MICROWAVE CHEMISTRY – A FERTILE FIELD FOR SCIENTIFIC RESEARCH AND INDUSTRIAL APPLICATIONS

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Abstract

This paper presents an overview of microwave chemistry, showing its evolution and applications as a part of ISM – Industrial, Scientific and Medical microwave applications.

Index Terms — industrial applications, microwave chemistry, microwave enhanced chemistry.

I. INTRODUCTION

Research and development in ISM (Industrial, Scientific and Medical) microwave applications require a close cooperation of a wide range of specialists from science and technology.

For industrial applications, in particular, which aim at increasing process productivity, quality control and efficiency (both technical and economical) it is essential that engineers from different fields of engineering work together as a team, which may also frequently include physicists, economists, administrators and other specialists.

Electronics engineers are not always aware that there is ample room in industrial microwave applications to exercise their expertise. Or else, they may not feel comfortable having to operate high-power microwave generators and face a multidisciplinary field of study, which requires the interest and cooperation of specialists from other fields; cooperation not always easy to obtain.

It may then be of interest to make a short survey of microwave industrial applications before focusing on the subject of microwave chemistry, a typical multidisciplinary activity as the name itself indicates.

II. MICROWAVE INDUSTRIAL APPLICATIONS

Industrial applications represent only a small fraction of the total microwave market, which is mostly dedicated to telecommunications. Nevertheless, they are economically important and are a source of both scientific advancements and practical developments.

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Microwaves in industry are found in low and high power applications. Typical low power applications are non-destructive measurement methods, used in process control, while the most common high power applications are to be found in processing industries utilizing microwave energy for heating.

Table I includes a listing of selected microwave measurements of industrial interest, which have been successfully applied in industry for over twenty years [1] [2].

Table I: Microwave measurements of industrial interest.

<table>
<thead>
<tr>
<th>Measured Quantity</th>
<th>Physical Phenomena Utilized</th>
<th>Electrical Parameter Measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Distances</td>
<td>Time elapsing</td>
<td>Phase</td>
</tr>
<tr>
<td>- Solid and liquid levels</td>
<td>between transmission and reception</td>
<td></td>
</tr>
<tr>
<td>- Small displacement</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Speed</td>
<td>Doppler effect</td>
<td>Doppler frequency</td>
</tr>
<tr>
<td>- Acceleration</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Flow rate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Thickness (metal sheet)</td>
<td>Reflection and cavity perturbation</td>
<td>Resonant frequency</td>
</tr>
<tr>
<td>- Degree of curing</td>
<td>Effects on dielectric properties</td>
<td>Transmission, reflection or cavity perturbation</td>
</tr>
<tr>
<td>- Moisture content</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Humidity</td>
<td>Effects on refraction index and cavity perturbation</td>
<td>Resonant frequency of cavity</td>
</tr>
<tr>
<td>- Detection of voids and cracks</td>
<td>Back-scattering and diffraction</td>
<td>Resonant signals (back-scattered)</td>
</tr>
<tr>
<td>- Products sorting</td>
<td>Diffraction or scattering</td>
<td>Reflected or transmitted signal</td>
</tr>
</tbody>
</table>

Telecommunications engineers will note that techniques familiar to them are extensively used.

The most common applications of microwaves in industry require high power levels for heating purposes.

Microwave heating is mostly used in drying processes for a large variety of materials, as paper, printing ink, leather, textiles, wood and plywood, plaster, concrete, ceramics, foundry moulds, rubber, plastics, pharmaceuticals and many others.

Applications in the food industry include cooking (well known in a domestic scale), thawing and tempering of frozen food, drying, freeze-drying, pasteurization, etc.

A large number of other processes utilize or are potential users of microwave heating. Worth mentioning are rubber vulcanization, disintegration of toxic gases, shale oil extraction, road repair, sintering of ceramics, nuclear waste treatment, soil treatment, hard seed germination, disinfection of grains and many other applications [3, 4].

Microwave processing may require the development of applicators of custom design.
Applicators are devices designed to transfer microwave energy from the generator to the processed materials.

The conventional microwave oven, basically a metal box, be it a small domestic model or a large industrial one, commonly is not the most efficient applicator, if specific energy consumption (joules per kilogram) is the reference.

Applicators for continuous processing generally are more efficient than static ovens for batch processing.

It is up to the microwave engineer to design the best applicator for the process being studied.

Basic electromagnetic theory concepts, inventiveness and computer modeling, are the ingredients for applicator design which are at disposal of most electronics engineers.

Figure 1 shows an applicator of modular design (it can easily be stacked in height and multiplied in a larger diameter) for the continuous processing of liquids or granulated materials. Figure 2 shows the same applicator being used in a laboratory pilot plant. [5]

Unfortunately, many economically feasible applications of microwave power did not progress beyond the experimental stage, generally for lack of support from conservative industry administrators, unwilling to take the risk of investing in the development of a new technology.

Figure 1 – Applicator of modular design.
III. MICROWAVE CHEMISTRY

Microwave Chemistry may be understood as a branch of Chemistry, which interacts with Electrical Engineering, more specifically with microwave applications. It is an evolution of chemical practices, where the traditional ways of heating with gas burners, electric heaters, steam and thermal fluid heaters were supplant by the microwave oven.

The use of microwaves as energy source for chemical reactions is not new. But in the past the field of "Microwave Chemistry" was mostly restricted to the study of reactions in electric discharges and plasmas excited by microwaves [6]. It was only when the widespread use of the domestic microwave oven reached the research laboratories, that a new era was open for microwave chemistry.

The first experiments, in the “domestic microwave oven era”, with microwave application to chemical reactions go back to the seventies, when the microwave oven was first used as a rapid heating source for sample open-vessel wet digestion [7].

This application was developed for elemental analysis purpose. It is usual to determine the amount of metals present in chemical products, in medicines, in food and others goods and also in wastes. The objective for this is to attend to FDA rules for consumption of goods and environmental rules on disposition of wastes. The metals are present in a organic or inorganic matrix, which needs to be destroyed to liberate them for analytical determination. The usual way of destruction of organic mater, or sample digestion, consists basically in the treatment with chemicals as sulfuric acid, nitric acid, perchloric acid, hydrogen peroxide or convenient
mixtures of them. These chemicals oxidize the organic matrix and liberate the metals as soluble salts. Finally these salts are submitted to appropriate analytical methods for their determination.

The usual procedures for sample digestion are very boring and tedious, worse they are very slow. They can require from two to 24 hours. The innovative heating of sample digestion with microwaves, in closed Teflon vessels, reduces this time to few minutes, usually about 20 minutes. Figure 3 shows a commercial microwave oven for sample digestion. It is similar to a domestic oven, but it is much more robust and it has microwave power control and temperature and pressure measuring devices. Figure 4 shows the digestion vessel closed in a Teflon vessel support. Nowadays this technique is extensively used in chemical analysis laboratories to speed the dissolution of solid samples. In 1986, Gedye [8] and Guiguere [9] published separately two papers reporting the enhancement of chemical synthesis by microwave irradiation. They used for synthesis the common microwave oven sold for sample dissolution and found that microwaves not only heat a reaction but also increase its rate.

Figure 3 – A commercial laboratory microwave oven for wet digestion of samples.

Figure 4 – Digestion vessel and its support.

It was an amazing surprise that changing the heat source changes the reaction velocity. So amazing that several organic chemists started to try their favorite reactions with microwave
rather than conventional, heating. Most results showed positive responses to microwave irradiation and some reactions did not show any effect. This was the period of dazzle, where it was valid the witticism: “all that I did with a Bunsen burner, I do better with microwave” and the knowledge about the observed new effects of microwave irradiation on chemical reactions grew fast.

It can be said that Gedye’s and Guiguere’s papers opened a new field for experimentation and publishing. Table II shows some typical examples of initial results observed in experiments with microwave heating. The volume of papers in this new area – microwaves enhanced chemical reactions – became so large that microwave conferences had to include specific sessions for this area of research, which now has entire conferences dedicated to it, such as: International Conference on Microwave Chemistry (Prague, September 1998 and Antibes, September 2000), Transforming Medicinal Chemistry (Cambridge, April 2000), Electronic Symposium on Microwave Assisted Synthesis (September 2001), Conference on Coherent Synthesis (San Diego, May 2002), International Microwaves in Chemistry Conference (Gainesville, March 2003), and CHI’s Microwave-Assisted Organic Synthesis Symposium (San Diego, February 2003). The number of papers has increased continually since those pioneering articles.

It is possible to evaluate the progress of microwave chemistry observing the increases of reactions and papers referred in reviews, from 11 reactions and 92 papers in 1995 to 402 reactions and 603 references in 2001, as shown in Table III.

Microwave chemistry may be accepted as a true branch of chemistry due to the enhancement of chemical reactions, as related in several papers.

Table II: Examples of reaction time reduction with microwave heating [7].

<table>
<thead>
<tr>
<th>Reactants / Product</th>
<th>Microwave Heating</th>
<th>Conventional Heating</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>reaction time (min)</td>
<td>yield (%)</td>
</tr>
<tr>
<td>mesitylene + polyoxymethylene / dimesitylmethane</td>
<td>4</td>
<td>75</td>
</tr>
<tr>
<td>benzoic acid + methanol / methyl benzoate</td>
<td>2</td>
<td>90</td>
</tr>
<tr>
<td>isoamyl alcohol + methanol / isoamyl acetate</td>
<td>2</td>
<td>100</td>
</tr>
<tr>
<td>anthracene + maleic anhydride / aduct</td>
<td>4</td>
<td>85</td>
</tr>
<tr>
<td>benzophenone + hydroxylamine / benzanilide</td>
<td>2</td>
<td>99</td>
</tr>
<tr>
<td>p-cresol + propyl iodide / propyl p-tolyl ether</td>
<td>4</td>
<td>96</td>
</tr>
<tr>
<td>cyclohexanol + sodium bromide / cyclohexyl bromide</td>
<td>10</td>
<td>49</td>
</tr>
<tr>
<td>acetanilide + hydrochloric acid / aniline</td>
<td>15</td>
<td>91</td>
</tr>
</tbody>
</table>

Table III: Evolution of reviews about microwave chemistry.

<table>
<thead>
<tr>
<th>Year</th>
<th>Author</th>
<th>Number of References</th>
<th>Number of Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1991</td>
<td>Mingos [10]</td>
<td>92</td>
<td>11</td>
</tr>
<tr>
<td>2001</td>
<td>Lidstrom [14]</td>
<td>603</td>
<td>402</td>
</tr>
</tbody>
</table>
IV. MICROWAVE ENHANCED REACTIONS

Microwave chemistry is one of the present subjects of scientific controversy. Some researchers attribute the observed increase of reaction rate to thermal effects of microwaves, and others attribute it to non-thermal effects. At the present time, after 17 years have elapsed, a complete explanation on how microwaves interact with chemicals has not been reached.

The initial observations were easy to explain, because reactions were performed in closed vessels used for sample dissolution. These vessels are made with an inner volume of 100-mL. Teflon vessel surrounded by a poly(ether ether ketone) resin (PEEK) shield and closed with a Teflon cup which has a pressure relief device (see figure 4). These dissolution vessels are filled with liquid reactants or solutions and then closed in a device, which compresses the vessel so that it may support an internal pressure up to 100 bar. When irradiated with microwaves the reactants are heated, because Teflon and PEEK are transparent to microwaves. As the inner temperature increases, the inner pressure builds up until it reaches the relief pressure of the dissolution vessel. Consequently, the liquid in the vessel boils at a higher temperature than obtained in an open reaction flask. Obviously, under pressurized conditions the reactants react more rapidly than in an open reaction flask, since higher pressure causes higher temperature and consequently, by Arrhenius law, higher reaction velocity.

This fact was the first contested question on microwave effects on chemical reacting systems. But it did not close the discussion, because new papers reported the same effect of increasing reaction rate by microwave irradiation under room pressure [15 – 18]. These new facts showed that microwaves really increased the reaction rate and that something more than Arrhenius law influenced the chemical system under microwaves. This fact justifies the terms microwave enhanced chemistry, microwave assisted chemistry or simply microwave chemistry.

V. EXPLANATIONS ABOUT MICROWAVE ENHANCED CHEMISTRY

There are two sets of probable explanations for experimentally observed enhancement of chemical reactions: the “thermal effects” and the “specific” or “non-thermal” effects. In the first case, the observed microwave effect is attributed to aspects of heat generation and transfer while in the second case the observed effect is attributed to interactions between electromagnetic irradiation and chemical structure or reaction mechanism. These specific effects may be observed when the same reaction is performed, at the same temperature, both with conventional heating and with microwave heating. Results are different.

One initial explanation was the volumetric heating [4,19], which is observed when polar molecules are exposed to a microwave field. The molecular dipoles are induced by microwaves to oscillate. This oscillation causes molecular collisions which generate heat. Since microwave irradiation is a volumetric phenomenon, heat is generated in the irradiated volume which will then have an homogeneous heat distribution. In conventional heating (heating fluid, gas burner, steam or electrical heating) there is a temperature gradient between the heat source and the mass to heat; consequently the temperature distribution is not homogeneous and the mean temperature of reactants will be lower than the set temperature. If two reactors, one heated by conventional heating and another heated by microwaves, are set for the same temperature, the microwave-irradiated reactor will operate at a temperature something higher than the conventional heated reactor. By this reason, the reaction rate will
be higher in the irradiated reactor. Unfortunately this mechanism does not explain the intensity of the observed microwave effects.

Another theory is related to a so-called superheating effect [20]. It is related with relaxation time, dielectric constant, loss factor and temperature. It may be observed with chemicals having a loss tangent increasing with temperature causing an increase of the normal boiling point.

Another possibility is the formation of small areas with elevated energy density, where the temperature increases more than around these areas, which were then called "hot spots". As the temperature in hot spots is higher than in the surrounding material, there the reaction rate is increased. The mean effect will be a whole reaction enhancement as compared to conventional heating for the same reaction [21, 22]. This theory is good for heterogeneous reactions as metal catalyzed reactions with polar reactants, but not for homogeneous reactions. Recently it has been argued whether this theory explains the observed kinetic effect [23].

Another theory considers the presence of ionic molecules in reactants, for example ionic salt. It explains that the ionic molecules will oscillate due to microwave irradiation and the kinetic energy acquired will be converted to heat [24].

There is a theory with a photochemical focus that attributes the observed effect to spins realignment due to microwave field [24, 25]. In accordance with this theory, the increase of reaction rate may be attributed to a new mechanism path that becomes possible with the change of spins alignment. A typical example is the oxygen that in nature is in the singlet form and when irradiated with microwaves it realigns its electrons spins and changes to triplet form, which is more reactive. This theory has already obtained its first experimental confirmation [26].

The controversy about the effects of microwaves on chemical reactions is enlarged by the difficulty to reproduce published data. This is due to several operational difficulties, as temperature measurement and definition of effective microwave power applied to a reaction.

At the beginning of microwave chemistry there was not a way to measure with precision the temperature under a microwave field, because the traditional chemical thermometers of mercury or thermocouple distorted the field and could act as an antenna taking microwaves out of the reactor cavity. Only recently thermometers with fiber optics, which are compatible with microwaves, were available at an affordable price.

Most papers are based on works with commercial laboratory microwave ovens which do not allow conditions to measure the effective power applied to the reactor.

VI. PURE AND APPLIED MICROWAVE CHEMISTRY

As observed in chemistry, it is possible to identify two sets of papers related to microwave chemistry. Papers that discuss fundamental aspects, for example how microwaves are absorbed by chemicals, kinetics changes in reactions, mechanism of interaction with chemicals, etc. And also papers which report results on microwave irradiation of chemical reactions, without attempting to explain how and why reactions are altered by microwaves. Both sets need to grow together to establish a scientific basis for industrial applications of microwave chemistry. The first one may be identified as “pure microwave chemistry” and the second as “applied microwave chemistry”.

A good example for the applied microwave chemistry kind of papers is the Lidström [14] collection of 406 microwave-enhanced reactions. And so is Table II. The abundance of these
kinds of papers originated two new abbreviations: MAOS which means Microwave-Assisted Organic Synthesis [27] and MAC which means Microwave Assisted Chemistry (includes organic and inorganic compounds) [38]. Table IV illustrates the evolution of molecular complexity and some recent products synthesized with microwave help.

The equipment which has been used for this kind of work is the commercial oven for laboratory work, as shown in figures 3 and 4. Nowadays laboratory microwave ovens became complex devices, which allow to perform up to 36 synthesis tests simultaneously.

Published results usually present a procedure for a synthesis, describing the proportion between reagents, the reaction solvent or support, the catalyst, the processing temperature and pressure, the overall irradiation conditions – nominal microwave energy power and irradiation time – and the yield and quality of the target compound.

Table IV: Evolution of products synthesized by microwave enhanced chemistry [39, 40].

<table>
<thead>
<tr>
<th>Products Synthesized by Microwave Enhanced Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2,4-triazines</td>
</tr>
<tr>
<td>2(1H)-pyrazinones</td>
</tr>
<tr>
<td>Diels-Alder reaction</td>
</tr>
<tr>
<td>2-acyl amino thiophenes</td>
</tr>
<tr>
<td>2-aryalbenzo[b]furans</td>
</tr>
<tr>
<td>3-aryl-5,6-dihydroimidazo[2,1]thiazole</td>
</tr>
<tr>
<td>3-isoxazolo[60]fullerene</td>
</tr>
<tr>
<td>amination of 1-bromonaphthalenes</td>
</tr>
<tr>
<td>amination of 5- and 8-bromoquinolines</td>
</tr>
<tr>
<td>aminopropenonaes / aminopropenoates</td>
</tr>
<tr>
<td>benzoazoles4,6-o-benzylidenes</td>
</tr>
<tr>
<td>benzylidenecineneole</td>
</tr>
<tr>
<td>chalcones</td>
</tr>
<tr>
<td>dihydropyrimidine</td>
</tr>
<tr>
<td>imidazo[1,2]pyridines</td>
</tr>
<tr>
<td>imidazo[1,2]pyrimidinea</td>
</tr>
<tr>
<td>isoflav-3-enes</td>
</tr>
<tr>
<td>isoxazoles one-pot synthesis</td>
</tr>
<tr>
<td>alfa-tosyloxyketones</td>
</tr>
<tr>
<td>pyrazoles one-pot synthesis</td>
</tr>
<tr>
<td>pyrimidines one-pot synthesis</td>
</tr>
</tbody>
</table>

Examples for the pure microwave chemistry kind of papers are the articles from Breccia [24, 26], Rybakov [23], Baghurst and Mingos [20], Jermolovicius and Senise [17, 28] and many others. The first difference with respect to applied microwave chemistry is the accuracy requirements in the microwave power measurement. This fact requires using equipment with more resources to measure the effective applied microwave energy, as shown for the chemical batch reactor in figure 5. In this kind of equipment it is possible to identify three parts: a) the
chemical reactor, which may be a Pyrex vessel closed in a multimodal cavity; b) the microwave source, usually a 2.45 GHz microwave generator with variable power up to 3 kW; c) the directional coupler and power meter.

![Figure 5 - Microwave irradiated chemical reactor at Instituto Mauá de Tecnologia – IMT.](image)

The chemical batch reactor may be described as a 0.5-1.0 L Pyrex kettle vessel with internal baffles to prevent whirlpool formation, with a top cover with four holes 24/40. A shaft of Pyrex rod and a paddle of Teflon are used to stir the reagents. A stirrer’s explosion proof electrical motor is assembled over the reactor top. The mixing velocity is measured by a stroboscopic digital tachometer. A total reflux Allihn condenser (Pyrex, 60 cm) with a Dean Stark flask (25 mL) is assembled at the vessel top. The condenser is cooled with cold water or water at room temperature. The sample collector is a 2-mm inside diameter Pyrex tube immersed into the reagents and with the other side connected to a vacuum vessel. It is fitted at the same hole used to feed the reagents. A digital fiber optic thermometer sensor protected by a thermometric well of Pyrex monitors the temperature of the reagents. The temperature control is done by an internal “U” tube of 6-mm diameter, where kerosene cooled at 30 ºC circulates with a convenient flow rate. This “U” tube is fitted at the same hole where the thermometric well is fitted. This assembled reactor is enclosed in an aluminum multimode cavity with mode stirrer, connected to a microwave variable-power generator of 2.45 GHz. A directional coupler and a power meter measure the irradiated and reflected microwave power.

For fast reactions the batch reactor may be substituted by a continuous flow reactor, which could be of two types: the continuous stirred tank reactor (CSTR) and the continuous plug flow reactor (CPFR). The CSTR is shown in figure 6 and the CPFR in figure 7. It is possible to identify the same electrical parts present in the batch reactor, but with a different reaction concept, namely the reagents flow continuously through the reactor. This flow is produced by means of a chemical pump.

Examples of typical data from kinetics analysis are the complete experimental kinetic equations for electric heating (1) and for microwave heating (2), for maleic anhydride esterification with 2-ethylhexanol-1 [29]:

\[-r_{MA} = 1.4E+25 \cdot \exp(-46300/RT) \cdot C_{MA}^{0.6} \cdot C_{2EH}^{2.2}\]  

\[-r_{MA} = 6.9E+21 \cdot \exp(-40700/RT) \cdot C_{MA}^{1.0} \cdot C_{2EH}^{1.9}\]  

(1)

(2)
where \(-r_{MA}\) is the maleic anhydride consumption rate (M/min), \(C_{MA}\) and \(C_{2EH}\) are molar (M) concentrations of maleic anhydride and 2-ethylhexanol-1, \(E\) is the activation energy (kcal/mol), \(R\) is the universal gases constant (1.9891 cal/mol.K), \(T\) is temperature (K).

Also the empirical kinetic equation for microwave enhanced styrene emulsion polymerization with high intensity irradiation (3) and for low intensity irradiation (4) and for conventional electric heating (5), all of them at 85 ºC with 0.11 % of potassium persulfate [26]:

\[
-r_{ST} = 0.011.C_{ST}^{0.8} \tag{3}
\]
\[
-r_{ST} = 0.078.C_{ST}^{1.0} \tag{4}
\]
\[
-r_{ST} = 0.077.C_{ST}^{1.0} \tag{5}
\]

where \(-r_{ST}\) is the styrene consumption rate (M/min); \(C_{ST}\) is molar (M) concentration of styrene.

Another example is the maleic anhydride catalytic esterification with 2-ethylhexanol-1 performed under conventional heating and under microwave heating. This exploratory experimental data showed a positive microwave synergic effect with the catalyst p-toluene sulfonic acid, which is the reduction of esterification global reaction order [30]. Explicitly, for this esterification at 142 ºC, with microwave heating and 0.1% of p-toluene sulfonic acid the apparent global simplified kinetic equation (6) was obtained and for 0.2 % equation (7). With conventional electric heating, for the same reaction conditions, the apparent global simplified kinetic equations, respectively (8) and (9), were obtained

\[
-r_{MA} = k. C_{MA}^{5.7} \tag{6}
\]
\[
-r_{MA} = k. C_{MA}^{3.0} \tag{7}
\]
\[
-r_{MA} = k. C_{MA}^{3.8} \tag{8}
\]
\[
-r_{MA} = k. C_{MA}^{1.4} \tag{9}
\]

where, \(k\) is the constant of chemical kinetic equation.

This fact brings an industrial advantage to the use of microwaves in chemical processes, which is the increase in process productivity when the global order of a reaction is lowered. A last example is the phenomenon observed by IMT researchers, namely a probable threshold value for microwave specific power, above which microwaves might influence the reaction mechanism. This experimental observation resulted when two reactions were irradiated under more drastic conditions (over 0.8 W/mL of chemical feed). One was the reaction of maleic anhydride esterification with 2-ethylhexanol-1 [31] and the other was the styrene emulsion polymerization [28]. These results agree with Wan [32] and Chiang [33] who used high energy pulsed microwaves to irradiate chemical reactions.
VII. APPLICATIONS

At this moment we do not have a consensual explanation for microwaves interaction with chemical reactions, but it is not necessary to know all the theory about something to make
profits with it.

There are several commercial applications for microwaves in the chemical processing industries, as shown in the Table II, most of them in chemical commodity industry, and in fine chemical or specialty industry as shown in Table IV.

Microwave enhanced chemistry brings an important tool to all involved with research of new pharmaceutical products. Usually the development of a new chemical structure with physiological effects requires about twelve years, from desk to final product. In this job, one of the first steps is the chemical synthesis trial that is a tedious and slow work. Chemists synthesize thousands and thousands of intermediate and target products. This demands a very long and expensive work, which represents about a quarter of the global development.

Since microwaves reduce reaction times by a factor of 10−10,000, then chemists found an alternative methodology to substitute the slow traditional and conventional methods of synthesis. A new brand of laboratory equipment was developed: the microwave oven for chemical synthesis. There are many manufacturers offering several options for these special oven, including closed vessels, open vessels, mini vessels (about 5 mL), low or high pressure, combinatorial version, plug flow continuous reactor, etc. All of them make viable the use of the most important benefit of microwave chemistry, namely higher reaction speed. With this benefit it is possible to optimize a procedure in hours instead of months or years.
Another benefit is the easy scaling up of microwave enhanced reactions. This fact might be attributed to the homogeneity of temperature in the reaction vessels [41]. It is necessary to observe that this scale-up means to scale from milligram to kilogram, in the specialty industries.

The success of the use of microwave irradiated reactors to process synthesis screening – up to 40% of all explorative chemistry is now done by microwave chemistry [41] - induced the creation of a trademark: Coherent Chemistry [39]. Coherent Chemistry is knowledge-based microwave synthesis for lead compound development [39].

In commodity scale of chemicals, some examples may be emphasized, such as methane and hydrocarbons oxidation [34,35], hydrogen cyanide [36] and acrylates polyesterification [37] enhanced by pulsed microwaves, or the manufacture of unsaturated orto-phthalic polyester enhanced by 2.45 GHz microwaves with a reduction of 36 % in processing time [18].

Obviously these experiments were done in small scale, while industrial production is in a big scale. Technology to scale up the microwave assisted chemical process from bench scale to pilot scale and finally to industrial scale is already available. For example, figures 8 and 2 show two pilot scale equipments. The first one is a batch reactor of 25 L for multipurpose processing, and the second is a continuous tubular flow reactor used for manioc hydrolysis.

On the bench scale it is necessary to develop the basic knowledge about the process. For this step the laboratory microwave ovens are used with success. Pilot plant tests require ovens or other kinds of large dimension applicators, where tests may be performed to try the applicability of the basic knowledge developed on bench scale. After the pilot test the initial knowledge is adapted to the pilot reality and then it is possible to design an industrial unit. Usually this design is not only a chemical one but also an electrical design of a microwave applicator.

VIII. CONCLUSIONS

As was shown in brief words, microwave enhanced chemistry is a frontier of scientific knowledge, because scientist observe phenomena that they cannot explain well enough to reach a consensus; thus it is an opportunity to create new theories for a new vision of the chemical world. At the same time, people from the chemical industry, whose interest is to make profit with the scientific knowledge or in other words to do technology, apply these initial and not explained ideas to their production units and increase the productivity of their plants.

Nowadays, microwave chemistry is really the point where it is possible to do science and technology, to find the unknown and the way to profit, to establish new concepts and new industrial processes. For all these facts, we can recognize that microwave chemistry is a fertile field for scientific research and industrial applications.

REFERENCES


