

REVIEW IN MICROWAVE HEATING APPLICATION IN PYROLYSIS

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Abstract:

The use of microwaves for heating is well established in society, being used in domestic and some industrial processes. However, there is potential for this technology to be introduced and applied to many other industrial heating processes, which offers unique advantages not attained with conventional heating. In this sense, microwave technology is being explored as one method to assist in waste management. The aim of this paper has been to provide the reader with a fundamental understanding of microwave-assisted pyrolysis processes. The unique internal phenomenon associated with microwave energy not only leads to significant savings in both energy consumption and process time during the pyrolysis process, but also allows for the development of chemical profiles of the volatiles, which enhances the overall quality of production. Both the influence of microwave heating on pyrolysis conditions (*distribution of temperature, heating rate and residence time of volatiles*) and raw materials have been discussed. Furthermore, special attention has been given to the microwave receptor, since it is an essential factor in any microwave heating process.

Key words : microwave ,heat application

1. Introduction

The use of microwaves for heating is well established in society, being used in domestic and some industrial processes. However, there is potential for this technology to be introduced and applied to many other industrial heating processes, which offers unique advantages not attained with conventional heating. In this sense, microwave technology is being explored as one method to assist in waste management. Currently, significant quantities of hazardous wastes are generated from a multitude of products and processes. The increase in both the quantity and of the diversity of waste production is now posing significant problems for their effective management. New technologies are being investigated to develop systems which shall support the safe handling, transportation, storage, disposal and destruction of the hazardous constituents of this waste. The recent interest in microwave technologies appears to offer the best solution to waste management, whereby a variety of microwave systems can be designed, developed and tailored to process many waste products. It is possible that microwave technologies shall provide for: (i) a reduction in waste volume, (ii) rapid heating, (iii) selective heating, (iv) enhanced chemical reactivity, (v) the ability to treat waste in-situ, (vi) rapid and flexible processes that can also be controlled remotely, (vii) ease of control, (viii) energy savings, (ix) overall cost effectiveness, (x) portability of equipment and processes, (xi) cleaner energy source compared to some more conventional systems, etc.

From existing processes for the harnessing of energy and raw materials from waste, thermo chemical conversion routes are suitable candidates for the application of microwave technology. One of the thermochemical processes which is rapidly gaining in importance in this field is pyrolysis. This process not only allows for higher energy recovery from the waste, but it also generates a wide spectrum of products. Hitherto, most published work on the pyrolysis process has dealt with conventional heating systems, although recent interest in microwave-assisted pyrolysis (MP) has highlighted its unique advantages, not within the scope of traditional methods.

The aim of this chapter is to emphasize the principles of MP and to show recent research on the application of this technology to waste treatment. As an introduction to the topic, a brief background on the pyrolysis process and the fundamentals of microwave irradiation as an energy source are presented.

2. General overview of the pyrolysis process

It is imperative that we make use of appropriate technologies for the recovery of resources from non-conventional sources such as waste, in order to ease the energy crisis and to slow environmental degradation which shall, in turn, reduce the percentage of land filled wastes. The choice of conversion process depends upon the type and quantity of waste feedstock, the desired form of energy (i.e., end use requirements), environmental standards, economic conditions and project specific factors. Many biochemical and thermo chemical processes have been researched for the purpose of waste upgrading (Faaij, 2006). While both methods of processing can be used to produce fuels and chemicals, thermochemical processing can be seen as being the easiest to adapt to current energy infrastructures, and to deal with the inherent diversity in some wastes.

Three different thermochemical conversion routes are found according to the oxygen content in the process: combustion (complete oxidation), gasification (partial oxidation) and pyrolysis (thermal degradation without oxygen). Among them, combustion (also called incineration) is the most established route in industry but this is also associated with the generation of carbon oxides, sulphur, nitrogen, chlorine products (dioxins and furans), volatile organic compounds, polycyclic aromatic hydrocarbons, dust, etc. On the contrary, gasification and pyrolysis offer the potential for greater efficiencies in energy production and less pollution. Although pyrolysis is still under development in the waste industry, this process has received special attention, not only as a primary process of combustion and gasification, but also as independent process leading to the production of energy-dense products with numerous uses. This makes the pyrolysis treatment process self-sufficient in terms of energy use, and also significantly reduces operating costs.

2.1 Principles of the pyrolysis process

The term “pyrolysis” is defined as a thermal degradation in the absence of oxygen, which converts a raw material into different reactive intermediate products: solid (char), liquid (heavy molecular weight compounds that condense when cooled down) and gaseous products (light molecular weight gases). The understanding of the pyrolysis process is a complicated one since many

factors have to be considered, such as raw material composition (see Section 2.2) and experimental conditions (see Section 2.3).

It is generally accepted that there are two possible steps in any pyrolysis process (Conesa et al., 1998): (i) *primary pyrolysis*, which comprises the devolatilization of the material where different reaction zones can appear corresponding to the thermal decomposition of the main constituents; and (ii) *secondary pyrolysis*, which covers the secondary decomposition reactions in the solid matrix, as well as secondary reactions between the volatiles release (homogeneous reactions), or between the volatiles and the carbonaceous residue (heterogeneous reactions). The first stage mainly involves dehydration, dehydrogenation, decarboxylation or decarbonilation reactions. The second comprises of processes such as cracking (thermal or catalytic), where heavy compounds further break into gases, or char is also converted into gases such as CO, CO₂, CH₄ and H₂ by reactions with gasifying agents, as well as partial oxidation, polymerization and condensation reactions.

2.2 Pyrolysis profiles

The diversity in chemical and physical properties of waste materials may imply significant differences between the corresponding pyrolysis profiles, since different levels of interactions between the components may occur. In this sense, an initial characterization of the material is of crucial importance to understand the pyrolysis dynamics, such as initial degradation temperature, conversion time, maximum volatile releasing rate and its corresponding temperature. Along with effective design and operation, each of the aforementioned represent the basic information required for full optimization of the process. Most of the studies on pyrolysis behaviour have been established for lignocellulosic materials, which comprise of a mixture of hemicellulose, cellulose, lignin and minor amounts of other organics. It is known that each of these components pyrolyze or degrade at different rates and by different mechanisms and pathways (Antal, 1983; Caballero et al., 1996; Branca & Di Blasi, 2003). While cellulose and hemicelluloses form mainly volatile products during pyrolysis due to the thermal cleavage of the sugar units, the lignin mainly forms char since it is not readily cleaved to lower molecular weight fragments. Wood, crops, agricultural and forestry residues, and sewage sludges are some of the main renewable energy resources available and subjected to pyrolysis processes, as are the biodegradable components of municipal solid waste (MSW) and commercial and industrial wastes.

There are different approaches that attempt to establish a correlation between the characteristics of the lignocellulosic materials and its final pyrolysis products. The first considers the biomass as a complex mixture of polymers consisting of carbon, hydrogen and oxygen (Couhert et al., 2009a). The second takes into account the functional groups presented (Savova et al., 2001), whilst the third is based on the biomass formed from cellulose, hemicelluloses and lignin (Couhert et al., 2009b). However, to date there is no model that predicts yield and composition of the final pyrolysis products, due largely to component interaction and the influence of mineral matter (Raveendran et al., 1995).

2.3 Pyrolysis technologies

Not only can raw material composition influence the yield and characteristics of the pyrolysis products, but the pyrolysis conditions can also modify the course of reactions and, therefore, strongly affect the yield and properties of products. Consideration should be taken of temperature, heating rate and residence time of vapours present in the reactor. Depending on these variables, the pyrolysis process can be divided into three subclasses: *slow*, *fast* and *flash pyrolysis* (see Table 1).

Pyrolysis technology	Residence time (s)	Heating rate (K / s)	Temperature (K)
Slow	450-550	0.1-1	550-950
Fast	0.5-10	10-200	850-1250
Flash	<0.5	>1000	1050-1300

Table 1. Range of the main operating parameters for pyrolysis processes (Elías, 2005)

Earlier literature generally equates pyrolysis to carbonization (*slow pyrolysis*), in which the principal product is a solid char (Antal & Gronli, 2003). Today, the term pyrolysis often describes processes in which oils are preferred products (Mohan et al., 2006). Hence *fast* and *flash pyrolysis* technologies have been considered as a good solution to convert materials to liquid fuel (Bridgwater & Peacocke, 2000). Nevertheless, pyrolysis as a means to convert a diversity of waste materials to combustible gas or syngas is receiving the increased attention which it deserves. In addition, microwave technology when applied to fast or

flash pyrolysis is suitable for producing higher gas yield with more syngas content (Domínguez et al., 2007; 2008; Dufour et al. 2009).

Some interventions in the operating parameters may induce and/or alter particular chemical reactions, resulting in different chemical profiles of the volatiles. Generally, increasing the pyrolysis temperature reduces the char yield and increases the gas yield (Domínguez et al., 2007; 2008). The liquid yield reaches a maximum value at intermediate temperatures and decreases at higher temperatures due to thermal cracking of heavy compounds. Long residence times of volatiles in reactor and high temperatures decrease tar production but increase char formation as a result of the extension of secondary reactions (Fernández et al., 2009). Higher heating rates favour a quick release of volatiles, modifying the solid residue structure with an increased yield of the liquid and gaseous fractions (Menéndez et al., 2007). Other variables that have to be considered in a pyrolysis process such as the reactor type (Bridgwater, 2003), sample size (Tsai et al., 2007), pressure (Cetin et al., 2005), etc., might also alter the final product distribution.

The optimization of each of the final pyrolysis products can also be done by catalytic means. The use of catalysts or additives to improve the yield or quality of pyrolysis gas or liquid fuels is still in its infancy. While there is fundamental work underway (Bridgwater, 1996; Williams & Nugranad, 2000; Wang et al., 2006), more research is necessary to explore the wide range of conventional and unconventional catalysts. Catalytic pyrolysis has been reported to be a productive means to increase gas yield by decreasing the amount of liquid, as well as positively affecting the quality of the organic composition of the oils – *in situ* upgrading (Domínguez et al., 2003).

Pyrolysis products

Pyrolysis process has the ability to provide three end products: gas, oil and char, which all have the potential to be refined further if required. The concentrations and characteristics of each product can vary considerably according to the feed characteristics and the operating conditions of the pyrolysis process. The main properties and applications of each pyrolysis fraction are presented below:

Solid fraction

Pyrolysis char is a carbonaceous residue mainly composed of elemental carbon originating from thermal decomposition of the organic components, unconverted organic compounds, e.g. solid additives, and even carbon nanoparticles produced in the gas phase secondary reactions. This carbonaceous

residue plays an important role in the pyrolysis process since it contains the mineral content of the original feed material, relevant to specific catalytic processes (Raveendran et al., 1995). The importance of the char cannot be understated as it may be involved as a reactive in heterogeneous or catalytic heterogeneous reactions (Menéndez et al., 2007).

The utilization of the char can vary considerably according to its characteristics. The main industrial uses of char can be summarized as follows: (i) as solid fuel for boilers which can be directly converted to pellets or mixed with other materials such as biomass, carbon, etc., to form the same, (ii) as feedstock for the production of activated carbon, (iii) as feedstock for making carbon nanofilaments, (iv) as feedstock for the gasification process to obtain hydrogen rich gas, (v) as feedstock for producing high surface area catalysts to be used in electrochemical capacitors, etc.

Liquid fraction

Pyrolysis oil is a complex mixture of several organic compounds which may be accompanied by inorganic species. In the case of biomass, the liquid or oil fraction (bio-oils) is found to be highly oxygenated and complex, chemically unstable and less miscible in conventional fuels (Demirbas, 2002). Thus, the liquid products still need to be upgraded by lowering the oxygen content and removing residues.

The oil obtained from pyrolysis can have the following industrial uses: (i) combustion fuel, (ii) used for power generation, (iii) production of chemicals and resins, (iv) transportation fuel, (v) production of anhydro-sugars like levoglucosan, (vi) as binder for pelletizing and briquetting combustible organic waste materials, (vii) bio-oil can be used as preservatives, e.g., wood preservatives, (viii) a suitable blend of a pyrolysis liquid with the diesel oil may be used as diesel engine fuels, (ix) bio-oils can be used in making adhesives, etc. Moreover, the oil may be stored and transported, and hence need not be used at the production site.

Gas fraction

The gas produced in a pyrolysis process is mainly composed of combustible gases, such as H₂, CO, C₂H₂, CH₄, C₂H₄, C₂H₆, etc. Other gases, such as CO₂ and pollutants (SO₂, NO_x), can also appear, although in lower concentrations.

The gas produced from pyrolysis can be used directly as a fuel in various energy applications, such as: (i) direct firing in boilers without the need for flue gas treatment, and

(ii) in gas turbines/engines associated with electricity generation. Pyrolysis gas containing significant amounts of hydrogen and carbon monoxide might be utilized in syngas applications. It is known that synthesis gas ($H_2 + CO$) having different H_2/CO molar ratios is suitable for different applications. For example, synthesis gas having a high H_2/CO molar ratio is desirable for producing hydrogen for ammonia synthesis. This ratio is increased further during the water-gas shift reaction for the removal of CO.

3. Background information on microwave heating

Since Percy Spencer accidentally discovered the possibility of cooking food with microwaves in the 1940s, research on microwave heating has continued unabated. Current investigations into the application of microwave technology across a number of fields may lead to significant savings in both energy consumption and process time. Moreover, the unique internal heating phenomenon associated with microwave energy can enhance overall production quality, allowing for the development of new end products and processes that cannot be realised using conventional methods.

3.1 Fundamentals of microwave heating

Microwaves lie between infrared radiation and radio waves in the region of the electromagnetic spectrum. More specifically, they are defined as those waves with wavelengths between 0.001 and 1 m, which correspond to frequencies between 300 and

0.3 GHz. Within this portion of the electromagnetic spectrum there are frequencies that are used for cellular phones, radar, and television satellite communications (van Loock, 2006). For microwave heating, two frequencies reserved by the Federal Communications Commission (FCC) for industrial, scientific and medical (ISM) purposes are commonly used, which are 0.915 and 2.45 GHz.

As all electromagnetic waves, microwaves consist of electric and magnetic field components, both perpendicular to each other. Generally, there are three qualitative ways in which a material may be categorized with respect to

its interaction with the electric field component of the microwave field: (i) insulators, where microwaves pass through without any losses (transparent), (ii) conductors, where microwaves are reflected and cannot penetrate, and (iii) absorbers. Materials that absorb microwave radiation are called dielectrics, thus, microwave heating is also referred to as dielectric heating.

There exist a number of mechanisms that contribute to the dielectric response of materials (Thostenson & Chou, 1999). These include electronic polarization, atomic polarization, ionic conduction, dipole (orientation) polarization, and interfacial or Maxwell-Wagner polarization mechanisms. At microwave frequencies, only dipole and Maxwell-Wagner polarizations result in the transfer of electromagnetic energy to thermal energy (Mijovic & Wijaya, 1990). In polar organic-solvent systems at non-extreme temperatures, the dipolar polarization mechanism accounts for the majority of the microwave heating effect, while in some carbon-based materials is the interfacial polarization the principal head. With respect to the former, dipoles may be a natural feature of the dielectric or they may be induced (Kelly & Rowson, 1995). Distortion of the electron cloud around non-polar molecules or atoms through the presence of an external electric field can induce temporary dipoles. The dipoles in the material exposed to the alternating electromagnetic field realign themselves approximately 2.5 billion times per second (for a microwave frequency of 2.45 GHz). This movement results in rotation of the dipoles, and energy is dissipated as heat from internal resistance to the rotation. On the other hand, the Maxwell-Wagner polarization occurs at the boundary of two materials with different dielectric properties, or in dielectric solid materials with charged particles which are free to move in a delimited region of the material, such as π -electrons in carbon materials (Zlotorzynski, 1995). When the charged particles cannot

couple to the changes of phase of the electric field, the accumulation of charge at the material interface is produced and energy is dissipated in the form of heat due to the so-called Maxwell-Wagner effect (Zlotorzynski, 1995). The interaction of microwaves with metals or metal powder (Marken et al., 2006) may further contribute to the energy absorption effect. The response to an applied electric field is dependent on the dielectric properties of the material (Thostenson & Chou, 1999). The polarization takes place when the effective current in the irradiated sample is out of phase with that of the applied field by a difference (termed δ). This difference defines the tangent loss factor, $\tan \delta$, often named the dissipation factor or the dielectric loss tangent. The word "loss" refers to the input microwave energy that is lost to the sample by

being dissipated as heat. Thus, microwave energy is not transferred primarily by convection or by conduction, as with conventional heating, but by dielectric loss. The tangent loss factor is expressed as the quotient, $\tan \delta = \epsilon''/\epsilon'$, where ϵ'' is the dielectric loss factor, indicative of the efficiency with which electromagnetic radiation is converted to heat, and ϵ' is the dielectric constant describing the ability of molecules to be polarized by the electric field. A high value for $\tan \delta$ indicates a high susceptibility to microwave energy. Because the dielectric properties govern the ability of materials to heat in microwave fields, the measurement of these properties as a function of temperature, frequency, or other relevant parameters (moisture content, density, material geometry, etc.) is important (Meredith, 1998). Many authors (Carpenter, 1991; Tinga, 1992; Guillon, 1994) have reviewed different techniques for dielectric property measurements at microwave frequencies. Unfortunately, $\tan \delta$ values are not easily found in the literature, and for most common solvents have only been determined at room temperature (Gabriel et al., 1998). Furthermore, the loss tangent of the material depends on the relaxation times of the molecules in the material, which, in turn, depends on the nature of the functional groups and the volume of the molecule (Gabriel et al., 1998). But not only microwave heating is a function of $\tan \delta$, but also other parameters related to the material, such as ionic strength, specific heat capacity, thermal conductivity and emissivity, and related to the applied field and the operating conditions have to be taken into account as well (Mingos & Baghurst, 1991).

ungrounded or exposed. At the tip of a grounded junction probe, the thermocouple wires are physically attached to the inside of the probe wall. This results in good heat transfer from the outside, through the probe wall to the thermocouple junction. In an ungrounded

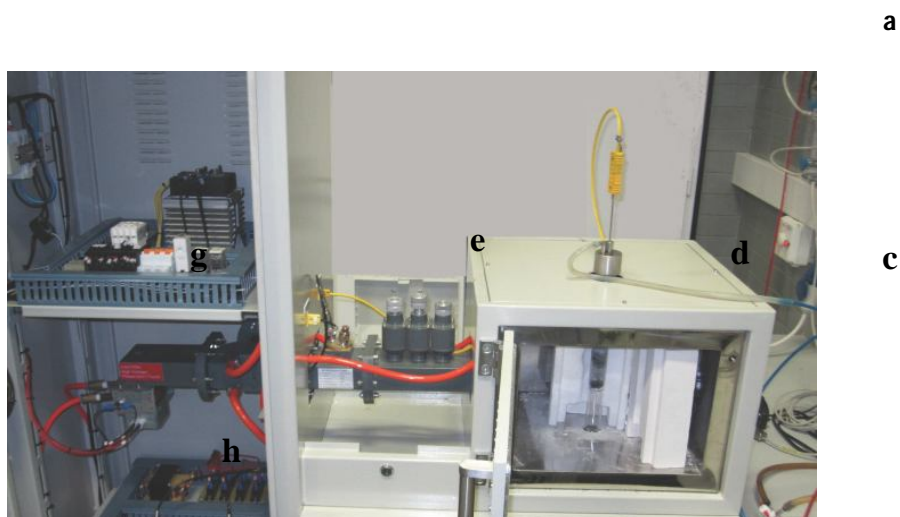


Fig. 1. Photographs of singlemode (upper) and multimode (lower) microwave ovens at INCAR (www.incar.csic.es) showing: a) magnetron; b) waveguide; c) circulator with reflected power meter; d) tuning screws; e) resonant cavity; f) reactor; g) terminator with transmitted power meter; h) infrared optical pyrometer; i) thermocouple; and j) insulating material probe, the thermocouple junction is detached from the probe wall. Response time is slower than the grounded style, but the ungrounded offers electrical isolation, and therefore, no interaction with the electromagnetic field. Therefore, ungrounded probes are usually employed under microwave radiation.

However, accurate measurement of the evolution of temperature is difficult due to inherent difficulties involved in measuring this variable in microwave devices (Menéndez et al., 1999). On one hand, the way in which temperature is monitored is dependent upon the type of temperature sensor. While infrared optical pyrometers give a temperature measurement by default, the thermocouple probes provide an over-temperature (Cloete et al, 2001). The combination of optical pyrometers together with thermocouple probes may alleviate the intrinsic error in both instruments. On the other hand, because not all materials or substances are similar microwave absorbers, it is accepted that temperature measurement corresponds to the average temperature of the bulk. When heating non-polar substances, the temperature registered on the probe will in fact be that of the

probe itself and not of the specimen. In this respect it is particularly difficult to determine the temperature in nonwater-soluble substances. Moreover, it is not always easy to determine the correct temperature for a substance during microwaving, even if it is soluble in water. As long as the load of water is large and the specimen not too small, the temperature of the water coincides with that of the substance. However, when specimens take the form of small droplets, these can be evaporated easily giving sudden unexpected temperature rises. Examples of accurate temperature measurements may be seen in the articles of Feirabend et al. (1991; 1992).

On the other hand, the temperature-feedback control should be capable of a fast reduction of power in cases where either the exothermic reaction energy becomes pronounced, or when the dissipation factor increases rapidly, to avoid thermal runaways. Most of the microwave ovens work at full power, and the power levels commonly fluctuate as a result of the patterns-of-switching of on-off cycles (Mingos & Baghurst, 1991). However, other models can set the power required, emitting only part of the full power, and thus, reaching a better control of temperature.

4. Approach to the microwave-assisted pyrolysis (MP)

Microwave heating is emerging as one of the most attractive alternative technologies in the pyrolysis process. MP not only overcomes the disadvantages of conventional pyrolysis (CP) methods such as slow heating and necessity of feedstock shredding, but also improves the quality of final pyrolysis products. At the same time it significantly saves processing time and energy. However, there are several major limitations which are preventing this technology from being widely employed in the waste manufacturing industry. These include the absence of sufficient data to quantify the dielectric properties of the treated waste streams, the need of a multi-disciplinary approach to design and develop the related conversion units, and the uncertainty about the actual costs.

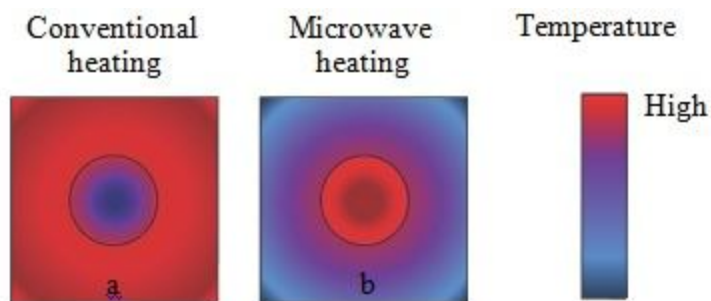
Material properties and operating conditions are the main factors affecting any pyrolysis process, since they determine the characteristics and yields of the final products. However, when microwaves are used as heating method in the pyrolysis process, one must consider additional complications which may affect the heat, mass transportation mechanism and chemical reactions. In order to examine further the novel conditions achieved through MP, in this section the more traditional approach to the pyrolysis process is used as a reference point.

Role of microwave heating on the pyrolysis conditions

When microwave heating is applied to a pyrolysis process, novel conditions in the temperature distribution, the heating rate and the residence time of volatiles are observed when compared with those achieved by conventional heating. Therefore, different chemical profiles of the volatiles in both heating systems are obtained allowing for modification of final pyrolysis products.

Conventional heating means that heat is transferred from the surface towards the center of

the material by convection, conduction and radiation. On the contrary, microwave heating represents the transfer of electromagnetic energy to thermal energy. Because microwaves can penetrate materials and deposit energy, heat can be generated throughout the volume of the material, rather than from an external source (volumetric heating). Therefore, microwave heating is energy conversion rather than heat transfer. As a result, opposite thermal gradients, i.e. temperature distribution, are found in both heating systems (see Fig.2). In microwave heating the material is at higher temperature than the surrounding area, unlike conventional heating where it is necessary that the conventional furnace cavity reach the operating temperature, to begin heating the material. Consequently, microwave heating favours the reactions involving the solid material, e.g. devolatilization or heterogeneous reactions (Zhang & Hayward, 2006), and conventional heating improves the reactions that take place in surroundings, such as homogeneous reactions in the gas-phase. Additionally, the lower temperatures in the microwave cavity can be useful to avoid undesirable reactions and condense the final pyrolysis vapours in this area.



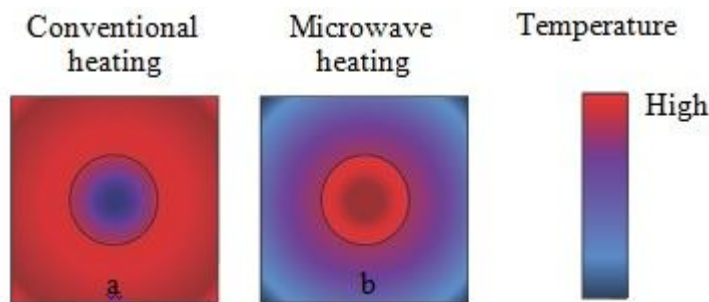


Fig. 2. Quality comparison of temperature gradient within samples heated by (a) conventional heating and (b) microwave dielectric heating. While the circles represent the sample, the squares correspond to the cavity used in both heating systems

From the different thermal gradients, it can be assumed that there are differences in final yields and composition of the pyrolysis products under both heating systems. Several authors (Menéndez et al., 2004; Domínguez et al., 2007) have observed greater gas yield and lesser carbonaceous residue in the MP experiments of different wastes, which demonstrate the efficiency of microwaves in carrying out heterogeneous reactions. Some of the heterogeneous reactions observed in pyrolysis processes, such as gasification reactions with CO_2 or H_2O , have been executed individually at different temperatures under both heating systems (Menéndez et al., 2007). The conversions in MW are always higher than those observed in conventional heating at any temperature. Additionally, the differences between both heating methods seem to be reduced with the temperature increase, which points to the higher efficiency of microwave heating at lower temperatures. Other heterogeneous reactions that can be found in a pyrolysis process are those in which the solid char not only act as a reactive, but also as a catalyst owing to the carbonaceous or metallic active centres located in the surface. These provide a catalytic effect for specific reactions, such as the methane decomposition reaction. This reaction has also been proved separately to give better conversion under microwave heating (Domínguez et al., 2008).

The differing performance between conventional and microwave heating is also translated

into differential heating rates of the material. Microwave heating reveals higher heating rates due to the fact that microwave energy is delivered directly into the material through molecular interaction with the electromagnetic field, and no time is wasted in heating the surrounding area. Therefore, significant savings of time and energy are achieved in MP, although other effects can also be deduced affecting the volatiles profiles. Generally, high heating rates improve the devolatilization of the material reducing the conversion times. The heating rate also has an influence on the residence time of volatiles, whose flow occurs from the more internal hot zones towards the external cold regions of the sample. The higher heating rate, the shorter residence time, and the faster the volatiles arrive to the external cold regions which, in turn, reduces the activity of secondary reactions of vapour- phase products. This results in high yields of liquid and reduced deposition of refractory condensable material on the char's internal surface (Allan et al., 1980).

In the case of materials with significant moisture content, like most biomass feedstocks, MP offers a different paradigm in particle heating where the electromagnetic field penetrates the solid, and interacts directly with dipoles in the chemical structure. Due to the high affinity of water molecules with microwaves, moisture content within a given biomass particle is selectively targeted by incidental microwaves. Microwaves vaporize moisture in the depth of the particle, prior to volatilizing organic content. The steam generated is rapidly released into the surrounding area, not only sweeping volatiles, but also creating preferential channels in the carbonaceous solid that increase its porosity. This, in turn, favours the release of volatiles at low temperatures, and hence, its reaction with the steam produced (Minkova et al., 2001) which leads to partial oxidation and formation of permanent gases (H_2 , CO, CH_4 , CO_2).

Role of microwave heating on the material

In terms of its physical form (structural arrangements, thermal conductivity and specific heat) and chemical characteristics (organic and inorganic composition), the efficiency of MP processes depends greatly on the nature of the material being processed. Hence, not all materials present the same dielectric behaviour, and therefore, not all materials are similarly heated by microwaves. In fact, there are generally three qualitative ways in which a material may be categorized with respect to its interaction with the microwave field (insulators, conductors and absorbers), as mentioned in Section 3.1. However, a fourth type of interaction is that of a mixed absorber. This type of interaction is observed in

composite or multi-phase materials where one of the phases is a high-loss material while the other is a low-loss material. Mixed absorbers take advantage of one of the most significant characteristics of microwave processing - that of selective heating. The microwaves are absorbed by the component that has high dielectric loss while passing through the low loss material with little drop in energy. In some processes and products, the heating of a specific component (whilst leaving the surrounding material relatively unaffected) would be of great advantage (Dernovsek et al., 2001). Microwave may also be able to initiate chemical reactions not possible in conventional processing through selective heating of reactants. Thus, new materials may be created.

Normally, waste materials have poor dielectric properties, being unable to absorb enough microwave energy to achieve the temperature necessary for pyrolysis. The amount of water present contributes to heating at insufficient temperatures at which it is merely possible to dry the material. Consequently, the use of a “microwave receptor”, also called microwave- absorbing dopant (Robinson et al., 2010) or antenna (Hussain et al., 2010), is necessary. Different types of microwave receptors can be used, such as inorganic matter (Monsef- Mirzai et al., 1995) or substances with conduction electrons, e.g. activated carbon, char, graphite, etc (Chanaa et al., 1994; El harfi et al., 2000).

Influence of the microwave receptor on the pyrolysis conditions

The microwave receptor is perhaps the primary factor in the MP, directly affecting pyrolysis conditions, which mainly include temperature profiles and heating rate. Maximum temperature is primarily determined by the dielectric properties of the receptor, while heating rate is likely to be dependant upon the chemical composition of the material and, to a much lesser extent, by its physical structure. Numerous studies have shown that the temperature evolution of a material during MP could be divided in four stages (Zhao et al., 2010): stage I, the heating of the sample could be explained by the dielectric relaxation

phenomenon of water molecules, which is responsible for the initial heating of the sample; stage II, the temperature reaches a plateau before attaining the pyrolysis temperature, which significantly depends upon the use of receptor; stage III, the temperature rises rapidly corresponding to an acute loss of mass, and normally a flex point appears; and stage IV, the thermal equilibrium is achieved, which depends on the receptor. Changes in the microwave receptor

can alter the conductivity and permittivity of the sample, and hence the strength of the electric fields in the sample and the power dissipated in it. Meanwhile, a phenomenon known as “thermal runaway” can also occur, where the microwave energy is concentrated in the receptor, whose rate of absorption (referred to as the thermal absorptivity) increases with temperature, leading to an exponential increase in heating rate.

During the course of the MP, it is important to emphasize that not only the receptor will absorb microwave energy to produce heat; the solid residue produced in the process also contributes to the final pyrolysis temperature. In Fig. 3, a simple sketch shows the different stages during the MP of a mixture of materials/microwave receptors.

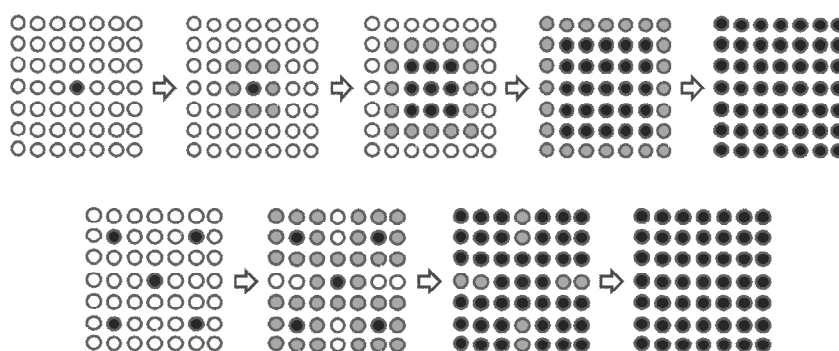


Fig. 3. Phases during MP of mixtures material particles (white circles)/microwave receptors (black circles), where it is shown the creation of first, second, third, etc. generations of microwave receptors (gray circles)

In the initial phase, only the added microwave receptor is able to absorb microwaves and produce heat, which allows the nearby particles of the materials to be heated by conventional methods (convection, conduction and radiation). Then, the removal of volatiles produces char, which will act as a microwave absorber, so that the pyrolysis process can then be sustained. Depending on the dispersal of the initial microwave receptor, first, second, third, etc. generations of microwave receptors may be found. The lower the number of generations, the better the dispersal of the added microwave receptor. This sustains higher temperature uniformity and faster heating rates, improving the pyrolysis rate of the material.

Although the majority of studies into MP consider microwave receptors to be an essential

part of the process, more recent investigations have proved that there is a MP of biomass which does not require the addition of microwave absorbers. Robinson et al. (2010) have confirmed that MP can be achieved without the use of carbon-rich dopants, and that the heating of water alone can be used to induce the pyrolysis of wood.

Influence of the microwave receptor on the pyrolysis products

The incorporation of receptors in the material can also be used to alter or tailor the products of pyrolysis. Apart from its chemical composition, its dielectric properties, which determine the heating mechanism, have to be considered, because all these factors will establish the interactions with volatiles.

Previous studies have shown the advantageous effects of microwave receptors on pyrolysis

products. Domínguez et al. (2003) compared the effects of char and graphite as microwave

receptor on yield and property of oil products. The results showed that the oil yields obtained from MP with char as receptor were higher than those obtained with graphite. Moreover, it was proved that the use of graphite instead of char as a microwave receptor, favored the cracking of large aliphatic chains to lighter species in oil products. Another example is the influence of an iron mesh as antenna in the MP of polystyrene (Hussain et al.,

2010). The rate of reaction was found to depend upon the size and shape of the mesh, in such a way that when the mesh was cylindrical, the conversion was greater and the rate of reaction was much faster. On the other hand, Wan et al. (2009) studied the influence of different catalysts to improve product selectivity during the MP of corn stover and aspen wood. They found that the catalysts, apart from working as microwave absorbents to speed up heating, participate in the so-called *in situ* upgrading of pyrolytic vapors.

The state of the art in microwave-assisted pyrolysis

This section examines the state-of-the-art in the use of microwave technology as an energy- efficient alternative to current heating technologies employed in the pyrolysis process. A significant number of articles have concentrated on exposing the limitations of CP and suggesting where MP can offer both technical and financial benefits. A summary of the main advantages of the MP is presented as follows:

- Fast and uniform heating
- Selective heating
- Direct utilization of large-sized feedstocks
- Treatment of non-homogeneous wastes
- Waste reduction and material recovery
- Better production quality
- New materials and products
- Enhanced chemical reactivity
- Energy efficiency
- Overall cost effectiveness/savings
- Improved process control
- Ability to operate from an electrical source
- Ability to treat wastes in-situ
- Flexible process that can also be made remote
- Portability of equipment and process
- Reduce hazards to humans and the environment

Biomass wastes

Several pyrolysis studies have been conducted using microwaves as a heating source, with lignocellulosic feedstocks that included wood (Miura et al., 2004; Chen et al., 2008), coffee hulls (Domínguez et al., 2007), rice straw (Huang et al., 2008), waste tea (Yagmur et al., 2008) and wheat straw (Budarin et al.,

2009). As a result of the aforementioned research, various products were generated, including gas, liquid and solid phase products. The primary factors affecting the product distribution and components include reaction temperature, reaction time, microwave power, particle size, additives, and the original characteristics of feedstock.

Microwave heating has also been considered as an alternative for carrying out the pyrolysis

of sewage sludges (Menéndez et al., 2004). The use of microwave-assisted processes in sewage sludge handling or treatment is not entirely new. In fact, a variety of processes involving microwaves have already been investigated. These have focused mainly on the pretreatment, including enhancement of anaerobic digestion (Hong et al., 2006; Climent et al., 2007), desaturation (Wojciechowska, 2005), cell destruction (Hong et al., 2004) and solubilization of organic solids (Eskicioglu et al., 2006), but also on the vitrification of the solid residue using microwave heating for the purpose of decreasing the leaching of heavy metals (Menéndez et al., 2005). Various patent applications describing procedures or apparatus for carrying out the drying and/or pyrolysis of waste materials, including sewage sludge, have also been presented during the last 20 years (Sullivan III, 1986; Marks & Fluchel, 1991).

Several researchers have indicated that MP produces more gas and less oil than CP

(Domínguez et al., 2007; 2008; Fernández et al., 2009; 2010). In addition, the major constituents in the gas pyrolysis products that can be seen as source of energy and fuel include H₂, CO, CH₄, and other light hydrocarbons. The MP of sewage sludge (Menéndez et al., 2004) produced H₂, CO and CH₄ with percentages of 22-43%, 23-30% and 2-7%, respectively. For the MP of coffee hulls (Domínguez et al., 2007), the percentages of H₂, CO and CH₄ in the gas product were 36-40%, 26-33% and 7-8%, respectively. Compared with CP, which is carried out using an electric furnace, MP produces more H₂ and CO content (Menéndez et al., 2004; Domínguez et al., 2007; Fernández et al., 2009; 2010), which is so-called syngas. The work of Huang et al. (2008) over the MP of rice straw shows that about half of rice straw sample is transformed into H₂-rich fuel gas, whose H₂, CO₂, CO, CH₄ percentages are 55, 17, 13 and 10 vol.%, respectively. These authors suggest that the difference in the production of H₂ obtained through MP, and through TA-MS analysis could be due to a hot spot generated by the focused heating of microwaves.

When considering bio-oils, MP satisfies the technical challenge directed to bring the biomass rapidly at the reaction temperature and to avoid exposition of

vapor-phase pyrolysis products in a hot environment. In addition, MP is a novel approach to improve the quality and consistency of bio-oil through the *in situ* upgrading of the biomass pyrolysis vapors (evolved volatiles from thermal decomposition of organics). Three approaches of such *in situ* upgrading have been reported in the literature; (i) catalytic pyrolysis (Williams & Nugranad, 2000), where the volatiles react directly and immediately on catalysts pre-mixed with the biomass feedstock, (ii) microwave-assisted pyrolysis (Domínguez et al., 2007; 2008; Huang et al., 2008), where the microwaves are not only useful as alternative method of heating, but also cause specific molecular activations (De la Hoz et al., 2005), and recently (iii) microwave-assisted catalytic pyrolysis (Chen et al., 2008; Wan et al., 2009), which involves the combination of the former. Both the use of catalysts or microwaves during the pyrolysis process improves the yield or quality of the final products. In fact, both aspects together may be assigned to a synergistic effect in such a way that, the result of using catalysts is improved under microwave heating, and vice versa (Fernández et al., 2009). For example, Wan et al. (2009) ascribe catalysts an important role in solid-to-vapour conversion and in reforming of vapors during the pyrolysis of biomass. The use of microwaves is known to create a different temperature gradient which permits the catalyst to be at higher temperature, promoting its catalytic activity. Moreover, the appearance of hot spots is also an important factor to take into account. Their nature is not completely understood, but in a sense they can be put on a level with a catalytic effect.

Significant differences appear in the bio-oils generated with MP. Domínguez et al. (2003)

carried out MP of different sewage sludges and found that the pyrolyzing oils have a high calorific value and a low proportion of compounds of considerable environmental concern, such as polycyclic aromatic hydrocarbons (PAHs). Apart from providing less hazardous compounds, MP generates some chemicals of interest in industry in higher proportions than CP. For their part, Wan et al. (2009) found that microwave-assisted catalytic pyrolysis usually produced additional water and coke-solid residue, and thus, reduces the yield of the organic phase of the bio-oil. Besides, that it is possible to control the product profiles by varying the catalysts and the dosages used. Much literature exists which have examined the use of a range of catalysts. Research has also been directed towards the design of selective catalysts for either increasing the production of specific compounds (e.g. phenols) or minimizing the formation of undesirable compounds (e.g. acids, carbonyls). However, it is still necessary to

study how catalysts change the chemical profiles of bio-oils under MP conditions.

Apart from biomass wastes which have already been examined, studies have also concentrated on the main component of biomass: cellulose. Budarin et al. (2010) espouse a mechanism for the specific microwave effect on cellulose to explain the lower temperature at which carbonization occurs, the higher calorific value of the final char and the improvement in the properties of the oils produced, in comparison with CP. There are also studies that have investigated the pyrolysis or thermal cracking of glycerin to produce synthesis gas under microwave heating (Fernández et al., 2009; 2010). From those studies, it was concluded that the use of microwave heating in glycerol pyrolysis ensures a higher gas fraction with an elevated content of syngas compared to conventional heating, even at low temperatures (400 °C). It is accepted that vegetable oil residues offer little hope as a renewable fuel for compression ignition engines, due to its high viscosity, low volatility and the polyunsaturated character of triglycerides which leads to incomplete combustion and a decrease in the performance of the engine. The microwave treatment of these oil residues could present some interest as the transesterification can be significantly accelerated (Fukuda et al., 2001). The biodiesel preparation time is considerably reduced (i.e. more than 10 times in comparison with conventional heating), and its properties are similar to those of diesel. Interestingly, MP offers an alternative to most CP methods which generally require a reduction in the size of the material, largely necessary when materials have low thermal conductivity (Miura et al., 2004; Ciacci et al., 2010). Large-sized feedstocks can be heated with microwave irradiation, and thus it is possible to reduce pretreatment processing costs. A few studies of MP of wood block (Krieger-Brockett, 1994; Miura et al., 2004) and corn stalk bale (Zhao et al., 2010) demonstrate that it is possible to pyrolyze thick blocks given that the heat exchanged from the external surface is lower than the heat produced by dielectric loss. The radiation energy is dissipated within the sample more or less uniformly, giving rise to much higher heating rates, although significant temperature gradients may be established between the hot internal regions and the surface of the sample (see Fig. 5). Conversion times are also shorter than those of conventional heating. Consequently, this could result in huge reductions in the electricity consumption normally used in the grinding and shredding processes.



Fig. 4. Cross-section of wood after 3 minutes of microwave radiation (Reprinted from Miura et al., 2004, with permission from Elsevier)

Other microwave-assisted pyrolysis processes

Experimental investigations about MP date back to the 1980s, after the discovery of substances which heat rapidly in a microwave field (microwave receptors) inducing the pyrolysis of other materials. From that moment, several researchers deal with MP of coals of different ranks. Monsef-Mirzai et al. (1995) observed evidence that volatile material undergoes significant secondary cracking, which may be enhanced by the presence of the receptor, to still condensable products. The tar yields depend on the type of microwave receptor, e.g. up to 49 wt% with CuO, 27 wt% with Fe₃O₄, or 20 wt% with coke. Jie & Jiankang (1994) studied the behavior of coal pyrolysis desulfurization by microwave radiation. The microwave method decreases the volatile matter loss and slightly improves the desulfurization efficiency, as compared with external heating pyrolysis. Lester et al. (2006) have indicated a potential new method for coke production from high volatile bituminous coal using MP. The time taken to generate the graphitized coke under microwave irradiation is surprisingly short compared with conventional methods. They suggest that the sample has either reached temperatures well in excess of 1000 °C or that microwaves have a non-thermal effect on coal structure that increases the rate of the structural ordering of the carbon atoms. There are also studies that have evaluated the change in electric and dielectric properties of some Australian coals during the process of pyrolysis (Zubkova & Prezhdo, 2006).

Microwave irradiation has also been applied by El harfi et al. (2000) and Bilali et al. (2005) in the pyrolysis of oil shales and rock phosphate, respectively. The former found that the oils produced by microwave heating are more maltenic,

less polar and contains less sulphur and nitrogen than those obtained by CP and the latter found to contain more paraffinic compounds.

Finally, some wastes are subjected to frequent variations and/or consisted of mixed materials which make the monitoring of the pyrolysis process difficult, such as municipal solid wastes (MSW). These ones are highly non-homogeneous in terms of material composition and size, and contain a large amount of ash, heavy metals and chlorine which increases the process cost and lower the quality of the products. However, studies on pyrolysis of MSW demonstrate that it is possible to produce valuable final products. To date, only conventional heating systems have been use in the pyrolysis of MSW (Buah et al., 2007; He et .

final pyrolysis products by reducing processing time and making cost savings. On the other hand, some segregated waste materials from MSW (e.g. paper, cardboard, waste wood, textiles or plastic) may also be suitable candidates for feedstock production by MP on small-scales.

Additional microwave heating applications in waste management

Microwave technology has also been employed in the sterilization of hospital wastes (Drake, 1993; Blenkarn, 1995). Hospital wastes (HW), comprising pathological, microbiological, sharps and associated contaminated waste, produce an environmental problem due to the very large volumes produced each year. The rapid and in-situ treatment of HW with microwave irradiation sterilizes and reduces it to inert ash prior to final disposal, as well as minimizes the contact with hazardous components.

In the case of nuclear wastes, there are certain components that are very good insulators and, therefore, conventional heating is not effective in their treatment. However, microwaves can selectively heat these waste mixtures, and thus, can be used for the *in situ* desaturation of low level nuclear waste, in the same waste storage vessel that the waste was deposited. This minimizes the handling of the radioactive waste and reduces the waste volume by about 5% (Oda, 1993).

Studies of thermal remediation using microwave heating enhanced by strong microwave absorbers have also been performed on soil contaminated with organic pollutants or toxic metal ions. George et al. (1992) investigated soil

decontamination via microwave heating enhanced by carbon particles. The decontamination process was performed under reduced pressure and an inert gas presence to prevent the combustion of the contaminant. Their results showed that removal efficiencies of near 10% could be achieved for phenanthrene using microwave heating enhanced by 40 wt.% carbon particles. The decomposition of polycyclic aromatics and polychlorobiphenyl in soil using microwave energy, with the addition of NaOH in company with Cu₂O (powdered Al, metal wire, etc.) serving as both reaction catalysts and microwave absorbers was also investigated (Abramovitch & Huang, 1994; Abramovitch et al., 1998; 1999). The results show that the decomposition products were probably either mineralized or very highly bonded to the bed. Furthermore, Abramovitch et al., (2003) reported that, with the addition of pencil lead or iron wire, the contaminated soil could be remediated safely to preset depths without the toxic metal ions leaching out for a long time. Yuan et al. (2006) investigated the microwave remediation of the oil contaminated with hexachlorobenzene (HCB) using powdered MnO₂ as microwave receptor. Their results revealed that a complete removal of HCB was obtained with 10 min microwave treatment by the addition of 10 wt.% powdered MnO₂ and about 30 wt.% H₂SO₄ (50%). A successful remediation of crude oil-contaminated soil (99% oil removal) using carbon fibers has been recently reported by Li et al. (2009). They concluded that microwave thermal processes can not only clear rapidly up the contaminated soil, but also recover the usable oil contaminant efficiently without causing any secondary pollution.

Conclusions

The aim of this paper has been to provide the reader with a fundamental understanding of microwave-assisted pyrolysis processes. The unique internal phenomenon associated with microwave energy not only leads to significant savings in both energy consumption and process time during the pyrolysis process, but also allows for the development of new chemical profiles of the volatiles, which enhances the overall quality of production. Both the influence of microwave heating on pyrolysis conditions (*distribution of temperature, heating rate and residence time of volatiles*) and raw materials have been discussed. Furthermore, special attention has been given to the microwave receptor, since it is an essential factor in any microwave heating process.

A significant number of articles have been reviewed for the purpose of demonstrating the limitations of conventional pyrolysis and suggesting where

microwave-assisted pyrolysis can offer advantages. Essentially, microwave-assisted pyrolysis is a novel approach in the in-situ upgrading of pyrolysis vapors. The oils produced under this technique, offer less hazardous compounds and produce a greater number of chemicals which are of interest to industry, than those obtained under conventional pyrolysis. As equally desirable and advantageous, is the fact that the gas fraction presents higher yields of hydrogen or syngas. In essence, microwave-assisted pyrolysis offers a superb opportunity to divert waste from the present eco-damaging disposal techniques such as from landfill and incineration, and it also presents a worthy means of recovering commercially valuable products from wastes.

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