Microwave Assisted Process
A need of chemical synthesis and Green chemistry approach

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Abstract:

Green world is the need of the time to save the earth. In the field of synthetic chemistry, there is a need to introduce safer, environment friendly reactions with modification in routes and alteration in use of instrumentation. The microwave assisted synthesis is one of best method to achieve faster product reaction along with efficiency. This review article includes information about various microwave synthesis, comparison between traditional method and microwave assisted synthetic route and benefits of microwave assisted synthetic routes over regular reported methods. It also adds constructive information and awareness about atom economy of the process by using radiations.

Key Words: Benefits, comparison, microwave assisted synthesis, traditional route.

Introduction:

Chemical industry is one of the key elements in leading industrial world. This industry has very key role to play when it comes to major impact on environment as well as economy of any sector. All industries are already spending lot of capital investment in research and development, production unit and finally in quality control department. Most of the reactions use costly chemicals, instrumentation, analysis and purification of the products. In many chemical reactions by using traditional path of designing, chemical synthesis, analysis cycle, it is observed that reactions end up with less yield, time required to achieve the product is high. Reaction conditions are critical with respect to maintain the temperature and pressure and assemble required is huge. Time to time monitoring is required to complete the process. Overall impression for such processes is negative. To overcome all the factors, we need to find an alternate route of synthesis which is more beneficial as compared to traditional route. Sir Paul Anaesthese suggested concept of green chemistry [1]. According to his concept of green chemistry, there must be minimum use of chemicals and reagents, reaction conditions should be easy to maintain, lesser use of solvent or if possible solvent free reaction, minimum time required to complete the process and many more[2].In 1991, scientist Trost had suggested concept of atom economy[3].This concept had included maximum conversion of staring material in product without byproduct formation or with minimum byproduct formation. The microwave assisted synthesis fits with maximum parameters of green chemistry. Temperature maintenance is less. Time required for synthesis is minimum [4]. As a result, it saves

energy and cost of reaction. Most of the reactions are solvent free [5]. If solvent required is polar like water [6] [7]. As a result, uniform heating and purity of product is better. Isolation of product is easier as minimum chance of byproduct formation [8]. All the factors improve selectivity and sensitivity of the process. Therefore, microwave assisted synthesis is more advantageous over a traditional route [9].

Now a day's microwave assisted synthesis is becoming more popular because of above mentioned parameters. It is used in all types of chemical industries for better and efficient productivity. Pharmaceutical and medical industries are taking more advantage of these new synthetic routes. Many antitumor drugs [10], bioactive compounds [11] are prepared using this technique.

This paper is an effort to summarize overall review of the microwave assisted synthesis in chemical process and its corresponding advantages.

Synthesis and review:

Metal oxide synthesis -

Jesus Prado-Gonjal, Rainer Schmidth and Emilio Moran prepared metal oxides and nano material using microwave irradiation using heat energy as a source.[12] For preparation solid solid state synthesis, single mode solid state microwave and microwave assisted hydrothermal methods are used. Concept of soft chemistry is used for the synthesis. It includes reaction at low temperature, intercalation, ion exchange, hydrolysis and redox reaction. Fast chemical process is used for preparation of lanthanide complex. By using sms $CaTMO_3$ complexes are prepared of Al, Cr, Mn, Fe Co using all required components with 5% weight of carbon black under microwave irradiation for 30 minutes. In traditional route it requires high temperature about 3000^0c and for about 24 hrs.

Carbon black helps thermal adsorption material to increase the kinetics of reaction. It was observed that excessive irradiation did not yield crystalline material. All these materials used as solid oxide fuel cell, as membrane for separation reaction, gas sensors in automobiles, magneto resistive material. Rare earth pyrochlore oxide compounds are synthesized with fast speed from nitrates in 20 minutes microwave irradiation followed by calcination.Material obtained by this method is nano sized, high homogeneity and sponge like structure. $Ba_xMn_8O_{16}$, $LaCrO_3$ Perovskite are prepared by single mode solid state microwave synthesis. Instruments used for heating was polarized and exhibits range amplitude across the cavity. Electric, magnetic fields were well defined, stable under operational condition.Ba_xMnO_{16} material shows antiferromagnetism with semi conductive property. It is prepared with mixture of $Ba(NO_3)$, Mn_2O_3, KCl for 5 minutes in silica crucible under microwave irradiation. In traditional method temperature maintained was 850^OC for 72 hours and in other reported method 900^0C for 48 hours.LaCrO3 pervoskite is prepared in 2 minutes with microwave irradiation starting from nitrates in SMMR. Solid state reaction works on diffusion of row material at their interfaces whereas hydrothermal or solvothermal reaction, the reaction ions or molecules works in solution. It affects morphology of compound and speed of reaction.$H_2v_3O_8$ material prepared using this technique at 120^oC per minute and at 200^oC with 20ml water used as solvent gives wire like structure and it used as semi conductive material as compared to quartz material more suitable to prepare.

Antioxidant synthesis -

Microwave assisted extraction of natural antioxidants from the exotic Gordiania axillaries fruit: optimization and identification of phenolic compounds.

Antioxidants plays vital role in digestive system therefore synthesis of such material is important. Many antioxidants are extracted from natural source. One of them is Gordiania axillaris fruit.

Gordianiaaxillaris fruit contains antioxidants and phenolic compounds which shows anticancer, anti stomach ache activity.YaLi, Sha Li, Sheng-Jun Lin, Jiao-Jiao Zhang, Cai-Ning Zhao and Hua-Bin Li microwave assisted extraction of Gordania axillaris fruit to study the antioxidant properties[13]Comparison between traditional methods like use of maceration and soxhlet extraction is carried out. In MAE method, results are much better which shows shorter time for extraction and lower temperature conditions. At high temperature antioxidants or bioactive compounds may under goes decomposition. If extraction time increases, then also biodegradation of compounds occurs. In soxhlet method, 0.500g of powdered fruit was wrapped in whatmann filter paper and placed under soxhlet extractor with ethanol for 4 hours and 95^{o}C temperature. In maceration extraction 0.500 g powder placed in centrifuge tube with 36.89% ethanol for 24 hours at 25^{o}C.By using microwave assisted synthesis for0.500g of powder with ethanol at 40^{O}C just for 75 minutes at 500W microwave better extraction is achieved. Microwave has dual influence on extraction because it accelerates solvent movement, cell rupture and diffusion of extractives into solvent.

Anticancer drug -

Microwave assisted synthesis of Imidazo [4,5-f][1,10] phenanthroline derivatives as apoptosis inducers in chemotherapy by stabilizing Bcl-2 G-quadruplex DNA

Cancer is one of the major life threatening diseases. Li Li, Jie-Qiong Cao, Hui- MIN Liu and co-workers worked on anticancer drug preparation through microwave synthesis.[14]The series of Imidazo [4, 5-f][1,10] phenanthroline derivatives, phenanthroline were synthesized. Nitro, trifloro, trichloro, hydroxyl derivatives are prepared at 100^{0}C for 20 minutes and yield obtained about 90%. Rapid temperature setting, higher stability with constant pressure this process proves to be more advantageous as compare to traditional methods .1,10-phenanthroline-5,6-dione (315.06 mg), 3-nitrobenzenaldehyde(339.6 mg), ammonium acetate(4g), glacial acetic acid(20 ml) at 100^{0}C for 20 minutes irradiated with microwaves. After 20 Minutes, add 20 ml of water at pH7 followed by filtration and drying process, which results in formation of yellow precipitate. This compound exhibit good anticancer activity against breast cancer, lung cancer, esophageal cancer by killing cancer cells, inhibiting growth of a549 cells, binding and stabilization to bcl-2-G-quadruplex DNA.

Uric acid de-crystallization -

De-crystallization of crystals using gold nano bullets and the metal assisted and microwave-accelerated de-crystallization technique.

Saturation of uric acid across muscles and joints end up with chronic disorders like gout. It is caused by improper renal filtration and decreases metabolism rate of digestive system. Traditional treatment methods against disease gout have major side effects like gastrointestinal toxicity, renal toxicity, gastrointestinal toxicity,

gastrointestinal bleeding and multiple organ failure. In some cases, Sevier side effects are also observed. Patient ends up with coma and may be followed by death. Nishone Thompson, Zainab Boone-Kukoyi did research on microwave assisted de-crystallization of uric acid and alanine responsible for gout [15]. Experiment is based on evaporation time, size of crystals and concentration of crystals to de-crystallization of the uric acid. In this work de-crystallization is carried out using two different ways, one with use of gold silver particles and another is without use of gold silver particles. It was observed that uric acid in presence of Ag/Au nano particles shows faster de-crystallization as compare to without these metal ions. Gold particles show better effect than silver because gold has good thermal stability than silver. In presence of gold nano particles rate of de-crystallization is very high because of irradiation collision energy of culture increases as gold particles bombards on each another and on crystals of uric acid as well. It increases kinetics of process as well as decreases concentration of crystals. It was observed that mediational microwave was more effective than domestic as it is designed for thermal ablation of tissue which controls their denaturization.

Bioactive compound -

Microwave assisted synthesis and antifungal activity of some novel thio ethers containing 1, 2,4-Triazole moiety.

Phenoxy ion containing compounds shows key interest for antifungal, antibacterial and antiherbicide activity. According to rule of bioisostere replacement of oxygen by sulfur improves bioactivity therefore thio compound synthesis is more important. Among all heterocyclic compounds sulfur and nitrogen containing heterocyclic systems shows effective anticancer, anti-inflammatory, antioxidants, antiherbicide, antifungal, antitumor activity. Compounds containing phenolic ring and sulfur provide potential design for drug against microbes. The scientist Jing Min, Yan-Xia shi and group had communicated in their research comparison between traditional and microwave assisted synthesis of heterocyclic compounds [16]. In this paper it was communicated synthesis of 1, 2, 4-triazole and thio ether compounds showing good antifungal activity. In traditional synthesis it was prepared by using 4-chlorophenol and 2- ethyl 2- chloro acetate in presence of KI, DMF and K_2CO_3. It is multistep synthesis under room temperature condition for 24 hours. Same compound was prepared under microwave condition at 90^0C in presence of NaOH/ DMF/ H2O with few steps in 10 to 20 minutes.

Ester Synthesis -

Microwave assisted synthesis of Cinnamyl long chain aroma esters.

Marta Worzakowska had synthesized Cinnamyl long chain aromatic esters.[17]Aroma compounds play key role in food, pharmacy, cosmetic, chemical industry. Ester shows characteristic aromatic property. These aroma compounds are derived from natural plant extract. On account of operational cost we end up with low yield of extract. In traditional synthesis, we required variety of chemicals and organic solvents. Proposed ester was prepared conventionally by using Cinnamyl alcohol, acid anhydride, diol and catalyst at 140^oC in thermostatic oil bath under reduced pressure for the period of 30 to 65 hours. Therefore, we need to find an alternative route for synthesis. However, by using same chemicals and temperature conditions in microwave it was prepared just within 10 to 20 minutes. It resulted in drastic reduction in time for required preparation.

Antifungal antitumor drug -

Microwave assisted synthesis of Naval Pyrazolo [3,4-g][1,8] naphthyridin-5-amine with potential antifungal and antitumor activity.

Cancer is complex and critical disease and multidrug therapy is used for the treatment. Synthesis of such drug involved multiple stage synthesis which ends up with minimum yield, potential toxicity and higher side effects. Drug toxicity is major issue because of enantiomer formation. However, by using microwave route the problem was resolved along with yield. Under microwave synthesis single product formation takes place. Scientist Paola Acosta, EstefaniaButassi, BraulioInsuastyand group suggested synthesis of pyrazole napthyridine compounds [18].These compounds exhibit quite positive potential for antitumor and antifungal activity. Under traditional synthesis by using $AlCl_3$, para CH_3-C_6H_4-SO_3H up to 30% to 40% yield was obtained. Varity of catalyst were tried for this, among them was zinc chloride which provides best results under microwave condition. By using same reaction conditions in microwave it has provided up to 75% yield at 120^0C, 300w.

Heterocyclic compounds -

Microwave assisted synthesis of Noval 2H- Chromene derivatives bearing phenyl thia zolidinones and their biological activity assessment.

Coumarins are group of compounds shows bioactivity which includes antitumor, anti HIV, antifungal, antibacterial and anti-inflammatory. Islam H.EI Azab, Mohamed M. Youssef and Mahmoud A. Amin, a group of scientist had synthesized phenylthiazolidinone and corresponding Coumarins by traditional as well as by using microwave radiations[19].Under traditional synthesis it took 5 to 7 hours for derivative preparation where as in microwave assisted synthesis same compounds are prepared within 8 to 10 minutes.

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