Chapter 2
Microwave Reactors for Chemical Synthesis and Biofuels Preparation

Cristina Leonelli and Paolo Veronesi

Abstract Microwave reactors are among the most novel thermochemical technologies to treat biomass and improve process sustainability. The microwave-assisted process offers several advantages over the traditional ones in terms of uniform internal heating of heterogeneous low-thermal conductivity loads, ease of control, saving of time and heat energy for properly designed or selected reactors. The geometries and the functioning principles of microwave reactors commonly adopted for chemical synthesis and biofuels are discussed in this chapter. Temperature monitoring, output microwave power control and product enhancement are critical to obtain process efficiency with microwave reactors.

Keywords Microwave technology · Equipment · Power · Energy · Dedicated microwave ovens · Autoclave

2.1 Introduction

In the 1980s microwave (MW) ovens dedicated to acidic dissolution (pressurized vessels) and ashing (furnaces up to 1,000 °C) of analytical samples were commercially available. At that time microwaves were exclusively adopted by analytical chemists [1] while the evolution of microwave reactors started some years after the pioneering works of synthetic chemists, Gedye et al. [2]. Inorganic syntheses using microwaves as heating source came to the forefront a few years later [3] jointly with materials preparation at high temperatures [4] showing that either dedicated equipment or furnaces could be fabricated for syntheses.

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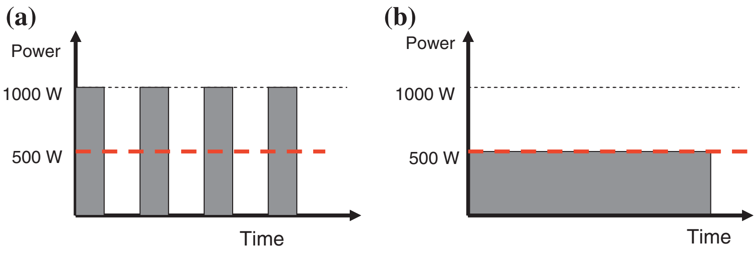


Fig. 2.1 Duty cycles of **a** pulsed and **b** continuously variable power microwave source at same average power

Several observations such as an abnormal increase in boiling temperature of organic solvents of 18–26 °C [5] or modified reaction path in organic synthesis [6] may be part of the so-called "microwave-effect". There are claims that specific microwave effects do occur, however, it must be stated that in the majority of cases where microwave-assisted reactions are carried out, the systems do not permit a precise control of power and temperature that is necessary for good reproducibility of the results [7].

One of the main differences between laboratory dedicated microwave ovens and domestic microwave ovens is the output power control, i.e. the duty cycle. In a domestic oven the power control of the microwave irradiation is usually a simple on/off type and the "irradiation time" does not coincide with the time during which the reaction vessel is kept inside the oven (Fig. 2.1). Hence it is common not to correctly estimate the microwave power used to heat a certain volume, since irradiation is not continuous [6]. Moreover, domestic microwave ovens use power sources whose progressive heating, as they are operated, causes the system to change their power efficiency. Power efficiency is also changed when the sample is being moved within the domestic microwave oven. The mismatching, power pulling and frequency pulling due to sample movement can also influence the final power efficiency of the process as described in all the comments and modifications have been accepted and integrated in the text by Metaxas and Meredith [8].

Apart from a number of commercially available microwave reactors, which will be discussed in the next section, there is a number of laboratories that developed dedicated MW reactors for synthesis and biofuel preparation under well controlled conditions equipped with proper temperature and output power control [9–17].

Such reactors operate with continuous microwave irradiation (Fig. 2.1b) making it easier to control heating cycles and process reproducibility.

2.2 The Microwave Reactor

In obtain efficient conversion of electromagnetic (EM) energy into heat, so that an extremely fast heating rate occurs in a reproducible way, laboratory-dedicated microwave reactors should be used in scientific studies as opposed to domestic ovens.

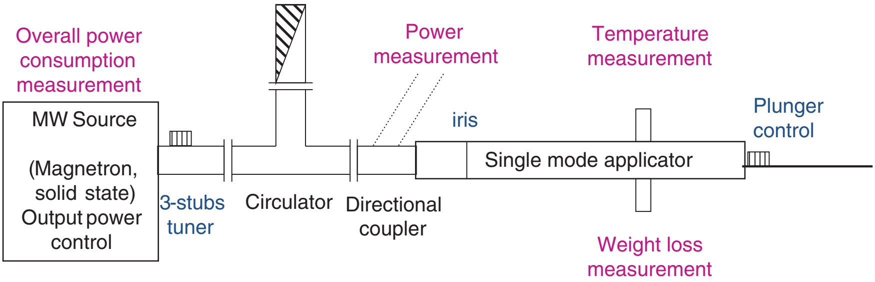


Fig. 2.2 General scheme describing a complete arrangement of a microwave system dedicated to heating in a closed applicator (single mode, in this case), where a colour code has been used to rapidly identify the components of the system, evidencing the impedance matching ones (*in blue*) and the possible measurement ports (*in purple*), together with an example of filter structure to avoid the microwave leakage

A microwave oven is essentially composed of a microwave source (magnetron or, more recently, solid state generators) with its power supply and controls, connected to a transmission line (waveguide for higher power, coaxial cables for lower power) that conveys the electromagnetic energy in a metallic cavity (commonly referred to as an applicator) into which the actual chemical reactor is inserted [18] (Fig. 2.2). The latter can be composed of a common borosilicate or quartz reactor or of microwave transparent polymer, usually Polytetrafluoroethylene (PTFE or Teflon®), PTFE-TFM (or Dyneon™, modified PTFE for high chemical and heat resistance) or Polyether ether ketone (PEEK). Care must be taken to ensure that the reactor vessel, tube or balloon is constructed of a material that is transparent to microwave energy to allow the transfer of electromagnetic energy to the reactants. In other cases, the reactor can be made of microwave-absorptive material (usually silicon carbide), to supply additional heat contribution to the load, via thermal conduction. These materials are commonly known also as susceptors.

Other important components are those dedicated to impedance matching (Fig. 2.2). The 3-stubs tuner allows the impedance matching between generator and load, by inserting metal posts along the transmission line with manual or automatic system. The 3-ports circulator allows to redirect the power reflected from the load to an auxiliary load (usually water) positioned on the third port. It protects the microwave source from reflected power and, if the third port is equipped, it can be used also to measure reflected power by a calorimetric system. The coupling iris is another impedance matching device composed of tailored openings along the transmission line to achieve the maximum energy transfer from the source to the load. It can be inductive, capacitive or resonant.

Finally along the line a directional coupler can be positioned; it measures emitted (forward) and reflected power, and hence to quantify the amount of energy dissipated into the load.

The geometry adopted for the cavity is of various forms, chosen according to the process to be performed.

At the end of the waveguide transporting the microwave energy to the applicator, a pressure window can be inserted. It is a “microwave transparent” safety window that ensures that any solvent vapours or small particles from reaction vessel do not reach the microwave source. Its insertion is also essential when the vessel is operated at elevated pressures as is often the case with chemical reactions initiated by microwave energy. Care must be taken with those windows since they can cause breakdown phenomena and undesired reflections. Therefore, precise information about maximum handled power and mismatch data should be taken into account [8].

Upon switching the microwave power on the energy is transferred to the cavity where the reflections from the metallic walls generate the well known interference phenomenon characterized by positions of decreased field intensity alternated by positions with enhanced intensity (Fig. 2.3). While in a single-mode cavity the regions of high and low EM field are relatively easy to measure or calculate, in a multi-mode cavity one needs to resort to an optimization process using numerical models to obtain the corresponding EM field distribution. The advantages and disadvantages of these two basic applicator geometries are discussed in the following paragraphs.

A microwave oven for treatment of biomass or for chemical synthesis necessitates the inclusion of a number of sensors for process monitoring. Temperature, pressure, reflected or absorbed microwave power, as well as FT-IR sensors jointly with thermal cameras are those most utilized in commercial ovens as in self-assembled ones.

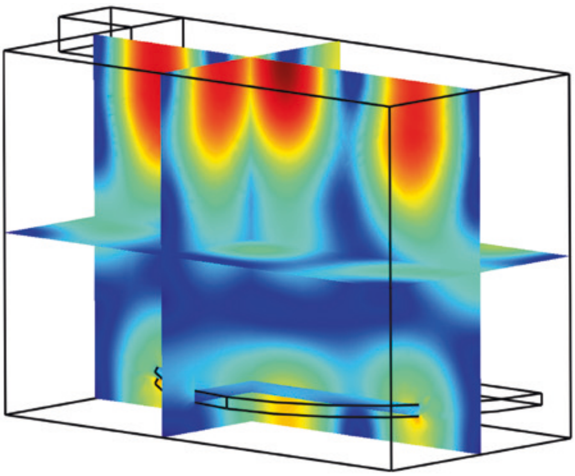


Fig. 2.3 Electric field distribution in a loaded multi-mode oven (half oven, symmetrical), showing the presence of regions with higher or lower electric field strength (colour scale: *red* high intensity). The scale and magnitude are missing since the intent is to explain the qualitative distribution of fields inside the microwave applicator or load

2.2.1 Commercial Microwave Ovens

Over the last 20 years we have assisted in establishing reactor geometries dedicated to synthesis, extractions, fermentations, and digestions [19].

The general features that characterize these commercial applicators can be summarized as follows:

1. homogenization of the electric field profile, through mode stirrers or of reaction vessel rotation;
2. reactor geometry design taking into account the penetration depth of the microwaves;
3. temperature and pressure control within the reaction chamber for continuous monitoring of process parameters;
4. optimized cost of reactor and spare parts;
5. safety issues and microwave leakage.

To evaluate the most recent developments in chemical reactors adapted to microwave heating, the most popular commercial geometries (Table 2.1) capable of reaching high temperature and pressureregimes will be described.

For more precise equipment description, refer to each producer web site. A good review paper on the use of microwave reactors for biodiesel production, we suggest the dedicated chapter by Coquerel et al. [20] and the article by Gude et al. [21].

2.2.2 Self Assembled Microwave Reactors

A very interesting review paper [15] reports on a number of self assembled microwave equipment for the pyrolysis of biomass. Zhao et al. [9] reported the effect of temperature on the pyrolysis of wheat straw in a 3,000 W, 2.45 GHz domestic microwave oven equipped with a two-digit electronic balance, a thermocouple, an electric heating device to circulate the air in the reactor for preventing the condensation of liquid phase products on the quartz reactor wall and pipelines, and a control function to produce constant temperatures during the whole process.

Huang et al. [12] studied the production of H_2-rich fuel gas from pyrolysis of rice straw using in a 2.45 GHz single-mode microwave cavity with maximum power of 2 kW. The reactor used was made of high quality quartz and was positioned in a quartz tube. A flux of nitrogen was used as carrier gas.

Salema and Ani [13] studied the effect of microwave irradiation on the pyrolytic process of two types of biomass, namely oil palm shell, OPS, and oil palm fibers, in the presence of char obtained from conventional pyrolysis of OPS as the microwave absorber. A 1 kW, 2.45 GHz domestic microwave oven was modified to perform the experiments. This oven was equipped with a fluidized bed quartz glass reactor, a steel distributor plate, and two k-type metallic thermocouples to record the temperatures on the surface and within the material.

Table 2.1 Description of the most popular commercial microwave ovens dedicated to biomass treatment and chemical synthesis

Producer/model	Description	Max power (W)	Max temperature (°C)	Max pressure (bar)	Max vessel volume (L or mL)
Anton Paar/Synthos 3000	Autoclave/multiple vessels (16)	1,400	240	40	16 × 100 mL
Anton Paar/Masterwave BTR	Multi-mode/single vessel	1,700	250	30	1 L
Anton Paar/Monowave 300	Single-mode/single vessels	850	300	30	30 mL
Biotage/Advancer Kilobatch	Multi-mode, autoclave/single vessel	1,200	250	20	350 mL
CEM/MARS 6	Radiant/multiple or single vessel	1,800	300	100	5 L
CEM/Voyager	Radiant, autoclave/stop-flow	300	250	20	80 mL
MILESTONE/FlowSYNTH	Multi-mode/continous flow	1,000	200	30	12–100 mL/min
MILESTONE/UltraCLAVE	Multi-mode, autoclave/multiple vessel	1,200	300	200	2 L
SAIREM/MiniFlow 200SS	Single-mode/continous flow	200	250	1.5	5 L/min
SINEO/MWave-5,000	Multi-mode, autoclave/single vessel	1,500	220	20	500 mL

2.3 Microwave Cavity Design and Selection

One of the main concerns when deciding to set up a microwave assisted process is the selection of the cavity type. The correct geometry of the cavity should allow the experimenter to gather the required information on the reactions yield and energy efficiency, but also to provide experimental parameters for possible scaling up (total gas evolved, throughput production etc.).

Often the choice is between selecting and adapting an existing microwave applicator, or to design a new one dedicated to the process of interest. In both cases, careful process analysis is essential. The process requirements should be known in detail, and most of the relevant properties of the materials to be processed should be known. Process analysis is a typical method to determine the process requirements, and the range of variability of some of the parameters involved. First of all, the kind of process must be identified (drying, tempering, heating, melting, …), taking into account that sometimes more than a single operation could be performed in the same applicator (e.g. defrosting + heating; heating + solvent removal + melting; …). It is important to know if the process is continuous or a batch. The materials properties play a fundamental role, and usually they are difficult to determine with good approximation, since they can change, also abruptly, as the microwave treatment proceeds and new products are formed, or the temperature is changed. Thermal, dielectric and electrical properties knowledge is required to properly design a new applicator, especially if modelling software is used. In general, most parameters referring to the product (dielectric properties, shape, dimensions, …) vary as a function of time (or temperature or space). A good process analysis makes the subsequent steps easier, and, due to the peculiarities of the microwave heating, some aspects usually neglected in conventional heating must be taken into account, such as the dielectric and electrical properties of the supporting materials (belts, trays, …) or of the materials to be used to build the applicators wall. Compliance to national or world-wide regulations on emission and safety are also an issue. A comprehensive list of questions, whose answer should be known before starting the design, is reported in Meredith's book [22].

The process analysis should give a "go or no-go" response, usually concerning both the technical and economic feasibility. In case of a favorable evaluation related to microwave processing, the next step could be deciding which kind of microwave applicator to use, ranging from single-mode applicators to multi-mode ones, or radiating structures. This depends crucially on the nature of the process and of the materials to be treated, as well as of their size. Remembering that the distinction of these types is purely for comparison because, for instance, radiating structures can be used to feed a multi-mode applicator, explained below.

2.3.1 Multi-mode, Single-mode and Radiant Applicators

Multi-mode applicators (Fig. 2.4) are generally simple and relatively cheap to build. Their main advantage is that they can have large dimensions—i.e. large

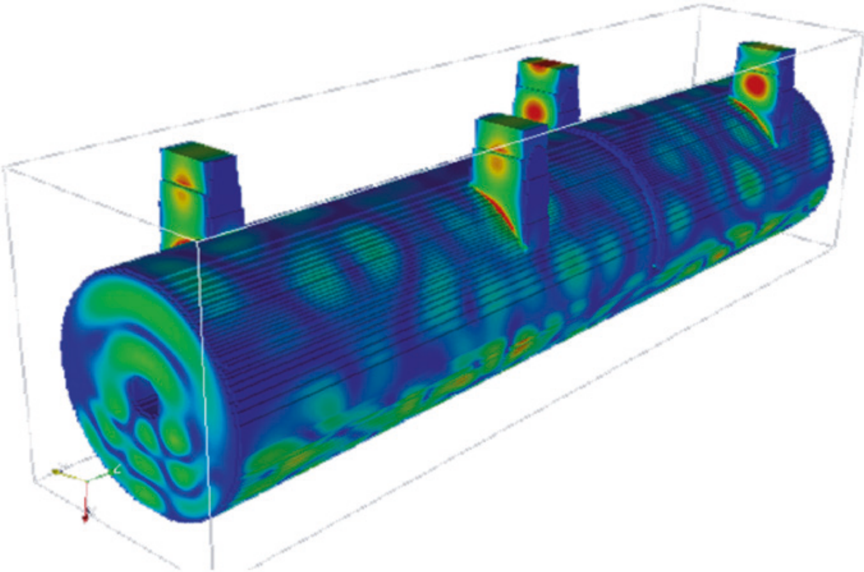


Fig. 2.4 Example of a partially loaded 4-ports microwave reactor for pyrolysis, showing the electric field strength distribution (colour scale: *red* = high intensity) [23]

volumes of material to be processed—and the use of mode stirrers, rotating dishes, or other means to improve heating homogeneity (Fig. 2.5). However, the loaded applicator can not be treated analytically and despite all the efforts in design or optimization, inherent heating inhomogeneity persists.

On the contrary, single-mode applicators (Fig. 2.6) can usually be treated analytically, and the distribution of the EM field in such applicators is well known and is controllable. Single-mode applicators are relatively simple to build and to

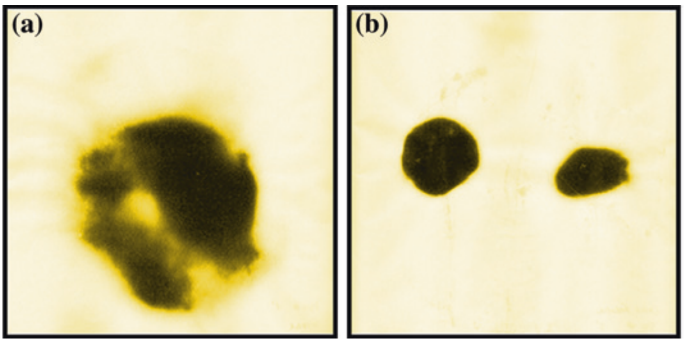


Fig. 2.5 Thermal paper images following microwave heating of a dielectric slab in multi-mode applicator: **a** in the presence of a mode stirrer; **b** without mode stirrer (*dark areas* correspond to highest temperature)

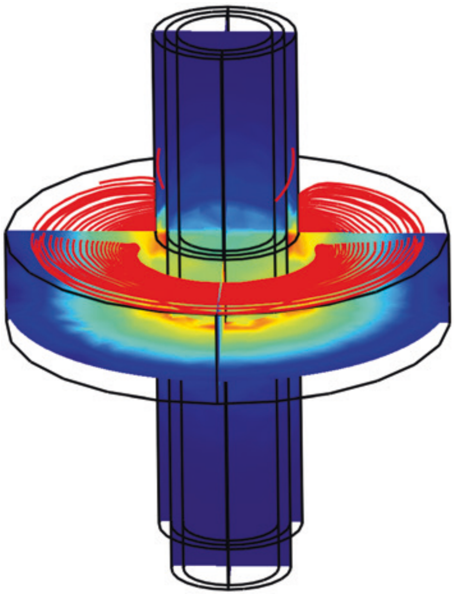


Fig. 2.6 Example of a loaded single-mode cylindrical applicator, showing contours of the electric field strength distribution (colour scale: *red* high intensity) and the magnetic field lines

adapt to achieve maximum efficiency, at least at the beginning of the process. The processing volume is usually small, however, this results in high power densities, with extremely high electric fields. On the one hand, this can help processing low loss material, but on the other hand, breakdown phenomena (arcing and plasma formation) can occur. One way to increase the processing load is to resort cavities operating higher order mode designs or running the system at a lower ISM frequency, as for example 915 MHz [8, 22]. It is important to comment that single-mode applicators suffer from increasing mismatching during the process due to changes in materials' dielectric properties. This implies that proper mechanical or electrical adapting techniques should be used to avoid power reflections during the heating process.

Radiating structures (Fig. 2.7) are designed to present good heating homogeneity. They tend to be less sensitive to the load variations compared with single-mode applicators. They can have large dimensions and an open structure, and this can pose some problems when shielding the openings to prevent leakage of EM energy. This is usually accomplished by adding chokes or filters at the edges of the radiating structure as described by Thuéry [24].

Each one of the three geometry presents different options such as whether to use a single feed or multiple generators, or which mode should be predominant in the applicator. The advent of solid-state sources offer a low cost possibility to also control the frequency and phase of each source, enhancing the possibilities of a microwave assisted process.

Due to the generally low efficiency of current microwave sources, that range from 0.5 to 0.85 for the most popular ISM frequencies, it can be useful to consider

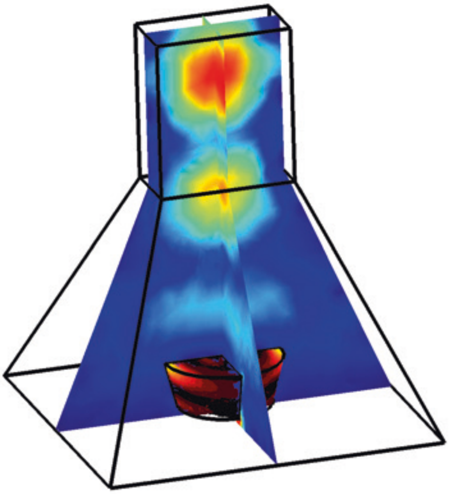


Fig. 2.7 Example of a radiating structure—horn, with cylindrical load placed at its exit: electric field strength distribution (colour scale: *red* = high intensity) and average power density (in thermal plot)

the use of hybrid systems where other heating techniques transport energy or heat to the load, and, in specific cases, allow auxiliary operations. Hot air generators, infra-red lamps, laser beams, and burners are some of the examples of systems that can be used in conjunction with microwaves, provided their interaction with the EM field occurs at safe conditions [22]. If the hybrid heating is not performed simultaneously, but in sequence (e.g. hot air, then microwaves, then IR), the exact sequence should be known, since the heat treatment is not invariant in the case of a different mode of treatment: previous "conventional" treatments can deeply alter the dielectric properties of the material, or other important characteristics as in the case of permeability to gases. A typical example is the pre-sintering process of ceramic disc in resistance heated furnace followed by sintering in microwave oven [25].

2.3.2 From the Cavity to the Reactor

After selecting the applicator, taking into account also the power requirements of the envisaged process, another demanding problem is how to distribute the power. One possible solution is using high power magnetrons, which present the advantage of a relatively high efficiency and ease of installation (1 single feed = 1 port), but they can have problems relating to the power handling capabilities of the transmission line and the protection from the reflected power. Another possible solution, which generally leads to good heating homogeneity and to the possibility of good distribution and control of the power in the applicator, relies on multi-feed techniques. In this case many lower power microwave sources (and their transmission lines), not necessarily operating at the same frequency are converging on a single cavity. The wiring of such systems is complicated, but they are generally more flexible compared with single feed applicators, especially in the event of microwave source failure. One of the major problems connected with the use of multi-feed systems is the cross-coupling inconvenience, i.e. energy entering from port “i” partially or completely flows into port “j”, thus reducing the efficiency of the whole system and potentially damaging the generator connected to the port “j” [26]. Careful design helps reduce the cross-coupling, but different load conditions of the applicator should be taken into account: a completely loaded applicator will not have cross-coupling between the sources, but if partially loaded, or loaded with a different load, then cross-coupling could occur [27]. Alternatively, there is the possibility of using internal filters to transform the cavity in different modules that can be designed independently [28].

After the applicator type has been chosen, which may have to be revised or modified as the investigation proceeds, the design or selection phase can begin. The simplest way to obtain a suitable applicator, is to adapt an already existing cavity, preferably being available on the market and not too expensive. Unfortunately, this may seldom lead to the best results. Fortunately, there are many different ways to obtain a “different” applicator starting from the same structure: movable parts, impedance matching devices, mode stirrers all assist, but also control strategies of the microwave sources help confer high flexibility to an applicator by allowing its use for a certain range of loads with satisfactory performance [26, 29].

2.3.3 Numerical Simulation as Design Tool

For a new process or a new product completely new designs are usually required. The design step can be conducted using modelling tools (computer simulations), or by trial and error approach which requires high expertise and is best suited to the modification of existing applicators. Each one of the approaches is not definitive and presents some advantages and drawbacks. Considering the design of a multi-feed applicator, the use of modelling software can lead to the best solution (not merely to the satisfactory one) regarding the feed positions for a certain load conditions without having to drill holes and relying on experience. On the other hand, if many ports are present, with no symmetry, the modelling can become quite time-demanding, and the difference between the modelled material and the real one can sometime lead to large discrepancies. The most updated simulation software allows simultaneous excitation of different sources with consequent reduction of computational times.

As a matter of fact, the information required for the model to be representative of reality is difficult to obtain, and they should be expressed as a function of temperature or other process variables. Coupling the EM field modelling and the thermal/fluid-dynamics can be sometimes very difficult. Taking into account the variation of the dielectric properties with temperature is relatively easy, since there is a 1:1 spatial correspondence among model referring to different temperatures or times. Instead, if the materials undergoes a pronounced dimensional change (shrinkage, foaming, …), a complete description of its deformation and its effects on the EM field distribution can be very difficult to obtain. Thus, the two approaches seem separate, but it is only by combining the two that an effective applicator can be designed.

2.3.4 Materials Choice

As described in Chap. 1, materials can be roughly classified into three categories, based on their interaction with microwaves:

1. materials that reflect microwaves (good conductors), generally bulk metals and alloys used to produce microwave cavities, wave guides, antennas and mode stirrers;
2. materials that are transparent to microwaves (low loss materials), such as fused quartz, some glasses, some ceramics, PE, PP, Teflon®, used to build load supports, turning tables, pressure windows, piping lines and so on;
3. materials that absorb microwaves (lossy materials) which usually constitute the load to be heated via direct microwave exposure, e.g. aqueous solutions, biomasses, polar solvents or materials that can be used as auxiliary microwave absorbers, commonly referred to as susceptors, to heat the load by conduction or irradiation.

The microwave absorption ability of a material is also dependent on its magnetic permeability, and in particular on the imaginary part of the complex permeability [26], but in the case of biomass this contribution is usually negligible and hence not taken into account (see Chap. 1).

Electric and magnetic properties of the materials are only the starting point, but their proper choice can make the difference between a working reactor and a poorly performing one. Cavity walls should be built using high electrical conductivity materials, or at least using highly conductive coatings, in order to minimize wall losses. The introduction of "microwave transparent" material, according to the previous classification, does not imply that it will not affect the EM field distribution: the lossless nature of such materials means only that it will not be significantly heated by microwaves, but it can severely alter the electromagnetic field distribution, depending on the real part of its complex permittivity [30].

Particular care must be taken when addressing the materials to be used as thermal insulators of microwave cavities: if such insulating materials are to going to be exposed to the microwave energy, then they should preferably be low loss materials, unless it is required that they act as auxiliary absorbers [31]. Such properties should not vary with temperature and their exposure to the reaction environment should not affect their properties. However, it is possible that during use the insulating materials undergo degradation or corrosion phenomena, or even are contaminated by some of the reactants or products, thus changing their microwave interaction characteristics. In this case, something meant to be practically lossless can become highly absorptive, a condition particularly dangerous when it comes to microwave pressure windows on waveguides since it may cause arcs or windows fracture.

2.4 Filters

The filters in microwave systems are very diffused; they are structures that are intended to avoid microwave leakage, usually by hindering the microwave transmission. The simplest filters are waveguides under cutoff conditions, or quarter wave chokes. Periodic structures such as doubly corrugated filters can be used to build wide band filters useful to prevent leakage from normally open large ports in microwave tunnel kilns [32].

Filters that work in absorbing microwave energy are often found as polymer contour of oven doors.

Very often these filters are used to introduce sensors or to introduce or extract gases from the applicator. They are also used in doors to avoid excessive leakage according to the limits set by national regulations and to allow continuous production by using open waveguide filters.

2.5 Sensors

Last, but not least, microwave assisted processes require particular care when it comes to measurement and control. This is essential to achieve the highest degree of reproducibility of a microwave-assisted process: the control system must be robust and reliable. Typically this includes multiple sensors, some of which are entirely dedicated to safety (microwave leakage meters), other used to monitor the main process variables such as forward or reflected power (usually embedded in the microwave source and transmission line) and load temperature or cavity pressure sensors. However, other control strategies can be implemented, for instance based on weight variation, degree of completion of a certain reaction, or even on variations of reflected power ascribable to variations of the dielectric properties of the load, as it evolves into the final product or simply changes in temperature.

Measuring temperature in microwave-assisted processes is probably one of the most demanding tasks. Many apparently outstanding results addressing lower temperature processes, claimed when applying microwaves, usually are due to errors in measuring temperature [33]. The most common and versatile temperature sensor is the thermocouple, however, since it is constructed of metal, its use in the presence of EM fields has been debated for a long time [34]. The presence of a thermocouple induces perturbations in the EM field distribution, and in particular its point-shaped tip favors electric field concentration near the tip itself, making

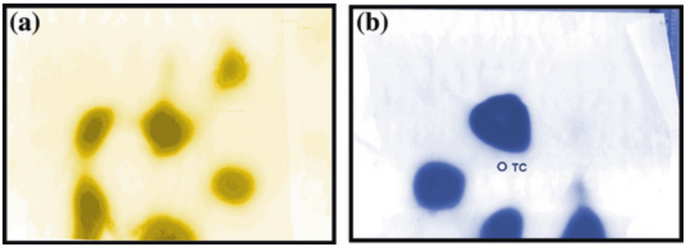


Fig. 2.8 Thermal paper images of the microwave heating of a dielectric slab in multi-mode applicator: **a** without metallic thermocouple; **b** with centrally positioned thermocouple (*dark areas* correspond to highest temperature)

it a perturbating measurement system [35, 36]. The higher electric field near the thermocouple tip can cause localized overheating, which is recorded by the thermocouple as representative of the state of the load (Fig. 2.8). However, depending on the reactor geometry and nature of reactants, thermocouples have been successfully used, especially immersed in a high loss dielectric fluids [37].

If non-perturbating methods are preferred to non-contact methods, or the use of optical fibers should be adopted. Non-contact methods, like optical pyrometers, have the drawback that only surface temperature is measured, and this temperature is not always representative of the load temperature: the load surface is exposed to the generally colder furnace atmosphere, and hence, under certain conditions, it could be the coldest part of the load. Moreover, pyrometers are line of sight methods, and require direct access to the surface to be measured, and so must avoid smoky environments. Measuring temperature through a viewing port with pyrometers (for instance to maintain a controlled atmosphere in the microwave cavity) requires that the port material (window) is transparent to the infrared radiation used by the pyrometer. This excludes most of the commonly used window materials, like fused silica or quartz, requiring their substitution by different window materials.

If information must be gathered on a wider area, other non contact methods, such as thermal cameras can be used, but then a proper control strategy must be implemented, that is able to represent the whole image data as a number, or to extract values in multiple points. A typical use of thermal camera is for safety issues, i.e. to verify that the load surface does not exceed a given temperature.

If the temperature information must come from within the load, then probes must be used. Non perturbating, or slightly perturbating probes, are optical fibers. Glass based fibers, optionally coated by PTFE are used to operate in the most severe reaction environments. Commercially available optical fibres can cover a wide temperature range, starting below the freezing point of water to 2,000 K. However, a single optical fiber usually is not able to cover the entire temperature range of interest, requiring that multiple optical fibers and controllers are installed.

The drawback of the aforementioned temperature sensor is the impossibility to provide the complete temperature distribution in the load volume. Only surface temperature or point information can be gathered, and given the nature of the microwave heating process, such data are not representative of the actual process. On the other hand, volumetric temperature sensors, like radiometers, are expensive and not so easy to use.

Global information on the process can be extracted using pressure sensors. Measuring pressure is usually easier than measuring temperature, since in most cases pressure is nearly constant in the whole reaction volume. Of course there are many exceptions, ranging from non-equilibrium rapid processes to particularly complex cavity or load geometries, inducing pressure losses. During microwave processing, in some cases gases can be generated, and this must be taken into account since their partial pressure adds up to the system pressure. Classical pressure sensors (piezoelectric, membranes, load cells, …) can be used provided they are positioned so that they do not to perturb the process and are not affected by the EM field. Some devices have been devised specifically for use in the presence of high strength EM fields, based on the variation of optical properties or of an optical path. In the first case, optical properties of a sensing material, like a glass ring exposed to polarized light, undergoes a change in color of the transmitted light, depending on the pressure that the ring is exposed to (usually proportional to the pressure within the reaction volume). Fiber optics, similar to the ones used for temperature measurements, can be used also to measure pressure, exploiting the change of the length of a cavity (Fabry-Perot cavity) enclosed between two semi-transparent mirrors. Forces, in the case of pressure measurements, or thermal expansion, in the case of temperature measurements, cause the variation of length of the Fabry-Perot cavity walls.

Pressure must be monitored in all the reactions occurring in closed environments, to avoid the generation of overpressure that can hinder the safety of the equipment or of the operator. This is why, regarding pressure, open microwave applicators are intrinsically safer, since they can be operated at atmospheric pressure. On the other hand, a closed vessel system allows control of the cavity atmosphere (or pressure).

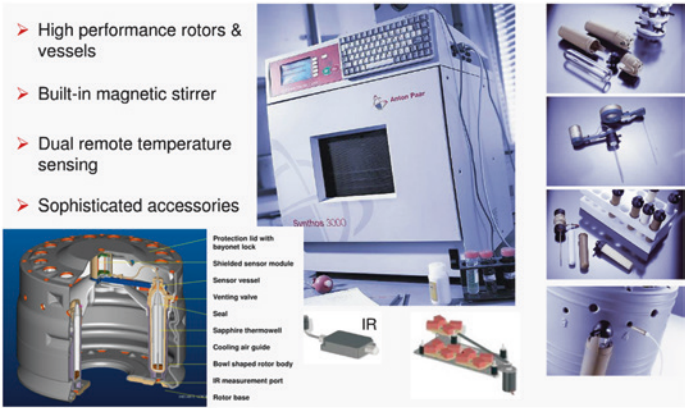
2.6 Guidelines for Equipment Selection

All commercial equipments dedicated to laboratory experimentation cover a range of temperatures up to 250–300 °C or even higher, depending on whether polymer or quartz is used in the construction of the internal reactor. The associated pressures commonly found are 30 bar for single-mode reactors and 80 bar for multimode reactors.

The operation time can reach several hours, but usually for most of the chemical reactions, digestions, fermentations and extractions, process time on the order of minutes is sufficient.

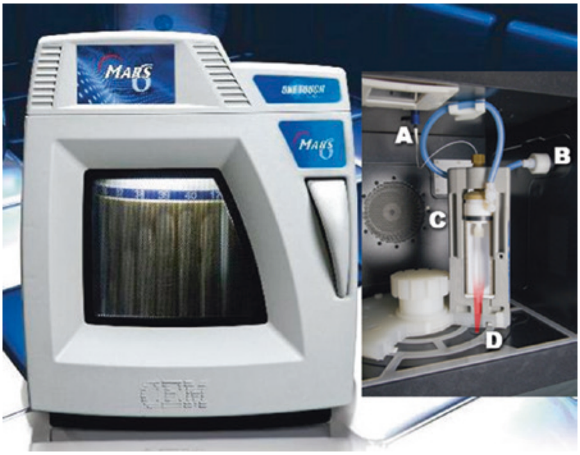
The following table shows the relevant features and options of some of the commercial systems dedicated to microwave chemistry (Table 2.2).

Table 2.2 Commercial microwave ovens for chemical synthesis and biomass treatment

Producer/model	Description
Anton Paar/ Synthos 3000	
Anton Paar/ Masterwave BTR	
Anton Paar/ Monowave 300	

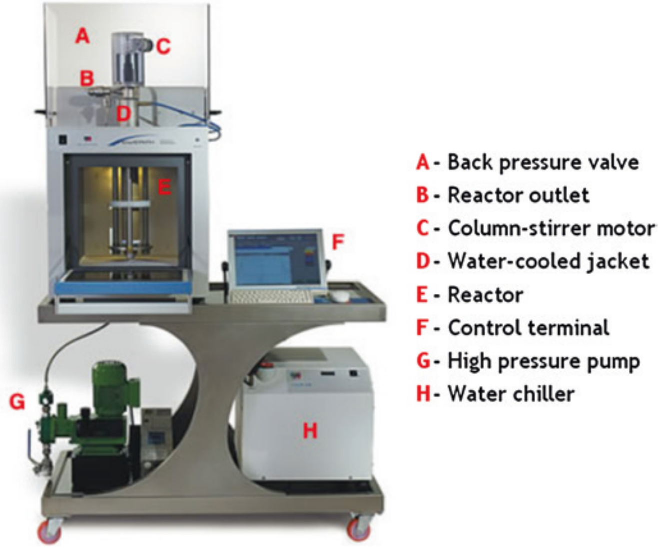
(continued)

Table 2.2 (continued)

Producer/model	Description
Biotage/ Advancer Kilobatch	
CEM/MARS 6	
	(A) Direct fiber optic temperature sensor of the reference vessel
	(B) Single vessel reference pressure sensor
	(C) Contactless pressure sensor
	(D) Contactless all-vessel temperature sensors

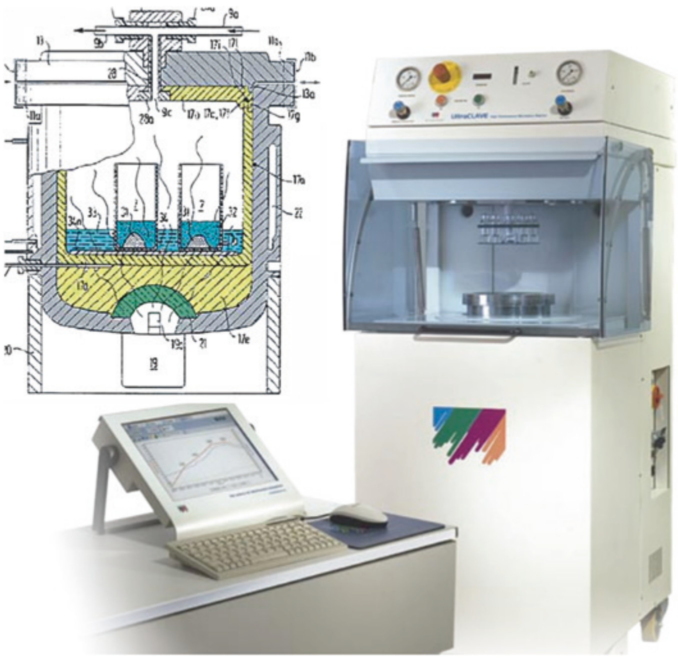
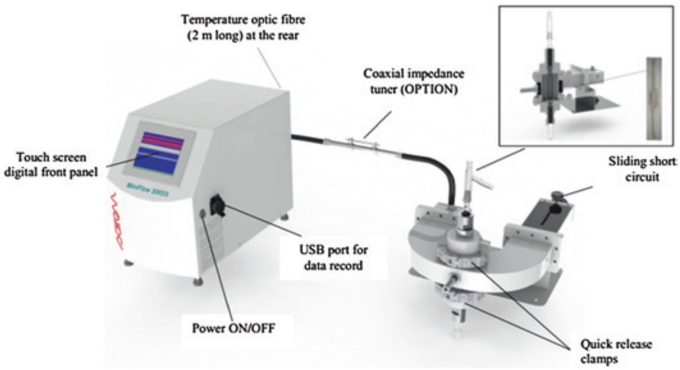
(continued)

Table 2.2 (continued)

Producer/model	Description
CEM/Voyager	
MILESTONE/ FlowSYNTH	

(continued)

Table 2.2 (continued)

Producer/model	Description
MILESTONE/ UltraCLAVE	
SAIREM/ MiniFlow 200SS	

(continued)

Table 2.2 (continued)

Producer/model	Description
SINEO/ MWave-5000	

Examination of the reactants or the biomass to be treated is necessary. A list of general questions that aim to highlight the more critical aspects of a sample to be inserted in a microwave oven, adapted from Meredith [22], is given below.

1. *Is the load composed of a single phase?* More than one phase? If yes, are all of these known? What is their chemistry? Dispersed metallic particles-such as catalysts—might strongly interact with microwave energy, even though metals have been accounted as fully reflective materials.
2. *Is it toxic? Does it become toxic during thermal treatment?* Evolved gases must be properly managed.
3. *Is it corrosive, flammable or explosive?* It must be stressed that in single-mode cavities the electric field density can be so high as to cause plasma formation which can have adverse effects on the reactor integrity.
4. *Are there any incompatibilities with other materials?* Reactivity with the reactor walls or with submerged sensors must be considered.
5. *In which shape and size is the sample at the beginning and at the end of the process?* Provided that the penetration depth has been considered, bear in mind that powders, liquids, solids, bulks, particles require specific manipulation within the EM field so that they show specific behaviour, not least the reflective surface of a continuous liquid phase which may prevent microwave absorption.

6. *What is the mass flow at the entrance and at the exit of the reactor?* Puffing, bloating and foaming are often observed in the heating zone and when a continuous flow process is adopted, these phenomena can create problems.
7. *What is the process time?* A rough estimate of the time required for heating the sample is good practice especially when temperature sensors are not submerged in the sample.
8. *What is the specific heat and the thermal conductivity of the material?* Poor thermal conductors might increase their inner temperature at dangerous levels before a surface temperature sensor records the event.

As stated above, the majority of the chemical reactors are designed for batch processes while a limited number are suitable for continuous processing.

Given these parameters for commercial microwave oven design the choice is dictated by:

1. the required scale (milligrams to gram or higher) or the throughput (g/min) for continuous process;
2. the preferred processing technique (batch, continuous, open vessel, closed vessel, etc.…);
3. the preferred workflow (with or without automation, sequential or parallel processing, etc.).

As the annual number of publications on microwave-assisted synthesis and biomass treatments exceed one thousand, it is recommended that the reader review the literature and some to the main texts on the this subject [6, 37–41].

2.7 On the Use and Modification of Existing Ovens

Some comments have already been reported on the emitted/forward microwave power, but when facing the issue of the scale-up, the power required for completing a certain process via microwave energy is the critical issue. In some cases, it could be feasible to adapt an existing microwave oven (either domestic of laboratory dedicated), but some care must be taken when modifying commercial ones.

As stated above, the power preferably can be supplied continuously or with on/off type feeding devices. It would be helpful to be able to calculate the power absorbed by the load, but not all the lab scale commercial ovens posses dedicated sensors, hence an estimation of the nominal output power is often the only evaluation possible. When the output power is supplied in a on/off regime, it is really difficult to calculate the actual irradiation time and from that the overall power used in the process. Apart from thermodynamics' calculations based on the temperature increase, elapsed time, specific heat, phase change rate and heated mass. Domestic ovens have the microwave source fed in on/off regime, so when modified by non-expert users, they tend to maintain this feature.

Additionally it should be taken into account that commercial microwave oven designed for the chemical laboratory are multimode cavities fed with continuous microwave irradiation which is not optimized for any specific chemical compound. This means that, as in the case of domestic oven, the metallic cavity containing the EM field is not adapted to the load being processed. In terms of efficiency it means that the microwave incident beam geometry has not been optimized for any specific chemical in the reactor and more often than not it has not been optimized for a specific reactor geometry, given that the reactor itself is interchangeable with other structures provided by the producer.

Concluding, when trying to estimate the power necessary to run a scale-up process attention should be paid to the microwave equipment chosen for the laboratory: if the equipment was not dedicated to that process, it may give an unacceptably low efficiency. In this case, the best solution is to start from scratch and design a fully dedicated equipment.

2.8 Conclusions and Future Outlook

Early work on the use of microwaves to produce biofuels dates back to the end of the previous century, when synthesis of biodiesel was conducted in domestic kitchen ovens by reaction between methanol and commercial seed oils [42]. Despite the lack of reproducibility and low efficiency typical of such microwave systems, the promising results led to the use of a laboratory scale plant for continuous process, which allowed to conclude that the application of microwave energy both in continuous and batch-wise process was proven to be practical on an industrial scale. A step further was accomplished by Mazzocchia et al. [43], who performed the biodiesel synthesis by heterogeneous catalysis using zeolites. This permitted to operate at temperatures as low as 170 °C and to achieve moderate yields of biodiesel in less than 2 h.

A significant step towards the large scale use of microwaves for biofuels production occurred some year later, in 2006, when researchers [44, 45] from the University of Connecticut operated at atmospheric conditions, on a 3 kg reactor and in presence of hydroxides (KOH and NaOH), to achieve good yields of biofuel in times of the order of minutes. This rapidly led to the possibility to go for a continuous flow system, which successfully processed more than 7 l/min flow in a 4 L vessel, with yields, for a similar system [46] and process, surpassing 90 %.

However, the use of homogeneous catalysts requires that a time- and resources-demanding procedure of neutralization and washing of products is applied, with the drawback of generating large amounts of wastewater. This led the research to investigate the use of inexpensive heterogeneous catalysts suitable for microwave irradiation, in order to keep high yields but to avoid separation stages. Moreover, research is focused on the identification of various alternative oil feedstock, preferably from agricultural waste or no-food crops. These, together with the development of large scale dedicated microwave equipment, with better process control and safety, is considered to be the key factor for a successful implementation of the microwave assisted synthesis of biofuels, and in particular of biodiesel and biomass-derivable ethyl tert-butyl ether.

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