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From Field to Shelf: How Microwave-Assisted Extraction Techniques Foster an Integrated Green Approach

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Abstract

Microwave-assisted extraction of organic compounds from vegetal matrixes is a relatively young field of research. The exceptional results achievable at the laboratory scale by microwave-assisted extraction, like shorter extraction times, lower average temperatures, reduction of organic solvents use, higher yields and selectivity, as well as energy and cost saving, are not always accompanied by a successful scale up. Nevertheless, microwave-assisted techniques of extraction have been multiplying during last decades. In this framework, a deeper knowledge of microwave applicator design criteria is mandatory. This chapter starts from the basis of microwave heating and the relevant material properties involved in a successful microwave-assisted extraction application, to continue with a short overview on how such properties can be measured and used to optimize the experimental setup or a possible scale up of the process under investigation. A comprehensive review of recent applications of microwave-assisted extraction, applied to vegetal matrixes, is presented next. The chapter ends reviewing duplex treatments of vegetal matrixes for extraction purposes, where microwave heating is coupled to other techniques, like ultrasounds, and indicating new paths, where the recent advent of new microwave solid-state generators has led to better process control and higher yields and energy efficiency.

Keywords: extraction, LCA, modeling, green chemistry, process intensification, energy efficiency

1. Introduction

The concept and principles of green chemistry as formulated by Anastas and Warner [1], were used as a guide in order to promote the concept of sustainable development also in the

analytical procedures, particularly in the sample preparation techniques, leading to what is nowadays recognized as green analytical chemistry [2], that is characterized by the following 12 principles [3]:

i. Direct analytical techniques should be applied to avoid sample treatment.

ii. Minimal sample size and minimal number of samples are goals.

iii. In situ measurements should be performed.

iv. Integration of analytical processes and operations saves energy and reduces the use of reagents.

v. Automated and miniaturized methods should be selected.

vi. Derivatization should be avoided.

vii. Generation of a large volume of analytical waste should be avoided and proper management of analytical waste should be provided.

viii. Multi-analyte or multi-parameter methods are preferred versus methods using one analyte at a time.

ix. The use of energy should be minimized.

x. Reagents obtained from renewable source should be preferred.

xi. Toxic reagents should be eliminated or replaced.

xii. The safety of the operator should be increased.

The first and fundamental step at the basis of most of the analytical procedures is represented by the extraction of the target analyte, therefore green extraction procedures need to be implemented as well in any analytical procedure. This led to the so-called green extraction, and particularly by focusing on the extraction of natural compounds from matrices of vegetal origin, to the concept of green extraction of natural products which was for the first time defined by Chemat et al. [4] as "based on the discovery and design of extraction processes which will reduce energy consumption, allowing the use of alternative solvents and renewable natural products, as well as ensuring a safe and high quality extract/product". In order to pursue this highly desired goal, six principles were defined by the same researchers group as follows:

i. Innovation by selection of varieties and use of renewable plant resources.

ii. Use of alternative solvents and principally water and agro-solvents.

iii. Reduce energy consumption by energy recovery and using innovative technologies.

iv. Production of co-products instead of waste to include the bio- and agro-refining industry.

v. Reduce unit operations and favor safe, robust and controlled processes.

vi. Aim for a non-denatured and biodegradable extract without contaminants.

It immediately appeared clear, as the use of microwave heating rather than more conventional heating strategies, represented in all likelihood the most suitable solution in order to pursue,

at least, the above-mentioned principles (ii) and (iii) of green extraction of natural products. Water and most of the preferred agro-solvents (e.g. ethanol) are known to be excellent chemical environments to interact with the electromagnetic energy at the microwave frequencies [5, 6]. Moreover, at a more microscopic level, direct interaction of the cell structure with microwave energy, was reported to lead a completely different extraction mechanism, based on the synergistic action of heat and mass transfer, working in the same direction (i.e. at the opposite of what happens with conventional extraction techniques), as depicted in **Figure 1** [7].

All of these unique characteristics instantly gave rise to a wide variety of different extraction processes employing microwave energy, that started being developed and investigated, giving rise to what is nowadays known as microwave-assisted extraction (MAE) [8].

The persistent increase in the interest toward chemical compounds of natural origin is due to the great number of epidemiological investigations that continuously highlight the human health benefits deriving from a regular consumption of fruits and vegetables [9, 10]. Moreover further driving forces are the toxicity of some synthetic analogs, the cost of raw materials and manufacture, as well as the possibility to obtain significant amounts of such chemicals also from by-products deriving from food industries [11–13].

The most representative MAE techniques (both performed in the presence of an extracting solvent and in solvent-free conditions) will be accurately reviewed in Section 2. Despite the exceptional results achievable at the laboratory scale, like shorter extraction times, lower average temperatures, reduction of organic solvents use, higher yields and selectivity, as well as energy and cost saving, they are not always accompanied by a successful scale up. Therefore, a deeper understanding of how microwave extraction works and of the related microwave equipment design is required in order to better exploit the benefits deriving from dielectric
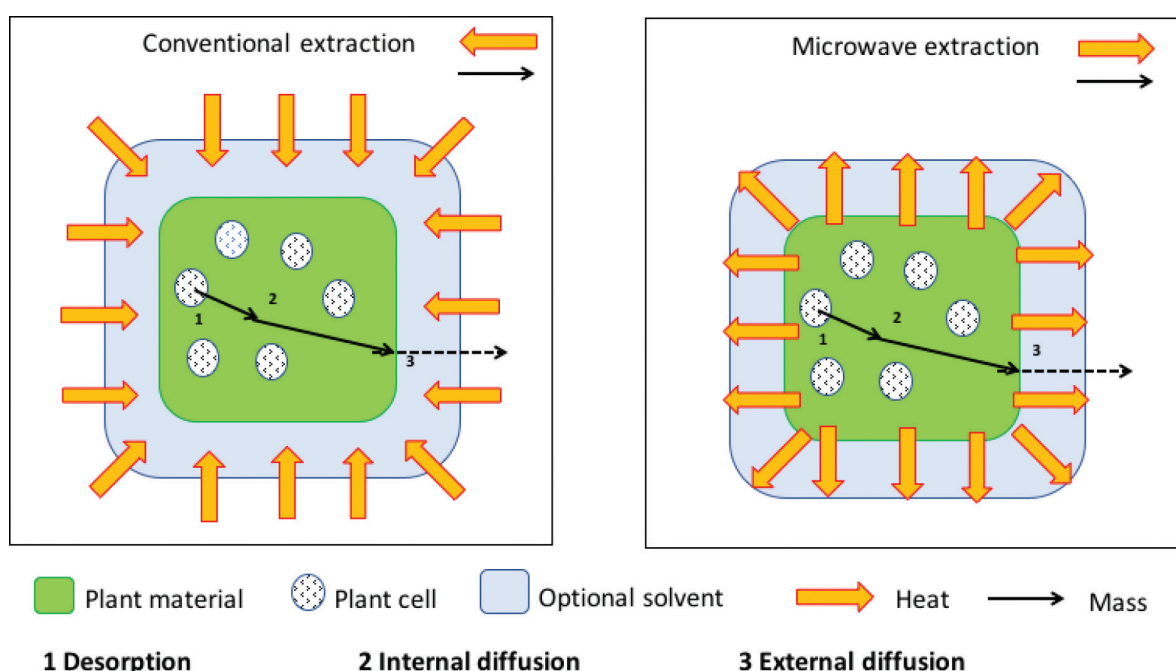

Figure 1. Heat and mass transfer mechanisms involved during conventional and microwave-assisted extraction. Adapted from [7].

heating of vegetal matrixes, with the ideal result of being able to achieve greener extraction processes, with almost no preparatory or separation steps, literally "from the field to the shelf". This is indeed the main focus of Section 3.

Section 4 is devoted to the environmental assessment evaluation of MAE with respect to traditional Soxhlet-based extraction, presenting a cradle to the grave life cycle assessment (LCA) study for the case of curcumin molecule extraction at a laboratory scale.

In Section 5, advantages deriving from the coupling of microwaves with further innovative techniques/extraction systems will be reviewed, highlighting their consequences in a process intensification perspective.

2. Microwave-assisted extraction (MAE): state of the art

Extraction of natural occurring chemical compounds is only one of the plenty food-processing technologies in which the use of microwave energy demonstrated significant advantages and unique possibilities [14]. The existing microwave-based techniques have been extensively reviewed [15–18], thus the present section is dedicated only at presenting the principles at the basis of the mostly employed ones, essentially presenting a major classification among those based on the use of a solvent and those operating in solvent-free conditions.

2.1. Microwave-assisted solvent extraction (MASE)

The first use of microwave energy for extraction purposes [19] was practically reported simultaneously with the first experiments performed in organic synthesis field which led to tremendous increase in yields and reduction in reaction times [20, 21]. Similarly, the use of water, methanol or a mixture of both solvents resulted in higher extraction yields, as a consequence of the polarity of the employed solvents, thus of their ability to efficiently be heated under a microwave field. Indeed, most of the solvents recommended by both green chemistry and green extraction principles can be efficiently heated when exposed to electromagnetic fields at the microwave frequencies. Therefore, necessarily the first use of microwave energy in the extraction of naturally occurring chemical compounds involved the use of solvent, leading to the group of experimental techniques called microwave-assisted solvent extraction (MASE) [22].

The extraction mechanism when using microwaves absorbing solvents is fundamentally similar with those of conventional extraction procedures. Nevertheless, the possibility of microwave to instantly and precisely furnish energy to the extraction mixture led first of all to advantages in terms of extraction times.

A further possibility is represented by the use of non-polar microwave-transparent solvents, like hexane and toluene, for example, even if not properly recommended in a green chemistry perspective [23]. In this latter case, the plant matrix needs to be wet in order to well couple with microwave energy. In doing so, the analytes of interest are then released in the solvent. The reported advantages of this latter approach in the green chemistry perspective are the typical less amount of solvent needed when compared to extraction technique based on a conventional mechanism.

Independently by the solvent employed, MASE techniques can be performed by employing both closed and open vessels, each of which possesses the proper advantages. When closed vessels are employed, temperature higher with respect to the boiling point of the used solvent can easily be reached, therefore typically reaching higher extraction yields. This could potentially be performed also by exploiting conventional heating strategies (e.g. by using an autoclave), but it would, however, need longer times to reach the selected extraction temperature.

In case of open vessels, the peculiar heating mechanism of microwaves together with its volumetric character is considered responsible for significant reduction in the processing time.

2.2. Solvent-free microwave extraction (SFME)

The unique possibility offered by microwave energy to directly interact with the plant cells containing the target chemicals together with the possibility to realize a heat transport occurring in the same direction as the mass transport (see **Figure 1**), led to the development of extraction technique characterized by the absence of any extraction solvent.

Indeed, solvent-free microwave extraction (SFME) techniques, invented in 2004 [24, 25] needs to be performed on fresh plant matrices, since the water contained in it is directly heated by interaction with microwaves, breaking the plant gland and releasing, for example, the essential oil. The water steam generating from the plant drives the essential oil recovered outside the microwave furnace, where a condenser is employed in order to cool down the distillate. The plants that have been efficiently exposed to SFME of essential oils have been reviewed in [26].

A further extraction technique employing microwave energy and solvent-free conditions is the so-called microwave hydrodiffusion and gravity (MHG) patented by Chemat et al. in 2008 [27]. In this configuration, the effect of the gravity is exploited synergically to the warming of the water (and other polar molecules) contained in the plant matrix, the latter leading to the disruption of the cell walls and the releasing of these substances (hydrodiffusion) outside the plant matrix. The extract is recovered at the bottom, outside the microwave furnace, where a refrigerator is placed.

3. Microwave reactor

Electromagnetic energy at the microwave frequencies can interact with matter according to its electric, dielectric and magnetic properties. In case of extractions from vegetal matrixes, usually the electric field component of the electromagnetic field is predominant in determining the heat generation inside the load, according to the simplified equation of the power density:

$$Pd \ = \ 2\pi f \, \varepsilon_0 \, \varepsilon'' \, |E|^2 \tag{1}$$

where Pd is the power density in W/m³, f is the frequency of the oscillating electromagnetic field in Hz, ε'' the imaginary part of the complex permittivity (loss factor) and $|E|$ is the

electric field strength, in V/m at a given position in space (i.e. for instance, inside the load). Power density, at its turn, determines how heat is generated and hence the temperature distribution inside a given load.

Limitedly to microwave-assisted extraction we can easily assert that it is possible to limit the heating preferably to the plant material, especially to the water therein contained, provided the proper choice of the optional solvent is made so that it has lower values of the loss factor. Otherwise, concurrent absorption of the microwaves occurs both from the plant material and the solvent. This can be used to achieve peculiar temperature distributions inside the reactor, as shown in **Figure 2**, where the early stages of heating in a single mode applicator (see next) of a load composed of a cylindrical shaped container (40 mm diameter), filled with solvent, containing dispersed spheres (2 mm radius) of plant material, 100 W power, 2450 MHz frequency, has been simulated. In this extremely simplified model, involving only the applicator, up to the movable short circuit (right end of color plots in **Figure 2**) the ambient temperature in the applicator has been set to 20°C and convection has been neglected, to better evidence the different heat generation pattern and relative temperature difference between solvent (permittivity of $2.41 - i \times 0.096$ for toluene and of $81 - i \times 12$ for water) and plant material (permittivity of $8 - i \times 3$).

The thermal plot sows, also another important phenomenon which can occur during microwave heating, depend on the load thermal properties, that is, the presence of overheated regions inside the load, with an external lower temperature (the so-called "inversion of temperature profiles", as it is opposite to what happens during conventional heating, where the maximum temperature, in absence of exothermal reactions, occurs at the load borders).

Another important aspect, shown by the thermal plots, is that microwave heating is not necessarily homogenous, and this can be ascribed once again to the electric field distribution, which, at its turn, depends also on the applicator geometry.

According to previous equation, another possibility would be changing the operating frequency, but this can be done provided the chosen frequency falls within the Industrial, Scientific and Medical (ISM) allowed ones, or proper shielding of possible emitted fields is provided. **Figure 3** shows an example of operating at higher frequency (5800 MHz) on the same load of **Figure 2**. At that frequency, the applicator used is no longer classifiable as a single mode one, as there is more than one mode inside the applicator (see next), and this is reflected into the electric field and temperature distribution.

Another possible option could be to change the dielectric properties of the load, but they are usually given by the nature of the plant material. However, additives like conducting or semiconducting particles could be added to modify the loss factor, but then subsequent separation would be needed.

Hence, it is evident that with a limited choice of available ISM frequencies and permittivity values given by the load nature, the proper control of the electric field strength inside the load becomes relevant. This can be accomplished by the proper design of the microwave applicator, that is, of the space where microwave-matter interaction occurs.
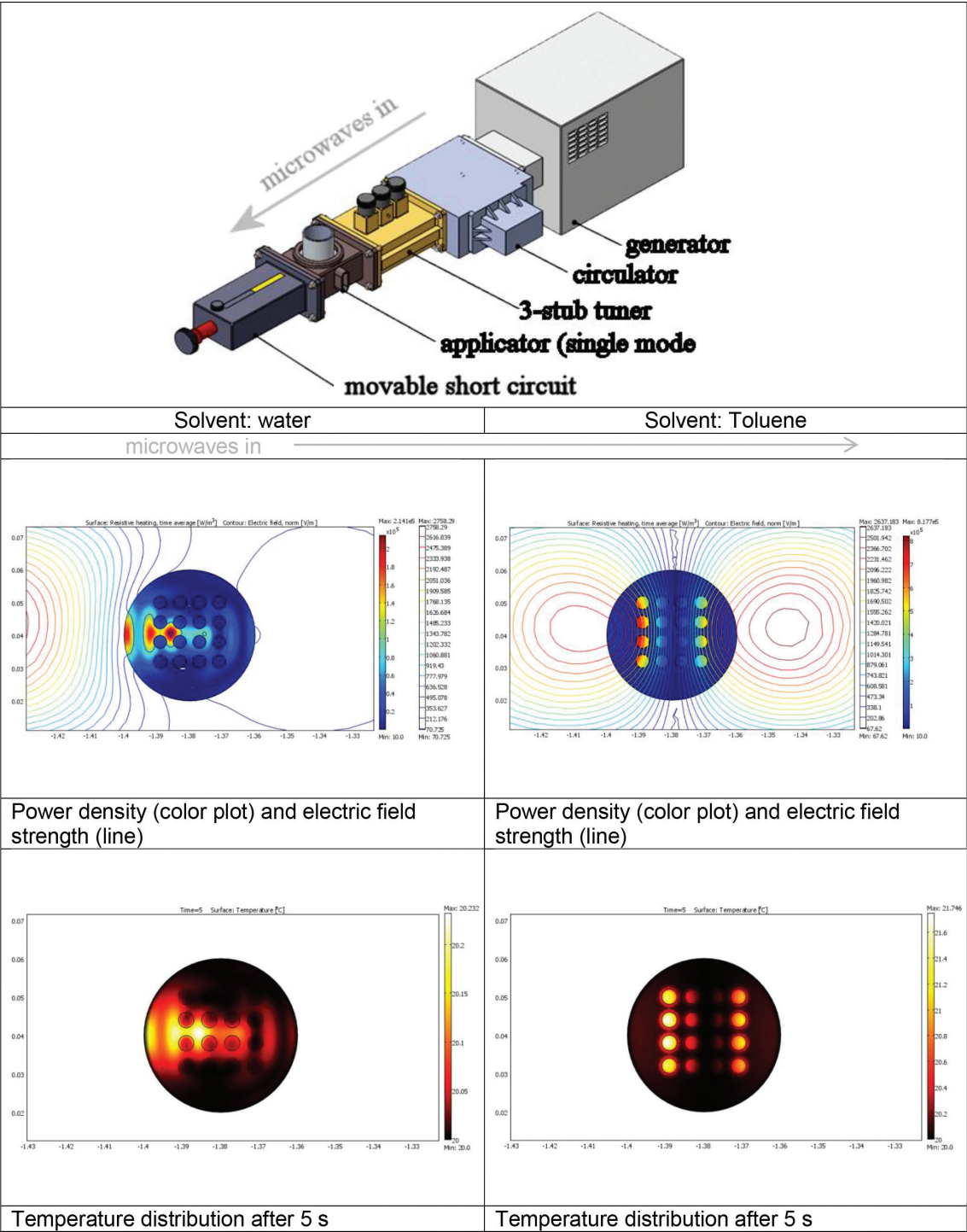
Figure 2. Power density, electric field strength and temperature distributions inside a microwave single mode applicator with a load constituted by plant material (depicted as the 16 spherical particles) and the extraction solvent (water or toluene).

3.1. Permittivity measurement techniques

In order to properly design (or select) a microwave applicator, the load permittivity should be known, as it affects both how heat is generated inside the load itself and the energy efficiency
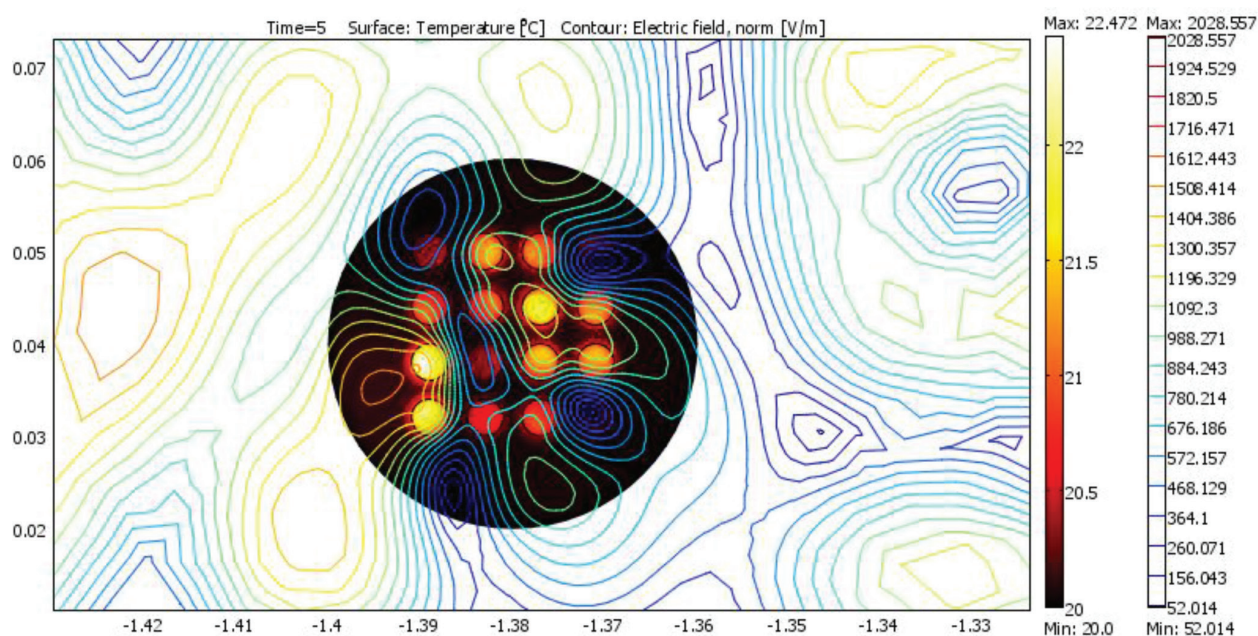
Figure 3. Temperature distribution and electric field strength inside the same microwave single mode applicator of **Figure 2**, in which the irradiating frequency was set to 5800 MHz. Again the 16 spherical particles represent the plant material and the surrounding environment is the solvent (toluene).

of the microwave applicator (i.e. the ratio between the power emitted from the microwave generator and the power transmitted to the load). As a matter of fact, every time an incident electromagnetic field passes through a different medium (for instance, from air, to solvent, to plant material), it is partly transmitted, partly absorbed and partly reflected. Hence, it can happen that only a small portion of the incident power is effectively absorbed and converted into heat, while the remaining could be reflected back to the generator, lowering the efficiency and requiring means to protect the generator from such reflections.

There is not a universal measuring technique to determine the permittivity of materials: it strictly depends on the frequency range of the measurement, on the state of the materials (liquid, solid, etc.) and on the expected values of permittivity.

Permittivity at the microwave frequencies is a complicated function which relates the electric flux density to the electric field in the medium [28]. It describes the interaction of a material in the presence of an electric field. It is a complex number and it accounts for different dispersion phenomena, like dipolar polarization, ionic polarization, interfacial polarization, etc. Its real part accounts for energy stored in the material, while the imaginary part, known also as loss factor, accounts for losses. The real part is sometimes indicated as dielectric constant, but this term is deprecated as it would suggest a "constant" behavior that does not correspond to the reality, given the strong dependence of permittivity on frequency. The ratio between the imaginary and real part of the complex permittivity is indicated as tanδ.

Depending on the expected values of permittivity and frequency, different techniques can be used to measure such parameter:

- Parallel plate: (sometimes called capacitance method) uses a parallel plate capacitor, with the material sandwiched in between (**Figure 4**). This method uses an impedance analyzer. It is typically used at the lower frequencies, below 1 GHz. Accuracy is typically ±1% for ε_r' and ±0.005 for tanδ.

- Coaxial probe: this method uses an open-ended coaxial probe, usually with a network analyzer (**Figure 5**). Cheaper measurement systems are nowadays available on the market [30]. It is the easiest method to use for liquids, or soft semi-solids, although very flat hard solids can be measured as well, provided an excellent contact (i.e. with no air gaps) is achieved. As a matter of fact, the assumption is that the material under testing is of "semi-infinite" thickness, homogenous, non-magnetic and isotropic. Typical ranges of frequency are from 200 MHz to 50GHz, with the possibility of continuous sweeping of frequency during the measurement (wide band). The method is usually not suitable for materials having a low (<0.1) tanδ or high ε_r' (>100). Accuracy is typically ±5% for ε_r' and ±0.05 for tanδ.

- Resonant cavity: this method uses a resonant cavity for the sample holder, and a network analyzer. Instead of using expensive network analyzers, a lower cost version uses a source (PLL Microwave Synthesizer), which generates the microwave stimulus, a set of directional couplers to separate reflected and transmitted signals, a microwave receiver based on the AD-8302 integrated circuit for magnitude and phase detection and a measurement probe, where the material to be measured is placed. A control unit (Microprocessor System) is connected through a USB link to a personal computer which includes all the required processing to determine dielectric properties from the measurements and to transform the outputs into the desired representation. The dielectric probe is designed as a microwave resonator where the interaction of the signals with the material takes place. In the embodiment shown in **Figure 6**, vials containing the material under test are introduced in the microwave resonator through a hole at the top of the probe. After sample insertion, the probe response (resonant frequency and quality factor) is shifted depending on the sample dielectric properties. From the measurement of the new response, the complex permittivity of the sample
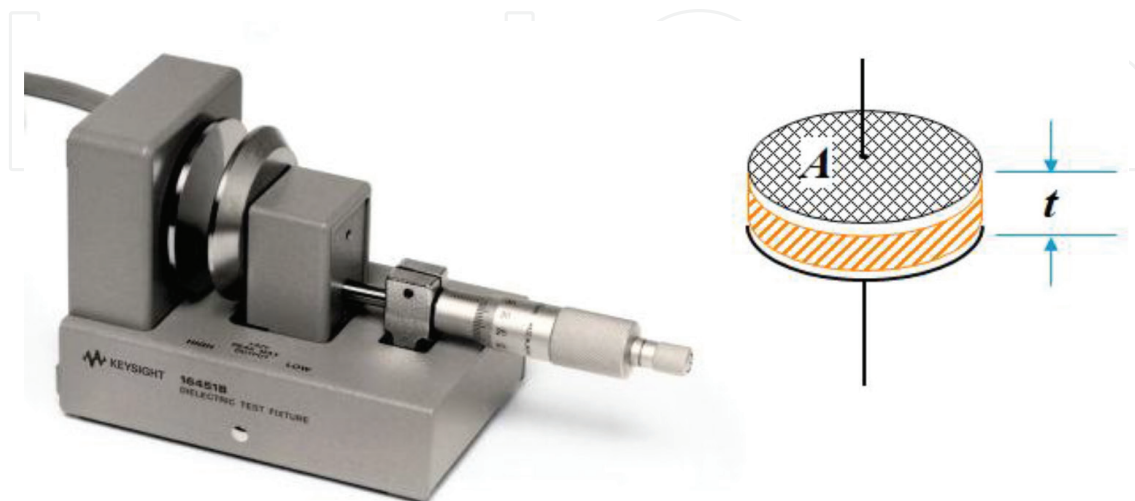

Figure 4. Parallel plate fixture and schematic functioning—Keysight technologies [29].
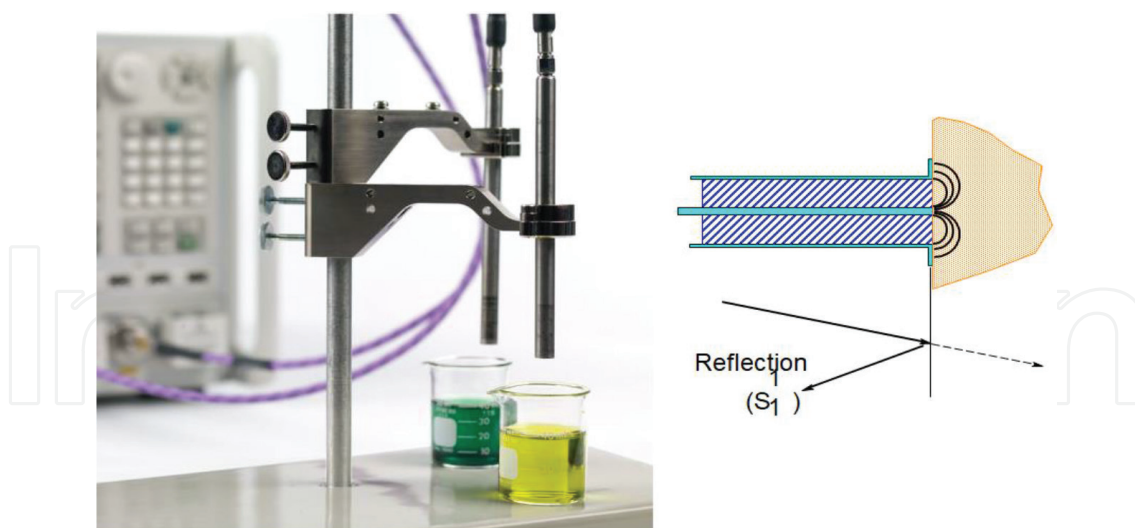
Figure 5. Coaxial probes and schematic functioning—Keysight technologies [29].

is calculated by using the electromagnetic model of the structure by a numerical procedure. This method has the best loss factor resolution. However, it is a narrow band method, giving information only at some specified frequencies, and requiring different cavities for different frequencies. However, as it is a differential measurement technique, no special calibration of the network analyzer is needed. It can be used also on thin films. In order to achieve precise measurements, the sample volume must be precisely known, and its dimensions should be chosen so that they do not shift excessively the resonant frequency of the cavity (out of cavity frequency range). This can occur also with small but highly lossy samples. Accuracy is typically ±1% for ε_r' and ±0.00001 for tanδ.

• Transmission Line: this method (**Figure 7**) can use a variety transmission lines for sample holders with a network analyzer (or equivalent). Lines can be coaxial, waveguide and even free space is considered a transmission line technique, in the "transmitter-receiver" configuration. It is useful for a broad frequency range, from the low microwave region to the mm-wave one. Sample preparation can result difficult, as samples must be precisely machined, and thus it is best indicated for hard machineable solids (liquids and powders must be contained), but it can be applied also to magnetic materials. This technique, based on the propagation trough the dielectric, needs large samples for low frequencies and small samples for high frequencies. Accuracy is typically ±2% for ε_r' and ±0.01 for tanδ.

3.2. Applicator design and selection

The choice or the proper design of an applicator is mandatory to determine the success of a microwave-assisted heat treatment. A typical sequence of actions leading to the development and industrialization of the chosen solution starts from very simple experimental tests, then moving to more complex questions (and answers) aimed at determining the effective yield and efficiency of the process and its correlated costs. An estimation of the costs of the whole sequence is difficult to be made in advance, except for the preliminary tests, which usually
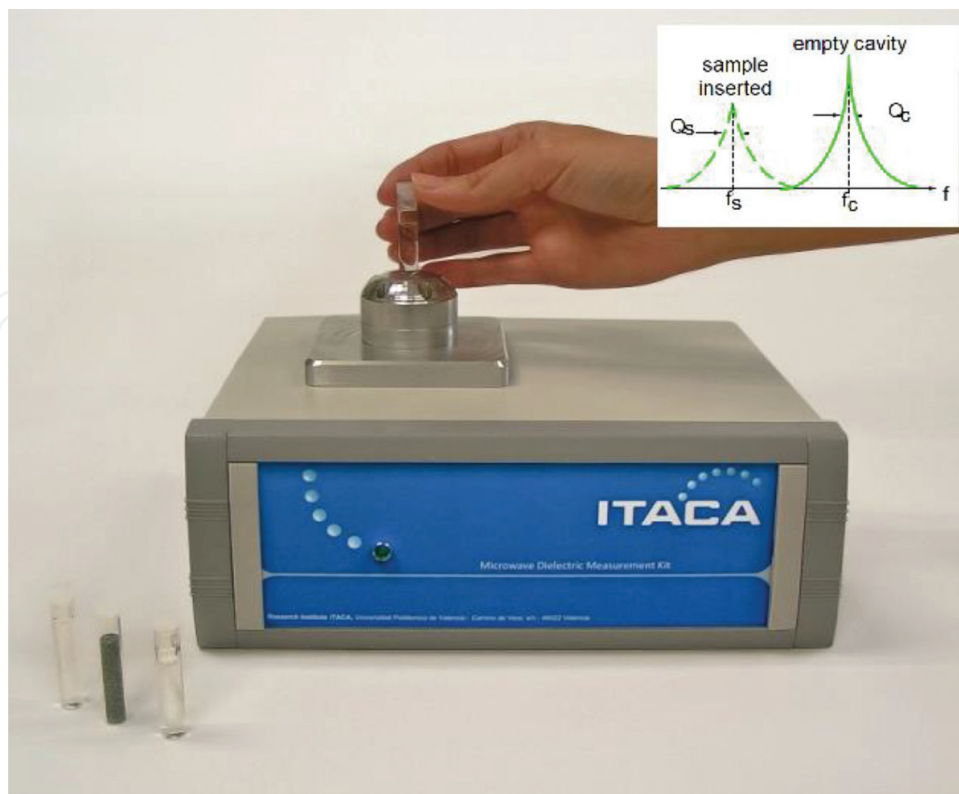
Figure 6. Resonant cavity and schematic functioning—ITACA [30].

require some thousands of euros. Sometimes, the preliminary tests costs can be quite high, depending on the amount and kind of material to be treated. The costs due to the subsequent steps (i.e. prototype and industrialization), as a rule of thumbs, increase dramatically as the sequence tends to the full industrialization of the investigated process.

The path leading to the full scale up, however, is not as straight as it could seem from the preliminary microwave heating tests results, and the proper applicator choice must take into account the characteristics of the process to be implemented.
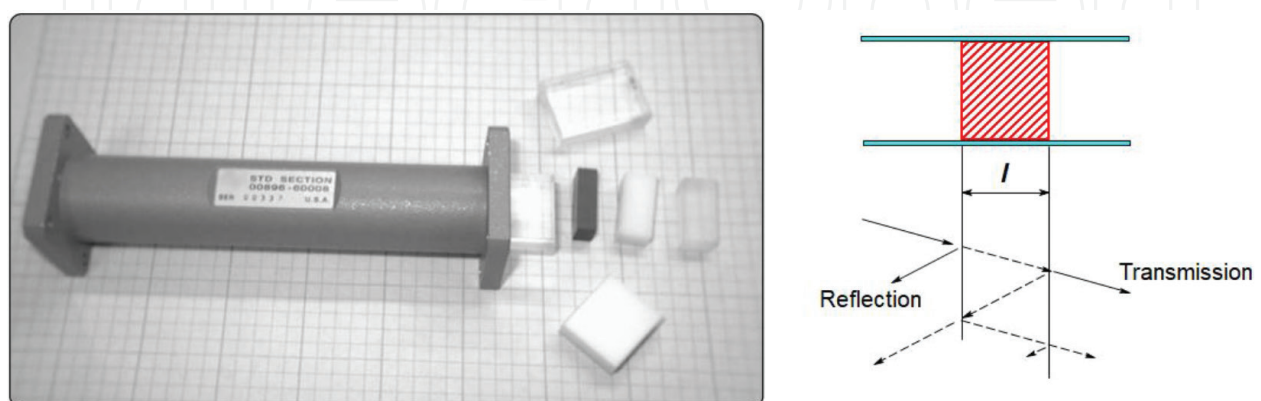

Figure 7. Transmission line and schematic functioning—Keysight technologies.

The process analysis is a typical tool to determine the mandatory process requirements, and the range of variability of some of the parameters involved. First of all, the process must be identified (drying, tempering, heating, melting, etc.), 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; etc.). It is important to know if the material will flow continuously or if the process is suitable for batch loading of the applicator. The properties of materials 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. The knowledge of temperature-dependent thermal, dielectric and electrical properties is mandatory to properly design a new applicator, especially if modeling software will be used.

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, like the dielectric and electric properties of the supports (vials, stirrers, belts, trays, etc.) or of the materials used to build the applicators wall, and the compliance to national or worldwide regulations on emission and safety. A comprehensive list of questions, whose answer should be known before even starting the design, is reported in [31].

The objectives of the microwave heating application should be also stated clearly, trying to understand whether homogenous heating or efficient heating is the key issue, or a tradeoff between the two. As a matter of facts, having a good energy efficiency does not necessarily means that homogenous heating can be achieved, as all the incident power could be dissipated in only small portions of the load.

The process analysis should then lead to the selection of the preferred applicator geometry, which could be summarized as follows:

- Single mode applicators: applicators where there is only one mode (i.e. the electromagnetic field pattern inside the applicator, generally quantified for rectangular applicators as the number of half wavelengths which can exist in each one of the three applicator dimensions). Such applicators are generally small and can reach extremely high electric field strengths (used also for plasma generation). Numerical solutions for the electromagnetic field distribution inside single mode applicators exist, but the presence of the perturbing load must be taken into account. Many single mode applicators are based on cylindrical or prismatic shapes, where one of the dimensions is of the order of magnitude of the microwave wavelength.

- Multimode applicators: applicators where multiple modes exist, each one with its own pattern and the resulting electromagnetic field is given by the superimposition of such modes, at the operating frequency of the microwave generator. They can have even large dimension and have room to install rotating dishes or mode stirrers, that is, reflecting movable surfaces used to perturb the electromagnetic field distribution, randomly, thus improving the homogeneity of heat generation. Domestic microwave ovens belong to this class of applicators.

- Radiant applicators: applicators which are antenna-like, that can be used to irradiate the load both in free space or used as feeds in closed applicators. In the second case, shielding is easier, while in the former case, care must be taken in order to avoid unwanted microwave leakage. If properly designed, they can guarantee a good heat generation homogeneity,

also on large dimensions. Usually they are less dependent on load position and nature compared to the resonant applicators, like the single mode ones.

Single mode applicators are the preferred choice in laboratory scale equipment, as they usually allow the repeatable positioning of the load, providing extremely high repeatability of results, which is not guaranteed in case of multi mode applicators, where load positioning is severely affecting the performances of the applicator itself.

Another problem rises when selecting the type (and number) of microwave sources required for a given application. Multimode applicators allow to install more than one source on the applicator walls, while single mode applicators are more difficult to be adapted for multi-feeds, given their generally smaller dimensions. Moreover, the source itself can affect the selection of the applicator, as the recent advent of solid-state microwave generators, as opposed to the more conventional magnetrons, is changing the way microwaves can be delivered to the load. This has been recently addressed in the AMPERE (Association for Microwave Power in Europe for Research and Education [32]) freely accessible newsletter: Trends in RF and Microwave Heating: SPECIAL ISSUE ON SOLID-STATE MICROWAVE HEATING [33].

Transitions from vacuum tubes to solid-state electronics had already occurred decades ago in the areas of communication, computers and control, and microwave heating is next, thanks to the availability of generators of higher and higher power (but still much lower than a high power magnetron, for the time being). The solid-state microwave heating technology offers several advantages over magnetrons, like frequency and phase variability and control, low input-voltage requirements, compactness, longer life span and reliability. On the other hand, solid-state generators are more sensitive to reflected power and they should be protected using expensive ferrite isolators. Their efficiency is currently similar to the magnetron's one, but their cost for unit power is much higher than magnetrons. However, the cost predictions are subjected to uncertainties, such as the market response to the new technology and the level of mass demand for such products.

Solid-state generators emit at one precise frequency, and not with a relatively large band, like magnetrons. They are more stable in frequency over time, hence they behave quite much as an ideal source which is used in modeling microwave heating. The possibility to control the relative phase and amplitude of multiple generators has opened new possibilities, like the localized overheating of certain load parts and the advent of "autotuning" algorithms which allow to achieve the maximum efficiency by controlling the emitted frequency, in real time.

After the type of applicator has been chosen (a choice which probably will have to be revised or modified as the investigation proceeds), the design phase can begin. The simplest way to obtain a suitable applicator, is to adapt something already existing, preferably if available on the market and not too expensive. This way, unfortunately, is not generally the one leading to the best results. Theoretically, there should be an applicator for each load (and loading conditions). Luckily, there are many different ways to obtain a "different" applicator starting from the same structure: movable parts, impedance matching devices, mode stirrers, they all help conferring a higher flexibility to a given applicator, allowing its use for a certain range of loads, with satisfactory performances.

For a new process or a new product, however, a completely new design is usually required. The design step can be conducted using modeling tools (computer simulations), or by subsequent trials and errors (this approach requires a high expertise and suits best the modification of existing applicators). Each one of the approaches is not definitive and presents some advantages and drawbacks. Considering, for instance, the design of a multi-feed applicator, the use of modeling software can lead to the best solution (and not only to the satisfactory one) regarding the feed positions for a certain loading condition, without having to rely solely on experience. On the other hand, if many ports are present, with no symmetry, the modeling can become quite time-demanding; moreover, models are always a simplification of the real device, and the difference between the modeled material and the real one can sometime lead to big differences between the modeling results and the real testing. For instance, permittivity measurements can be affected by large errors, especially when referring to high temperatures or in presence of phase changes.

Usually the information required for the model to be representative of reality are difficult to be obtained, and they should be expressed as a function of temperature. Coupling the electromagnetic field modeling and the thermal/fluid-dynamical one 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 material undergoes a pronounced dimensional change (shrinkage, foaming, etc.), a complete description of its deformation and its effects on the electromagnetic field distribution can be very difficult to obtain.

Thus, the two approaches seem separate, but combining the two is probably the best choice to design the applicator. Starting from the model, there is always something in the real world (a deformed welded zone, some deformation in handling, a slightly different material than the one modeled) which needs to be compensated. But, also, there is always some model which should be examined to understand how a variation of a certain component or geometry of one part of the applicator influences the overall applicator performance.

In the field of microwave-assisted extractions, there are some aspects of the applicator design which require a more detailed discussion.

One of these is the evaluation of the required installed power to achieve a certain productivity. The determination, or rather, the estimation of the required installed power, can be performed by two different means. The theoretical approach uses relatively simple equations (if some simplifying assumptions are made) to determine the power required to achieve the desired result (heating, drying, etc.), using the heat equation. Taking into account, at this preliminary design stage, which will be the applicator efficiency and the power losses due, for instance, to heat losses, which is almost impossible. The theoretical approach uses thermodynamics equations to calculate the power consumption, assuming that there is no difference of the energy balance between a conventional and a microwave-assisted process. This assumption applies to almost all cases, but some chemical reactions paths seem to be quite different under microwave irradiation, requiring low activation energies or occurring with faster kinetics, probably due to the localized overheating not detectable by conventional temperature measurement systems. However, since in these cases the theoretical approach would overestimate the installed power, it can still be considered satisfactory.

The experimental approach, instead, allows to determine an upper constraint to the power to be installed to achieve the desired result. However, it suffers from the fact that the data used for the installed power calculation are dependent on the type of applicator used and on the load itself, as shown in **Figures 8** and **9**, where the same applicator has been loaded with different amounts of load (**Figure 8**) and where different applicators have been used to process the same load (**Figure 9**).

In the case shown in **Figure 8**, it is evident a nonlinear dependence of the specific power consumption on the load mass, due to excessive power reflections in case of small loads, which then tends to become constant when the reflections are low enough not to become predominant. In the other case (**Figure 9**), the different electric field strength on the load, due to different applicators geometries and efficiency (affected by the reflection coefficient), is responsible for such differences in the specific energy consumption.

The experimental approach is definitely rough, but at least it allows to determine the maximum power which will be required by the process (it is the maximum since there is always an applicator able to perform the desired treatment using an amount of energy equal or less than the energy consumption recorded in the preliminary tests).

Moreover, when deciding the installed power, it is mandatory to consider that there could be some physical limits to the power density. The main limits concern the product's integrity, the completion of reactions and the prevention of arcs or plasma formation.

A particular care must be taken in case of thermal runaway. This phenomenon often occurs when the loss factor of the material increases as temperature increases: in this case, if a region of the material exposed, for instance, to higher electric field, reaches a temperature higher than the surrounding material, it tends to increase its temperature much more than the surroundings. As a matter of fact, the higher loss factor, if the electric field is constant, leads to a higher power density, and thus to an increased heat generation and temperature increase, which, at its turn, causes a further increase of the loss factor.

Another important aspect in designing or selecting a microwave applicator for microwave-assisted extraction is the tradeoff between heating homogeneity and energy efficiency. If the load can be moved, mixed, stirred, then it is easier to achieve more uniform heating [36] due to mass transfer, but if heating homogeneity has to rely solely on heat generation and transfer,
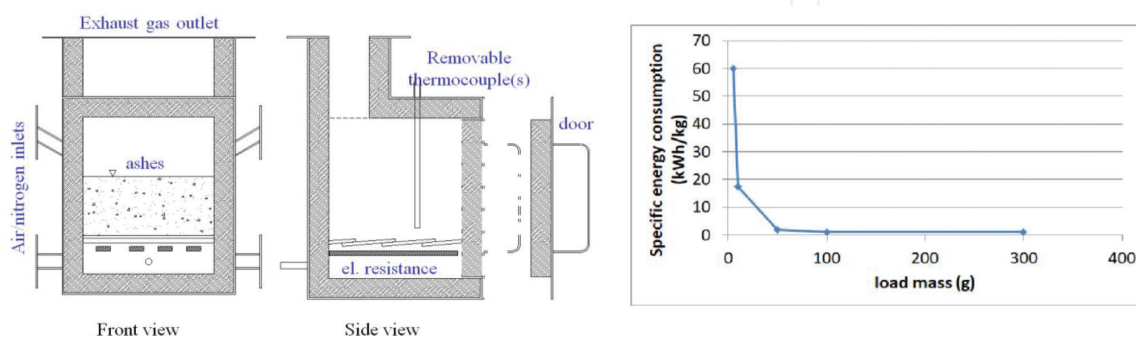

Figure 8. Specific energy consumption as a function of load mass during the 2.45 GHz microwave heating of ashes from lignite combustion power plants [34].
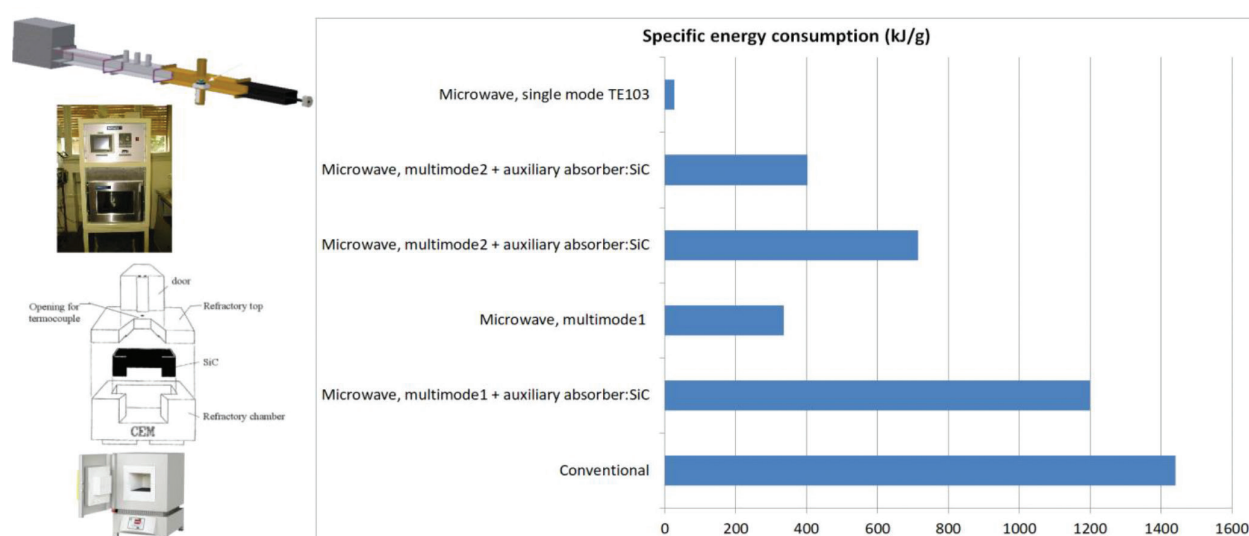
Figure 9. Specific energy consumption measured during the synthesis of the cobalt aluminate pigment in four different furnaces: conventional—Nannetti, Italy; Multimode1—CEM MAS (USA); Multimode2—Radatherm (Australia); single mode—self-assembled. Data from [35].

then the design becomes more critical and the use of multiple microwave sources is generally preferable. Control systems should be faster and robust, preferably adaptive, since the load usually is of natural origins, and thus it has a higher variability compared to pre-processed or synthetic starting materials.

Last but not least, since during pure (i.e. not hybrid) microwave processing heat is generated in the load and the surrounding environment remains colder, it is important also to provide sufficient thermal insulation to avoid heat losses. This is generally accomplished using insulating materials, but care must be taken when inserting them in the microwave applicator, as they could be (or become) good microwave absorbers, with the result of competing with the load in microwave power absorption and to fail as insulating materials. In this framework, another important component which is usually subjected to high electric field strength is the pressure window: in some installations, where it is required to separate the microwave generation zone from the microwave application one, like in vacuum processing, or even in case of pressurized environments, there is the need for a material able to transmit microwaves and to isolate the two environments. The requirement of materials for pressure windows are very demanding: they should withstand the load (pressure difference), with large safety coefficient, they must hold the pressure and being cleanable to avoid possible overheating of deposited particles of the load, they should present high transmission and low absorption or reflection of microwaves; they should be thermo-mechanically stable and chemical inert; they should withstand the process temperature without carbonizing, they should resist also to thermal shock and the thermal fatigue. Optionally, they should be optically transparent (common devices for arc detection are light sensors that are installed along the microwave transmission line), hence an opaque window would mask the occurrence of an arc. Moreover, for safety reasons, generally it is preferable to install two pressure windows (the second for safety in case of failure of the first one, but also for impedance matching purposes, that is, to minimize reflected power).

4. Is MAE really green?

Even if microwave-assisted extraction techniques are typically considered greener with respect to more conventional extraction processes mainly as a consequence of the enhanced heating rates which are obtainable with the use of microwaves and the resulting reduction in processing time, together with the reduction and sometimes elimination of any solvent, the accurate comparison between the environmental assessments of the different extraction procedures is surprisingly scarce in the scientific literature, making any trustworthy conclusions a sort of act of belief.

Recently, cradle to the grave environmental evaluations of laboratory scale conventional Soxhlet-based extraction as well as of microwave-assisted extraction were performed by applying the life cycle analysis (LCA) methodology [37]. This approach allows considering practically all the fundamentals damage categories that could have an impact on this particular process, thus including, for example, energy consumptions, abiotic resources depletion, transport, laboratory facilities, emissions as well as the disposal of waste [38].

Particularly, that study focused on the natural compound Curcumin that is actually under exponentially increasing investigation for its antioxidant, anti-inflammatory and anticancer properties [39]. In order to realize the most suitable comparison between conventional and MAE procedures, the evaluation of the total potential damage of both approaches was referred to the same mass unit or curcumin molecule (i.e. 1 kg). Both experiments were performed exploiting a similar configuration and the same extractive solvent (i.e. acetone), with the same solid to liquid ratio. In detail, conventional extraction was performed using a conventional Soxhlet apparatus reported on the left of **Figure 10**, while MAE was performed in a TE_{103} single mode applicator operating at the frequency of 2.45 GHz that is reported on the right of **Figure 10**.
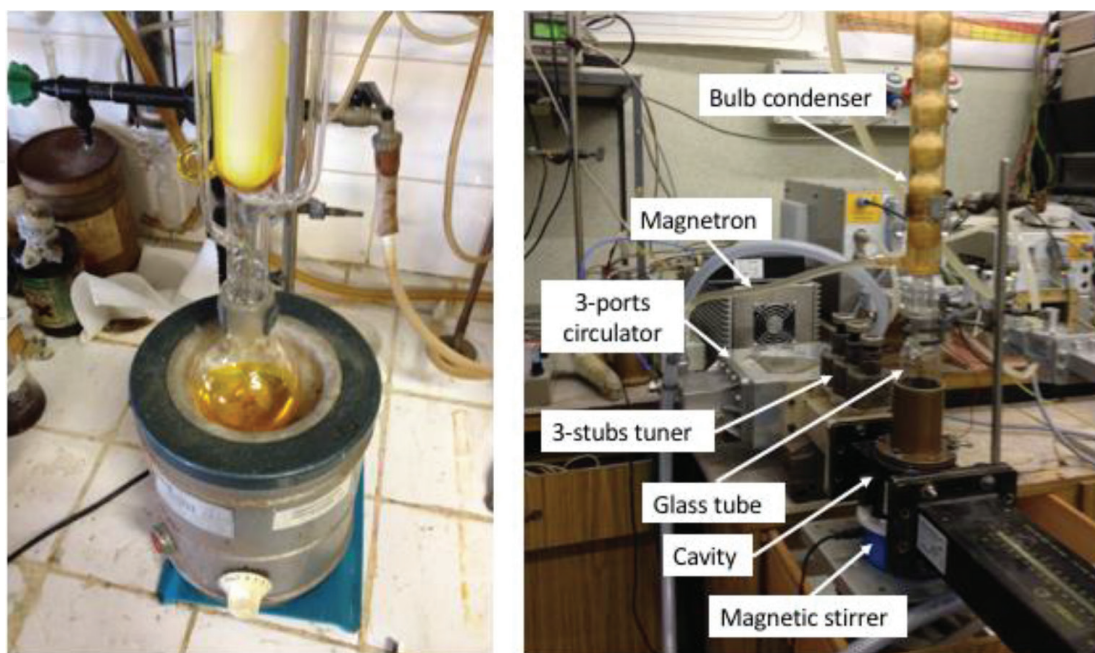

Figure 10. Conventional Soxhlet-based apparatus (left) and microwave-assisted extraction applicator (right).
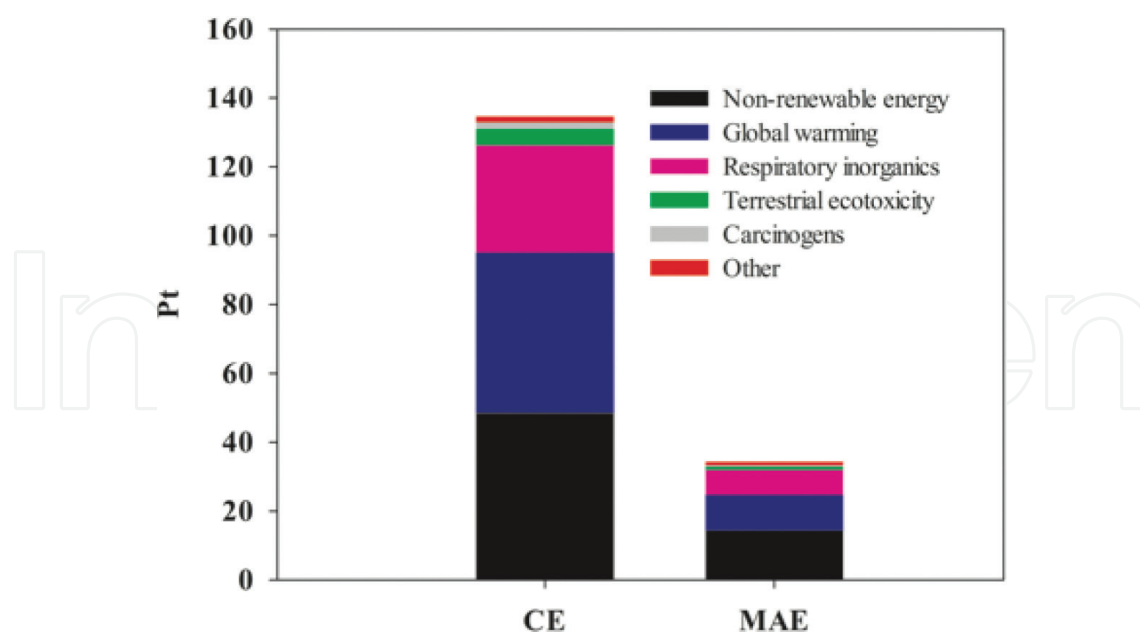
Figure 11. Comparative analysis of curcumin life cycle produced by conventional extraction (CE) and by MAE technique, at a laboratory scale. Adapted from [37].

Conventional Soxhlet extraction was prolonged for 24 h, while the use of microwave energy allowed obtaining comparable extraction yields in only 5 min of heating at reflux conditions. Single score evaluation results are reported in **Figure 11**, where Pt represents the eco-indicator points: the lower its value is the better that particular process will impact on the environment. Particularly, the conventional Soxhlet-based extraction resulted in 135 Pt, while the environmental damage associated with the proposed MAE resulted ca. 75% lower (i.e. 34.4 Pt), thus suggesting a greener character of microwaves with respect to conventional extraction procedures, at least in the considered lab-scale scenario. In both cases the three most impacting categories resulted "non-renewable energy", "global warming" and "respiratory inorganics", primarily as a consequence of consumptions of abiotic resources and emission of inorganic species, which are associated to the processes used to describe the electrical energy demand of the extraction techniques compared.

These results are worth to note also because they were obtained taking into account the poor efficiency a 2.45 GHz microwaves magnetron generators.

5. Coupling with further techniques

In an effort to continuously improve extraction efficiency and contemporary increase the green characteristics of microwave-assisted extraction in a process intensification (PI) perspective [40], several integrating technologies have recently been coupled with microwave heating [15]. The most widely employed ones are summarized in the next sub-sections.

5.1. Ultrasonic microwave-assisted extraction (UMAE)

Similar to MAE techniques, the use of ultrasounds (US) was also reported to tremendously increase extraction yields and reduce extraction time as well as the amounts of solvents needed, as a results of a combination of different extraction mechanisms like fragmentation, erosion, capillarity, detexturation and sonoporation [41].

Independently by the mechanism (or combination of different ones) which are responsible for a given extraction procedure, acoustic cavitation is at the basis of ultrasound-assisted extraction (UAE), since it lead to high shear forces, generation of microjets, shock waves and pressure variations.

Simultaneous irradiation of microwaves and ultrasounds for extraction purposes was firstly reported by Cravotto et al. [42] for the extraction of vegetable oils, resulting in higher yields in comparison with the sole use of microwave energy (employing both open and closed vessels). A dedicated PEEK horn was used in order to avoid arcing and further unwanted phenomena, into the multimode microwave cavity, as a consequence of the use of metallic horns. In all likelihood, the higher extraction yields typically reported when microwave energy is combined with ultrasounds is related to the further contribution offered by ultrasounds to the disruption of plant cell walls (manifested at lower frequencies), thus further enhancing the mass transfer from the plant to the extracting solvent.

A further peculiarity of US is the acceleration in the rehydratation and swelling of the plant, therefore, this can be exploited in the use of a combination of both microwaves and ultrasounds for the extraction from previously dried matrices.

5.2. MAE in ionic liquids (ILs)

The nature of ionic liquids (ILs) makes them suitable candidate solvents to efficiently couple with the electromagnetic energy at the microwave frequencies, mainly due to the ionic losses contribution to the loss factor value. Indeed, ILs are organic salts existing in the liquid state, constituted by an organic cation and an organic or inorganic anion [43].

Further properties (different from their chemical structure) of ILs that led to intensification of extraction processes from plant materials are their excellent solvating properties, a high thermal stability together with an easy to tailor viscosity. These properties significantly contributed to spread their utilization in extraction of both polar and non-polar natural compounds.

Despite the reported advantages, several concerns related to the use of ILs still exist. Indeed, even if considered green solvents as a consequence of their extremely low volatility, issues related to their toxicity and the high cost associated to their preparation remain.

5.3. Deep eutectic solvents (DESs)

In a continuous research for new green solvents for extraction purposes, deep eutectic solvents (DESs) were recently investigated for the extraction of bioactive compounds [44]. Even if they

can be seen as ILs analogs (since they possess similar physicochemical properties), they have been reported to be biodegradable and to possess lower toxicity and production costs.

DESs are systems composed by an eutectic mixture of Lewis or Brønsted acids and bases characterized by melting points much lower with respect to the individual constituents [45].

More recently natural deep eutectic solvents (NADESs) were developed by combining primary metabolites and bio-renewable starting materials, like sugars, amino acids and organic acids [46].

Similar to ILs, their chemical structure (or better in this case the chemical structure of the constituents the eutectic mixture) assure an excellent microwaves absorbing ability, thus making them suitable candidate solvents to be used in MAE as recently proposed, for the extraction of genistin, genistein and apigenin from pigeon pea roots [47]. Efficiency of DESs in coupling with microwave energy, was recently proved to lead to a greater (with respect to more conventional MW-coupling solvents like water and methanol) degree of disruption of cell walls [48].

5.4. Design of experiments (DoE)

A further tool that can significantly intensify every kind of extraction process (and not only), thus including also microwave-assisted procedures, is represented by design of experiments (DoE). DoE is a well-recognized collection of statistical and mathematical tools that has been widely exploited to improve and optimized extraction processes [49], as well as many other application fields in chemistry and materials science [50–53]. It relies in a statistical-based methodology used to systematically plan all the experiments to perform in order to obtain trustworthy and robust data without loosing extremely useful information on individual variables as well as interaction effects among different variables on the final goal of the study that could be, for example, the optimization of a certain MAE protocol. Indeed, traditionally the optimization of the extraction conditions for a certain technique and a certain matrix, are performed by the one-factor-at-time (OFAT) approach, that is extremely time and energy demanding and moreover, it could lead to the loss of the effects caused by several extraction parameters acting in combination. Therefore, in this perspective DoE approach can be easily considered an important tool to pursue a more rapid green process intensification development.

In a recent work [49], these statistical techniques were applied to the microwave-assisted extraction of phenolic compounds from *Juglans regia* L. fresh male flowers and unripe walnuts seeds, with the aim to investigate the role on the extraction efficiency of temperature, extraction time and number of microwaves heating cycles.

6. Conclusions

Microwave-assisted extraction (MAE) of naturally occurring chemical compounds is an extremely efficient extraction technique mainly as a consequence of the unique heating mechanism that is able to generate peculiar and otherwise impossible to reach extraction mechanisms. Different variants of MAE can be though according to the system matrix-solvent to be employed. Indeed,

the choice of the kind of MAE technique to be applied, cannot discern from a fundamental aspect to be considered, that is represented by the detailed knowledge of the dielectric properties of the matrix as well as the solvent, to be used. They represent important parameters to be used as input information for numerical simulation studies aimed at predict the microwave power distribution and the temperature evolution into the load during the extraction process.

Numerical simulation is fundamental also since it allows to rapidly select the optimal dimensions of the microwave cavity for a particular load (with particular dielectric properties).

In this view, it can be seen in a process intensification perspective.

In the same perspective, MAE has been shown to significantly benefit from the coupling of a different number of integrating technologies and tools.

However, it has been shown that although MAE can effectively and quantitatively considered greener with respect to conventional soxhlet-based extraction, for example, in the case of lab-scale extraction of curcumin molecule, general conclusions cannot be drawn, since case to case evaluations are mandatory. The use of cradle to the grave LCA evaluation is highly recommended to reach such assessments.

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