Microwaving Wastes for Producing Syngas

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Several thousands of million tons of wastes are generated worldwide every year. Of these, organic solid wastes have the potential to partially satisfy the production of chemicals, whilst the environmental impact can be minimized and the sustainability of the processes increased compared to those based on fossil resources. However, these wastes are complex due to their high heterogeneity, and new conversion processes are necessary before they can be converted into high value products. One possibility is to process these wastes using the microwave-induced pyrolysis (MIP), as an alternative to the conventional pyrolysis or gasification processes, that lead to the production of simple molecules, mainly H_2 and CO, a mixture known as synthesis gas or syngas (see Figure 1).

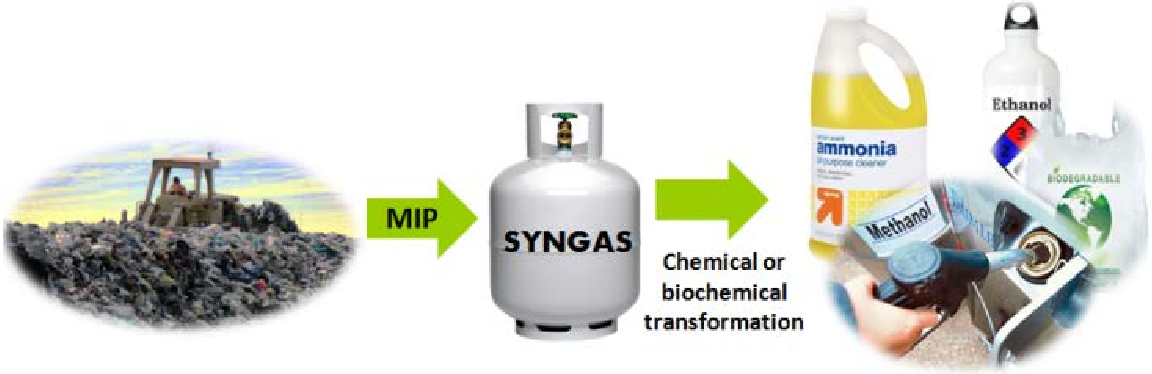

Figure 1. The MIP syngas production concept.

MIP provides the following advantages over conventional gasification and pyrolysis processes: (i) easy conditioning and handling of the biomass, (ii) higher gas yields (and, in consequence, lower oil and solid fraction yields) compared to conventional pyrolysis, (iii) no need of gasifying agent, (iv) no need of catalysts (v) high concentration (up to 95 vol% in some cases) of the syngas in the resulting gas fraction.

A major drawback of MIP is, however, the scaling up of the process. At present, there is yet no commercially available microwave equipment able to process several tons of wastes in a reasonable time. Nevertheless, a lot of investigation is being made in this field and some promising prototypes or demo plants are currently working. Some of these are shown in Table 1.

Table 1. Energy consumption of different technologies for producing syngas

Process	**Processing Capacity**	**Energy Consumption** [kWh/kg]
Scandinavian Biofuel[1]	70 T/day	0.15
Payakkawan et al.[2]	1 T/day	1.5
Rotawave Ltd.[3]	3-12 kg/load	0.5-1.3

What follows is focused on the use of MIP for producing syngas i.e., maximizing the gas fraction and, at the same time, the H_2 and CO content of this fraction.

Why syngas from MIP?

Pyrolysis is defined as a thermochemical and irreversible decomposition of organic materials at elevated temperatures in the absence of oxygen. It involves the simultaneous change of physical phase and chemical composition. Pyrolysis gives rise to three end products: gas, oil and char, which all have the potential to be further refined if required (see Figure 2). The relative amounts and characteristics of each product vary considerably depending on the feed and the operating conditions of the process (i.e., temperature, heating rate, inert gas flow, presence of catalysts, etc.).

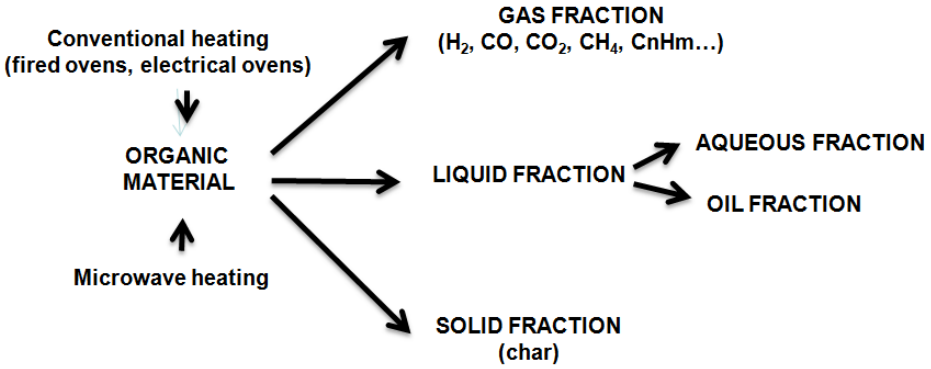

Figure 2. Pyrolysis-derived products

The main properties and applications of each fraction are the following:

Solid fraction

The pyrolysis char is a carbonaceous residue mainly composed of elemental carbon originated from thermal decomposition of the organic components, unconverted organic compounds, e.g. solid additives, and even carbon nanoparticles produced during secondary reactions between the evolved volatiles and the char itself. This carbonaceous residue plays an important role in the pyrolysis process since it also contains other inorganic compounds (i.e., ashes or mineral matter) of the original feed material, which are relevant in specific catalytic processes. The importance of the char cannot be understated as it may be involved as a reactant or catalyst in heterogeneous reactions. On the other hand, the utilization of the char depends considerably on its characteristics. Some possible uses of char are: (i) as solid fuel for boilers, either directly converted to pellets or mixed with other materials such as biomass, carbon, etc., (ii) as feedstock for the production of activated carbon, (iii) as feedstock for the gasification process to obtain hydrogen rich gas, (iv) as additive for soil amendment.

However, these char fractions often contain an important amount of heavy metals making difficult their industrial use. When MIP is aimed to produce syngas, the solid fraction is minimized. Moreover, part of this fraction can be recirculated into the process acting both as microwave susceptor and as catalyst of certain reactions to promote syngas production[4-6].
Depending on the operational conditions of MIP it is possible to attain very high temperatures at the end of the pyrolysis process and so obtain a solid residue which is partially vitrified (see Figure 3). Unlike other methods aimed to maximizing the porous texture of the solid residue in order to produce adsorbents, this particular MIP process is designed to obtain a solid residue with minimal porous textural development, where the heavy metals present in the residue are occluded in a glassy-like matrix[7]. The advantages of this technique are the substantial volume reduction with respect to the initial feedstock and a solid residue that is more resistant to the leaching of organic substances and heavy metals than the char obtained by conventional pyrolysis. This can be of particular interest to process organic residues containing high amounts of toxic heavy metals.

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. Thus, the liquid products still need to be upgraded by lowering the oxygen content and removing residues.

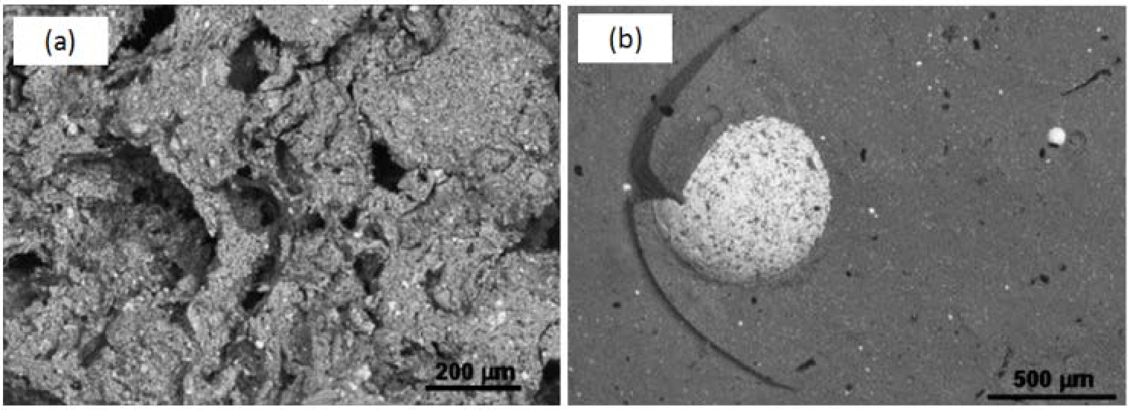

Figure 3. SEM microphotographs of the solid residues obtained after conventional pyrolysis in (a) an electric furnace and (b) high temperature MIP[7].

The oil obtained from pyrolysis can have the following uses: (i) combustion fuel, (ii) power generation, (iii) production of chemicals and resins, (iv) transportation fuel, (v) production of anhydro-sugars like levoglucosan, (vi) binder for pelletizing and briquetting combustible organic waste materials, (vii) fuel for diesel engines, normally by blending with the diesel oil.

However, this liquid fraction is composed of a complex mixture of organic compounds making it difficult to upgrade for use as biofuel. It may also contain hazardous compounds such as polycyclic aromatic hydrocarbons (PAH). In the case of MIP for syngas production, the high temperatures reached during the process also minimizes the production of oils, which, in addition, contain less hazardous compounds[8,9].

Gas fraction

The gas produced in a pyrolysis process is mainly composed of permanent gases, such as H_2, CO, CO_2, CH_4, C_2H_2, C_2H_4, C_2H_6, etc. The gas fraction collected from pyrolysis can be used directly as fuel for 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. Moreover, pyrolysis gas containing significant amounts of hydrogen and carbon monoxide might be used for syngas applications. These range from the production of ammonia, methanol and the Fischer-Tropsch process to produce hydrocarbons, biopolymers, etc.

In the case of MIP, depending on the operating conditions and the organic substrate, the gas yield can be as high as 58 wt%, while the maximum gas yield attained in conventional pyrolysis at a similar temperature (800 ºC) is only 37.6 wt%. Moreover, the amount of syngas (H_2 + CO) can reach values up to 95.2 vol% in the case of MIP, while the maximum value obtained when the same substrate is pyrolyszed in an electric furnace at similar temperatures is 79.8 vol% (see Table 2). That is, MIP not only gives rise to a higher production of gases but also these gases have a higher proportion of syngas than the equivalent process carried out in an electric furnace.

Use of microwave susceptors

The dielectric properties of the dried biomass (and organic wastes, in particular) are very poor, i.e., it is very difficult to heat it, up to the high temperatures needed, by microwave radiation, unless very high power is used[12]. In order to achieve the high temperatures required to carry out the pyrolysis, it is necessary to use very high powers, if possible. One way to overcome this problem is to use microwave susceptors. Among the different microwave receptors than can be used, carbonaceous materials are particularly good microwave absorbers (see Figure 4).

Thus, recycling part of the char produced in the pyrolysis to the pyrolysis process itself can be a smart solution. The heating process during MIP of two different biomass/microwave susceptor blends is sketched in Figure 5.

Table 2. Comparison between MIP and conventional pyrolysis (both at 800 °C) for different substrates[10,11].

		Microalgae[a]	**MSW**[b]	**Straw**[c]
MIP Gas Yield	[wt%]	57.2	48.3	55.9
Conv. Gas Yield	[wt%]	34.7	36.1	37.6
Increment	[%]	64.8	33.8	48.7
MIP Syngas	[vol%]	94.0	94.6	95.2
Conv. Syngas	[vol%]	53.0	72.5	79.8
Increment	[%]	77.4	30.5	19.3

[a] **Microalgae:** A residue, after methanol extraction, of the microalgae scenedesmus almeriensis.
[b] **MSW:** Municipal solid wastes
[c] **Straw:** Agricultural residue, used in a biodiesel production plant, that is mainly composed by straw.

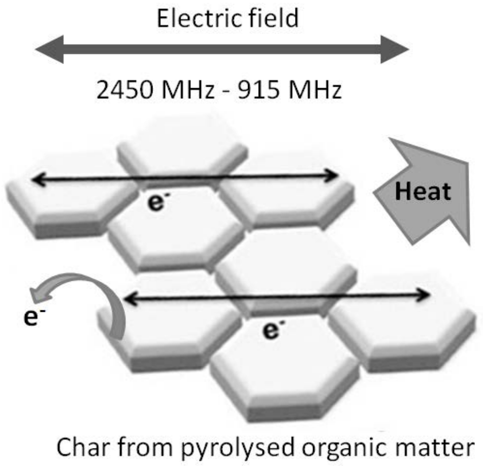

Figure 4. Char from organic feedstock pyrolysis is a microwave-absorbent material due to the delocalized π-electrons, which cannot couple to the phase changes of the electric field, hence the accumulated energy dissipates as heat[6]. Eventually, electrons may jump out of the material, ionizing molecules of the surrounding atmosphere, and form micro-plasma[13].

Obviously, the more homogeneous is the blend, the more homogeneous the temperature of the bed will be, and, in consequence, the MIP process will be completed faster and in a reproducible way.

It is worth mentioning that there is a minimum concentration of the microwave susceptor below which MIP does not take place unless a higher power is used. But, interestingly, this is also the optimal concentration, since at higher concentrations the pyrolysis progresses in an uneven way. This is due to a decrease of the skin depth, or penetration of microwaves, because of the formation of an outer layer of good microwave absorber char that hinders the penetration of microwaves into the bed of biomass[12]. This effect is schematized in Fig. 6.

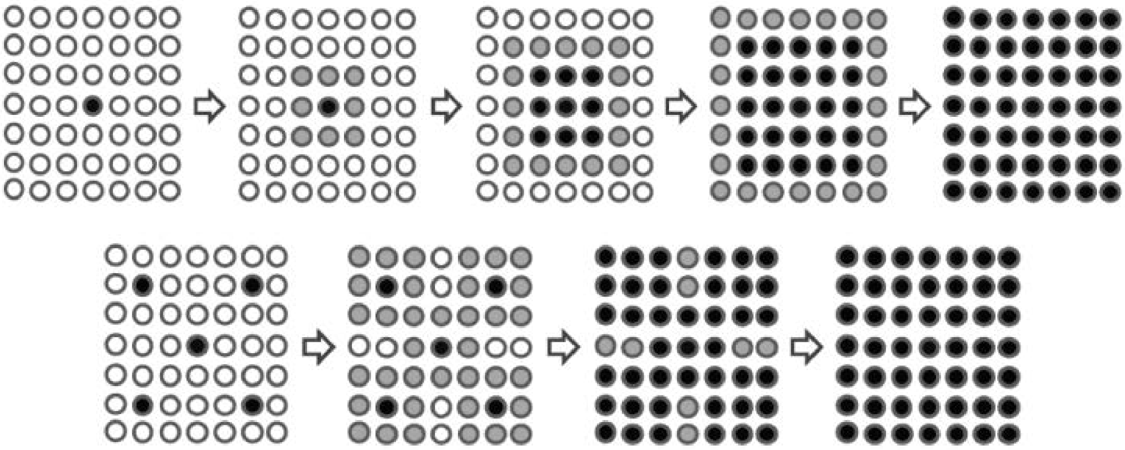

Figure 5. Evolution of organic particles (white circles) and microwave susceptor particles (black circles) during MIP, creating second, third and more generations of microwave receptors (gray circles)[5,12].

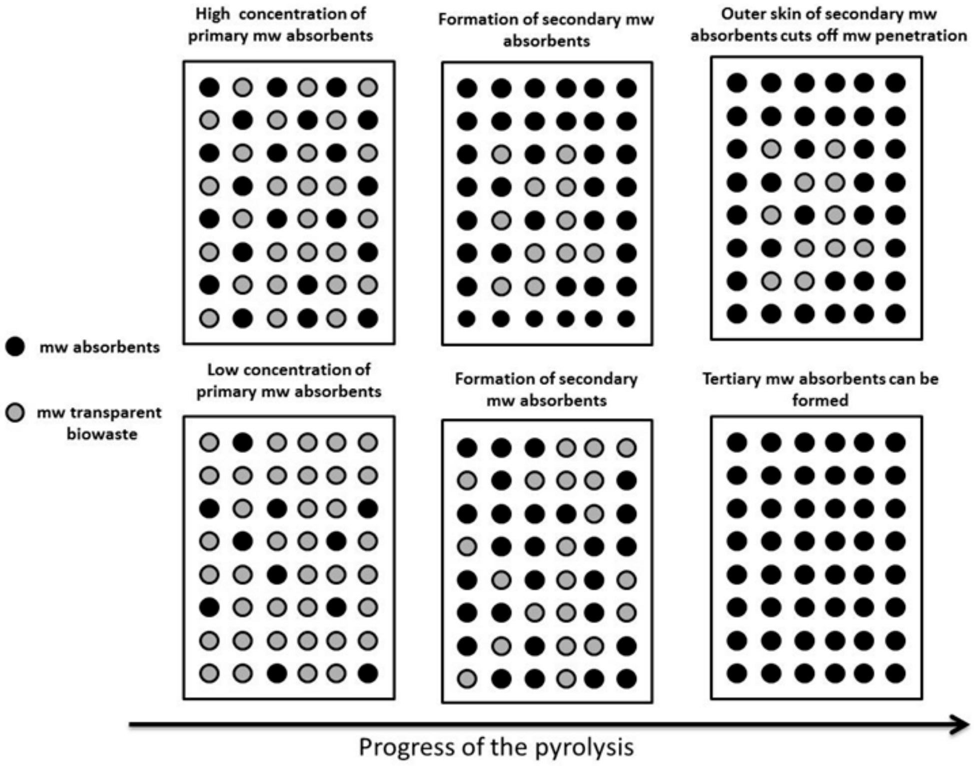

Figure 6. Evolution of organic particles (gray circles) and microwave susceptor particles (black circles) during MIP, for high and low concentrations of primary susceptors (upper and lower rows, respectively)[12].

Triple role of char as susceptor, reactant and catalyst

As microwave energy is transferred directly to the material that is heated (volumetric heating), the temperature inside the material is usually higher than the temperature of the surrounding atmosphere, unlike conventional heating. Figure 7 shows an illustrated comparison between temperature gradients caused by microwave and conventional heating.

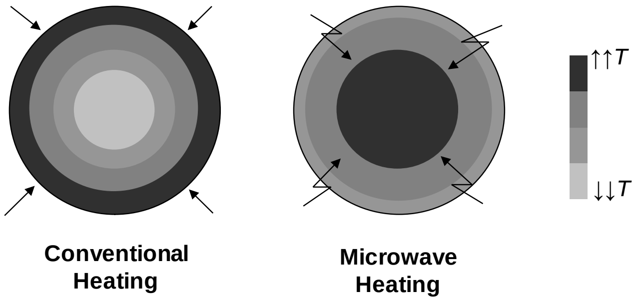

Figure 7. Temperature gradients produced by microwave and conventional heating.

In MIP, gases evolve from high temperature regions, inside the particles, to the lower temperature of the surroundings. This gives rise to different cracking and recombination reactions than in the case of conventional heating. For instance, the following heterogeneous endothermic gasification reactions are favored (with respect to conventional heating) since the solid reactant is being directly heated by the microwaves:

$$C_{(s)} + CO_{2\,(g)} \leftrightarrow 2CO_{(g)} \qquad (1)$$

$$C_{(s)} + H_2O_{(g)} \leftrightarrow CO_{(g)} + H_{2\,(g)}. \qquad (2)$$

In this case, the char used as susceptor (and that being formed as MIP progresses) is also a reactant. Moreover, this char can also act as catalyst favoring the endothermic gasification reactions[14-16]:

$$(\text{-}CH_2\text{-})_{(g)} + H_2O_{(g)} \leftrightarrow CO_{(g)} + 2H_{2\,(g)} \qquad (3)$$

$$(\text{-}CH_2\text{-})_{(g)} + CO_{2\,(g)} \leftrightarrow 2CO_{(g)} + H_{2\,(g)} \qquad (4)$$

and the exothermic water gas shift reaction:

$$CO_{(g)} + H_2O_{(g)} \leftrightarrow CO_{2\,(g)} + H_{2\,(g)} \qquad (5)$$

Since the char added as susceptor and that produced in the pyrolysis acts as catalyst, the MIP can be considered as a self-catalytic pyrolysis[16]. Moreover, it seems reasonable to suppose that the direct heating of microwaves reinforces the catalytic performance of the catalyst (char). On the other hand, recombination of light molecules, once they are released from the material, is unpaired by the lower temperature (compared to the core of the particle) of the surrounding atmosphere[15]. More important than these effects might be, however, the presence of micro-plasma during the MIP.

The pseudo-catalytic effect of micro-plasma

The microwave heating of carbon-based material can give rise to hotspots, which appear here as small sparks or electric arcs (considered as micro-plasma since confined to a >1-mm space and last for a fraction of a second). These electric arcs are caused by uneven distribution of the EM field and by preferential heating (due to differences in dielectric properties, impurities or geometric defects within the particle). These hotspots may cause ionization of the surrounding atmosphere. Moreover, in the case of carbons, the increase in the kinetic energy of the delocalized π electrons, which are free to move in relatively broad regions trying to align themselves with the alternating electric component of the microwave field, may give rise to the ionization of the surrounding atmosphere caused by electrons that eventually jump out of the material (see Fig. 4).

Evidence of the micro-plasma is presented in Fig. 8. It may appear in a quasi-spherical shape (ball lightning) or as an arc discharge. Although the temperature of these hotspots is orders of magnitude higher than the mean temperature of the bed, because of its ephemeral nature the average bed temperature remains virtually unaltered. This is quite an interesting fact since the “chemistry” inside the micro-plasma differs from that in a non-ionized atmosphere. Thus, complex gas molecules are ionized when they hit the micro-plasma, and these ions are then recombined resulting in simpler molecules like H_2 or CO rather than CH_4 or CO_2. This can explain why MIP favors the production of gases in general, and syngas in particular, when compared with conventional pyrolysis at similar temperatures. In this sense, one may consider a pseudo-catalytic effect of micro-plasma that selectively favors the production of syngas.

Figure 8. Different types of micro-plasma occurring in MIP and some of the species formed in it (down right)[13]

The energy costs of producing syngas by MIP

Since most of the data available in scientific literature are obtained from lab experiments, it is difficult to establish the energy required for producing syngas using a possible MIP industrial process. However, a rough approximation based on an extrapolation of several microwave heating processes can be done in order to have a first estimation of the energy consumption to scale up a MIP process[17]. Comparatively, the energy cost for producing syngas from MIP processes is higher than the energy consumed in other conventional processes (see Table 3).

Table 3. Energy consumption of different technologies for producing syngas

Process [Ref.]	**kWh/m^3 of syngas**
Steam CH_4 reforming [18]	1.46
Partial oxidation of CH_4 [18]	0.01
Auto-thermal CH_4 reforming [18]	0.14
Microwave-assisted dry CH_4 reforming [19]	2.20
Pyrolysis-gasification of MSW [20]	0.38
Gasification of refused-derived fuel [20]	0.41
MIP of straw [21]	1.88
MIP of biowastes [21]	1.63 – 3.89

Nevertheless, this comparison is somewhat uneven since some of these processes use CH_4, light hydrocarbons or alcohols as raw material, which has to be previously produced. This can have an important impact in the total energy consumption of the process, depending on the method of production. In addition, these processes need the application of specific catalysts to induce the production of H_2 and CO. Moreover, an exhaustive care must be taken to avoid catalyst deactivation; for instance, a higher steam/C ratio than expected from the stoichiometry of the reaction is usually required to drive the steam-methane reforming in order to avoid coke deposition onto the catalyst surface. The comparison is more even in the case of gasification. However, it is important to bear in mind that gasification needs a gasifying agent like steam, oxygen, CO_2, etc. In addition, char combustor and reformer reactors are usually required. These hurdles are absent when it comes to the MIP process, as no operating costs regarding to pre-treatment steps, gasifying reagents (hence additional capital expenditure if air separation units are required to produce O_2), or expensive catalysts are envisaged. This leaves some room to the higher energy consumption reported for the MIP processes.

Concluding remarks

Syngas production by microwave induced pyrolysis of organic wastes and other bio-solids is an attractive technology from an environmental point of view, giving that hazardous and pollutant materials are converted into a clean and valuable gas. Moreover, the collateral pollution released (in the oil and solid sub-products) is lower as compared to other alternatives used for valorizing organic residues. This is due to the high degree of cracking of the organic molecules because of the micro-plasma occurring during pyrolysis, which in turn gives rise to a high syngas production. If the saving that represent the cost of getting rid of the organic residues is not contemplated, the energy costs of using this technology are still higher than other conventional technologies for producing syngas. However, this is an incipient technology that largely depends on the advances in the design of new microwave furnaces able to operate efficiently at a large scale. Therefore, the viability of this technology will be linked to the evolution of the waste management cost and to the development of new microwave equipment capable of operating on large scales.

Acknowledgements

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J. Angel Menéndez Díaz, researcher, science popularizer, and entrepreneur, was born in Lugones, Asturias, Spain. He graduated from University of Oviedo, Spain, where received his M.Sc. in Chemistry and Ph.D. in Chemical Engineering in 1988 and 1994, respectively. He worked as research assistant at the Penn State University, USA, from 1995 to 1996. In 1997, he joined INCAR-CSIC, Spain, where he is currently working as a scientific researcher. His research activity is mainly focused in carbon materials and the use of microwave heating applied to industrial processes, leading various research projects on these fields. He is author and co-author of more than 200 scientific publications including books, diverse book chapters and patents. He has served as the Doctoral advisor of several students. He is a former member of the executive committee of the Spanish Carbon Group (GEC) from 2003 to 2011; Founder Editor of the GEC Bulletin (2005-14), and a cofounder of Xerolutions Ltd.