

Final version published in *Fuel Processing Technology*, 2010, 91 (1), 1-8

Microwave heating processes involving carbon materials

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Abstract

Carbon materials are, in general, very good absorbents of microwaves, i.e., they are easily heated by microwave radiation. This characteristic allows them to be transformed by microwave heating, giving rise to new carbons with tailored properties, to be used as microwave receptors, in order to heat other materials indirectly, or to act as a catalyst and microwave receptor in different heterogeneous reactions. In recent years, the number of processes that combine the use of carbons and microwave heating instead of other methods based on conventional heating has increased. In this paper some of the microwave-assisted processes in which carbon materials are produced, transformed or used in thermal treatments (generally, as microwave absorbers and catalysts) are reviewed and the main achievements of this technique are compared with those obtained by means of conventional (non microwave-assisted) methods in similar conditions.

Keywords: Microwaves, carbon materials, coal, catalysis, pyrolysis

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1. Introduction to the microwave heating of carbons

Microwaves lie between infrared radiation and radiowaves 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. The microwave band is widely used in telecommunications. In order to avoid interference with these uses, the wavelengths of industrial, research, medical and domestic equipment are regulated both at national and international levels. Thus, the main operating frequency in the majority of countries is 2.450 (+/- 0.050) GHz [1, 2].

Dielectric heating refers to heating by high-frequency electromagnetic radiation, i.e., radio and microwave frequency waves. The interaction of charged particles in some materials with the electric field component of electromagnetic radiation causes these materials to heat up. The heat resulting from this interaction is mainly due to two different effects. In the case of polar molecules, the electric field component of the microwaves causes both permanent and induced dipoles to rotate as they try to align themselves with the alternating field (2450 million times per second). This molecular movement generates friction among the rotating molecules and, subsequently, the energy is dissipated as heat (Dipolar Polarization). This is the case of water and other polar fluids. In the case of 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, a current traveling in phase with the electromagnetic field is induced. As the electrons cannot couple to the changes of phase of the electric field, energy is dissipated in the form of heat due to the so called Maxwell-Wagner effect (Interfacial or Maxwell-Wagner Polarization) [1, 2].

The materials which interact with microwaves to produce heat are called microwave absorbers. The ability of a material to be heated in the presence of a microwave field is defined by its dielectric loss tangent: $\tan\delta = \epsilon''/\epsilon'$. The dielectric loss tangent is composed of two parameters, the dielectric constant (or real permittivity), ϵ' , and the dielectric loss factor (or imaginary permittivity), ϵ'' ; i.e., $\epsilon = \epsilon' - i\epsilon''$, where ϵ is the complex permittivity. The dielectric constant (ϵ') determines how much of the incident energy is reflected and how much is absorbed, while the dielectric loss factor (ϵ'') measures the dissipation of electric energy in form of heat within the material [1, 2]. For optimum microwave energy coupling, a moderate value of ϵ' should be combined with high values of ϵ'' (and so high values of $\tan\delta$), to convert microwave energy into thermal energy. Thus, while some materials do not possess a sufficiently high loss factor to allow dielectric heating (transparent to microwaves), other materials, e.g. some inorganic oxides and most carbon materials, are excellent microwave absorbers. On the other hand, electrical conductor materials reflect microwaves. For example, graphite and highly graphitized carbons may reflect a considerable fraction of microwave radiation. In the case of carbons, where delocalized π -electrons are free to move in relatively broad regions, an additional and very interesting phenomenon may take place. The kinetic energy of some electrons may increase enabling them to jump out of the material, resulting in the ionization of the surrounding atmosphere. At a macroscopic level, this phenomenon is perceived as sparks or electric arcs formation. But, at a microscopic level, these hot spots are actually plasmas. Most of the time these plasmas can be regarded as microplasmas both from the point of view of space and time, since they are confined to a tiny region of the space and last for just a fraction of a second. An intensive generation of such microplasmas may have important implications for the processes involved.

The microwave heating of a dielectric material, which occurs through the conversion of electromagnetic energy into heat within the irradiated material, offers a number of advantages over conventional heating such as: (i) non-contact heating; (ii) energy transfer instead of heat transfer; (iii) rapid heating; (iv) selective material heating; (v) volumetric heating; (vi) quick start-up and stopping; (vii) heating from the interior of the material body; and, (viii) higher level of safety and automation [3]. Due to these advantages, microwaves are used in various technological and scientific fields in order to heat different kinds of materials [2-4]. Most of the industrial applications of microwave heating are based on heating substances that contain polar molecules, for example: food processing, sterilization and pasteurization, different drying processes, rubber vulcanization, polymerization or curing of resins and polymers by elimination of polar solvents, etc. In addition, solid materials with a high dielectric loss factor, i.e., microwave absorbers, can be subjected to different processes based on microwave heating. Among these materials, carbons are, in general, very good microwave absorbers, so they can be easily produced or transformed by microwave heating. Moreover, carbon materials can be used as microwave receptors to indirectly heat materials which are transparent to microwaves. Thus, carbon materials have been used as microwave receptors in soil remediation processes, the pyrolysis of biomass and organic wastes, catalytic heterogeneous reactions, etc. The high capacity of carbon materials to absorb microwave energy and convert it into heat is illustrated in Table 1, where the dielectric loss tangents of different carbons are listed. As can be seen, the loss tangents of most of the carbons, except for coal, are higher than the loss tangent of distilled water ($\tan\delta$ of distilled water = 0.118 at 2.45 GHz and 298 K). The search and compilation of these data is no a straightforward matter. Although this parameter is helpful for the study of microwave heating, few research groups have determined the

dielectric loss tangents of carbons and the data that can be found are scattered throughout bibliography.

Table 1. Dielectric loss tangents for different carbon materials at a frequency of 2.45 GHz and room temperature, ca., 298 K

Carbon material	$\tan\delta = \epsilon''/\epsilon'$	Reference
Coal	0.02-0.08	[5, 6]
Carbon foam	0.05-0.20	[7]
Charcoal	0.11-0.29	[8, 9]
Carbon black	0.35-0.83	[10, 11]
Activated carbon	0.57-0.80	[9, 12, 13]
Activated carbon ^a	0.22-2.95	[14]
Carbon nanotube	0.25-1.14	[15, 16]
CSi nanofibres	0.58-1.00	[17]

^a Activated carbon at a mean temperature of 398 K

The first commercial microwave oven was developed in 1952, although it was during 1970s and 1980s when the widespread domestic use of microwave ovens occurred, as a result of Japanese technology transfer and global marketing [18]. Curiously, the industrial applications of microwaves were initiated by the domestic ovens. However, in recent years, the number of processes that combine the use of carbons and microwave heating to obtain benefits with respect to other traditional methods based on conventional heating has increased enormously. Thus, as can be seen from Figure 1, the number of scientific publications related to these topics was very low until the late 1990s, but interest has risen drastically in the last decade and especially so in the last five years.

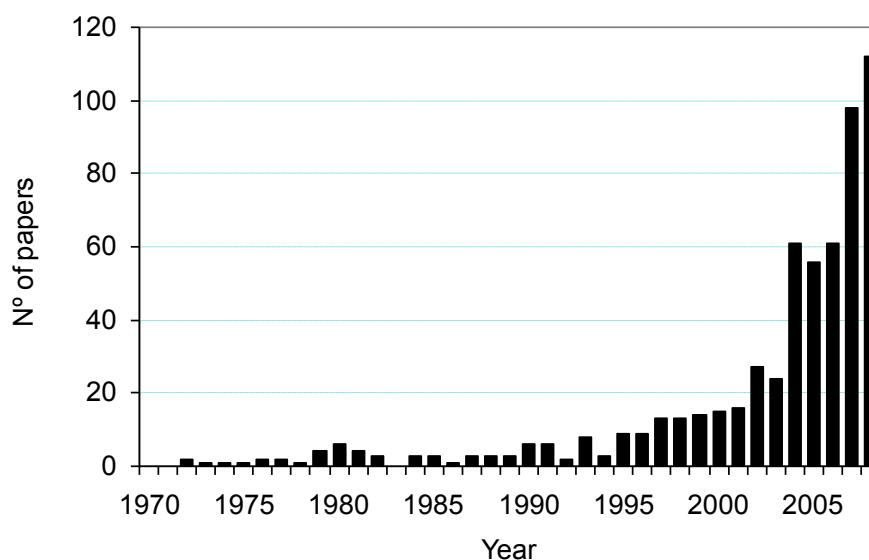


Figure 1. Evolution of the number of research papers published on microwave-assisted processes involving carbon materials (Source: Scopus®).

The aim of this work is to review examples of different microwave-assisted processes involving carbon materials. In these processes, microwave heating is used either to produce or modify different carbon materials or is employed in combination with carbons acting as microwave absorbers to enhance different processes in technological applications. The amount of published work is relatively large, so an effort has been made to be representative rather than comprehensive. Thus, the synthesis of a wide range of carbon materials by microwave techniques is reviewed in section 2. Due to the widespread use of activated carbons, their production, modification and regeneration is treated in a separate section (section 3). The use of microwave heating in various metallurgical and mineral processes is presented in section 4. Moreover, microwaves can be used not only to treat and modify solid carbons but also for purposes of revaluation, to obtain other products of high added value, such as gases. This is the case of thermal valorisation of biomass and biosolids, which is dealt with in section 5. Finally, the use of microwaves to enhance the reactions catalysed by carbons is growing in importance and is discussed in section 6.

2. Synthesis of carbon materials

Microwave plasma-enhanced chemical vapor deposition (CVD) has been widely used for growing carbon nanotubes [19, 20] or diamond deposition [21]. Although very few works have been described, the synthesis of nanocarbons by the direct microwave irradiation of catalyst particles on a solid support is another possibility for producing carbon nanofilaments by CVD [22, 23]. Thus, carbon nanofilaments were formed through microwave-assisted CH_4 decomposition over an activated carbon, acting as catalyst and microwave receptor, using a combination of CH_4/N_2 . The same method was also used to grow carbon nanofilaments on carbon fibers doped with Fe and Ni [23], giving rise to structures similar to those shown in Figure 2. Mixtures of CH_4/CO_2 were also used to produce nanofilaments using a char as catalyst and microwave receptor [22]. Since no nanofilaments were observed after analogous tests carried out under conventional heating, it must be concluded that it is the different mechanism involved in heating the supports by microwaves that promotes the formation of nanofilaments.

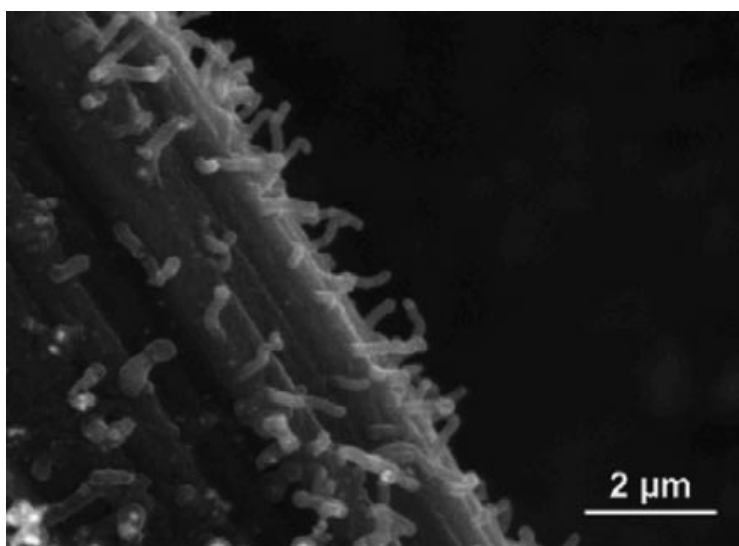


Figure 2. Carbon nanofilaments grown on a carbon fiber. (Reprinted from Ref. [23] with permission from Elsevier).

Carbon materials can act not only as a support for growing nanostructures but also as the carbon-source for the synthesis of nanotubes and nanofibers via microwave heating. It has been reported that is possible to synthesize these nanostructures by simply microwave heating of graphite for 60 min [24] or of organometallic compounds like ferrocene, $\text{Fe}(\text{C}_5\text{H}_5)_2$, for just 30 min [25]. In addition, microwave irradiation seems to be an effective option for purifying nanotubes. Thus, the refining of raw samples of nanotubes, that is the elimination of the amorphous carbon formed during the synthesis and metal impurities (the remains of the catalyst), has been carried out by microwave heating, at 433 K for 30 min., in nitric acid. [26]. The microwave-induced functionalization of carbon nanotubes is another option. Reactions such as amidation and 1,3-dipolar cycloaddition have been performed in a matter of minutes, which is a significant reduction in time compared to conventional functionalization processes. In addition, the number of steps involved in the reaction procedure has been reduced, which opens the door to a fast and inexpensive process for producing functional singlewall carbon nanotubes [27]. The multifunctionalization of carbon nanotubes using a combination of two addition reactions, the 1,3-dipolar cycloaddition of azomethine ylides and the addition of diazonium salts, has also been achieved in solvent free conditions via a simple and fast microwave-induced method [28]. This method reduces not only the reaction time but it also avoids the need for using toxic solvents. Another example of the use of microwaves in the functionalization of carbon materials is the oxidation of carbon nanohorns [29]. Furthermore, carbon nanotubes can be incorporated into ceramic matrices using microwave irradiation. The use of a microwave-induced reaction may be able to overcome some of the problems of the conventional methods of synthesis, i.e., non-uniform dispersion and damage to the nanotubes during high temperature processing in the reacting media. As an example, a carbon nanotube-silicon

carbide composite has been synthesized by this method in only 10 minutes at temperatures between 673 and 1173 K [30].

Another application of microwave heating is the production of graphitic carbons from various precursors, such as isotropic or anisotropic pitch-based carbon powders [31]. Moreover, Mitsubishi Heavy Industries, Ltd. (MHI) has claimed ⁽¹⁾ to have produced superior-grade graphite from carbon powder by using a microwave process at 3473 K. Expanded graphite, a modified graphite which retains its layered structure and is similar to natural graphite but with larger interlayer spacing and abundant micropores, has been produced by the microwave irradiation of both natural graphite, mixed with HNO₃ and KMnO₄ [32], and expandable graphite [33]. A microwave-based device specially designed for the production of expanded graphite has been patented [34]. It has also been claimed that powdered carborundum, i.e., silicon carbide, with diameters in the nanometer range, can be produced by a microwave-assisted process that involves reducing SiO₂ with various forms of carbon in a nitrogen atmosphere [35]. In a similar way, Changhong et al. used microwave heating to induce the direct reaction between silicon and charcoal powder, at temperatures lower than 1273 K, in order to synthesize silicon carbide [36].

Microwave irradiation has been used to synthesize ordered mesoporous carbon materials (OMC) by employing a nano-casting technique and ordered mesoporous silica as the template. Thus, microwave heating techniques have been applied to synthesize nano-structured materials such as zeolites and ordered mesoporous silica materials under hydrothermal conditions [37], the result being a remarkable enhancement in the efficiency of sol-gel synthesis, as manifested by the shorter time or lower temperature

required for the synthesis, and the unique and uniform properties of the products. The ultrarapid production of OMC materials, which utilizes the intense heat generated by microwaves during the carbonization step, offers a number of advantages, such as energy saving, low temperature preparation (even at 673 K), controllable oxygen content, i.e., a wide range of hydrophilicity without the need for post-activation, and an enhancement of the conductivity of the carbon materials [38].

Another use of microwave heating in the synthesis of carbon materials is derived from the capacity of microwaves to interact with polar solvents (Dipolar Polarization). In this case, interaction can produce a more uniform dispersion of metal particles in the synthesis of carbon-supported catalysts by means of the so-called microwave-assisted polyol process [29, 39, 40]. Another advantage of the interaction of microwaves with polar solvents is that they can be eliminated by evaporation, thereby saving both energy and time. Thus, microwave heating can be used to facilitate the polymerization or curing of polymers by eliminating solvents. The application of microwave irradiation to polymer chemistry has also revealed potential advantages in its ability not only to drive chemical processes but also to perform them in a short time [41]. A particular case of industrial interest is the microwave-assisted vulcanization of rubber [42]. The use of microwave heating in rubber vulcanization is now a well-established technique. Interestingly microwave heating can also be used to devulcanize elastomer waste [43]. In the field of carbon materials, microwave heating has been applied in the drying step of the synthesis process of carbon xerogels [44, 45]. Microwave drying has been used to prepare resorcinol–formaldehyde gels by employing methanol [44] and water [45] as solvents. By using microwave drying, the process for obtaining carbon gels has been greatly simplified. As with other drying methods, the textural properties can be

controlled, but time has been considerably reduced by changing from conventional drying techniques to microwave drying (up to 90% reduction in the drying stage), no pre-treatment being necessary. Taking into account that one of the disadvantages of carbon gels, compared to other carbon materials, was the complexity, long time required and the high costs of the traditional synthesis methods, this improvement (i.e., the use of microwaves in the synthesis of carbon gels) makes these materials more economically competitive in a large number of applications.

3. Production, modification and regeneration of activated carbons

Activated carbons are, in general, produced from different organic precursors, such as biomass, coal, polymers, natural or synthetic fibres, etc, which are subjected to carbonization and activation processes. The activation process can be carried out by making steam, CO₂ or air react with a char or a carbonized material at relatively high temperatures, i.e., 873 to 1173 K. This kind of activation is commonly referred as physical or thermal activation. On the other hand, chemical activation consists in the simultaneous carbonization of the precursor with an activating agent, such as ZnO, H₃PO₄, KOH, etc, at temperatures ranging from 673 to 1073 K. Both microwave-assisted activation processes have been recently reviewed by Yuen and Hameed [46].

Since carbonaceous materials are good microwave absorbers, the microwave-assisted physical activation of chars from different organic precursors has been widely studied over the last few decades. Norman and Cha reported a method for producing highly microporous activated carbons by the CO₂ activation of coal chars [47]. More recently,

a research group from Kunming University of Science and Technology in China has claimed to have obtained activated carbon by the steam activation of coconut shells in a pilot-scale device of 60 kW with considerable saving of time and energy [48], whilst another group from the University of Huddersfield in the United Kingdom has reported activating a phenolic resin-derived carbon in air using constant rate microwave thermogravimetry [49].

On the other hand, few attempts have been made to develop microwave-based processes for chemical activation. The non-carbonized organic precursors of activated carbons impregnated with activating agents are, in general, poor microwave absorbers. This characteristic makes it difficult to heat them up with microwaves to the high temperatures required, although this problem could be overcome by using microwave receptors, e.g. carbonaceous materials [50]. Additionally, Yagmur et al. [51] reported a microwave-induced impregnation method applied prior to the carbonisation stage saving both time and energy.

A way of exploiting the excellent dielectric properties of carbon materials, i.e., their high microwave absorption capacity, is the use of microwave heating to tailor their surface chemistry either by introducing or by removing surface functionalities. As was discussed in section 2, the microwave-assisted functionalization of carbon nanotubes and nanohorns has already been successfully carried out. By contrast, in the case of activated carbons, microwave heating has mainly been used for the rapid elimination of surface functionalities that are often present on the carbon surface. Thus, microwave heating has been used to remove oxygen functionalities and produce a highly-basic activated carbon in just a few minutes, basic properties lasting upon air exposure [52].

Similar results were obtained for carbon fibres subjected to thermal treatments in a microwave oven [53, 54]. In the case of granular activated carbons, the main advantage of employing microwave as opposed to conventional heating seemed to be the saving of time and energy, as the chemical changes observed on the carbon surface did not differ very much regardless of the method used, provided that similar temperatures were used [55]. However, whereas in the case of the activated carbons the porous texture remained more or less unaltered after microwave treatment, the carbon fibres subjected to microwave treatments exhibited a reduction in micropore volume and micropore size. This effect has been used to produce carbon molecular sieves (CMS) by subjecting acrylic textile fibres to microwave action [56]. This novel method of producing and improving the properties of molecular sieves of carbon fibres seems to be more economical than the conventional one. In particular, CMS produced by this method showed a very high selectivity for CO₂/CH₄ and O₂/N₂ gas separations [57].

Another topic of investigation has been the microwave-induced regeneration of exhausted activated carbons. Thus, Price et al. [58] and Cha et al. [59] have reported microwave-assisted regeneration processes of activated carbon saturated with volatile organic compounds (VOC). As well as of carbons used in gas phase applications, the regeneration of activated carbons used in liquid phase adsorption has been studied. Thus, different activated carbons polluted with phenol [60] and pharmaceuticals [61] have been subjected to thermal regeneration under N₂ and CO₂ atmospheres, using both conventional and microwave heating. It was found that the rapid heating of the exhausted activated carbons by microwave energy leads to a quick regeneration. Furthermore, microwave technology allowed the activated carbons to be recycled and reused several times. Thus, it was shown that microwave heating preserves the porous

structure of the regenerated activated carbons more efficiently than treatment in a conventional device. The use of this technique causes no damage to the carbon; rather, it increased the surface area, at least during the first regeneration cycles [62]. Figure 3 illustrates the changes in the adsorptive capacity of a commercial activated carbon exhausted with phenol, after subsequent cycles of regeneration at 1123 K in N_2 and CO_2 atmospheres, using both conventional and microwave heating. Interestingly, regeneration in the microwave oven doesn't just preserves (or even increases) the adsorptive capacity of the activated carbon, the regeneration time is reduced by 90% as well.

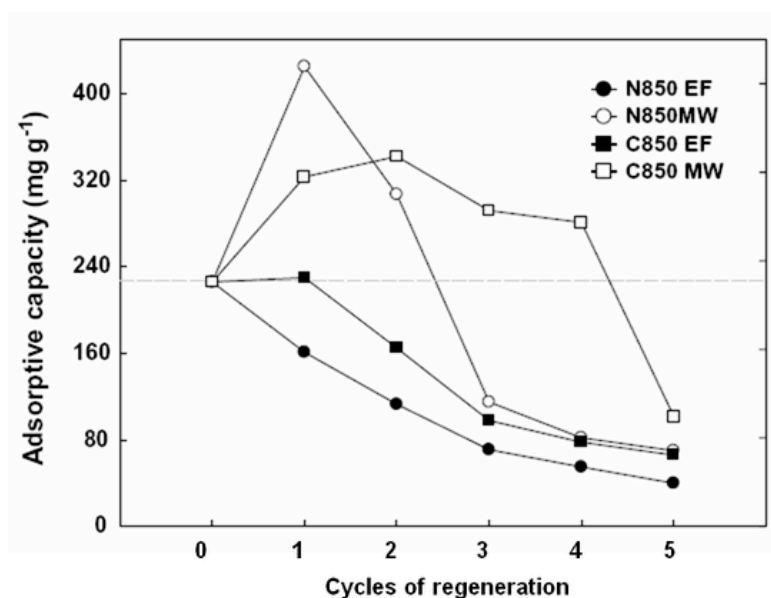


Figure 3. Comparison of the phenol adsorptive capacities of an activated carbon after various cycles of regeneration: (N850EF) electric furnace at 1123 K in a N_2 atmosphere; (N850MW) microwave furnace at 1123 K in a N_2 atmosphere; (C850EF) electric furnace at 1123 K in a CO_2 atmosphere; (C850MW) microwave furnace at 1123 K in a CO_2 atmosphere. Adapted from reference [60].

One more example of the application of microwave-assisted regeneration of activated carbon is its use in certain gold recovery industries which is described in the next section.

4. Metallurgy and mineral processing

Microwave heating has been investigated for use in various metallurgical processes, including pyrometallurgy, hydrometallurgy [63] and mineral processing [3].

Yet in the particular case of processes involving carbons, the microwave-assisted reduction of metal oxides with different carbon materials has been extensively investigated. Thus, hematite fines and magnetite concentrates have been mixed with different carbons like charcoal or coke and then subjected to microwave heating up to 1273 K [64]. It was found that the process is influenced by the type of carbon used and that, under similar conditions of temperature, microwave reduction produces better results than those attained by conventional heating. Recently, a process for carrying out the carbothermic reduction of iron oxides using microwave heating has been patented [65]. Similar processes that combine microwave heating with the use of various kinds of carbons as reducing agent and microwave absorbers are applied to other metallic oxides [66].

Microwave heating is also employed in the gold mining industry to recover gold from the activated carbon used in the so called carbon-in-pulp process (CIP). The carbon, which is used to adsorb the gold cyanide molecule, is periodically removed from the adsorption tanks to allow removal of the gold by elution. Then, after the carbon is subjected to an acid wash to remove inorganic compounds, it is regenerated at 923-1123 K in a steam atmosphere to remove other foulants such as flotation reagents, lubricating oils and humic acids which would foul the carbon and undermine its performance. The regenerated carbon is then sized and returned to the CIP circuit.

Regeneration is conventionally done in rotary kilns or vertical tube furnaces. However, it has been demonstrated that the use of microwave heating can be also an alternative economically feasible, with a saving of energy and time consuming [67].

Another field of application of microwave heating is the processing of coals. Coals are, in general, very poor microwave absorbers (see Table 1), since they do not possess graphene lattices of a size large enough to allow delocalized π -electrons to move in order to couple with the electromagnetic field of the microwaves (i.e., heating by interfacial polarization). Thus, only devolatilized coals, chars or cokes, with a relatively large amount of delocalized π -electrons that move on the incipient graphenic structures, show good microwave absorbance properties (see Figure 4).

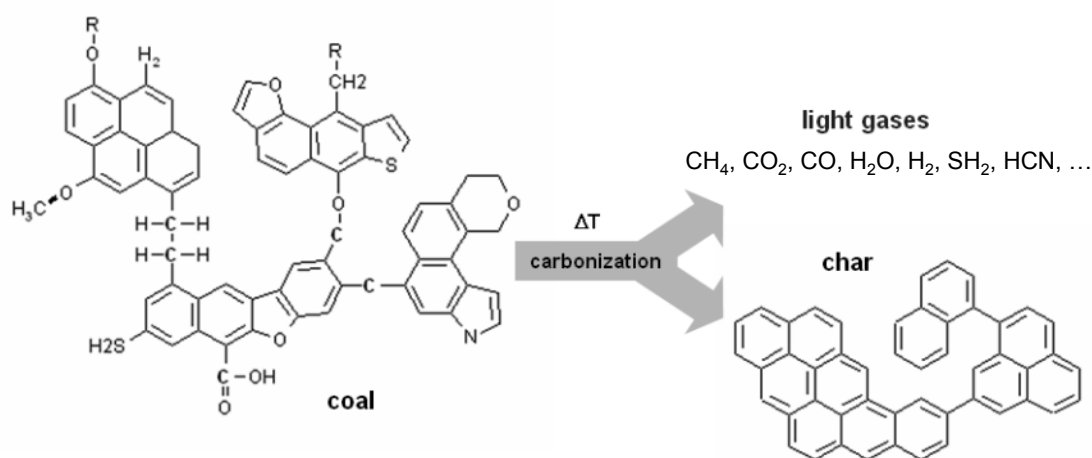


Figure 4. Representative coal molecular structure and char after devolatilization. Coal doesn't possess many delocalized π -electrons. After devolatilization aromatic rings fuse given rise to small graphitic planes with π -electrons free to move.

Despite this, the microwave heating of coals is used in the industrial processing of coal. For example, a process for the microwave-assisted grinding of coals has been described [68]. In this process, coals of various ranks were exposed to microwave radiation to

quantify the effect on grindability. Reductions of up to 50% of relative grindability were reported after 5 minutes of microwave exposure. These reductions are believed to be due to fracture mechanisms; inherent moisture within the coal structure absorbs microwaves changing phase, and producing considerable pressure and differential expansion by gangue mineral components. Another example is the microwave-assisted desulphurization of coals which is based on the fact that pyrite heats more rapidly than coal. This heating has the effect of enhancing the magnetic susceptibility of pyrite thereby improving the removal rates by magnetic separation [69]. In addition to these two industrial applications of microwave heating of coals, the possibility of using microwave heating of a high volatile bituminous coal for rapid coke making has been studied at the bench scale [70]. In the cited work it is suggested that devolatilization starts due to the moisture content and -OH bonds present in the coal, and then, when the aromaticity of the devolatilized material increases, the absorption of microwaves allows temperatures in excess of 1273 K, which produces graphitized coke in less than 2 h.

5. Thermal valorisation of biomass and biosolids

Microwave heating is a good alternative for carrying out the pyrolysis of biomass [71, 72], coal [73, 74], oil shale [75, 76], glycerol [77] and various organic wastes [78]. In general, these materials are poor receptors of microwave energy, so they cannot be directly heated up to the high temperatures usually required to achieve total pyrolysis. However, microwave-induced pyrolysis is possible if the raw material is mixed with an effective microwave receptor, such as certain metal oxides [73, 74] or carbon materials [50, 71, 72, 75-78]. The latter are usually preferred for this particular application, not only because they are very good microwave absorbers, but also because they are

inexpensive, easily available in different textures, sizes, forms, etc; and do not add any extra inorganic component to the solid residues obtained after pyrolysis. Moreover, the carbonaceous residue itself which is obtained from the pyrolysis of the organic materials can be used as an excellent microwave absorber [50, 71, 79, 80].

A case of particular interest is the pyrolysis of sewage sludge [50, 79-85], often called biosolids. Handling of this waste, which can be considered as biomass, represents a challenge in industrialized countries. So far, none of the methods used, from land reclamation, such as landfill or organic fertilisers, to incineration, is exempt from drawbacks, like collateral pollution or high costs of treatment. These high costs are in part due to the need to remove the high water content of the sludge. Microwave heating could be a highly efficient alternative for drying these biosolids [81]. Moreover, a process that uses the steam produced by microwave drying to gasify the products generated during subsequent pyrolysis has been described [80]. In this method, drying, pyrolysis and gasification of the sewage sludge take place at the same time, giving rise to a larger gas fraction with a high syngas ($\text{CO}+\text{H}_2$) content [79, 84, 85] and to an oil fraction with a low polycyclic aromatic hydrocarbons (PAHs) content [82, 83]. In contrast, the oil from the conventionally heated sludge consists primarily of PAHs. Unlike other conventional pyrolysis methods and due to the high temperatures that are reached during the process, a partially vitrified solid residue can be obtained by microwave-assisted pyrolysis [80]. This is particularly useful in the case of sludges with high heavy metal content.

A unique characteristic of microwave-assisted thermal treatments of biomass and biosolids is that they produce a considerable higher amount of H_2 and CO (syngas) and

much less CO₂ than similar treatments carried out using conventional heating. This feature is illustrated in Figure 5, where the compositions of the gas fractions obtained from the pyrolysis of a biomass residue using both methods of heating are compared. Given that microwave-assisted pyrolysis maximizes the gas fraction obtained (oils are produced but in very small amounts) and the fraction of the carbonaceous residue can be used as microwave receptor and consumed by auto-gasification with the CO₂ obtained in the process [72], this method can be used for the thermal valorisation of biomass and biosolids, by producing mainly syngas-rich gases.

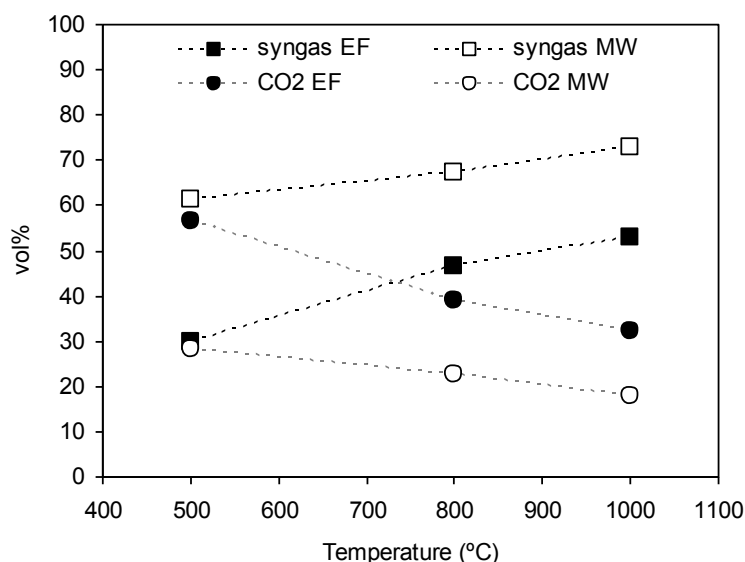


Figure 5. Variation, with temperature, in the gas composition obtained from the pyrolysis of a biomass residue using conventional (closed symbols) and microwave-assisted (opened symbols) pyrolysis. Adapted from reference [72].

Microwave heating combined with the use of carbons as microwave receptors has also been used in soil remediation to eliminate organic pollutants. Thus, the use of graphite fibres, as microwave receptor, in microwave-assisted extraction (MAE) has been shown to be a successful method for the extraction of contaminants in soils, rivers and marine sediments [86]. Similar microwave-induced thermal treatments employing granular

activated carbon as microwave absorber to achieve the appropriate temperature were used to decontaminate the soil [87].

6. Microwave enhancement of carbon catalyzed reactions

Owing to their particularly strong interaction with microwave radiation and high thermal conductivity, graphite and certain other carbons are efficient sensitizers. They are capable of converting radiation energy to thermal energy, which is then transmitted instantaneously to supported chemical compounds. Two types of reaction are favored by carbons-microwave coupling: (i) reactions which require a high temperature, and (ii) reactions involving chemical compounds which, like the organic compounds, have a low dielectric loss and do not heat up sufficiently under microwave irradiation. Thus, microwave heating is a valuable, non-conventional energy source for organic synthesis, which can produce spectacular accelerations in many reactions [88]. Carbons and carbon-supported catalysts are used as sensitizer or sensitizer-plus-catalyst in several organic microwave-assisted synthesis reactions, such as Diels-Alder reactions, the thermolysis of esters, the decomplexation of metal complexes, the pyrolysis of urea, esterifications, etc. [89]. Carbon particles are used to selectively heat the catalyst and substrate without bulk heating the solution. A case of particular interest is fullerene chemistry under microwave irradiation [90], where fullerenes are subjected to different organic reactions in order to functionalize them.

Carbons can be used as catalyst in a variety of heterogeneous gas-phase catalytic systems [91]. Besides, they are good microwave absorbers. These two characteristics have been combined to enhance various catalytic reactions, in which carbons play the

double role of catalyst and microwave receptor. In fact, the interaction of microwave irradiation with some heterogeneous catalytic systems has been proven to enhance the reaction rates, the selectivities of the products and the conversion values [92-94].

NO_x reduction [95, 96], SO₂ reduction [97], catalytic CH₄ decomposition for H₂ production [98, 99] and CO₂ reforming of CH₄ (dry reforming) [100, 101] are just some examples in which the use of carbon materials as catalyst and microwave receptor resulted in a considerable improvement in the yield of the reactions. A variety of carbon materials, such as activated carbons, metallurgical cokes, chars or anthracite, were used. Several microwave-enhanced heterogeneous catalytic reactions, in which carbons acted as catalyst and microwave receptor, are shown in Table 2.

Table 2. Examples of microwave-enhanced heterogeneous catalytic reactions, in which carbons are used as catalysts and microwave receptors

Reaction	Catalyst/microwave receptor	Reference
$C + 2NO \rightarrow CO_2 + N_2$	Subbituminous coal char, anthracite, metallurgical coke	[95-97]
$C + NO \rightarrow CO + 1/2N_2$	Subbituminous coal char, anthracite	[95-97]
$C + SO_2 \rightarrow CO_2 + S$	Subbituminous coal char, anthracite	[97]
$2C + SO_2 \rightarrow 2CO + S$	Subbituminous coal char, anthracite	[97]
$C + CO_2 \leftrightarrow 2CO$	Biomass char	[72]
$CH_4 \rightarrow C + 2H_2$	Activated carbon	[98, 99]
$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$	Activated carbon	[100, 102]

The improvement in the results is attributed to the way the catalyst is heated by microwaves. Thus, in the case of microwave heating, the catalyst (i.e., the carbonaceous material) is heated directly by the action of the microwaves, and so it is at a higher temperature than the surrounding atmosphere. However, under conventional heating,

heat is transferred through the surface of the catalyst, mainly by conduction and convection, resulting in a totally different temperature gradient. In addition to this, as mentioned before, microplasmas are commonly produced during the microwave irradiation of carbons. The temperature in these microplasmas (also called hot spots) is believed to be much higher than the overall temperature of the system, which usually favours heterogeneous reactions between the solid catalyst and the gases taking part in the reaction. It should therefore be possible to apply this technique to other catalytic reactions in which a carbon-based catalyst is used.

7. Conclusions

Carbon materials are, in general, very good microwave absorbers. This explains the increasing interest over the last decade in using them in a wide variety of microwave-assisted thermal processes. These processes include the synthesis of a wide variety of carbon materials (i.e., nanostructures, graphite, active carbons, polymers, etc.), the purification or even chemical and/or physical modification of carbons in a quick and controlled way, the enhancement of different processes involving coal, chars or even biomass/biosolids, and the clear improvement in the efficiency of some carbon-catalyzed reactions. These processes are attracting considerable attention given their possible use in commercial applications and some of them have already been demonstrated at pilot or even industrial scale. The main advantage of using microwaves, instead of traditional heating techniques, is because of the different mechanism involved in heating carbons, leading to, (i) a considerable decrease in the time scale, which in most cases implies a smaller consumption of energy, (ii) a reduction in the number of steps involved in the global process, eliminating the need for other reagents, devices, etc.

and (iii) an increase in the efficiency of the global process. These advantages mean that the final products obtained from microwave-assisted processes will probably be more economically competitive than the ones obtained using traditional techniques.

Acknowledgements

B.F., Y.F and L.Z. are grateful to CSIC of Spain and the European Social Fund (ESF) for financial support under thesis grant I3P-BDP-2006. Financial support from the PCTI-Asturias (Project PEST08-03) is also acknowledged.

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