

# Green Chemistry

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## ABSTRACT

Green chemistry, also known as sustainable chemistry, refers to the development of chemical products and processes that minimize or eliminate the usage and production of harmful compounds. They only utilize environmentally friendly chemicals and chemical procedures. It is built on twelve principles that can be used to develop or reproduce molecules, materials, reactions, and processes that are safer for human health and the environment from the ground up. Green Chemistry decreases the environmental impact of chemical processes and technologies, as demonstrated in this article. The goal of this review is to learn more about the role of catalysts in green chemical synthesis for a more sustainable future. In the ecologically friendly synthesis of novel and existing compounds, catalysis plays a critical role. Catalysed processes require less energy to produce and produce fewer by-products, co-products, and other waste items, indicating increased efficiency. Catalysts can be created in such a way that they are not harmful to the environment. Catalysts come in a variety of shapes and sizes, and some of them have positive effects in the chemical industry. The aim of present review is to synthesize the organic compounds by using green chemistry approach and understand the methods and the alternative economically used chemical initiators.

## Module 1: Introduction to green chemistry and catalysis Basic principle and concept of green chemistry

**Definition of green chemistry:** Green chemistry is the design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances. Green chemistry applies across the lifecycle of a chemical product, including its design, manufacture, use, and ultimate disposal.

1. Prevent waste: Design chemical syntheses to prevent waste. Leave no waste to treat or cleanup.
2. Maximize atom economy: Design syntheses so that

the final product contains the maximum proportion of the starting

materials. Waste few or no atoms.

3. Design less hazardous chemical syntheses: Design syntheses that use and generate substances with little or no toxicity to either humans or the environment.
4. Design safer chemicals and products: Design chemical products that are fully effective yet have little or no toxicity.
5. Use safer solvents and reaction conditions: Avoid using solvents, separation agents, or other auxiliary chemicals. If you must use these chemicals, use safer ones.
6. Increase energy efficiency: Run chemical reactions at room temperature and pressure whenever possible.
7. Use renewable feedstocks: Use starting materials (also known as feedstocks) that are renewable rather than depletable. The source of renewable feedstocks is often agricultural products or the wastes of other processes; depletable feedstocks are often fossil fuels (petroleum, natural gas, or coal) or mining operations.
8. Avoid chemical derivatives: Avoid using blocking or protecting groups or any temporary modifications if possible. Derivatives use additional reagents and generate waste.
9. Use catalysts, not stoichiometric reagents: Minimize waste by using catalytic reactions. Catalysts are effective in small amounts and can carry out a single reaction many times. They are preferable to stoichiometric reagents, which are used in excess and carry out a reaction only once.
10. Design chemicals and products to degrade after use: Design chemical products to breakdown into innocuous substances after use so that they do not accumulate in the environment.
11. Analyze in real time to prevent pollution: Include in-process, real-time monitoring and control during syntheses to minimize or eliminate the formation of byproducts.
12. Minimize the potential for accidents: Design

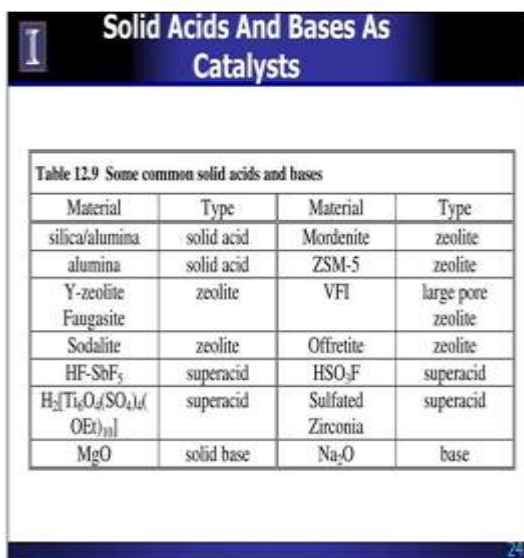
chemicals and their physical forms (solid, liquid, or gas) to minimize the potential for chemical accidents including explosions, fires, & releases to the environment.

## MODULE: 2 CATALYSIS

### 1. THE ROLE OF CATALYSIS:

The creation of chemical products and processes that minimize or completely do away with the usage and production of dangerous materials is known as "green chemistry." Green chemistry has gained recognition as a novel, scientifically grounded strategy for environmental conservation throughout the past ten years. The function of catalysis as a vital instrument in preventing pollution has become apparent. Although catalysis has long been used to boost yield, efficiency, and selectivity, it is now known to achieve a variety of green chemical objectives.

### 2. SOLID ACIDS AND BASES:



Material	Type	Material	Type
silica/alumina	solid acid	Mordenite	zeolite
alumina	solid acid	ZSM-5	zeolite
Y-zeolite	zeolite	VFI	large pore zeolite
Faujasite	zeolite		
Sodalite	zeolite	Offretite	zeolite
HF-SbF <sub>5</sub>	superacid	HSO <sub>3</sub> F	superacid
H <sub>2</sub> [Ti <sub>6</sub> O <sub>4</sub> (SO <sub>4</sub> ) <sub>2</sub> (OEt) <sub>10</sub> ]	superacid	Sulfated Zirconia	superacid
MgO	solid base	Na <sub>2</sub> O	base

### 3. CATALYTIC REDUCTION:

Diesel engines now use selective catalytic reduction (SCR) technology to help them comply with upcoming and present regulations requiring reduced emissions of NO<sub>x</sub> and CO<sub>2</sub>. For reliable operation and excellent NO<sub>x</sub> reduction efficiency, a consistent flow is necessary to distribute the reductant at the SCR catalyst inlet. Reduced exhaust temperatures from highly efficient engines need minimizing thermal losses between the engine outlet and the SCR catalyst. This can be accomplished by either integrating the SCR capability

with the diesel particulate filter (DPF) or relocating the SCR catalyst upstream of the DPF. The shorter mixing times available for the AdBlue® injection.

### 4. ENZYME TECHNOLOGY IN BIOCATALYTIC REDUCTION:

Notable advancements persist in broadening the range of enzyme engineering applications available to synthetic chemists and in increasing the creation of biocatalysts that are incredibly stable, selective, and active. For instance, Frances Arnold's 2018 Nobel Prize in Chemistry, which she received for developing directed evolution techniques for enzyme engineering, helped to establish biocatalysis. After previous editions in 2014, 2011, 2006, and 2002, Organic Process Research & Development hasn't featured a special feature in this sector for the past eight years. Therefore, it gives us great pleasure to provide this Special Issue, Biocatalysis: Enzyme Process Improvement via Protein and Reaction Engineering. The compilation includes a range of review and research articles written by renowned professionals from academia business throughout.

### 5. CATALYTIC OXIDATION:

The employment of substitute reactants, the creation of novel catalysts, novel reactions, and novel reactor technologies are just a few instances of the noteworthy advancements made in the direction of a more sustainable chemical industry that can be seen in catalytic oxidation. It is evident from the recent advancements covered in this Review that enhanced sustainability and improved economics frequently go hand in hand.



From an industrial perspective, this review details a few recent advances in the field of catalytic selective oxidation. The article discusses the utilization of alkanes as building blocks for the synthesis of intermediates and bulk chemicals. It

also cover the essential characteristics that catalysts must have to effectively catalyze the selective oxidation of these hydrocarbons. The established procedures for propene oxidation in use and the novel procedures being researched.

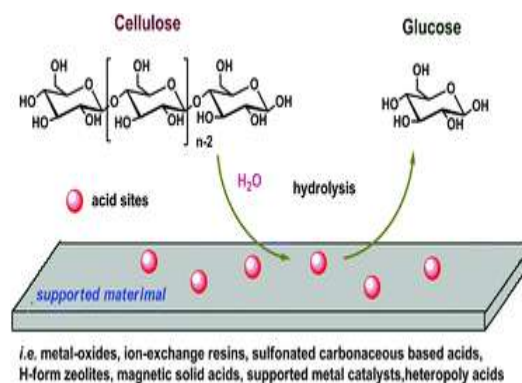
## 6. CATALYTIC CARBON-CARBON BOND FORMULATION:

The fundamental processes of both classical and contemporary chemical synthesis have been organometallic reactions, including conjugate additions, nucleophilic additions (such as the Grignard reaction), and different cross-couplings. 1. Numerous commodity chemicals, fine chemicals, agrochemicals, medicines, dyes, perfumes, and different polymeric materials can now be synthesized thanks to the advancements in these processes. The fact that they were awarded the Nobel Prizes in 1912 and 2010 serves as much more evidence of their significance. 2. However, these reactions also have significant limitations and common drawbacks from the perspective of futuristic sustainability, or "green chemistry": a) they must all begin with highly reactive stoichiometric metals, necessitating strictly anhydrous conditions in volatile flammable solvents; b) non-natural organic halides are typically used as the feedstocks, which require pre-synthetic preparation; c) most of these reactions are intolerant of water and a variety of common functional groups found in naturally occurring compounds, necessitating lengthy protection and deprotection steps that ultimately reduce synthetic efficiency. d) Stoichiometric metal and halide wastes are invariably produced.

## 7. HYDROLYSIS:

Cellulose, the primary constituent of lignocelluloses, is a biopolymer made up of many glucose units joined by  $\beta$ -1,4-glycosidic linkages. Acids that break the  $\beta$ -1,4-glycosidic linkages cause the cellulose polymers to hydrolyze, producing glucose or oligosaccharides, which are sugar molecules. The hydrolysis of cellulose has been accomplished through the application of mineral acids like HCl and H<sub>2</sub>SO<sub>4</sub>. Nevertheless, they have issues with reactor corrosion, poor catalyst recyclability, product separation, and the requirement to treat waste effluent. Some of these issues can be resolved by using heterogeneous solid acids because of their excellent catalyst recyclability and ease of product separation. This article outlines current developments in the

hydrolysis of cellulose by several solid acid types, including polymer-based acids, sulfonated carbonaceous based acids and bases.



## 8. CATALYSIS IN NOVEL REACTION MEDIA:

Many of the volatile organic compounds (VOCs) that are now utilized as solvents in organic synthesis are facing pressure to be replaced by alternatives in the chemical industry. Many solvents are poisonous or hazardous, most notably chlorinated hydrocarbons, and their use is prohibitively expensive due to these qualities as well as a major environmental problem such as air emissions and contaminated aqueous effluents. This is a major motivator behind the search for innovative reactive media. For example, Curzons and colleagues have recently observed that strict control over the use of solvents is probably going to produce the biggest progress toward more environmentally friendly methods for producing pharmaceutical intermediates. The current focus on innovative reaction media is also driven by the requirement for effective homogeneous catalyst recycling techniques. These efforts aim at minimizing chemical waste.

## 9. CHEMICALS FROM RENEWABLE RAW MATERIAL:

Chemists' approach to the synthesis of organic compounds in the lab and in business has altered dramatically in the last few years. In order to address global environmental issues like soil, water, and air pollution, researchers are urged to use "greener" reagents, solvents, and techniques. New green solutions have been made possible by the use of plant and animal derivatives that are typically considered "waste material." The most significant developments in this discipline have been emphasized in this study, with special attention

paid to wool, silk, and feathers—materials that have been essential to organic reactions. Additionally, we made the decision to concentrate on the other key supports and catalysts in green syntheses, namely proteins.

#### 10. PROCESS INTEGRATION AND CASCADE CATALYSIS:

In order to carry out cascade reactions by the skillful combination of required enzymes, nature has evolved extremely complex and efficient systems. This provides a method for attaining effective bioprocess intensification.

Chemoenzymatic cascade reactions (CECRs) combine the advantageous aspects of both chemo- and bio-catalysis, such as the high selectivity of biocatalysts and the broad reactivity of chemo-catalysts. This is a significant step toward mimicking natural processes in the creation of artificial systems that enhance bioprocess intensification. Nevertheless, CECRs are extremely difficult due to the incompatibilities between the two catalytic disciplines. Great progress has been achieved in developing methods to build CECRs in the last few years. Regarding this, the broad ideas and representative approaches—such as chemobionanoreactors, spatial compartmentalization, and temporal compartmentalization—are introduced in this chapter.

#### MODULE 3: MICROWAVE ASSISTED SYNTHESIS

##### 1. Theoretical aspects of microwave dielectric heating:

In addition to being a well-known method for preparing meals at home, microwave dielectric heating is also frequently utilized in industry to process food and other materials. Applications for microwaves have been developed to include waste materials into glasses and to heat, rubber, wood, paper & agricultural items volumetrically<sup>1</sup>. In order to power chemical reactions, microwave dielectric heating makes use of certain liquids' and solids' capacity to convert electromagnetic radiation into heat. But it wasn't until the middle of the 1980s that the benefits of doing organic transformations using microwave dielectric heating became apparent. The synthetic chemist now has access to novel reactions that would not be feasible with traditional heating thanks to this technique. Recent advances in this area indicate that most reactions requiring heating could benefit from the application of microwave-assisted chemistry.

In the past, microwave chemistry was often used only when all other options to perform a particular reaction had failed, or when exceedingly long reaction times or high temperatures were required to complete a reaction. This practice is now slowly changing and, due to the growing availability of microwave reactors in many laboratories, routine synthetic transformations are now also being carried out by microwave heating. Microwave include following advantages, over the conventional heating.

- Uniform heating occurs throughout the material
- Process speed is increased · High efficiency of heating
- Reduction in unwanted side reaction
- Purity in final product,
- Improved reproducibility
- Environmental heat loss can be avoided
- Reduce wastage of heating reaction vessel
- Low operating cost

Microwave technology uses ionic conduction or dipolar polarization to introduce heating into the reacting system. Electromagnetic waves that go through the sample's ions or dipoles when exposed to microwave radiation cause the molecules to vibrate. This process results in the loss of energy as heat due to dielectric loss and molecular friction. Microwave radiation can induce a quick temperature increase throughout the sample, resulting in fewer byproducts or decomposition products, because it is introduced into the reaction system remotely and does not come into direct physical contact with the reaction components. In contrast, conventional heating of organic reactions such as oil baths, sand baths, or heating mantles is quite slow and creates an internal temperature gradient that can cause local overheating and reagent degradation during prolonged heating.

##### 2. Microwave-accelerated metal catalysis:

The effectiveness of microwave heating in accelerating organic changes (reaction times reduced from days and hours to minutes and seconds) has recently been demonstrated in several different areas of organic chemistry. This special report mainly summarizes our experience in developing fast, robust and selective microwave catalyzed homogeneous reactions. Applications include selective Heck couplings, cross couplings and asymmetric compensations.



The science of green chemistry was developed to meet the growing demand for environmentally friendly chemical processes. We believe that the combination of metal catalysis and microwave heating is important in the pursuit of green laboratory-scale synthesis.

Catalysis is a hot topic in organic chemistry today. In the last 10-15 years, there has been an impressive increase in the number of publications on the discovery and application of catalytic methods for organic transformations and organic synthesis. The main topics are transition metal catalysis, organo catalysis, biocatalysis and recently photocatalysis and electrocatalysis. Ever since it was discovered that MW has a profound effect on the reaction time, conditions and product purity, organic chemists were metal-catalyzed reactions are attractive because they are very sensitive to MW radiation. Hydroformylation is one of the oldest metal-catalyzed organic reactions.

### 3. Heterocyclic chemistry using microwave-assisted approaches:

The term green chemistry is defined as "the invention, design and application of chemical products" and processes to reduce or eliminate the use and production of hazardous substances. Strong, efficient, a cost-effective chemical process is required for process chemical approval. Synthetic formulas green chemistry is designed to pollute the environment the least. transmitted A variety of chemical synthesis methods are very well written and implemented. Microwave assisted organic Synthesis has emerged as the new "master" of organic synthesis. This technology is simple, clean, fast, efficient and effective and it can revolutionize the economy for the synthesis of many organic molecules. In recent years Microwave-assisted carbon reactions have emerged as a new tool for carbon synthesis. traditional culture Organic synthesis means longer warm-up times and tedious equipment setup, which can lead to higher costs. Excessive use of processes and solvents/reagents lead to environmental pollution. The main principle of heating in a microwave oven is due to the interaction of charged particles. A substance reacts with electromagnetic waves of a specific frequency. situation in which you are working. The heat of electromagnetic radiation becomes etheric by collision or conduction, or both. Two basic principle mechanisms involve the heating of material:

Heterocyclic chemistry using microwave-assisted approaches:

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#### a) Dipolar Polarization:

Dipolar polarization is a cycle by which intensity is created in polar particles. On openness to a swaying electromagnetic field of fitting recurrence, polar particles attempt to follow the field and adjust themselves in stage with the field. Heat can be produced by dipolar polarization through one or both of the following mechanisms:

Cooperation between polar dissolvable atoms like water, methanol and ethanol  
Interaction between molecules of polar solutes like formic acid and ammonia

#### b) Conduction mechanism:

The conduction system creates heat through protection from an electric flow. The swaying electromagnetic field produces a wavering of electrons or particles in a conveyor, bringing about an electric flow. These ongoing countenances interior opposition, which warm the guide. Microwave warming is not quite the same as ordinary warming in many regards.

#### ➤ Advantages:

- Fast responses
- High virtue of items
- Less side-items
- Further developed yields
- Streamlined and worked on engineered method
- More extensive usable scope of temperature
- Higher energy proficiency
- Refined destination and well being innovation
- Measured framework power changing from mgtokgs cal

e.

• **Disadvantages:**

- Heat force control is troublesome
- Water dissipation
- Shut compartment is hazardous in light of the fact that it very well may be exploded

**4. Microwave-assisted reductions:**

Organic compound reductions are crucial for industrial and laboratory synthesis [10]. In synthetic chemistry, they are strong transformations, particularly in the synthesis of natural products, fine pharmaceuticals and chemistry. Both the synthesis of fine chemicals and the production of commodities benefit from the decrease of C-C multiple bonds, particularly C-C double bonds. The process of hydrogenating unsaturated carbonyl yields saturated derivatives, which find extensive use in the pharmaceutical industry and in the synthesis of tastes and fragrances. In organic synthesis, one of the various methods for reducing C-C double bonds is catalytic transfer hydrogenation (CTH). For CTH, there are a few potential H donors, such as formic acid, cyclohexadiene, and hydrazine; however, the most common and conventional donors are formic acid and its corresponding salts, which include ammonia, sodium, and potassium.

When compared to traditional reductions conducted under conventional heating, microwave heating results in shorter reaction times, high yields, and occasionally beneficial modifications in selectivity. Many functional groups can be chemoselectively transformed by utilizing various organic reduction techniques, including as hydrogenation, (catalytic) transfer hydrogenation, asymmetric hydrogenation, and ionic hydrogenation. The use of ionic hydrogenation and (catalytic) transfer hydrogenation is much more common than the use of hydrogen gas. This is undoubtedly a byproduct of the challenges in reactor design and reaction engineering when high- or medium-pressure reactions must be conducted under microwave heating conditions. After analyzing the synthetic instances provided in the previous chapters, it can be concluded that the majority of the reaction protocols are only proof-of-principle investigations, showing that reduction reactions may be carried out when microwave radiation is used.

**5. Microwave-assisted multi-component reactions:**

The use of multi-component reactions (MCRs) in the synthesis of physiologically significant chemicals is of great ecological interest. For medicinal and organic chemists, the invention of novel MCRs for the synthesis of various heterocycles has grown in importance. One major advantage of multi-component reactions is that they cut down on expenses and laboratory time (MCRs). In the majority of multi-component reactions, the result contains the majority of the reacting atoms. The great synthetic efficiency of multi-component reactions is one of their most significant features. In addition to their widespread use in pharmaceuticals and drug synthesis, MCRs are also widely used in materials science and in the synthesis of eco-friendly compounds, as well as in the preparation of chromatographic chiral stationary phases. MCRs can also be used to artificially synthesize amino acids and peptides, or in polymer manufacturing and the synthesis of a wider range of polymers, including polysaccharides.

From straightforward fused rings to intricate steroidal molecules, MWA-MCRs facilitate easy access to biologically relevant molecules. This productive consolidation remains a traditional illustration of innovation driven particles. The MCR shows a combination of sub-responses, for example, Knoevenagel response, Michael expansion, cycloaddition response and so on., in a one-pot way to conserve the economy of the response for a naturally harmless methodology. While MWA helps decrease the time from hours to minutes and even to seconds with better returns staying away from monotonous decontamination process. The last ten years has seen a speed up interest in MWA-MCR to foster atoms and has hurried the course of medication disclosure. Consistent endeavors can cook towards improvement of novel methodologies in age of significant pharmacophores with a greener engineered convention. Acridine, pyrenes, purines, pyrimidines, and other pharmacologically relevant heterocyclic molecules are among the examples presented in this review. aided by MW-MCR and their mechanical method. Without a doubt, there is as yet a massive opportunity for investigation in this field and a great deal still needs to be gotten on the table then not-so-distant future. Thusly, this survey might clear a course for some specialists and push them to examine and create

more current compound elements in light of MWA-MCRs.

#### 6. Integrating microwave-assisted synthesis and solid-supported reagents:

There are two particular manufactured strategies for applying microwave warming to responding tests. The simplest method is to carry out the reaction in an open reaction vessel under normal atmospheric pressure. This includes standard research facility dishes fitted with a changed reflux condenser housed remotely to the microwave hole, utilizing response temperatures at or just underneath the typical reflux point of the dissolvable.

This type of microwave reaction is increasingly being referred to as MORE chemistry (microwave-induced organic-reaction enhancement), although this is not entirely accurate. Despite their widespread use, we believe that these kinds of anagrams are not particularly useful for defining the region. Despite its characteristic similarity to standard synthetic methodology, this method has been utilized significantly less frequently than the alternative approach due to safety concerns. Microwave flash heating is an alternative strategy that makes use of rapid heating and cooling of a sample that is contained in a sealed reaction vessel. In such cycles, creating high-inward tensions as a result is conceivable of the raised response temperatures utilized, which are normally altogether higher than the standard edge of boiling over of the dissolvable. This type of fast warm change likewise is by all accounts useful concerning the overall respectability of the polymer lattice itself (counting polymer-upheld intermediates), which has expanded steadiness under such brief term, high-pressure warm openness. This is unquestionably rather than numerous different reports that express that critical disintegration of immobilized beginning materials and intermediates can happen with the activity of delayed regular warming cycles at encompassing strain. Thus, practically every one of the responses including polymer-upheld reagents are presently led utilizing microwave streak warming.

#### 7. Microwave-assisted solid phase synthesis:

The most popular and extensively studied use of microwaves in chemical processes has been in microwave-assisted organic synthesis. A review of the literature shows that a wide variety of organic reactions have been successfully carried

out by scientists. Diels-Alder, Heck, Suzuki, Mannich, Hydrogenation of [beta]-lactams, Hypoxylation, Dehydration, Esterification, Cycloaddition, Epoxidation, Reductions, Condensation s, Cyclization Reactions, Protection and Deprotection, etc. area few examples of these reactions.

The pharmaceutical industry makes extensive use of microwave-assisted organic synthesis, especially when creating molecules for the lead optimization stage of drug discovery and development. During this stage, chemists create candidate pharmaceuticals from lead molecules using a variety of synthetic approaches. The following methods can be used to conduct organic synthesis reactions, depending on the conditions of the reaction.

Radiopharmaceuticals have been synthesized in the pharmaceutical business using microwave-assisted organic synthesis at increased pressure. These radiopharmaceuticals are utilized as tracers to create nuclear medical images in pre-clinical investigations. In the first experiment of this type, a multimode microwave oven was utilized, and it was noted that the rate of reaction significantly increased. As a result, microwaves are being used more often to create radiopharmaceuticals. Microwaves have the advantage of quick reaction rates and excellent reaction yields. This can be explained by the short half-lives of the reactants; for instance, a synthesis involving carbon-11 that took five minutes less produced a 15% increase in production rate. Additionally, it has been shown that a few reactions could only be accomplished with the use of microwaves.

#### 8. Scale-up of microwave-assisted organic synthesis:

The direct scaling of organic synthesis facilitated by microwaves (MAOS) in a prototype multimode microwave laboratory device batch reactor is looked into. Numerous chemical reactions have been increased in size, usually from 1 mmol to 100 mmol. Among the changes are multicomponent chemistries, Diels-Alder cycloaddition processes using gaseous phase, solid-phase organic synthesis, and carbon-carbon cross-coupling procedures catalyzed by transition metals chemicals in reaction containers with PR pressurization. A variety of distinct Pd catalysts, high- and low-microwave-absorbing solvents (both homogeneous and heterogeneous), as well as different response times. These investigations have looked into and temperatures. It

was feasible to produce comparable isolated products in each scenario. yields starting at a small scale (about 5 milliliters of processing volume) scaled up (maximum 500 mL volume) without altering the reaction conditions that were already tuned (direct scalability). The current study's prototype benchtop multimode microwave reactor permits parallel processing in quartz or PTFE-TFM containers, with maximal operating temperatures and pressures of 80 bar and 300 °C. The system has the capacity to maintain an inert or reactive gas environment, magnetic stirring in all containers, and full online monitoring of temperature, pressure, and microwave power. Fast microwave synthesis has attracted much attention in recent years. reports on the use of microwave heating to accelerate organic heating chemical changes of groups Gedye and Giguere/Majetich in 1986<sup>2,3</sup> more than 2000 articles have been published in the field of microwave supported organic matter synthesis (MAOS).<sup>4</sup> Slow adoption in the early stages of the technology is due to its lack of controllability and repeatability and a general misunderstanding of the fundamentals of microwave dielectric heating.

#### MODULE 4. SONOCHEMISTRY

Sonochemistry is understanding the impact of sonic waves and wave characteristics on chemical processes is the goal of the study of sonochemistry in chemistry. The atomic and molecular chemistry that corresponds to the distinct physical characteristics of sonic waves is also unique. These effects frequently show up best in ultrasonic systems. Sonoluminescence, ultrasound, sonication, and sonic cavitation are examples of phenomena that illustrate this.

#### Green Sono chemical Approaches for Organics synthesis:

- The applications of ultrasound have long been known in both industry and academy, the green value of the non-hazardous acoustic radiation has been recognized by synthetic and environmental chemists only recently.
- The chemical and physical effects of ultrasound arise from the cavitation collapse which produces extreme conditions locally and thus induce the formation of chemical species not easily attained under conventional conditions, driving a particular radical reactivity.

- This rationale, accessible in a non-mathematical manner, anticipates the advantages of using this technology in a variety of processes that include milder reactions with improved yields and selectivity, easy generation of reactive species and catalysts or replacement of hazardous reagents.
- Sonication enables the rapid dispersion of solids, decomposition of organics including biological components, as well as the formation of porous materials and nanostructures.
- Ultrasound can be harnessed to develop an alternative and mild chemistry, which parallels the ability of acoustic waves to induce homolytic bond cleavage.
- Sonochemistry is thought to be a practical approach for conducting chemical reactions without the need for solvents.
- Among the main benefits of these Sono chemical processes are their high yields, low energy requirements, minimal waste, and solvent-free operation.
- The application of ultrasonography in particular activation is produced by chemical reactions in solution based on a physical phenomenon: cavitation caused by sound.
- During the process of cavitation, mechanical stimulation destroys the liquid phase's molecules' attraction force.

#### Solvent-Free Sono chemical Protocol:

##### ➤ Heterogeneous Catalysis in Organic:

Chemical catalysts that are heterogeneous have a physical phase that differs from the reactant and/or product phases of the chemical reactions they catalyze. Heterogeneous solid phase catalysts are typically used to speed up the chemical reaction between two gaseous reactants. The catalysis in these reactions occurs in the following three steps:

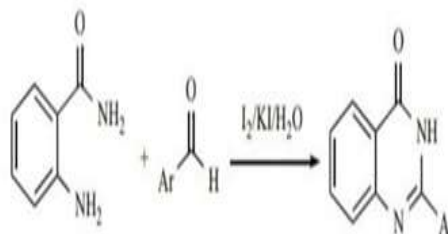
- The gaseous reactants' adsorption on the solid heterogeneous catalyst's surface.
- The product is created as a result of the chemical reaction between the adsorbed reactants.
- The catalyst's active catalytic surface regenerates when the resultant compound is desorbing from its surface.

Because they make it possible to produce a number of commercially significant compounds on a relatively large scale, heterogeneous catalysts are very helpful. For instance, iron oxides deposited on alumina, a chemical substance that



ng the formula  $Al_2O_3$ , are frequently employed as heterogeneous catalysts in the Haber process, which produces ammonia for industrial use.

Ethylene and oxygen undergo a reaction on alumina that is catalyzed by silver and a number of other promoters to produce ethylene oxide.



• **Examples of Heterogeneous Catalysis:**

The following list contains some typical instances of heterogeneous catalysis-related reactions, or processes where the catalysts and reactants are in distinct physical states:

- Vanadium oxides catalyze the interaction between oxygen and sulfur dioxide in the contact process that results in sulfuric acid.
- Iron oxides on alumina catalyze the reaction between hydrogen and nitrogen in the Haber-Bosch process, which produces ammonia for industrial use
- An unsupported platinum-rhodium gauze catalyzes the reaction between ammonia and oxygen in the Ostwald process, which produces nitric acid.
- Methane and water react in a process called steam reforming, which is aided by potassium nickel oxide to produce hydrogen.

➤ **Heterocyclic Synthesis in Water:**

A heterocyclic compound has at least two different elements as a member of its ring. The most common heteroatoms found on a cyclic ring are Oxygen (O), Nitrogen (N) and Sulphur (S). Example: Synthesis of Quinazolinone derivatives. Bakavoliet al. have reported oxidative cyclocondensation of o-aminobenzamide with various aldehydes in water using  $I_2/KI$  as catalyst and oxidizing agent to obtain the corresponding quinazolin-4(3H)-ones. Quinazolin-4(3H)-one derivatives were previously prepared by thermolysis of 3-arylideneamine-1,2,3-benzotriazine-4-ones in paraffin oil at 300 degree Celsius or by condensation of aryl, alkyl and heteroaryl aldehydes in refluxing ethanol in the presence of  $CuCl_2$ , but both these methods require high-temperature reaction, low yield, long-reaction time as well as were not environment friendly.

i. **Solvent Free Reactions-**

One of the most promising ways to achieve this goal is the solution-less technique, a strategic position because solvents are often toxic, expensive, and difficult to use and remove. This is the main reason for its development in modern technologies. These approaches can also allow for experimentation works without strong mineral acids (e.g.  $HCl, H_2SO_4$ ) that can enter into corrosion, safety, handling and contamination problems as waste. These acids can be advantageously replaced by solid, recyclable acids such as kaolin clay.

• **Solvent-free Techniques- Three types of experimental conditions without solvents can be considered.**

➤ **Reaction on Solid Mineral Supports:**

Reactants are first impregnated as neat liquids onto solid supports such as alumina, silica, and clays or via their solutions in an adequate organic solvent and further solvent removal in the case of solids. Reaction in dry media is performed between individually impregnated reactants, followed by possible heating.

➤ **Reactions Without any Solvent, Support/Catalyst:**

These heterogeneous reactions are carried out between pure reactants in quasi-corresponding amounts without addition. In solid-liquid mixtures a reaction means either dissolution of a solid in a liquid phase or adsorption of liquid on a solid surface as an interfacial reaction.

➤ **Solid-Liquid Phase Transfer Catalysis (PTC):**  
Reactions occur between pure reactants as qua

si-equivalents complexation of a catalytic number of tetra-alkylammonium salts or cations. If carried out without a solvent, the liquid organic phase contains consists of an electrophilic reactant and then eventually a reaction product. Nucleophilic anionic species can be produced in situ by subjecting their conjugate acids with solid bases, whose strength is increased due to exchange of ion pairs  $R_4N^+X^-$ .

➤ **Advantages:**

- No reaction means are available to collect, clean or recycle
- The manufactured chemicals are often quite pure and avoid thorough chromatographic purification and in certain situations, recrystallization is not even necessary
- Sequential solvent-free in high-performance systems reactions are possible
- compared to organic solvents, reactions are fast, so sometimes reaching a remarkable completion in minutes
- specialized equipment is often not required
- energy consumption can be significantly lower
- preformed salts and metal-metal complexes often are unnecessary
- surgery may be prevented group protection removal
- at the time of establishment industrial processes may have less capital equipment
- methods without solvents can become more economically viable and ecologically friendly by significantly reducing sets and processing costs.

➤ **Disadvantages:**

formation of "hotspots" and the possibility of runaway reactions. Rather than continuing to operate under the outdated paradigm in which a reaction medium or solvent is used as a heat sink or agent for heat transfer, it would be preferable to work on designing reactors for continuous flow systems. In solvent-free processes, it is obvious that quantifying reaction heat is just as important.

1. **Reactions in Organic Solvents:**

Everyone uses organic solvents in most of their daily operations, from sanitizing procedures to removing stubborn grease stains. The perfume or cologne we use, the detergents used to keep our clothes fresh and clean, all these products contain ingredients called organic solvents.

Organic solvents are those chemical compounds that have a carbon-based molecular structure. They are widely used to

dissolve a material to create a solution or even to extract one material from another. In general, a solvent refers to a substance that can dissolve another substance. But since all these solvents are carbon-based, these compounds have carbon atoms in their structure. Consider the example of the organic solvent benzene, which has six carbon atoms in the organic solvent. The molecular structure of an organic solvent always contains a carbon atom and some have a hydrogen atom. These solvents are mainly classified into natural and synthetic solvents based on their molecular structures.

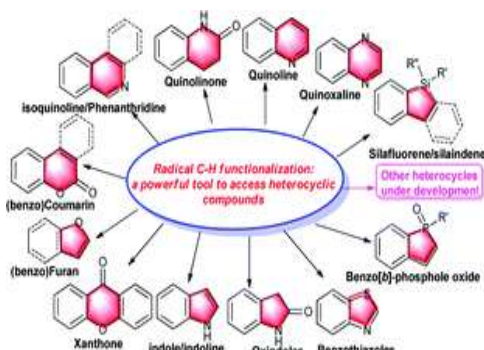
Natural solvents – These are the solvents which are naturally produced by living organisms. Synthetic Solvents – These are the solvents that are produced as a result of chemical reactions occurring in various organic compounds.

• **Applications of organic solvents:**

Organic solvents are used in various fields. They are used in coatings, polishes, paint thinners and removers (toluene), cleaning agents, nail polish removers (acetone, ethyl acetate, methyl acetate), industrial and consumer degreasers, detergents, perfumes, stains and various chemical syntheses and processes.

➤ **Heterocyclic Functionalization:**

Heterocyclic compounds are widely found in natural products, drugs and bioactive molecules. Thus, organic and pharmaceutical chemists have dedicated great efforts to the construction of these heterocyclic frameworks, developing versatile and efficient synthetic strategies. Direct C–H functionalization via the radical route has emerged as a promising and dramatic approach to heterocycles with high atom economy. Heterocyclic compounds such as coumarins, furans, benzofurans, xanthenes, benzothiazoles, indoles, indolines, oxindoles, quinolines, is quinolines, quinoxaline, and phenanthridines have been successfully synthesized by C–H functionalization via the radical route.



Heterocyclic compounds are widely present in the basic structures of several natural products, drugs and agrochemicals, and therefore efforts have been made to synthesize them in a much easier and simpler way. Over the past decade, significant progress has been made in the field of heterocyclic synthesis using C-H functionalization as an emerging synthetic strategy. Transition metal-catalyzed CH functionalization of arenes with various directing groups has recently emerged as a powerful tool for the creation of various classes of heterocycles. This review focuses primarily on recent advances in the synthesis of N, O heterocycles from olefins and allenes using nitrogen-based and oxidative directing groups.

#### ➤ **Organometallic Reactions:**

Organometallic compounds are chemical compounds that contain at least one bond between a metallic element and a carbon atom in an organic molecule. Even metalloids elements such as silicon, tin and boron can form organometallic compounds that are used in some industrial chemical reactions. Reactions where the target molecules are polymers or drugs can be catalyzed by organometallic compounds, which leads to an increase in the reaction rate. Generally, the bond between the metal atom and the carbon attached to the organic compound is covalent in nature. When metals with a relatively high electronegativity (such as sodium and lithium) form these compounds, the carbon attached to the central metal atom has a carbanionic character.

#### • **Properties of organometallic compounds:**

The bond between the metal and the carbon atom is often highly covalent in nature. Most organometallic compounds exist in solid form, especially compounds in which the hydrocarbon groups are aromatic or have a cyclic structure.

Compounds made of highly electropositive metals such as sodium or lithium are highly volatile and can ignite spontaneously. In many cases, organometallic compounds have been found to be toxic to humans (especially those compounds that are naturally volatile). These compounds can act as reducing agents, especially compounds formed by highly electropositive metals.

Grignard reagents are extremely useful organometallic compounds in the field of organic chemistry. They exhibit strong nucleophilic qualities and also have the ability to form new carbon-carbon bonds. Therefore, they display qualities that are also exhibited by organolithium reagents and the two reagents are considered similar.

#### ➤ **Reactions of Grignard Reagents:**

**Reactions with a carbonyl group:** These reagents form different products when reacting with different carbonyl compounds. The most common reaction of Grignard reagents is the alkylation of ketones and aldehydes with R-Mg-X. Reactions of Grignard reagents described above is also called the Grignard reaction. The solvent used in this reaction is tetrahydrofuran and diethyl ether.

**Reactions with non-carbon electrophiles:** Grignard reagents and some organolithium compounds are very useful for forming new carbon-heteroatom bonds. These reagents can also undergo a transmetalation reaction with cadmium chloride to give dialkylation. This reaction can be written as  $2R-Mg-X + CdCl_2 \rightarrow R_2Cd + 2Mg(X)Cl$ . Alkyl chains can be attached to many metals and metalloids using these reagents.

**Reactions with organic halides:** Usually, these reagents are quite unreactive towards organic halides, which differs significantly from their behavior towards other halides. However, carbon-carbon coupling reactions occur with Grignard reagents, which act as reactants when a metal catalyst is added. An example of such a coupling reaction is the reaction between methyl p-chlorobenzoate and nonyl magnesium bromide, during which the compound p-nonyl benzoic acid is formed in the presence of a catalyst - Tris(acetylacetonate)iron.

#### **MODULE 5. SOLVENT & IONIC LIQUID**

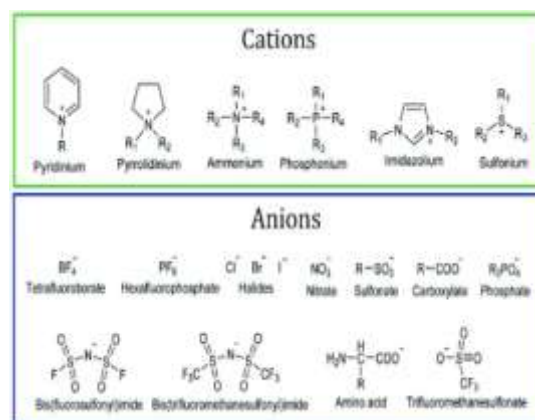
An ionic liquid (IL) consists of large nitrogen containing organic cation and smaller

inorganic anion. Generally ionic compounds are solid at room temperature due to strong electrostatic force of attraction between cation and anion in crystal lattice, but ionic liquids are liquid at room temperature due to presence of asymmetry in the compound which reduces the lattice energy of crystalline structure and hence melting point of the salt.

Conventional solvents are general laboratory solvents that were routinely used for laboratory and industrial purposes because of their volatility, melting point, better dissolving power, and yield. Apart from their direct exposure to laboratory workers, when released in environment (air, water, and soil), these can cause potential threat to plants, animals, and humans from ground level reaching to mass level when left untreated. Majority of chemicals can cause hazards if not handled carefully. Direct contact (inhalation, skin, and eye contact) and prolonged exposure (occupational) are the two major routes of chemical toxicity to humans. Damage to health can, depending on the chemical composition, damage to organs, weakening of the immune system, development of allergies or asthma, reproductive disorders and birth defects, effects on the psychological state, intellectual or physical development of children, cancer. Role of various types of solvents and ionic liquids used in green synthesis:

#### Ionic liquids:

An ionic liquid (IL) consists of large nitrogen containing organic cation and smaller inorganic anion. Generally ionic compounds are solid at room temperature due to strong electrostatic force of attraction between cation and anion in crystal lattice, but ionic liquids are liquid at room temperature due to presence of asymmetry in the compound which reduces the lattice energy of crystalline structure and hence melting point of the salt. Although these are liquid at room temperature, yet their vapor pressure is very low or negligible in comparison to conventional organic solvents. It can be explained on the basis of electrostatic force of attraction between ions in ionic liquids which hold them strongly and reduce their escaping tendency. Common cations and anions used in ILs.



#### ➤ Properties of ionic liquids:

Desirable ILs can be designed by suitable combination of cations and anions:

Multicomponent ILs can be formed by mixing of liquid salts with inorganic salts.

Certain properties such as miscibility, hydrophobicity, viscosity, density etc. can be adjusted or fine-tuned to suit a particular application.

The ions in ILs are held together by coulombic forces and thus exerts near-zero vapor pressure above the liquid surface. So ILs do not emit potentially hazardous VOCs during their transportation, handling and use.

ILs are non-oxidizing so non-flammable and non-explosive.

The velocity of the reaction increases in ILs due to its ionic character.

ILs can be stored without decomposition for a long time

ILs are suitable for stereoselectivity control.

ILs do not form coordinate bond with metal complexes.

ILs are stable over a wide range of temperature.

Common anions present in ILs are nitrate, phosphate, tetrafluoroborate, tetrafluoromethane sulphonate, hydrogen sulphate, benzoate, acetate, format & halides and commonly used cations in ILs are imidazolium, pyrrolidinium, ammonium, phosphonium & pyridinium cations. Large organic cationic part and smaller inorganic anionic part makes them capable for dissolving both organic and inorganic material.

#### ➤ Roles of ionic liquids:

1. In Electrochemistry:
  - Batteries
  - Solar panels



2. In chemistry:
- Synthesis
  - Catalysis
  - Polymerization

3. In Biotechnology:
- Biocatalysis
  - Protein purification

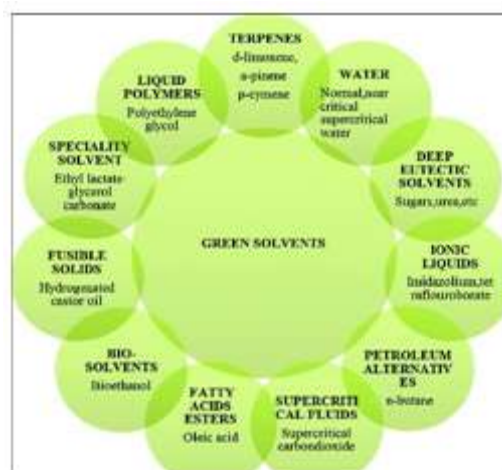
4. In Pharmaceutical industries:
- Drug delivery
  - Active pharmaceutical ingredients

**Solvents:-**

Solvents used in different chemical processes are found to be of major environmental concern. Thus, the reduction of the use of solvents or replacing them with less toxic green solvents is two major aims of green chemistry. According to Fisher, the green solvent expresses the objective of minimizing the environmental impact of the consumption of solvents in chemical production. Effective utilization of green solvents such as water, supercritical fluids, liquid polymers, and ionic liquids (ILs) can help achieve the aim to reduce environment degradation. Low toxicity, phase behavior, chemical, thermodynamics, biodegradability, and non-flammability are some of the properties of novel green solvents or bio solvents in extraction of natural products and oils, terpenes can be a good replacement to petroleum solvents like n-hexane. Water being universal solvent and non-toxic can be used in various reaction medium, extraction, separation, and organic synthesis. Deep eutectic solvent is another eco-friendly solvent which is widely used in dispersive liquid-liquid micro extraction and as green absorbents for volatile organic pollutants. Another wonder class of solvents includes the ILs, which is commercially used in desulphurization of fuel oils and carbon capture. Instead of using n-hexane, n-butane can be used as a sustainable solvent for natural product extraction. For processing of polymer melts and pre-treatment of lignocellulose biomass, supercritical fluids can be a good replacement to traditional solvents. For carotenoid extraction, fatty acid esters are good choice as solvent part. Bioethanol, for its low toxicity and reliable availability, is used as green solvent in various synthesis and industrial production. For its renewable nature, biodegradability, low costs, and eco-friendliness,

castor oil serves as a promising green solvent for nanoparticle synthesis, agriculture, food, textile, paper, plastic, rubber, cosmetics, perfumeries, electronics, pharmaceuticals, paints, inks, additives, lubricants, and biofuels.

➤ **ROLES OF SOLVENTS IN GREEN CHEMISTRY:**



**CONCLUSION**

There is a need to update or adapt traditional procedures that are not environmentally friendly, used dangerous solvents, and are not atom specific in the sense that they do not follow green chemistry principles. This could be beneficial to students 'safety while also being environmentally sustainable. For the first time, a new approach has been established. Inorganic synthesis, non-conventional approaches are used.

Catalysis is crucial in the environmentally friendly synthesis of compounds. By substituting an environmentally friendly synthetic approach for a standard synthetic pathway, several by-products, co-products, possible wastes, and pollutants can be avoided. The reduction of a number of steps that normally occur during synthesis shows the possibility for catalysts to be employed for environmentally friendly synthesis. The use of catalysts in chemical synthesis can be quite beneficial. Inventing environmentally friendly technology and producing ecologically friendly chemicals.

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