazardous **dipolar aprotic solvents**—such as **1,4-dioxane**, **N- methyl-2-pyrrolidone (NMP)**, and others—commonly used in the processing of industrially active compounds. These solvents pose risks to both human health and the environment, prompting the development of safer alternatives.
Recommended Alternatives in Synthetic Chemistry
In various chemical synthesis processes, greener solvent options are now being adopted, including:

- **Alcohols**
- **Carbonates**
- **Ethers**
- **Glycols**
- **Furans**
- **Water**

These alternatives are less toxic and more environmentally benign, making them preferable choices for sustainable chemical processes.

Supercritical CO_2 as a Green Solvent
Supercritical carbon dioxide (SC-CO_2) is increasingly being used as a green alternative to traditional organic solvents, especially in the extraction of compounds from natural materials. It offers several benefits, including low toxicity, non-flammability, and ease of removal from final products.

To further enhance extraction efficiency, SC-CO_2 is often used in combination with **natural co-solvents** derived from plant-based sources—such as **vegetables, legumes, seeds, and oats**. These materials can be incorporated into the process as **co-extractants**, helping to replace commonly used solvents like ethanol or methanol in SC-CO_2 extraction systems.

A) Ultrasound



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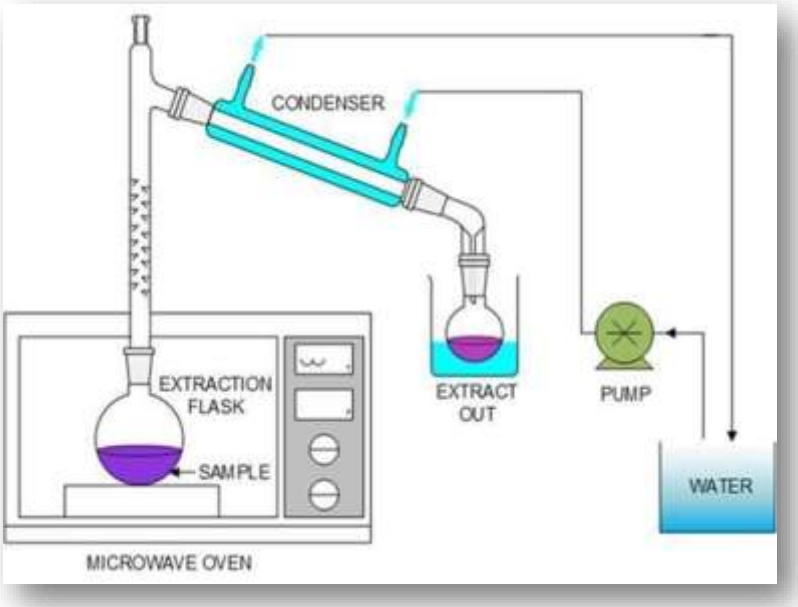
B) Microwave Assisted Extraction [MAE]

Microwave-Assisted Extraction (MAE): A Green Technology for Sustainable Processing

Microwave-Assisted Extraction (MAE) is considered a green and efficient technology that offers several environmental benefits. It enhances the extraction of compounds from various materials while reducing the environmental footprint of traditional methods.

Environmental Advantages of MAE

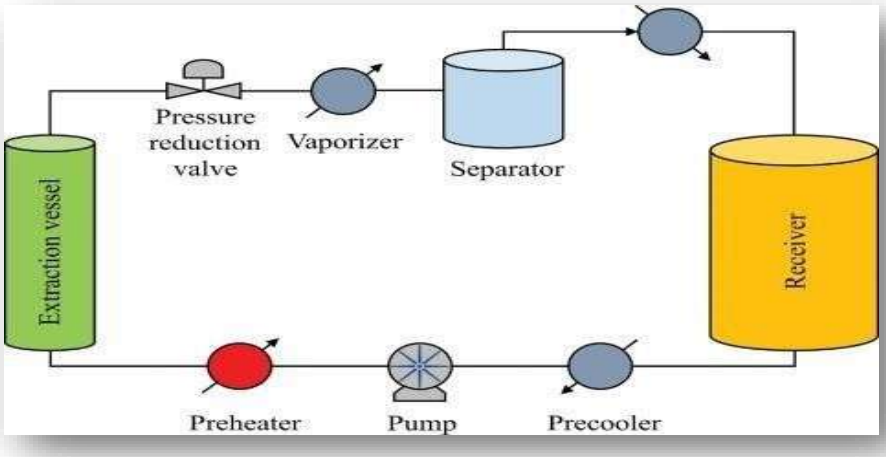
1. **Reduced Solvent Usage**
   MAE requires significantly less solvent compared to conventional extraction methods, which leads to a decrease in chemical waste and minimizes the impact on the environment.
2. **Lower Energy Consumption**
   The process is energy-efficient, as microwaves can rapidly heat samples, reducing overall processing time and lowering the energy required for extraction.
3. **High Throughput Capabilities**
   MAE allows for the simultaneous extraction of multiple samples—up to 40 at a time—improving efficiency and productivity in laboratory settings.



C) Supercritical Fluid Extraction (SFE)

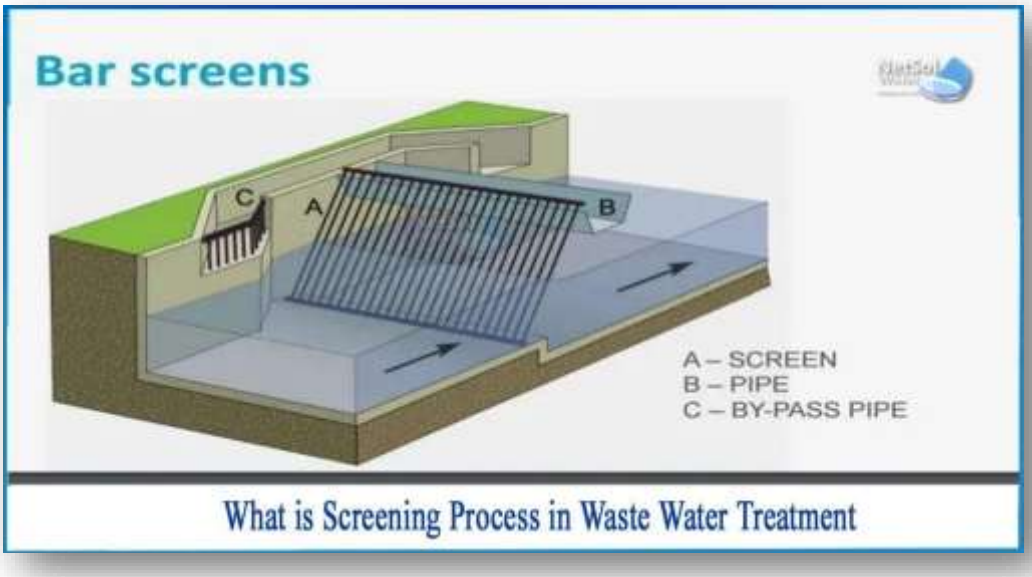
Supercritical Fluid Extraction (SFE) is an advanced technique that helps reduce the environmental impact of volatile organic compounds (VOCs) by preventing their release into the environment. This method utilizes supercritical fluids—such as **supercritical CO_2**—which are capable of selectively extracting compounds without generating harmful waste. Additionally, the solvents used in SFE can be **recaptured and reused**, making the process more sustainable and cost-effective.

SFE is particularly effective for extracting contaminants, such as **pesticides**, from soil and other environmental matrices, offering an eco-friendly alternative to traditional remediation methods.



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A) Greening through Screening



This refers to a range of processes designed to identify environmental and climatic issues, as well as opportunities for intervention. These processes typically utilize tools such as **Strategic Environmental Assessment (SEA)** and **Environmental Impact Assessment (EIA)**, which help evaluate the potential environmental effects of projects and policies before they are implemented.

6.1 SOLVENT ELIMINATION:

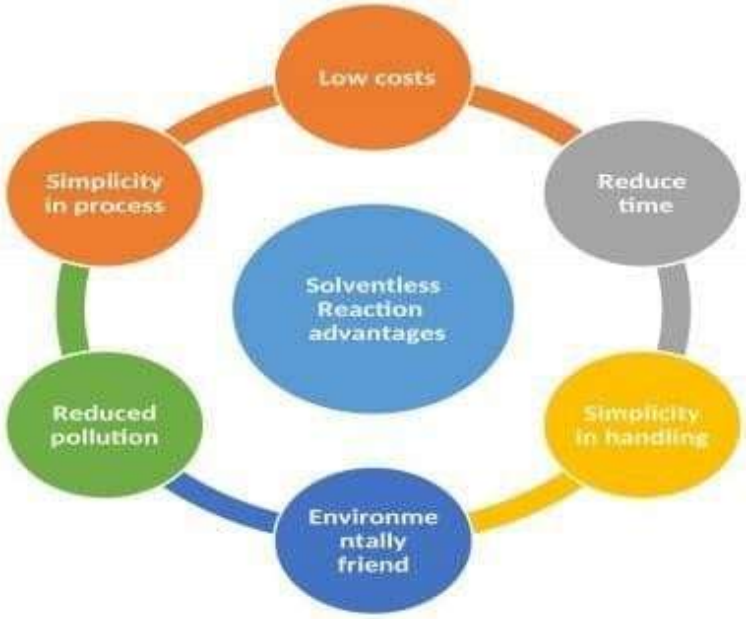
"No Co-Operation Without Fluids" – Aristotle's Belief

Aristotle once believed that "No reaction occurs in the absence of a solvent." However, this is not true.

A **solventless reaction**—also known as a **dry reaction** or **solid-state reaction**—is a chemical reaction that takes place without the use of a solvent. These reactions can occur in various states, such as between solid reactants, or on surfaces where no solvent is involved.

Advantages of Solventless Reactions

- **Economical**: No solvent is required, reducing costs associated with purchasing, disposing of, or recovering solvents.
- **Faster Reaction Rates**: Without solvents, some reactions proceed more rapidly due to the direct interaction of reactants.
- **Environmentally Friendly**: The absence of solvents eliminates the need for toxic chemicals, reducing the impact on the environment.
- **Simple to Handle**: Without solvents, handling and processing materials become simpler, and there is a reduction in the production of waste and pollution.

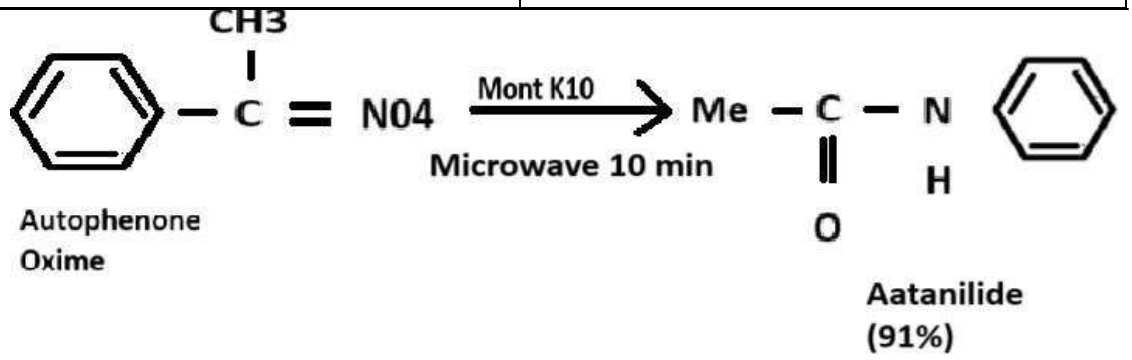


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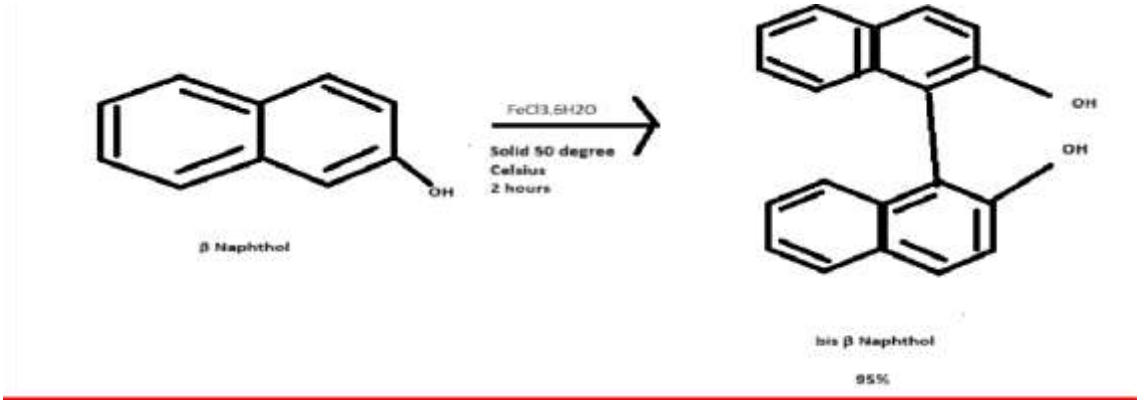
Ex;

- **Beckmann Rearrangement**

Usual Treatment	Green Synthesis
Backmann rearrangement of oximen of letoner are counted into any leader by hitting withreagents like PCI2, HCCOOH, SoCl2 etc.	Oximen of a lutone is mixed with mont monmorllonite and radiated for 7 minutes in microwave oven to give corresponding anilide in 91% yield.



- **Oxidative couplings of phenols**



Usual Treatment	Green Synthesis
oxidative couplings of phenols in solution with metal salts such as FeCl3 or Manganese bis(acetyabutonate) although the later one is too expensive to use in a large quantity.	In 1989, Toda et al have reported oxidative coupling of phenols in presence of FeCl36H2O proceed merge faster in the solid state than the solution.

5. RESEARCH AND DEVELOPMENT IN THE FIELD OFGREEN CHEMISTRY

Key Aspects of Green Chemistry R&D

1. **Developing Alternative Feedstocks**
   Green chemistry focuses on utilizing **renewable resources**, such as **biomass**, instead of relying on **fossil fuels** as starting materials for chemical synthesis. This reduces dependence on non-renewable resources and supports sustainability.
2. **Designing Safer Chemicals**
   The goal is to create **molecules with reduced toxicity** and **environmental persistence**, ensuring they fulfill their intended purpose without posing long- term risks to human health or the ecosystem.
3. **Optimizing Reaction Pathways**
   Green chemistry encourages the use of **catalytic processes** to minimize waste generation and maximize product yield. This approach enhances the efficiency of chemical reactions, reducing both material and energy waste.
4. **Solvent Selection**
   Green chemistry promotes the identification and use of **less hazardous solvents** or even **solvent-free reactions**. This helps reduce the environmental and health risks associated with traditional solvent use.
5. **Energy Efficiency**
   Processes are designed to operate at **lower temperatures** and **pressures**, reducing energy consumption. Energy efficiency is a critical aspect of reducing the carbon footprint of chemical processes.
6. **Waste Minimization**
   Green chemistry focuses on **preventing waste generation** through careful design and process optimization. **Atom economy** is a key principle, ensuring that the maximum amount of reactants is converted into useful products, leaving minimal waste behind.
7. **Biomimicry**
   By studying **natural systems**, green chemistry seeks to develop **environmentally friendly chemical processes** that mimic the efficiency and sustainability found in

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nature.

8. **Life Cycle Analysis**
   Green chemistry incorporates **life cycle analysis (LCA)** to assess the **environmental impact** of a chemical product from **production** to **disposal**, helping identify areas for improvement and ensuring the process is truly sustainable.

5.1 ALTERNATIVE FEEDSTOCKS

Green Chemistry and the Use of Renewable Resources

Green Chemistry encourages the development of innovative technologies that harness the potential of **renewable resources**. Traditionally, chemical products have been made using materials that are either **toxic** or derived from **non-renewable sources** such as **petroleum**. However, modern Green Chemistry research focuses on replacing these with **renewable**, **non-toxic**, and **environmentally friendly alternatives**, such as **plants** and **agricultural waste**.

Utilizing Biomass as a Resource

A significant portion of **biomass**—up to **80%**—consists of complex carbohydrates that can be broken down and **fermented** into valuable chemical commodities, including:

- **Ethanol**
- **Organic acids**
- **Glycols**
- **Aldehydes**

This process not only reduces dependence on fossil fuels but also contributes to waste valorization by utilizing by-products of agriculture.

Advancements in Biomass Conversion

The conversion of **biomass to ethanol** has become both **economically viable** and **technologically advanced**, thanks to **genetically engineered bacteria**. These microbes are capable of breaking down the diverse sugars found in **hemicellulose**, enhancing the efficiency of the fermentation process and enabling more effective use of renewable materials.



5.2 Benign Manufacturing

Benign manufacturing refers to the development of cleaner and safer methods for producing chemical materials. Traditional **synthetic methods**, commonly used in chemical manufacturing, have often resulted in the generation of large amounts of **hazardous waste**.

Green Chemistry aims to transform these methods by making them more **efficient** and **environmentally responsible**. Research in this area focuses on minimizing or eliminating unnecessary steps, such as:

- The use of **protecting or blocking groups**
- **Temporary modifications** of molecules during synthesis
- Unnecessary **physicochemical processing**

By reducing such steps, green synthetic methods not only cut down on waste but also lower energy consumption, improve **atom economy**, and enhance the **overall sustainability** of chemical production. These innovations are crucial in achieving the broader goals of Green Chemistry and creating safer industrial practices.



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METATHESIS IN GREEN CHEMISTRY: - Metathesis Reactions: Changing Places for a Sustainable Future

The term **"metathesis"** originates from the Greek word meaning **"to change places."** In chemistry, metathesis reactions involve the breaking and forming of **carbon–carbon double bonds**, leading to the exchange of atomic groups between molecules.

A simplified representation of a metathesis reaction is:

A–B + C–D → A–C + B–D

Significance in Green Chemistry

Metathesis reactions are highly valuable in modern chemical synthesis for the following reasons:

1. **Efficiency**
   These reactions often require **fewer steps**, consume **fewer resources**, and produce **less waste**, making the overall process more sustainable.
2. **Simplicity**
   Many metathesis reactions are **air-stable** and do not require extreme conditions, making them easier to handle and implement in laboratories or industry.
3. **Environmental Friendliness**
   The use of **non-toxic solvents**, **lower energy requirements**, and **fewer byproducts** makes metathesis a **green alternative** to traditional chemical reactions.

Olefin Metathesis: A Key Example

Olefin metathesis is a well-known example of a metathesis reaction, where **alkene groups** are exchanged using **metal catalysts**. First observed in the 1950s, it has since become a powerful tool in both industrial and academic chemistry.

This reaction aligns closely with the **principles of Green Chemistry**, promoting more sustainable and cleaner synthesis methods by:

- Reducing hazardous waste
- Minimizing energy consumption
- Enhancing atom economy

Olefin metathesis continues to play a central role in developing **eco-friendly** and **cost-effective** chemical processes across various fields.

6. CONCLUSION

Green Chemistry: A Path Toward a Sustainable Future

Green Chemistry seeks to develop new chemical practices and principles that provide solutions to global challenges such as climate change. It focuses on the creation of chemical methods and substances designed to protect the environment and reduce harmful impacts on human health and ecosystems. Understanding and applying the principles of Green Chemistry is crucial for ensuring a sustainable future for generations to come.

More importantly, it is essential that the scientific, technical, educational, and broader community work together to promote and implement Green Chemistry for a sustainable future. Many organic and inorganic materials currently have harmful effects on human health and the environment, but Green Chemistry offers a pathway for sustainable development through:

- **Green synthesis**
- **Energy-efficient production processes**
- **Recycling and reuse of materials**

Various international organizations are promoting Green Chemistry principles, which include:

- Waste prevention
- Reducing the use of harmful materials
- Development of less hazardous synthesis methods
- Creation of safer chemicals
- Biodegradable materials
- Use of renewable raw materials
- Energy-efficient processes
- Catalytic processes
- Environmentally friendly solvents

By adhering to these principles, Green Chemistry plays a pivotal role in building a more sustainable, eco-friendly world.

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