

A SIGNIFICANCE OF MICROWAVE ASSISTED TECHNIQUE IN GREEN CHEMISTRY

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ABSTRACT

Microwave Assisted Synthesis is rapidly becoming the method of choice in modern synthesis and discovery chemistry laboratories. Microwave-assisted synthesis improves both throughput and turn-around time for chemists by offering the benefits of drastically reduced reaction times, increased yields, and purer products. In this type of synthesis we applying microwave irradiation to chemical reactions. The fundamental mechanism of microwave heating involves agitation of polar molecules or ions that oscillate under the effect of an oscillating electric or magnetic field. In the presence of an oscillating field, particles try to orient themselves or be in phase with the field. Only materials that absorb microwave radiation are relevant to microwave chemistry. These materials can be categorized according to the three main mechanisms of heating, namely. Dipolar polarization, Conduction mechanism, Interfacial polarization. Microwave chemistry apparatus are classified: Single-mode apparatus and Multi-mode apparatus. Although occasionally known by such acronyms as 'MEC' (Microwave-Enhanced Chemistry) or 'MORE' synthesis (Microwave-organic Reaction Enhancement), these acronyms have had little acceptance outside a small number of groups. The ability to combine microwave technology with in-situ reaction monitoring as an analytical tools will offer opportunities for chemists to optimize the reaction conditions. Different compounds convert microwave radiation to heat by different amounts. This selectivity allows some parts of the object being heated to heat more quickly or more slowly than others (particularly the reaction vessel).

KEY WORDS: Microwave chemistry, Microwave synthesis, Microwave-Enhanced Chemistry.

1. INTRODUCTION^{1,2}

Green chemistry, is a sustainable chemistry and also a philosophy of chemical research and engineering that encourages the design of products and processes that minimize the use and generation of hazardous substances. As a chemical philosophy, green chemistry applies to organic chemistry, inorganic chemistry, biochemistry, analytical

chemistry, and even physical chemistry. While green chemistry seems to focus on industrial applications, it does apply to any chemistry choice. Click chemistry is often cited as a style of chemical synthesis that is consistent with the goals of green chemistry.

In Green chemistry, microwave technology has been used since the late 1970s, while it has only been implemented in organic chemistry since

the mid-1980s. The development of the technology for organic chemistry has been rather slow compared, to for example, combinatorial chemistry and computational chemistry. This slow uptake of the technology has been principally attributed to its lack of controllability and reproducibility, safety aspects and a generally low degree of understanding of the basics of microwave dielectric heating. Since the mid-1990s, however, the number of publications has increased significantly. The main reasons for this increase include the availability of commercial microwave equipment intended for organic chemistry and the development of the solvent-free technique, which has improved the safety aspects, but are mostly due to an increased interest in shorter reaction times. The short reaction times and expanded reaction range that is offered by microwave assisted organic synthesis are suited to the increased demands in industry. In particular, there is a requirement in the pharmaceutical industry for a higher number of novel chemical entities to be produced, which requires chemists to employ a number of resources to reduce the time for the production of compounds. Chemistry databases, software for diversity selection, on-line chemical ordering systems, open access and high throughput systems for analysis and high-speed, parallel and combinatorial synthesis equipment have all contributed in increasing the throughput. The common factors for these technical resources are automation and computer-aided control. They do not, however, speed up the chemistry itself. Developments in the chemistry have generally been concerned with novel highly reactive reagents in solution or on solid supports. In the electromagnetic spectrum, the microwave radiation region

is located between infrared radiation and radio waves. Microwaves have wavelengths of 1 mm±1 m, corresponding to frequencies between 0.3 and 300 GHz. Telecommunication and microwave radar equipment occupy many of the band frequencies in this region.

The microwave electromagnetic spectrum is divided into sub bands.

While the lower microwave frequency ranges (L band) are used for the purpose of communication, the higher frequency ranges (W band) in the spectrum are used for analytical techniques such as spectroscopy. Microwave RADAR equipment that operate at lower wavelengths (0.01-0.25 m) are used for communication.

2. BASICS AND THEORY^{1,6}

The basic mechanism of microwave heating involves agitation of polar molecules or ions that oscillate under the effect of an oscillating electric or magnetic field. In the presence of an oscillating field, particles try to orient themselves or be in phase with the field. However, the motion of these particles is restricted by resisting forces (inter-particle interaction and electric resistance), which restrict the motion of. Particles and generate random motion, producing heat. Since the response of various materials to microwave radiation is diverse, not all materials are amenable to microwave heating. Based on their response to microwaves, materials can be broadly classified as follows

- Materials that are transparent to microwaves, e.g., sulphur
- Materials that reflect microwaves, e.g., copper
- Materials that absorb microwaves, e.g., water

If two samples containing water and dioxane, respectively, are heated in a single-mode microwave cavity at a fixed radiation power and for a fixed time the final temperature will be higher in the water sample. In order to understand why this phenomenon occurs, it is necessary to comprehend the underlying mechanisms of microwave dielectric heating. As with all electromagnetic radiation, microwave radiation can be divided into an electric field component and a magnetic field component. The former component is responsible for the dielectric heating, which is effected via two major mechanisms.

2.1. Dipolar polarization mechanism

Dipolar polarization is a process by which heat is generated in polar molecules. One exposure to an oscillating electromagnetic field of appropriate frequency, polar molecules try to follow the field and align themselves in phase with the field. However, owing to inter-molecular forces, polar molecules experience inertia and are unable to follow the field. This results in the random motion of particles, and this random interaction generates heat. Dipolar polarization can generate heat by either one or both the following mechanisms.

1. Interaction between polar solvent molecules such as water, methanol and Ethanol.
2. Interaction between polar solute molecules such as ammonia and formic acid.

The key requirement for dipolar polarization is that the frequency range of the oscillating field should be appropriate to enable adequate inter-particle interaction. If the frequency range is very high, inter-molecular forces will stop the motion of a polar molecule before it tries

to follow the field, resulting in inadequate inter-particle interaction. On the other hand, if the frequency range is low, the polar molecule gets sufficient time to align itself in phase with the field. Hence, no random interaction takes place between the adjoining particles. Microwave radiation has the appropriate frequency (0.3-30 GHz) to oscillate polar particles and enable enough inter-particle interaction. This makes it an ideal choice for heating polar solutions. In addition, the energy in a microwave photon (0.037 kcal/mol) is very low, relative to the typical energy required to break a molecular bond (80-120 kcal/mol). Therefore, microwave excitation of molecule does not affect the structure of an organic molecule and the interaction is purely kinetic based.

2.2. Conduction mechanism

The conduction mechanism generates heat through resistance to an electric current. The oscillating electromagnetic field generates an oscillation of electrons or ions in a conductor, resulting in an electric current. This current faces internal resistance, which heats the conductor. The main limitation of this method is that it is not applicable for materials that have high conductivity, since such materials reflect most of the energy that falls on them.

The conduction mechanism. A solution containing ions, or even a single isolated ion with a hydrogen bonded cluster, in the sample the ions will move through the solution under the influence of an electric field, resulting in expenditure of energy due to able to believe that the more polar the solvent, (i.e. the higher the dielectric constant it possesses), the more readily the microwave irradiation is absorbed and the higher the temperature obtained. This would appear to correspond well to what

is observed in the case of water versus dioxane. If, however, two solvents with comparable dielectric constants, ϵ_s , such as acetone and ethanol are heated at the same radiation power and for the same period of time as the water described above, the final temperature will be much higher in ethanol than in acetone. In order to be able to compare the abilities of different solvents to generate heat from microwave irradiation, their capabilities to absorb microwave energy and to convert the absorbed energy into heat must be taken into account. These factors may be considered using the loss angle, δ , which is usually expressed in the form of its tangent.

$$\tan \delta = \epsilon''/\epsilon'$$

The dielectric constant, or relative permittivity, ϵ' , represents the ability of a dielectric material to store electrical potential energy under the influence of an electric field. At room temperature and under the influence of a static electric field, ϵ' , is equal to the dielectric constant, ϵ_s . The loss factor, ϵ'' , quantifies the efficiency with which the absorbed energy is converted into heat. For solvents with comparable ϵ' and low values of $\tan \delta$; the loss factor provides a convenient parameter for comparing the abilities of different materials to convert microwave into thermal energy. The dielectric constants of acetone and ethanol are, indeed, in the same range but ethanol possesses a much higher loss tangent. For this reason, ethanol couples better with microwave irradiation, resulting in a more rapid temperature increase.

2.3. Interfacial Polarization

The interfacial polarization method can be considered as a combination of the

conduction and dipolar polarization mechanisms. It is important for heating systems that comprise a conducting material dispersed in a non-conducting material. For example, consider the dispersion of metal particles in sulphur. And sulphur does not respond to microwaves, and metals reflect most of the microwave energy they are exposed to, but combining the two makes them a good microwave-absorbing material. However, for this to take place, metals have to be used in powder form. This is because, unlike a metal surface, metal powder is a good absorber of microwave radiation. It absorbs radiation and is heated by a mechanism that is similar to dipolar polarization. The environment of the metal powder acts as a solvent for polar molecules and restricts the motion of ions by forces that are equivalent to inter particle interactions in polar solvents. These restricting forces, under the effect of an oscillating field, induce a phase lag in the motion of ions. The phase lag.

2.4. Loss angle

As mentioned above, polar solvents and/or ions are needed for microwave heating. The dielectric polarization depends primarily on the ability of the dipoles to reorientate in an applied electric field. Besides the physical properties of the contents of the reaction vessel, both the volume of the contents and the geometry of the reaction vessel are crucial to provide uniform and reproducible heating. The load volume (i.e. the volume of the load with respect to the oven cavity) is the more important of the two factors. Dramatic effects may occur when using volumes greater or smaller than those specified by the manufacturer of the microwave apparatus. In order to achieve the best possible

reproducibility, reactions should be performed in carefully designed cavities and vessels, and, additionally, the use of a temperature control will help to overcome many of these problems.

2.5. Modes

When microwaves enter a cavity, they are reflected by the walls. The reflections of the waves eventually generate a three dimensional stationary pattern of standing waves within the cavity, called modes. The cavity in a domestic microwave oven is designed to have typically three to six different modes intended to provide a uniform heating pattern for general food items. Despite being a good solution for these purposes, the use of the multi-mode technique will provide a field pattern with areas of high and low field merely an effect of the thermal heat generated by the microwaves or is it an effect specific for microwave heating?

. The main advantage of using microwave assisted organic synthesis is the shorter reaction times. The rate of the reaction can be described by the Arrhenius Eq.

$$K = A e^{-\Delta G/RT}$$

Considering Eq. there are basically two ways to increase the rate of a chemical reaction. First, the pre-exponential factor A , which describes the molecular mobility and depends on the frequency of vibrations of the molecules at the reaction interface. We have described previously how microwaves induce an increase in molecular vibrations and it has been proposed that this factor, A , can be affected. Other authors, however, have proposed that microwave irradiation produces an alteration in the exponential factor by affecting the free energy of activation, ΔG .

3. MICROWAVE CHEMISTRY APPARATUS¹⁶

Most pioneering experiments in chemical synthesis using microwaves were carried out in domestic microwave ovens. However, developments in microwave equipment technology have enabled researchers to use dedicated apparatus for organic reactions. The following are the two categories into which microwave chemistry apparatus are classified:

3.1. Single-mode apparatus

3.2. Multi-mode apparatus

3.1. Single-mode Apparatus

The differentiating feature of a single-mode apparatus is its ability to create a standing wave pattern, which is generated by the interference of fields that have the same amplitude but different oscillating directions. This interface generates an array of nodes where microwave energy intensity is zero, and an array of antinodes where the magnitude of microwave energy is at its highest.(Fig:-2).¹⁴

The factor that governs the design of a single-mode apparatus is the distance of the sample from the magnetron. This distance should be appropriate to ensure that the sample is placed at the antinodes of the standing electromagnetic wave pattern.(Fig:-3).

One of the limitations of single-mode apparatus is that only one vessel can be irradiated at a time. However, after the completion of the reaction period, the reaction mixture can be rapidly cooled by using compressed air this is a built-in cooling feature of the apparatus. As a result, the apparatus becomes more user-friendly. These apparatus can process volumes ranging from 0.2 to about 50 ml under sealed-vessel conditions (250 °C, ca. 20 bar), and volumes around 150 ml under open-vessel reflux conditions 10.

Single-mode microwave heating equipment are currently used for small-scale drug discovery, automation and combinatorial chemical applications. An advantage of single-mode apparatus is their high rate of heating. This is because the sample is always placed at the antinodes of the field, where the intensity of microwave radiation is the highest. In contrast, the heating effect is averaged out in a multi-mode apparatus.^{13, 14}

3.2. Multi-mode Apparatus

An essential feature of a multi-mode apparatus is the deliberate avoidance of generating a standing wave pattern inside it. (Fig:- 4).

The goal is to generate as much chaos as possible inside the apparatus. The greater the chaos, the higher is the dispersion of radiation, which increases the area that can cause effective heating inside the apparatus. As a result, a multi-mode microwave heating apparatus can accommodate a number of samples simultaneously for heating, unlike single-mode apparatus where only one sample can be irradiated at a time. Owing to this characteristic, a multi-mode heating apparatus is used for bulk heating and carrying out chemical analysis processes such as a shing, extraction, etc. In large multi-mode apparatus, several liters of reaction mixture can be processed in both open and closed-vessel conditions. Recent research has resulted in the development of continuous-flow reactors for single- and multi-mode cavities that enable preparation of materials in kilograms. major limitation of multi-mode apparatus is that even with radiation distributed around them, heating samples cannot be controlled efficiently. This is largely due to the chaos generated, which makes it difficult to create equal heating conditions

for samples that are heated simultaneously.^{17,18}

4. ADVANTAGES OF MICROWAVE CHEMISTRY²¹

Microwave radiation has proved to be a highly effective heating source in chemical reactions. Microwaves can accelerate the reaction rate, provide better yields and uniform and selective heating, achieve greater reproducibility of reactions, and help in developing cleaner and greener synthetic routes.

4.1. Increased Rate of Reactions²²

Compared to conventional heating, microwave heating enhances the rate of certain chemical reactions by 10 to 1,000 times. This is due to its ability to substantially increase the temperature of a reaction, for instance, synthesis of fluorescein, which usually takes about 10 hours by conventional heating methods, can be conducted in only 35 minutes by means of microwave heating (Table:-2).

4.2. Efficient Source of Heating^{23, 24, 25}

Heating by means of microwave radiation is a highly efficient process and results insignificant energy saving. This is primarily because microwaves heat up just the sample and not the apparatus, and therefore energy consumption is less. A typical example is the use of microwave radiation in the ashing process they eliminate the lengthy heating-up periods associated with conventional electrical resistance furnaces. This significantly lowers average energy costs.

4.3. Higher Yields²⁶

In certain chemical reactions, microwave radiation produces higher yields compared

to conventional heating methods, for example, microwave synthesis of fluorescein results in an increase in the yield of the reaction, from 70% to 82% (Table:-3).

4.4. Uniform Heating²⁷

Microwave radiation, unlike conventional heating methods, provides uniform heating throughout a reaction mixture (Fig:-5).

In conventional heating, the walls of the oil bath get heated first, and then the solvent. As a result of this distributed heating in an oil bath, there is always a temperature difference between the walls and the solvent. In the case of microwave heating, only the solvent and the solute particles are excited, which results in uniform heating of the solvent. This feature allows the chemist to place reaction vessels at any location in the cavity of a microwave oven. It also proves vital in processing multiple reactions simultaneously, or in scaling up reactions that require identical heating conditions.

4.5 Selective Heating

Selective heating is based on the principle that different materials respond differently to microwaves. Some materials are transparent whereas others absorb microwaves. Therefore, microwaves can be used to heat a combination of such materials, for example, the production of metal sulphide with conventional heating requires weeks because of the volatility of sulphur vapors. Rapid heating of sulphur in a closed tube results in the generation of sulphur fumes, which can cause an explosion. However, in microwave heating, since sulphur is transparent to microwaves, only the metal gets heated. Therefore, reaction can be carried out at a much faster rate, with rapid heating, without the threat of an explosion.

4.6 Environmentally-friendly Chemistry²⁸

Reactions conducted through microwaves are cleaner and more environmentally friendly than conventional heating methods. Microwaves heat the compounds directly; therefore, usage of solvents in the chemical reaction can be reduced or eliminated, for example, Hamelin developed an approach to carry out a solvent-free chemical reaction on a sponge-like material with the help of microwave heating. There action is conducted by heating a spongy material such as alumina. The chemical reactants are adsorbed to alumina, and on exposure to microwaves, react at a faster rate than conventional heating. The use of microwaves has also reduced the amount of purification required for the end products of chemical reactions involving toxic reagents.

4.7 Greater Reproducibility of Chemical Reactions

Reactions with microwave heating are more reproducible compared to conventional heating because of uniform heating and better control of process parameters. The temperature of chemical reactions can also be easily monitored. This is of particular relevance in the lead optimization phase of the drug development process in pharmaceutical companies.

5. LIMITATIONS OF MICROWAVE CHEMISTRY^{23, 24}

The limitations of microwave chemistry are linked to its scalability, limited application, and the hazards involved in its use.

5.1. Lack of Scalability

The yield obtained by using microwave apparatus available in the market is

limited to a few grams. Although there have been developments in the recent past, relating to the scalability¹⁵ of microwave equipment, there is still a gap that needs to be spanned to make the technology scalable. This is particularly true for reactions at the industrial production level and for solid-state reactions.

5.2. Limited Applicability

The use of microwaves as a source of heating has limited applicability for materials that absorb them. Microwaves cannot heat materials such as sulphur, which are transparent to their radiation. In addition, although microwave heating increases the rate of reaction in certain reactions, it also results in yield reduction compared to conventional heating methods examples have been cited in the reference.

5.3. Safety Hazards Relating to the Use of Microwave-heating Apparatus

Although manufacturers of microwave-heating apparatus have directed their research to make microwaves a safe source of heating, uncontrolled reaction involving volatile reactants under superheated conditions may result in explosive conditions. Moreover, improper use of microwave heating for rate enhancement of chemical reactions involving radioisotopes may result in uncontrolled radioactive decay. Certain problems, with dangerous end results, have also been observed while conducting polar acid-based reactions, for example, microwave irradiation of are action involving concentrated sulphuric acid may damage the polymer vessel used for heating. This is because sulphuric acid is a strong coupler of microwave energy and raises the reaction temperature to 300 C within a very short time. As a result, the

polymer microwave-heating container may melt, with hazardous consequences. Conducting microwave reactions at high-pressure conditions may also result in uncontrolled reactions and cause explosions.

5.4. Health Hazards Relating to the Use of Microwave-heating Apparatus

Health hazards related to microwaves are caused by the penetration of microwaves. While microwaves operating at a low-frequency range are only able to penetrate the human skin, higher frequency-range microwaves can reach body organs. Research as proven that on prolonged exposure microwaves may result in the complete degeneration of body tissues and cells. It has also been established that constant exposure of DNA to high-frequency microwaves during a biochemical reaction may result in complete degeneration of the DNA strand. Research has been carried out to understand this phenomenon, and two schools of thought have evolved. The first is based on the thermal degeneration of DNA by microwave radiation, and believe that microwaves have enough energy to disrupt the covalent bond of a DNA strand. The other school of thought is emphatic about the existence of a 'non-thermal microwave effect'. Kakita *et al* have proved that in identical temperature conditions, microwave-irradiated DNA strands were different from those heated under conventional heating methods. Microwave-irradiated DNA strands were usually destroyed, which does not occur in conventional heating. This discovery has restricted the use of microwave heating to only a biological reactions.

6. APPLICATION OF MICROWAVE CHEMISTRY

Application of microwave radiation in chemical synthesis encompasses its use in the acceleration of chemical synthesis. Microwave-enhanced synthesis allows organic chemists to work faster, generate higher yields, and increase product purity. In addition, due to the availability of high-capacity microwave apparatus, the yields of the experiments have now easily scaled up from milligrams to kilograms, without the need to alter reaction parameters. Microwave organic synthesis is the main component of microwave-assisted chemical synthesis Technique.

6.1. Organic Synthesis

Organic synthesis is the preparation of a desired organic compound from available starting materials. Microwave-assisted organic synthesis has been the foremost and one of the most researched applications of microwaves in chemical reactions. The earliest of such reactions was conducted by Richard Gedye and his co-workers, in the hydrolysis of benzamide to benzoic acid under acidic conditions. They reported rate enhancements up to 5-1000 times in comparison to conventional heating methods. Since then, chemists have successfully conducted a large range of organic reactions. These include the following:

1. The Diels-Alder reaction
2. Racemisation of large organic molecules thorough Diels-Alder cyclo-reversions
3. The Ene reaction
4. Heck reaction
5. Suzuki reaction
6. Mannich reaction
7. Hydrogenation of beta-lactams
8. Hydrolysis

9. Dehydration
10. Esterification
11. Cycloaddition reaction
12. Epoxidation
13. Reductions
14. Condensations
15. Protection and deprotection
16. Cyclisation reactions, etc.

Microwave-assisted organic synthesis is being widely applied in the pharmaceuticals industry, particularly for developing compounds in the lead optimization phase of drug development. In this phase, chemists use diverse synthetic techniques to develop candidate drugs from lead compounds. Based on reaction conditions, organic synthesis reactions can be conducted in the following Technique:

1. Organic synthesis at atmospheric pressure
2. Organic synthesis at elevated pressure
3. Organic synthesis in 'solvent-free' open vessel reactions

6.1.1. Organic Synthesis at Atmospheric Pressure

Microwave-assisted organic reactions can be most conveniently conducted at atmospheric pressure in reflux conditions²⁶. A good example of microwave-assisted organic synthesis at atmospheric pressure is the Diels-Alder reaction of maleic anhydride with anthracene (Fig:-6). In the presence of diglyme (boiling point 162°C), this reaction can be completed in a minute, with a 90% yield. However, the conventional synthetic route, which uses benzene, requires 90 minutes²⁷. It is extremely important to use dipolar solvents for reactions in such conditions. Solvent systems with higher boiling

points are preferred in microwave-assisted organic synthetic reactions.

6.1.2. Organic Synthesis at Elevated Pressure

Microwaves can be used to directly heat the solvent in sealed microwave-transparent containers. The sealed container helps in increasing the pressure in the reactor, which facilitates the reaction that will take place at much higher temperatures. This results in a substantial increase in the reaction rate of microwave-assisted organic synthesis. However, increase in the reaction rate of any chemical synthesis depends on three factors: volume of the vessel, the solvent to space ratio, and the solvent boiling point.

6.1.3. Organic Synthesis in 'Solvent-free' Open Vessel Reactions

Microwaves have been applied to organic synthesis in dry media, using solid supports. Microwave radiation, based on solid supports, has been highly successful in reducing the reaction time for condensation, acetylation and deacetylation reactions, for example, deacetylation of a protected compound such as alcoholic acetate held on a support material. The microwave-assisted reaction could be completed within two to three minutes, compared to conventional oil-bath heating at 75 °C for 40 hours.

6.2. Microwave-assisted Synthesis of Organometallic and Coordination Compounds

Microwave radiation has been successful in accelerating the reaction rate for the generation of organometallic and coordination compounds, which are produced by generating covalent bonds between organic compounds and metals.

In case of organometallic compounds, it has been observed that the use of microwaves in the synthesis of organo-B-metal compounds has resulted in a 40-fold³⁰ increase in the rate of reaction. This enhanced rate of reaction was achieved under conditions identical to high-pressure organic synthesis³¹ in 100 ml Teflon pressure vessels, containing relatively small quantities of solvent (~12 ml). In addition, the synthesis of a variety of transition metal coordination compounds, under atmospheric conditions, has been successfully carried out under microwave radiation, for example, the reaction of hydrated rhodium chloride ($\text{RhCl}_3 \cdot x\text{H}_2\text{O}$) and cyclooctadiene C_8H_{12} , to produce $\text{Rh}(\text{cod})\text{Cl}_2$ in the presence of EtOH/H₂O, in microwave radiation, increased the rate of the reaction more than 1200-fold for the same Improved syntheses of $\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta\text{-arene})\text{PF}_6$ and $\text{Fe}(\eta\text{-arene})_2\text{PF}_6$ salts, using the microwave-heating properties of metal powders, have also been reported. Organometallic compounds are an important constituent of vitamins such as vitamin B-12. Their applications range from their use in the production of display screens and the manufacture of computer chips to their usage in electrolytic solutions for batteries. Like organometallic compounds, coordination compounds have a large variety of applications, for example, in the dye industry, and also in medical science.

6.3. Microwave-assisted Synthesis of Intercalation Compounds

Applications of microwave chemistry for intercalation compounds have been tested recently. Intercalation compounds comprise organic or organometallic compounds. Conventional heating methods for the preparation of

intercalation compounds, such as the intercalation of pyridine or its derivative into the layered compound α -VO(PO₄), are slow and have their stoichiometric limitations with respect to the yield obtained. The maximum stoichiometry obtained for this reaction, even after 64 hours, has been VO(PO₄)_{0.85}. The use of microwaves in this process has reduced the stoichiometric results. Intercalation compounds have found their applications in fields such as energy storage devices, impurity extraction from bauxite ore, etc.

6.4. Microwave-assisted Synthesis of Ceramic Products

Microwave processing of ceramic materials has reached a high degree of maturity. In the ceramic production industry, the removal of solvent or moisture is a critical step in the generation of ceramic products. Initially, the use of microwaves in this industry was limited to the effective removal of solvents from solid samples. It is estimated that for materials with a water content below 5%, microwave drying is more energy efficient than conventional drying methods. However, over the past few years, the utility of microwaves has increased due to the other advantages they provide. It has been proven that microwave heating provides better uniform heating than conventional heating methods. This has increased their utility over conventional methods, which provide non-uniform heating, and may generate solids with uneven properties. Ceramics are widely used in electrical components, sanitary-ware industries, and in many other industries. Microwaves have also found application in the sintering process. Sintering is the process of welding together the powdered particles of a substance or mixture by heating it to a temperature below the

melting point of the components. The particles stick together and form a sinter. Initial studies³⁴ in microwave-aided sintering were carried out by using a 400W microwave-tuned waveguide applicator, to effect the sintering of alumina and silica rods at >1700 °C. Since then, a wide range of materials has been processed with microwaves. A frequency range of 28 GHz is used to facilitate the generation of homogeneous profiles of the materials sintered. However, microwave sintering has not become an economically viable replacement for conventional methods. In the near future, improved product and process simplification may lead to an economically viable microwave-sintering operation.

6.5. Microwave-assisted Synthesis of Polymer Products

Polymer chemistry, including ceramic processing, forms the single-largest application area of microwave chemistry. The use of polar reactants in polymerization reaction results in controlled synthesis, and a combination of this with direct heating of reactants makes microwave heating an economically viable option. Economic analyses suggest that the cost of curing polymers may be reduced from 4-11 MJ/kg to 0.3-0.5 MJ/kg by switching over to the use of microwaves³⁵. Curing is a polymerization process, which transforms a liquid resin to a solid, creating the maximum physical properties attainable from the materials. Using microwave radiation in curing has greatly increased the rate of the reactions.

6.6. Solid-state Chemical Synthesis

The microwave dielectric losses of many solid compounds have been used to provide sufficient heat to drive a chemical reaction, for example, the high energy-

loss factor of copper oxide has been used to synthesis the high transition temperature(T_c) superconductor $YBa_2Cu_3O_x$. A number of other materials also display excellent heating properties, for example, boron and carbon have adequate heating characteristics and can be used as the only significant microwave absorber material for a solid-state reaction.

6.7. Processing of Radiopharmaceuticals

Microwave-assisted organic synthesis at an elevated pressure has been used in the pharmaceutical industry for the synthesis of radio labeled chemicals or radiopharmaceuticals. Radio pharmaceuticals are a genre of chemical compounds that have a radioisotope of an element used in drug making. During pre-clinical trials, these radiopharmaceuticals are used as tracers to generate a nuclear medical image. Positron Emission Tomography (PET) is a common technique used for the generation of nuclear medical images. The most critical aspect relating to radioisotopes is their decay time. The decay time of commonly used radioisotopes is given in Table:-5.

With so little decay time, radio pharmacists are always on the lookout for a method that can squeeze their production time. Microwave chemistry provides a solution to the radiopharmaceutical generation issue. A multi-mode microwave oven was used in the first trial of this kind and it was observed that the rate of reaction increased substantially. This has resulted in the enhanced use of microwaves to produce radiopharmaceuticals. Examples of rate acceleration caused by the use of microwaves are cited in the reference paper³⁷. Other advantages of microwaves include the high yield of the reaction. This

can be attributed to the short half-life of reactants, for example, saving five minutes in a synthesis with carbon-11 resulted in an enhanced production rate of 15%. It has also been observed that several reactions could only be achieved by using microwaves.

7. CONCLUSION

The dynamic microwave power system employed offered an efficient heating of the materials thus, reduced chemical reactions times and increased reaction yields were observed in most of the Literature Survey. In this type of synthesis we focused on the "Significance of Microwave Assist Technique in Green Chemistry" for chemical reactions. Microwaves act as high frequency electric fields and will generally heat any material containing mobile electric charges, such as polar molecules in a solvent or conducting ions in a solid. Polar solvents are heated as their component molecules are forced to rotate with the field and lose energy in collisions. Semiconducting and conducting samples heat when ions or electrons within them form an electric current and energy is lost due to the electrical resistance of the material.

Thus in last we can say only that the ability to combine microwave technology with in-situ reaction monitoring as an analytical tools which offer opportunities for chemists to optimize the reaction conditions.

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Table:-1 Microwave Frequency Bands

Letter Designation	Frequency range
<u>L band</u>	1 to 2 GHz
<u>S band</u>	4 to 8 GHz
<u>C band</u>	4 to 8 GHz
<u>X band</u>	8 to 12 GHz
<u>K_u band</u>	12 to 18 GHz
<u>K band</u>	18 to 26.5 GHz
<u>K_a band</u>	26.5 to 40 GHz
<u>Q band</u>	33 to 50 GHz
<u>U band</u>	40 to 60 GHz
<u>V band</u>	50 to 75 GHz
<u>E band</u>	60 to 90 GHz
<u>W band</u>	75 to 110 GHz
<u>F band</u>	90 to 140 GHz
<u>D band</u>	110 to 170 GHz

Table:-2 Comparison of Reaction duration (in Minutes)

Reaction	Conventional	Microwave
Synthesis of Fluorescein	600	35
Condensation of Benzoin with Urea	60	8
Biginelli Reaction	360	35
Synthesis of Aspirin	130	1
Synthesis of Phenothiazine	60	4

Table:-3 Comparison of Yields (%)

Reaction	Conventional	Microwave
Synthesis of Fluorescein	70	82
Condensation of Benzoin with Urea	70	73
Biginelli Reaction	70	75
Synthesis of Aspirin	85	92
Synthesis of Phenothiazine	71	86

Table:-4 Comparison Yield Under Microwave and Conventional Heating Method

Chemical Reaction	Temperature (°C)	Time(min)	Mw Yield(%)	Conventional (%)
Hydrolysis of Hexanenitrile	100	60	40	26
Oxidation of Cyclohexane	80	60	26	12
Esterification of Stearic Acid	140	120	97	83

Table:-5 Half Life of the Isotopes of Some Common Elements Used in Radiopharmaceuticals

Element	Half Life (in minutes)
Oxygen-15	2
Nitrogen-13	10
Carbon-11	20
Fluorine-18	110



Fig:-1. Dipolar molecules which try to align with an oscillating electric field

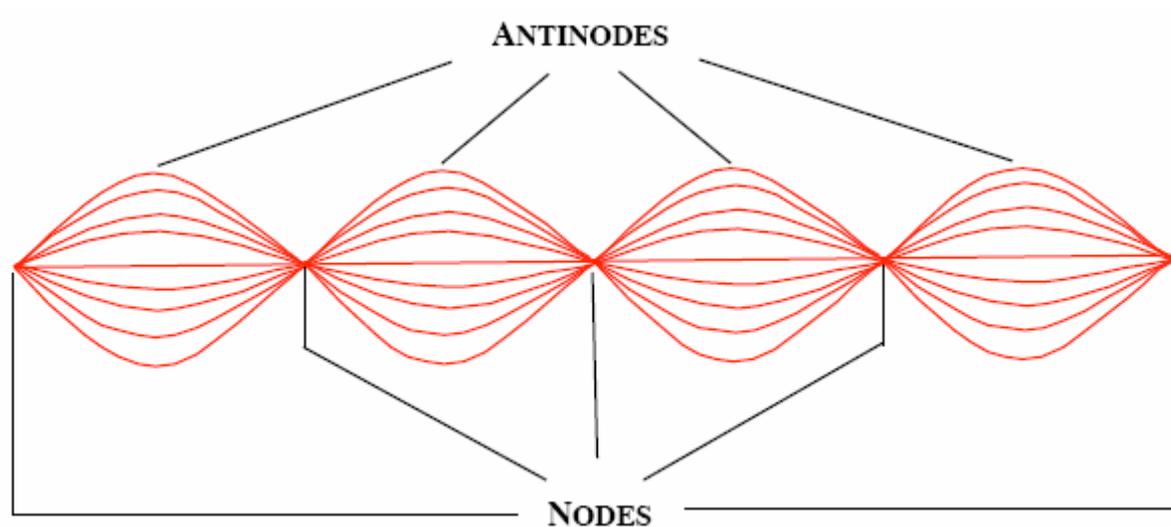


Fig:-2. Generation of a Standing Wave Pattern

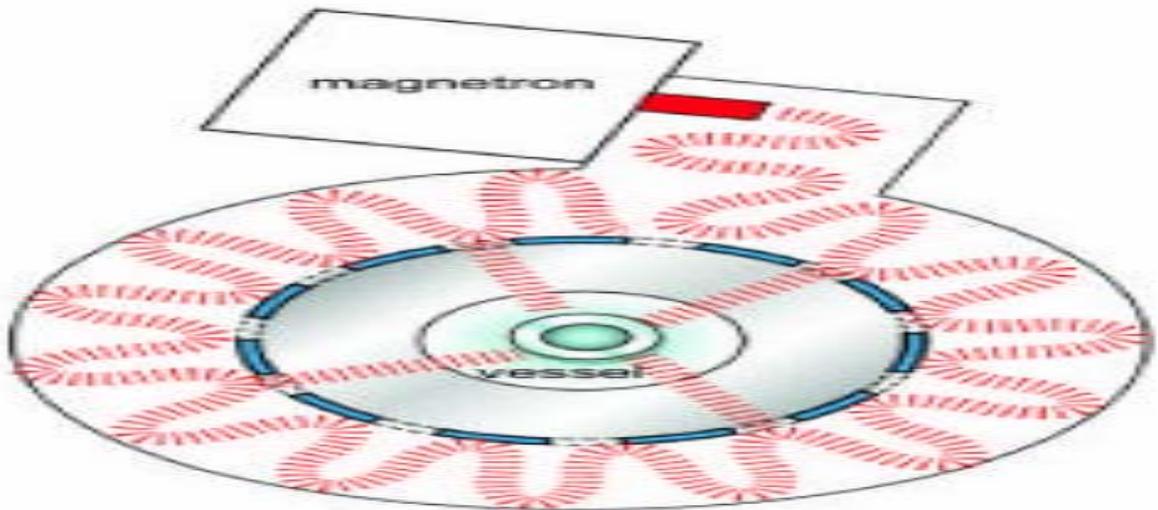


Fig:-3. Single mode heating apparatus

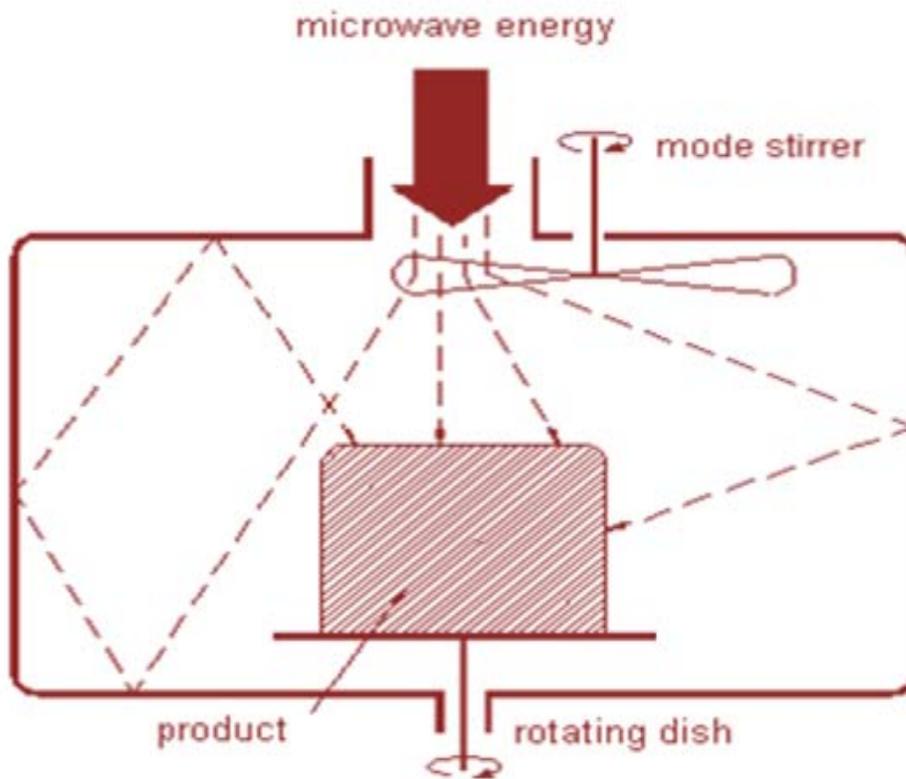


Fig:-4. Multi-mode Heating Apparatus

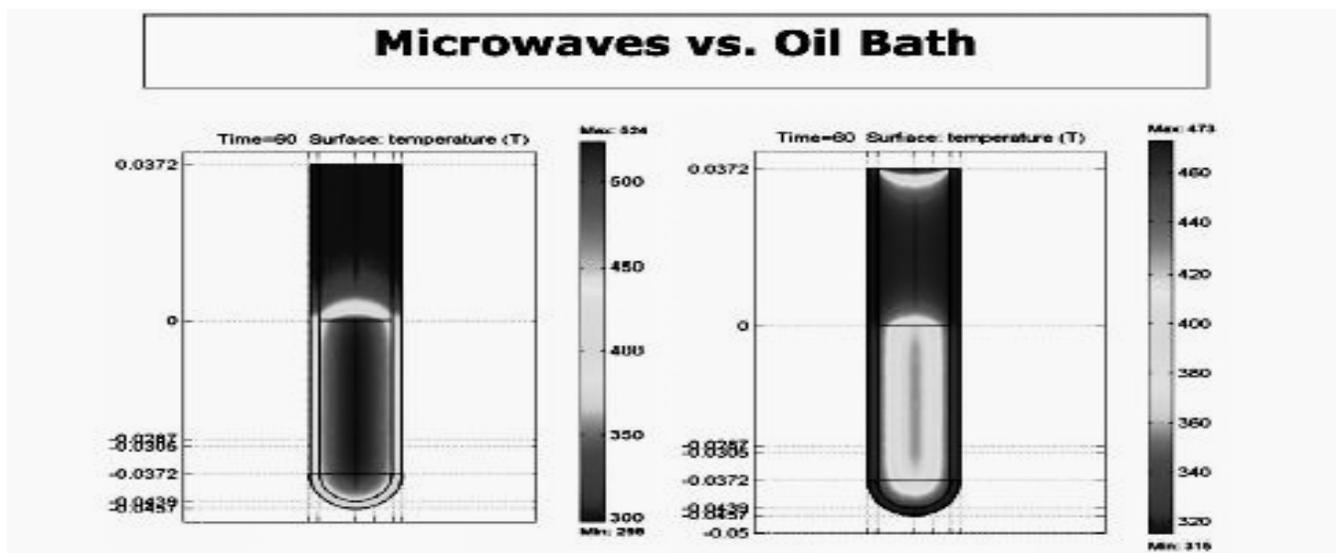


Fig:- 5. Uniform Heating through Microwave Irradiation

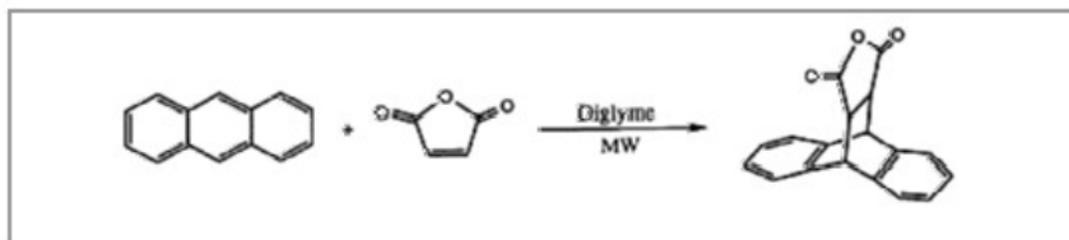


Fig:-6. The Diels-Alder Reaction with Microwave Radiation