MICROWAVE-ASSISTED SYNTHESIS: REVIEW OF RECENT DEVELOPMENTS

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ABSTRACT

The term green chemistry is defined as "the invention, design and application of chemical products and processes to reduce or to eliminate the use and generation of hazardous substances". The major applications of green chemistry principles and practice renders control, regulation, and remediation, hence resultant environmental benefit can be expressed in terms of economic impact .It also involves replacement of traditional methods of heating with that of modern methods of heating such as microwave radiations which helped to reduce carbon footprint as low as possible. Microwave assisted synthesis is an important tool for green chemistry. Microwave radiation, an electromagnetic radiation, which is widely use as a source of heating in organic synthesis. Microwave assisted organic synthesis has emerged as a new "lead" in organic synthesis which makes the chemistry to go green. This technique has provided the excellent momentum for many chemists to switch to microwave assisted chemistry. There has been a dramatic uptake in the use of microwaves as an energy source to promote synthetic transformations. Microwave-assisted synthesis is clearly a method by which the laboratory chemist can achieve goals in a fraction of the time as compared to traditional conductive heating methods . In the present article an attempt was made to focus on what is microwave assisted synthesis, how is it generated and recent development in this area.

I. INTRODUCTION

Microwave technology opens up new opportunities to the synthetic chemist in the form of new reactions that are not possible using conventional heating. The interest in the microwave assisted organic synthesis has been growing during the recent years[1-2]. The short reaction times provided by microwave synthesis make it ideal for rapid reaction scouting and optimization of reaction conditions, allowing very rapid progress through the hypotheses–experiment–results iterations, resulting in more decision points per unit time.

With the easy availability of microwaves its use in chemistry has gained momentum and this has led the microwave heating to emerge as powerful technique to promote a wide variety of chemical reactions[3]. The bottleneck of conventional synthesis is typically the optimization, i.e. finding the optimum conditions for a specific reaction to obtain the desired products in good yields and purities. Since many synthesis reactions require at least one or more heating steps for long time periods, these optimizations are often difficult and time-consuming. Microwave-assisted heating under controlled conditions has been shown to be a valuable technology for any application that requires heating of a reaction mixture, since it often dramatically reduces reaction times – typically from days or hours to minutes or even seconds. Compounds can therefore be rapidly synthesized in either a parallel or (automated) sequential way using this new promising technology. The great

invention of burner was done in organic chemistry 1899 by Robert Bunsen. This invention was so useful that it lead to provide heat in a much focused manner required to carry out any chemical synthesis[4] The Bunsen burner was later superseded by oil baths or hot plates, while in the 21st century reactions by microwave energy has been an increasingly popular topic in the scientific community[5].

The term microwave is inseperably linked in our modern society to the rapid heating and warming of food stuff. what is fascinating from a chemical synthesis stand point is the dynamic range of temperature afforded by modern laboratory microwave instrumentation to date most of efforts has been focused on elevated temperature transformation or reactions requiring heating synthetic transformation unachievable through conductive heating have recently been realized using microwave as the entery source. Low temperature reactions via microwave energy have been recenty introduced with the key point being that genteral reations conditions which are important to biochemical applications. Microwaves are in form of electromagnetic energy which lie in electromagnetic spectrum corresponds to wavelength of 1cm to 1m and frequency of 30GHz to 300MHz .This places it between infrared radiation and radiowaves. The typical bands for industrial applications are 915±15 and 2450 ±50 MHz. The shorter wavelength in the range 1-25cm is for radar, whereas remaining section are devoted to telecommunication. The entire microwave region is therefore not available for heating applications and equipment operating at 2.45GHz is most commonly used. Microwave energy consist of both electric as well as magnetic field.

The difference between microwave energy and other forms of radiation, such as X- and γ-rays, is that microwave energy is non-ionizing and therefore does not alter the molecular structure of the compounds being heated – it provides only thermal activation. The heating effect utilized in microwave assisted organic transformations is mainly due to dielectric polarization. When a molecule is irradiated with microwaves, it aligns itself with the applied field. The rapidly changing electric field (2.45 x 109 Hz) affects the molecule and consequently the molecule continually attempts to align itself with the changing field thus energy is absorbed. The ability of a material to convert electromagnetic energy into thermal energy is dependent on the dielectric constant. The larger the dielectric constant the greater is the coupling with microwaves. Thus, solvents such as water, methanol, DMF, ethyl acetate, acetone, acetic acid, etc. are all heated rapidly when irradiated with microwaves. However, solvents with low dielectric constants such as hexane, toluene, carbon tetrachloride, etc. do not couple and therefore do not heat that rapidly under microwave irradiation. Microwave heating has thus been found to be a very convenient thermal source not only in the kitchen but also in a chemical laboratory [1,6]. Chemists have explored the possibility of the application of a conventional microwave oven to carry out chemical reactions. However, the advantages of using microwave dielectric heating for performing organic transformations[7] have only emerged since the mid- 1980s. This technology opens up new opportunities to the synthetic chemist, in the form of new reactions that are not possible using conventional heating.

The concepts of atom economy and energy factors have eventually become a guiding principle of Green chemistry. These are embodied in the “12 Principles of Green chemistry” which are as follows:

• Prevention of waste
• Atom Economy
• Less Hazardous Chemical Syntheses
• Design Safer Chemicals

 ISBN: 978-93-86171-33-7

• Safer Solvents and Auxiliaries
• Design for Energy Efficiency
• Use Renewable Feedstocks
• Reduce Derivatives
• Catalysis
• Design for Degradation
• Real-time Analysis for Pollution Prevention
• Inherently Safer Chemistry for Accident Prevention

1.1 Principle of microwave reactions

The basic principle behind the heating in microwave oven is due to the interaction of charged particle of the reaction material with electromagnetic wavelength of particular frequency. The phenomena of producing heat by electromagnetic irradiation are either by collision or by conduction, sometime by both. All the wave energy changes its polarity from positive to negative with each cycle of the wave. This cause rapid orientation and reorientation of molecule, which cause heating by collision. If the charge particles of material are free to travel through the material (e.g. Electron in a sample of carbon), a current will induce which will travel in phase with the field. If charge particle are bound within regions of the material, the electric field component will cause them to move until opposing force balancing the electric force.[8-14] The key requirement for dipolar polarisation 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.

Microwave energy is such a tool which will not affect the activation energy but it provide a great momentum to complete the reaction more quickly and in more efficiently as compared to the conventional heating. In each cycle of electromagnetic energy the microwaves will transfer energy in 10-9 sec whereas the kinetic molecular relaxation will take 10-5 sec. This indicates thatenergy transfer is faster than the molecular relaxation.[15] This helps to create the high instantaneous temperature and non equilibrium condition which have a great impact on the kinetics of the reaction. This helps to increase the reaction rate in less time with greater yield[16]

The principle of microwave synthesis offers three major benefits to chemistry development: speed, reproducibility, and a scalable approach to compound synthesis. Additionally, significant advantages of our technical solution are ease of use, safety, verified synthesis methods to enable new users, and an efficient work flow that fits the drug discovery process.

II. SYNTHETIC APPLICATIONS

Microwave energy has found general, commercial application in very few areas. These include food processing, analytical chemistry, and heating and vulcanization of rubber. Food processing and rubber manufacture involve

relatively high-volume, continuous processing. Analytical chemistry applications are broad in scope and involve high-volume, repetitive, batch processing, often with long intermediate drying and reaction steps that can be shortened using microwave heating. Much work has been undertaken to investigate the use of microwaves for the processing of a wide range of materials, including ceramics, polymers, composites (ceramic and polymer matrix), powders, and minerals. Microwaves have also been investigated in a broad range of plasma processes (surface modification, chemical vapor infiltration, powder processing), chemical synthesis and processing, and waste remediation. Despite the considerable effort that has been expended in microwave process development, there has been little industrial application to date, with most of the effort still in the laboratory stage. The plethora of very recent articles describing a variety of new chemistries performed with microwave irradiation have appeared. This section will cover many of these synthetic applications.

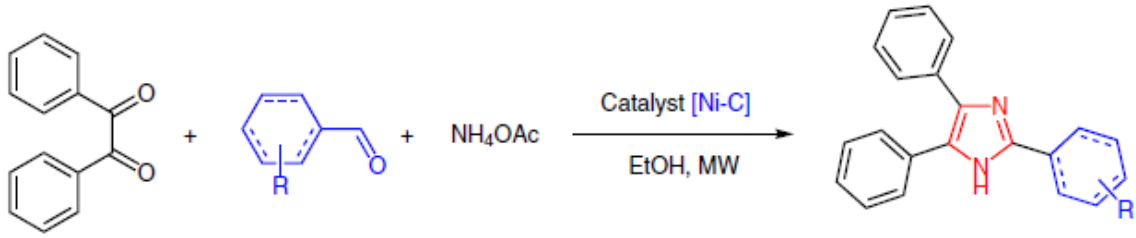
Roshni V [17]and coworkers recently developed a green approach towards synthesis of N-doped C.dots from sesame seeds using microwave-assisted pyrolysis. The fluorescence properties and photostability of C.dots are evaluated. These C.dots will be used to understand the metal sensing properties especially for Fe3+.Green, economical as well as waste recycling synthesis of C.dots was carried out from sesame seeds by energyefficient and time-saving microwave heating.

Sustainable industrial processes demand rapid and cost-effective synthesis procedures of zeolites. Umer Khalil[18] et al reported the synthesis zone of pure mordenite (MOR) zeolite under microwave irradiations. Phase purity, crystallinity, and morphology were carefully studied through optimization of synthesis parameters such as crystallization time, aging time and Si/Al ratio Calcium phosphate-based biomaterials have been frequently used as bone substitutes and osteoconductive scaffolds due to their chemical similarity to the inorganic phase of bone. Hydroxyapatite (HA) is the most frequently used calcium phosphate-based biomaterials and it could be prepared from natural or synthesized sources via several processes. Nano-HA (nHA) particles were suggested to have superior bioresorbtion and close chemical and crystallographic structure to natural bone apatite. Mahomad Nageeb Hassan & coworkers reviewed microwave-assisted (MW) processing of biomaterials, particularly bioceramics, has more appealing advantages than conventional heating methods. It works through an internally generated heat inside the materials molecules instead of originating external heating source and subsequent radiative transfer as in the conventional heating. Thus, MW synthesis of HA offers several benefits including rapid heating, shorter synthesis time, efficient energy transformation and throughout volume heating.[19]

A Schiff's base complex nickel catalyst (Ni-C) enabled a highly efficient one-pot microwave-assisted synthesis of 2,4,5-trisubstituted imidazoles in excellent yields from aldehydes, benzil, and ammonium acetate. The catalyst could be easily recovered by simple filtration and reused. Improved yields were observed under microwave irradiation com-pared with conventional heating as reported by researchers[20]. Overall, the reaction pro-vides a convenient and practical route to the preparation of imidazole derivatives from aromatic aldehydes, benzil, and ammonium acetate as a nitrogen source.

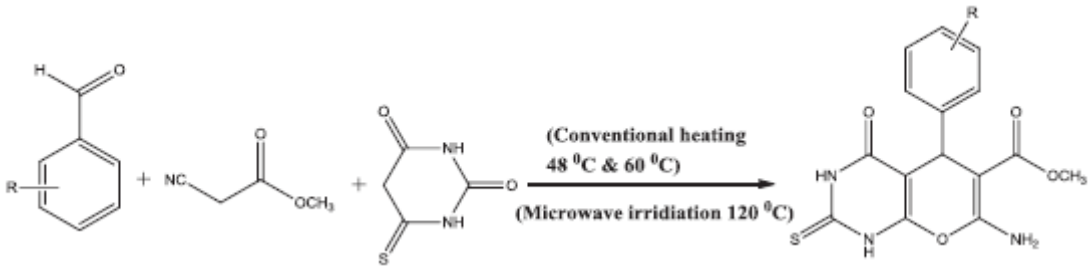
Researchers have developed a method for an efficient adsorbent, iron-modified activated carbon fiber (Fe_2O_3/ACF),which was rapidly fabricated by microwave-assisted heating treatment strategy, which is used to remove As(V) from simulated wastewater[21].

 ISBN: 978-93-86171-33-7



Hasanpoora M and coworkers[22] synthesized zinc oxide nanoparticle with different morphologies by using a microwave-assisted hydrothermal method. In this method, hydrothermal reaction conditions control the size and morphology of zinc oxide particles; although, in chemical methods the reaction time is generally too long

Ajmal R. Bhata[23] and coworkers designed an efficiently simple protocol for the synthesis of methyl 7 amino-4-oxo-5-phenyl-2-thioxo-2, 3, 4,5-tetrahydro-1H-pyrano[2,3-d]pyrimidine-6-carboxylates via one-pot three component condensation pathway via microwave irradiation using water as a green solvent. Researchers reported that synthesis of methyl 7 amino-4-oxo-5-phenyl-2-thioxo-2, 3,4, 5-tetrahydro-*1H*-Pyrano[2,3-d]pyrimidine-6-carboxylate derivatives under microwave irradiation. Initially, the same reaction has also monitored under conventional heating (48 °C and 60 °C). The result showed that reaction completed in 3–6 min with excellent yield (78–94%) under microwave irradiation as compared to conventional heating were obtained moderate yields (69–86%) in 2–6 h at 48 °C and (71–87%) in 1–4 h at 60 °C respectively. Further the yields (67–82%) of targeted compounds were obtained in 2–7 h under room temperature.



A new method[24] for prepration of cobinamide $(CN)_2$Cbi, a vitamin B_{12} precursor, that should allow its broader utility has been developed. Treatment of vitamin B12 with only NaCN and heating in a microwave reactor affords $(CN)_2$Cbi as the sole product. The purification procedure was greatly simplified, allowing for easy isolation of product in 94% yield. The use of microwave heating proved beneficial for $(CN)_2$Cbi(c-lactone) synthesis. Treatment of $(CN)_2$Cbi with triethanolomine led to $(CN)_2$Cbi(c-lactam)

Microwave irradiation in polymer chemistry is an emerging research field. This type of heating can enhance the rate of reaction and improve the specific characteristics of the formed polymer. Nassima Mazouzi-Sennour[25] et al presented a paper focusing on selective microwave (MW) heating and its influence on the polyesterification reaction. As a reaction model, the polyesterification of sebacic acid with decanediol, in bulk and in aqueous emulsion was investigated. The reaction was catalyzed by using 4-dodecylbenzenesulfonic acid (DBSA), which plays a catalytic and surfactant role. Both in bulk and in aqueous media, a polyester with higher molecular weight is obtained in MW heating compared to the conventional heating.

A facile and rapid microwave-assisted combustion method (MWAC) was developed to produce nanocrystalline ZnO powder using dissolution of zinc nitrate (as the oxidant) and urea (as fuel) as the starting materials and water as solvent, then heating the resulting solution in a microwave oven. The study done by L.C.Nehru [26] and

coworkers suggested that application of microwave heating to produce the homogeneous porous ZnO was achieved in a few minutes.

WHICH CHEMISTRY IS NOT SUITABLE FOR MICROWAVE[27] Reactions that are extremely exothermic should not be performed in the instrument. Hydrogen peroxide is, for example, not suitable to use at high temperature, regardless of the technique, because it is explosive. When working with reaction mixtures that contain large amounts of ions or that can release gases, extra precaution is advisable since the heating rate might be very high and the pressure increase may be correspondingly quick due to the closed vessel system. In this case, the experiment can be performed at low concentration (very diluted solution).

III. CONCLUSIONS

The fields of polymer science, bioinformatics, biotechnology as well as biochemistry have been attracted towards microwave assisted reactions in recent years. The chemical reactions can be effectively carried out with the use of microwave ovens. Rapid lead generation and optimization can be successfully done with this technology. All in all, microwave heating is undoubtedly a bonanza for organic and medicinal chemistry researchers. This enabling technique has changed from the 'last sort' in early days to the 'first choice' nowadays for carrying out synthetic transformations requiring heat. In the future, with lower costs, microwave synthesizers will become an integral part of and a standard technology in most synthetic laboratories and will continually make valuable impact on organic synthesis, fabrication of materials, synthesis of biomaterials . The future for the application of microwave technology looks bright because of its efficiency and its potential to contribute to clean products.

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