

Process Intensification Using Alternate Energy Sources

Part II: Use of Microwave and Light Energy

Parag R Gogate

This article highlights the mechanism of process intensification using microwave energy and light energy and the types of equipment used. The article is well illustrated with case studies are demonstrating the degree of process intensification achieved using alternate energy sources when compared with the conventional approach.

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Microwave assisted operations present undoubtedly a very promising electromagnetic field application to intensify chemical processes. Microwave heating of materials has been known for a long time and development of microwave ovens has more than 50 years of history. The classical publication by Gedye et al. (1986) has opened a period of very intensive investigations of the effects of microwave on chemical reactions.

In general, microwave frequencies range from 0.3 to 300GHz, which correspond to wavelength of between approximately 1mm and 1m. A major part of this range is occupied by the radar and telecommunication applications. Thus, in order to avoid interference, the domestic and industrial microwave appliances operate at several standard allocated frequencies, most often at 2.45GHz. Molecules that have a permanent dipole moment (for example water) can rotate in a fast changing field of microwave irradiation. As a result of this operation an internal friction occurs in the polar medium, which is heated directly and almost evenly. The magnitude of this effect depends on dielectric properties of the substance to be heated. Microwave has a capacity of heating the material at a significantly faster rate as compared to conventional modes of heating.

Organic and inorganic solvents with low molecular weights and high dipole moments (e.g. H₂O, MeOH, EtOH) couple effectively with microwaves at 2.45 GHz. At the same time, non-polar organic solvents have negligible dielectric losses and therefore they do not effectively couple with microwaves. If polar solvents are used, the main interactions occur between microwaves and polar molecules and it would be expected that any specific microwave effect related to the reactants and products would be masked by the solvent-microwave interaction. The reaction rates should, therefore, be basically the same as those observed under the conventional conditions. This hypothesis has been confirmed by a recent study of esterification reactions, where no enhancement by microwaves irradiation was observed compared with the conventional reaction, at the same reaction temperature (Raner and Strauss, 1992). Microwave effects depend on microwave-material interactions; the more polar a molecule, more significant is the microwave effect when the rise in temperature is considered. In terms of kinetic and reactivity, the specific heat has therefore been considered according to reaction mechanism and, particularly, how polarity of the system is altered during the progress of the reaction (Perreux and Loupy, 2002). Specific microwave effects can be expected for a polar mechanism, when the polarity of reaction is increased during the reaction from the ground state towards the transition state. The result is essentially dependent on the medium and reaction mechanism. Several articles contain examples of increased selectivity in which the chemo- or regioselectivity can be increased under the microwave dielectric heating compared to conventional heating (Langa et al., 1997; Almena et al., 1996). It can be foreseen that microwave effects could be important in determining the selectivity of some reactions. When competitive reactions are involved, the ground state is common for both processes. The mechanism occurring via the more polar transition state could, therefore, be favored under the dielectric heating (Perreux and Loupy, 2002). Finally, it is important to note that microwave heat is rapid because energy is absorbed directly by the material. The temperature of the reaction mixture is uniform, especially in comparison with conventional heating.

Reactors based on Microwave heating

Microwave equipment can be divided in to two categories: (a) multi-mode and (b) single-mode cavities. Considering an empty metallic volume, if the dimensions of that volume are too big compared to the wavelength, the electric field repartition into that volume is very heterogeneous. This is the case for multi-mode applicators (such as domestic microwave oven). The repartition is well mastered and stable if the applicator dimensions are close to the single-mode structure. The use of wave-guides emitting the fundamental mode at fixed frequency, allows to master and, above all control, the power transmission when the aim is to study the influence of microwave electromagnetic field on the behavior of chemical reactions. This approach makes it feasible to extrapolate the results to industrial scale.

Multi-mode cavities

Domestic microwave oven is a typical example of a multi-mode device. Such devices comprise of a large microwave cavity with reflective walls that are necessary to prevent leakage of a large microwave cavity with reflective walls that are necessary to prevent leakage of radiation and to increase the efficiency of the oven. Domestic microwave ovens are not intended for chemical applications. For instance, they do not allow application of high pressure since explosions could occur. Moreover, they are not compatible with corrosive and inflammable compounds. Domestic microwave ovens operate on duty cycles, with the intervals between zero and full power reaching several seconds (e.g. 600 W oven, 30 s duty cycle). Large duty cycles are undesirable in chemical applications since samples may cool dramatically between switching steps. However, self-modified microwave ovens were utilized in chemical applications about a decade ago since commercially produced equipment was not easily available.

Single-mode cavities

Single-mode units have a smaller cavity. These type of equipment have greater energy efficiency and more even temperature distribution in the reaction vessel than multimode units. Single-mode resonant heater allows a sample to be placed at a position of much higher electric field strength than can be obtained in a multi-mode oven. Single-mode equipment needs to have a built in protection of the magnetron and hence working with small samples does not cause problems. It also has a variable microwave power input, which means that the resulting temperature can be measured accurately and the pre-set temperature can be achieved. This requires a recording unit to read the signal from the measuring temperature device. It should be noted that, temperature measuring within microwave field is quite problematic and hence the temperature has to be measured by special techniques, like infrared pyrometry or fiber-optic devices.

The material to be treated must be located inside the vessel within the cavity. The vessel must be microwave transparent, (Teflon, quartz) chemically inert and resistant to high temperatures attained. Some chemical applications require high pressures. For temperatures up to 180°C, Teflon is a convenient choice. However, if higher temperatures are required, a quartz vessel is preferred.

Single-mode devices work well for either high-loss type of dielectric materials that are very microwave-transparent, such as hydrocarbons, the applicator must be resounded, while using a variable sliding short-circuit position and iris tuning. Multimode techniques are coupling with very high-loss materials which means that if the loss is moderate or low, multi-mode methods are less effective and single-mode methods are preferred. This method allows the microwave heating of relatively low-loss materials such as polymers or some ceramics, using low powers (<2.5 kW).

Currently only few microwave Reactors equipped with efficient temperature control system for safe microwave synthesis at laboratory scale are available. These systems lead to reproducible operating conditions. Several examples and detailed description of commercial laboratory microwave reactors are reported in the work of Stuerger and Delmotte (2002). Some of the specific case studies with spectacular effects of microwave irradiations are discussed here. Table 1 will illustrate process intensification using microwave irradiations.

Reaction	Reaction time		Product yield	
	Conventional	Microwave	Conventional	Microwave
Hydrolysis of benzamide to benzoic acid	1h	10min	90%	99%
Oxidation of toluene to benzoic acid	25 min	5min	40%	40%
Esterification of benzoic acid with methanol	8h	5min	74%	76%
S _N 2 reaction of 4-cyanophenoxide ion with benzyl chloride.	16h	4min	89%	93%
Heck arylations of Olefins	20h	3min	68%	68%

Case Studies

Pillai et al. (2002) studied microwave (MW) assisted olefin epoxidation over hydrotalcite catalyst, using excess of acetonitrile. Apparently, the selective epoxidation of a variety of olefins occurs more rapidly upon microwave irradiation, than by conventional heating in an oil bath. This is presumably due to the polar nature of the reaction intermediates that couple efficiently with microwaves and causes the dramatic rate acceleration. This approach significantly minimizes the longer reaction times required in conventional heating of olefins with H_2O_2 and avoids the use of large excess of volatile organic solvent usually employed.

Hajek et al. (1997) investigated rearrangement of 1,1,3-triphenylpropargyl alcohol under microwave irradiation (700 W) as well as conventional conditions in oil bath (100°C), in the presence of 10 g neutral alumina (Al_2O_3). Conversion of 1,1,3-triphenylpropargyl alcohol in nonstirred sample (temperature gradient 18°C) was three times higher under microwave exposure compared to the conventional heating. Conversion in stirred sample was almost the same under microwave and conventional heating. Local superheating effect is responsible for the acceleration of the reaction as indicated by these results.

Huber and Jones (1992) studied the acceleration of an Ortho-Ester Claisen rearrangement by clay-catalyzed microwave thermolysis. Conventional thermolysis was carried out in three-necked round bottom flask. The assembly was flushed with dry nitrogen gas and then triethyl orthoacetate was introduced, followed by 2-cyclohepten-1-ol and, finally, propionic acid. The mixture was heated to 140°C using an oil bath. In the case of microwave thermolysis, montmorillonite KSF was suspended in dry DMF in a flame dried sealed tube. 2-Cyclohepten-1-ol was added under stream of nitrogen followed by triethyl orthoacetate. The mixture was exposed to irradiation for 9 min (500 W) in a commercial microwave oven. Under traditional conditions, only moderate yields of the product were recovered, contaminated with varying amounts of starting alcohol and their derived acetates. By microwave thermolysis, high yields of pure product were obtained.

Application of microwave heating accelerates many ring opening reactions. For example, Villemin and Labiad (1992) investigated the opening of phenylthio dichlorocyclopropanes in the presence of $AgBF_4 / Al_2O_3$ under microwave irradiation (microwave oven, 650 W). Microwave heating allows working under solvent-free conditions and has potential for significant acceleration of the reaction rates. Calinescu et al. (2001) carried out catalytic dechlorination of chlorobenzene in a solution of NaOH in 2-propanol, at boiling temperature. It was found that Pd (supported alumina or aluminum silicate) is a very active catalyst. The microwave heating had very favorable effect: the conversions were almost double in comparison to conventional heating.

Use of Light Energy (UV/Sunlight) for process Intensification

The use of light, either artificial or solar for carrying out chemical and biochemical reactions may result in two sustainability related effects:

- Drastic increase of process selectivity to the required products (e.g. due to a different chemistry and / or low / ambient process temperature)
- Drastic decrease of the (non-renewable) energy consumption in the process (e.g. due to low temperature processing or use of solar light)

Photo activated chemical reactions are characterized by a free radical mechanism initiated by the interaction of photons of a suitable energy level with the molecules of chemical species present in the solution with or without the presence of a catalyst. The radicals can be easily produced using a UV radiation by the homogenous photochemical degradation of oxidizing compounds like hydrogen peroxide and ozone. An alternative way to obtain free radicals is the photocatalytic mechanism occurring at the surface of semiconductors (like titanium dioxide) and this indeed substantially enhances the rate of generation of free radicals and hence the rate of chemical reactions (Mazzarino et al., 1999). A major advantage of the photocatalytic oxidation based processes is the possibility to effectively use sunlight or near UV light for irradiation which should result in considerable economic savings especially for large-scale operations.

Various chalcogenides (oxides such as TiO_2 , ZnO , ZrO_2 , CeO_2 etc. or sulfides such as CdS , ZnS etc.) have been generally used as photo-catalysts. The surface area and the number of active sites offered by the catalyst for the adsorption of reactant species play an important role in deciding the overall rates as usually the adsorption step is the rate controlling step (Xu et al., 1999). Thus nature of catalyst i.e. crystalline or amorphous is important. It should be noted that the best photocatalytic performances with maximum quantum yields have been always with titania. In addition, Degussa P-25 catalyst is the most active form (hybrid mixture of rutile (approximately 70%) and anatase forms) among the various catalysts available and generally gives better efficiencies (Yamazaki et al., 2001)

though in some cases pure anatase based forms of TiO₂ such as Hombikat, PC-500 have also been reported to be more efficient (Lindner et al., 1997). Also the photocatalytic activity of titanium dioxide can be enhanced by pre-treating it with sulfuric acid (Yu et al., 2002) Or by increasing the cation strength e.g. doping with platinum (Lia and Li, 2002).

Reactors used for photocatalytic oxidation

The **photocatalytic process** can be carried out by simply using slurry of the fine particles of the solid semiconductor dispersed in the liquid phase in a reactor irradiated with UV light either directly or indirectly. Proper dispersion of catalyst in the liquid phase can be achieved using either mechanical or magnetic stirrers. Aeration usually maintained for scavenging the electrons (HO₂ radicals are formed in the valence bonds) to prevent electron / hole charge recombination, also helps in achieving dispersion of the catalyst. The extent of dispersion can also be increased by sonication of the slurry at low frequency (e.g. 20 kHz) using an ultrasonic bath for about 10-15 min (Mazarino et al., 1999). However, in the case of slurry reactors, the performance of the reactors might be severely affected by low irradiation efficiency due to the opacity of the slurry. Also the solid catalyst needs to be separated from the liquid, which is not so easy with small sizes of the catalyst particles (usually below 1 micron). Another problem is the fouling of the surface of radiations source due to the decomposition of the catalyst particles. Thus, the application of slurry reactors for the photocatalytic treatment on a large scale seems to be quite problematic.

An alternative to the use of catalyst in the suspended form is the use of supported photocatalyst. The key advantages are, obtaining an active crystalline. Structure and stability of the catalyst layer in the reacting media. Films obtained by wash coating using a suspension of commercial products with a well-known photocatalytic activity satisfy the first possibility, but can be very sensitive to erosion by the following liquid. Durable supported films can be obtained by different techniques like physical and chemical vapor deposition, but in this case the crystalline structure of the final product and consequently the catalytic activity might be difficult to control. Thermal treatment at 500°C can be used to increase the extent of crystalline nature of the catalyst obtained by physical or chemical vapor deposition. Scouring is another problem associated with films, comprising immobilized powders of TiO₂ (Bideau et al. 1995) and reduced catalyst area to volume ratio of the immobilized photocatalyst is likely to cause mass transfer problems. Butterfield et al. (1997) have reported a modified fabrication technique and design of the reactor in order to eliminate scouring. Here, the oxide is actually grown on a titanium substrate as a defect film (a film that is electronically conducting even in dark), which also allows application of electric field to enhance the overall rates. The batch reactor used in their work, for water disinfection has been reported to remove 100% of E-coli and 2 log units of Cl. Perfringens spores in 25 minutes whereas only about 20-30% disinfection was observed for UV light and UV light + photocatalyst.

Overall, the immobilized or supported catalytic reactors offer many advantages, most important being, the supported catalyst is not allowed to mix with the fluid thus avoiding the requirement of ultrafine particles separation. Various devices have been developed such as TiO₂ coated tubular photoreactor, annular and spiral photoreactors. Falling-film photoreactors and two commercial scale versions are also available (Matrix photocatalytic Inc, Ontario Canada and Purifiers Environmental Technologies Inc., London, Ont. Canada). It should be noted that any configuration can be selected but the most important point is to achieve uniform irradiation of the whole active surface. Some of the equipments used for carrying out photocatalytic oxidation have been represented in Fig 1.

Limitations of photocatalytic reactions

In the case of **photocatalytic oxidation**, the most common problem associated is the reduced efficiency of photo-catalyst with continuous operation possibly due to the adsorption of contaminants at the surface and blocking of the UV activated sites, which makes them unavailable for the favored reaction. Thus, it is necessary to devise a technique for proper continuous cleaning of the catalyst surface during the photocatalytic operation. Ultrasonic irradiation is one such technique that can be used simultaneously with UV/ solar irradiation. Moreover, photocatalytic oxidation technique is also affected by severe mass transfer limitations especially in the immobilized catalyst type of reactors, which are generally preferred over slurry reactors to avoid solid catalyst separation problems. One more factor suggesting that the two techniques will give better results when operated in combination is the fact that the basic reaction mechanism in both the techniques, i.e. UV and US is the generation of free radicals and subsequent attack by these on the reactant species. If the two modes of irradiations are operated in combination, more number of free radicals will be available for the reaction thereby increasing the rates of reaction.

Thus, the expected synergism between these two modes of irradiation can be possibly attributed to:

- Cavitation effects leading to increase in the temperature and pressure at the localized microvoid cavity implosion sites.
- Cleaning and sweeping of the TiO₂ surface due to acoustic micro-streaming allows for more active catalysts sites at any given time.
- Mass transport of the reactants and products is increased at the catalyst surface and in the solution due to the facilitated transport as a result of shockwave propagation.
- Surface area is increased by fragmentation or pitting of the catalyst.
- Cavitation induced radical intermediates participate in the destruction of organic compounds
- The organic substrate reacts directly with the photogenerated surface holes and electrons.

Most of these effects are likely to be occurring simultaneously and though their relative contributions to the ultrasonic enhancement of heterogeneous photocatalytic processes is far from understood, the overall global effect is the substantial enhancements in the rates of chemical processing applications. Toma et al. (2001) have given a brief overview of different studies pertaining to the effect of ultrasound on photochemical reactions concentrating on the chemistry aspects i.e. mechanism and pathways of different chemical reactions. Gogate and Pandit (2004) have given the detailed description of the sonophotocatalytic reactors concentrating on wastewater treatment applications.

Photocatalytic reactions

Some case studies

An excellent example of how light can be drastically improve the selectivity of industrially important chemical reactions are the studies carried out by the group of Frei at Berkeley University (Sun et al., 1994, 1996, b, Blatter et al., 1998). Oxidations of small hydrocarbons, carried out with visible light on various types of zeolites resulted in exceptionally high reaction selectivities. For instance complete (100%) selectivity was reported for oxidation of toluene to benzaldehyde on CaY Zeolite (Sun et al., 1994) and cyclohexane oxidation to cyclohexanone on NaY Zeolite (Sun et al., 1996a). Selectivities remained high even when more than 50% conversion of the hydrocarbon was loaded into the zeolite matrix. Quantum efficiencies of the processes were also relatively high on and average between 10-30% (Sun et al., 1996b).

Another area where light can be used to enhance the reaction selectivity is the field of asymmetric (chiral) synthesis. This area is of particular interest and importance to the pharmaceutical industry. The fact that circularly polarized light can be used to selectively obtain the required enantiomer from non-chiral starting material, has been confirmed in the literature. Enantioselective photoreactions can be carried out both in solutions and in the solid state and there are several literature reviews on this subject (Inoue, 1992; Everitt and Inoue, 1999; Feringa and Van Delden, 1999).

A step further in the area of photocatalysis is to replace the artificial light by the concentrated light, thus approaching the ideal 'green' process. Some possibilities with operating capacity of up to pilot scale have been demonstrated for synthesis of chemicals (Esser et al., 1994 and Schiel et al., 2001).

Conclusions

Use of alternative forms of energy has been reviewed in the present work concentrating on the mechanistic aspects, different reaction configurations and highlighting the specific case studies demonstrating the degree of process intensification achieved as compared to the conventional approach. The potential of alternative sources of energy (cavitation, microwave and light) as tools for process intensification appears to be very promising as it leads to intensification of practically all the processing steps including mass transfer, heat transfer, chemical reaction and the separation processes. It appears that the efficacy of these equipments has been well established at laboratory scale and to an extent at pilot scale operations. Close research collaboration of various disciplines such as chemical engineering, chemistry, material science and applied physics in particular is essentially required to harness the spectacular effects of these technologies at industrial scale operation effectively.

Author

Dr Gogate is currently associated with the Institute of Chemical Technology, Mumbai as Scientist A in the Information Processing center. His main research interests include cavitation phenomena, waste water treatment, advanced oxidation processes, design of multiphase reactors and process intensification. He has published over 40 research papers in International Journals. Dr. Gogate has recently received the young Scientist Award of the Indian Science Congress Association.

Reference Book:

Chemical Industry Digest
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