

*Chapter 5*

## **SYNGAS PRODUCTION BY CO<sub>2</sub> REFORMING OF CH<sub>4</sub> UNDER MICROWAVE HEATING – CHALLENGES AND OPPORTUNITIES**

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### **ABSTRACT**

The main industrial process used to produce synthesis gas (H<sub>2</sub> + CO) and its resulting byproducts is the steam reforming of natural gas. Methane reforming with carbon dioxide, or dry reforming, is a promising alternative that may lead to the reduction of CO<sub>2</sub> emissions and the production of a syngas with a lower ratio of H<sub>2</sub>/CO. The main obstacle to the industrial implementation of CH<sub>4</sub> reforming with CO<sub>2</sub> is that there are no commercial catalysts that can operate without undergoing deactivation due to carbon deposition. Consequently, new catalysts are being developed and changes are being introduced in the process in order to achieve high and steady conversions.

The microwave-assisted CO<sub>2</sub> reforming of CH<sub>4</sub> over carbon-based catalysts combines the catalytic and dielectric properties of carbonaceous materials with the advantages of microwave heating, which favours catalytic heterogeneous reactions due to, among other reasons, the generation of hot spots or microplasmas. Under certain operating conditions, the microwave-assisted dry reforming reaction can be considered as a combination of CH<sub>4</sub> decomposition and CO<sub>2</sub> gasification of carbon deposits, leading to the continuous regeneration of active centres. The most appropriate operating conditions to achieve high conversions for a long period of time are temperatures ranging between 700 and 800°C and the presence of high proportions of CO<sub>2</sub> in the feed (at least 50%).

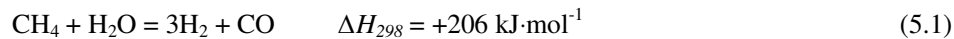
The use of catalysts with a good catalytic activity gives rise to high conversions at high values of volumetric hourly space velocity, making it possible to produce large amounts of syngas. Of the catalysts evaluated the most suitable for the microwave-assisted dry reforming of methane proved to be mixtures of carbonaceous material and metal catalyst. The carbon material should be microporous and have a good reactivity towards CO<sub>2</sub>. The metal catalyst with the best catalytic activity is Ni/alumina.

Energy consumption in the process of microwave-assisted reforming of methane with CO<sub>2</sub> is estimated to be 4.6 kW·h per m<sup>3</sup> of H<sub>2</sub>, which is a promising value compared to the energy consumption in the steam reforming of methane. Therefore, the

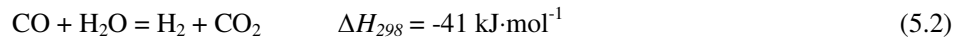
process promises to be competitive, both from the point of view of conversion and energy consumption

## INTRODUCTION

Synthesis gas can be obtained through various chemical and thermochemical processes from almost any carbon source, such as oil, carbon, biomass or biodegradable waste. However, natural gas is nowadays the dominant feedstock and steam reforming is the principal industrial process for the production of syngas (and hydrogen) [1-5]. Figure 5.1 shows the steps employed at the typical hydrogen production plants based on steam reforming. Steam reforming involves the endothermic conversion of methane and steam into hydrogen and carbon monoxide (reaction 5.1). It typically occurs at temperatures between 700 and 850°C, pressures between 3 and 25 bar and over Ni-based catalysts [5,6].



Steam reforming results stoichiometrically in a  $\text{H}_2/\text{CO}$  ratio of 3:1, which is higher than the ratio needed for the synthesis of byproducts, such as methanol or derivatives from the Fischer-Tropsch reaction [2,5]. Industrially, the  $\text{H}_2/\text{CO}$  ratio is adjusted by means of the water gas shift reaction (WGS, reaction 5.2), which is usually performed in two steps: a high temperature shift (350 – 400°C) over iron oxide-based catalysts and a low temperature shift (200 – 250°C) over copper-based catalysts [2,5,7,8].



Despite being a well-established process, steam reforming presents several drawbacks. The coupling of WGS for  $\text{H}_2/\text{CO}$  ratio adjustment is costly and it makes the global process more expensive [5,9,10]. In addition, an elevated heat supply is necessary in order to achieve a high methane conversion. The heat supply normally comes from combustion of part of the incoming natural gas feedstock ( $\leq 25\%$ ) or from burning waste gases, such as purge gas [6,11]. Therefore, a large quantity of  $\text{CO}_2$ , ranging from 0.35 to 0.42  $\text{m}^3$  of  $\text{CO}_2$  per  $\text{m}^3$  of  $\text{H}_2$  produced, is emitted due to both the reaction and the heat requirement [12].

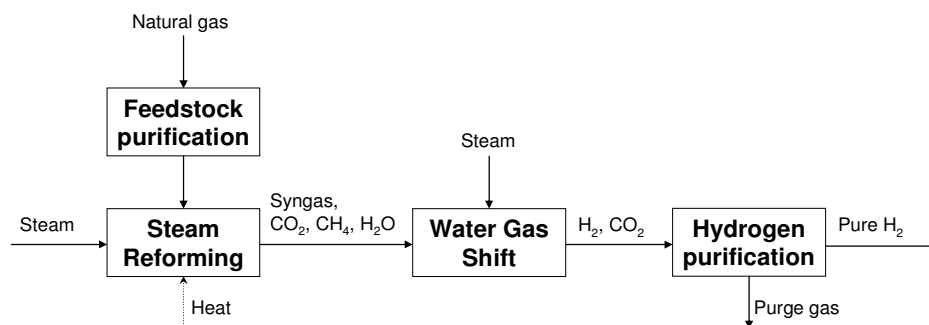
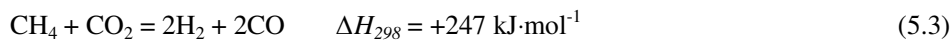


Figure 5.1. Steam reforming process for producing natural gas.

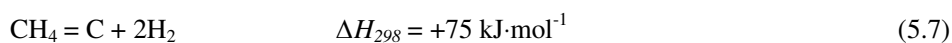
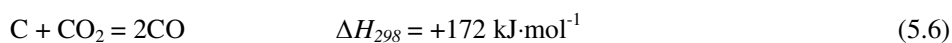
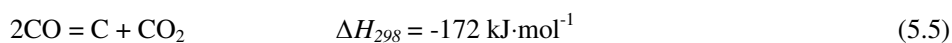
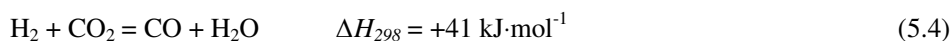
Moreover, an excess of steam must be introduced, approximately at a H<sub>2</sub>O/CH<sub>4</sub> ratio of 3 to 4, in order to avoid the deactivation of the metal catalysts due to carbonaceous deposits, and consequently, operation costs and energy consumption increase [4,8]. In addition, as the metal-based catalysts used in the steam methane reforming or the following syngas conversion processes may be poisoned by sulphur containing compounds (usually H<sub>2</sub>S and COS), expensive desulphurization units are needed to remove these compounds [5,7].

It is for these reasons that alternative processes to steam reforming are being investigated. The catalytic decomposition of methane is the preferred alternative for hydrogen production [12-17], while partial oxidation and CO<sub>2</sub> reforming are the two main options for replacing steam reforming to convert methane into syngas [2,3,8,10,11].

The CO<sub>2</sub> reforming of methane, or dry reforming (reaction 5.3) is an endothermic reaction, like steam reforming, but it yields a syngas with a lower ratio of H<sub>2</sub>/CO, i.e. 1:1 for a complete conversion. This ratio is preferable for the synthesis of higher hydrocarbons via Fischer-Tropsch and adequate for the production of oxygenated derivatives, which eliminates the need to adjust H<sub>2</sub>/CO ratio by means of the WGS reaction [8-10,18-21].



Dry reforming is favoured by high temperatures and low pressures. Thermodynamically, it can occur at temperatures higher than 640°C but, technically and assuming a stoichiometric ratio of CH<sub>4</sub>/CO<sub>2</sub> in the feedstock, temperatures higher than 800°C are needed to achieve acceptable conversions [9,21]. The process selectivity is determined by the occurrence of side reactions, which depend on the operating temperature (see Table 5.1). Thus, at temperatures lower than 800°C, the reverse water gas shift reaction (RWGS, reaction 5.4) occurs [4,9]. In addition, at temperatures lower than 700°C and a stoichiometric CH<sub>4</sub>/CO<sub>2</sub> ratio, i.e. 1:1, carbon deposits may be formed from the Boudouard reaction (reaction 5.5). However, the reverse reaction, i.e. the CO<sub>2</sub> gasification of carbon, occurs at high temperatures (reaction 5.6). Carbon deposition at high temperatures is produced by decomposition of CH<sub>4</sub> (reaction 5.7) [4,9,10].



**Table 5.1. Lower and upper limiting temperatures for reactions of the CH<sub>4</sub>/CO<sub>2</sub> system**

Reaction	Upper limiting <i>T</i> (°C)	Lower limiting <i>T</i> (°C)
CH <sub>4</sub> + CO <sub>2</sub> = 2H <sub>2</sub> + 2CO (5.3)		640
H <sub>2</sub> + CO <sub>2</sub> = CO + H <sub>2</sub> O (5.4)	820	
2CO = C + CO <sub>2</sub> (5.5)	700	
C + CO <sub>2</sub> = 2CO (5.6)		700
CH <sub>4</sub> = C + 2H <sub>2</sub> (5.7)		557

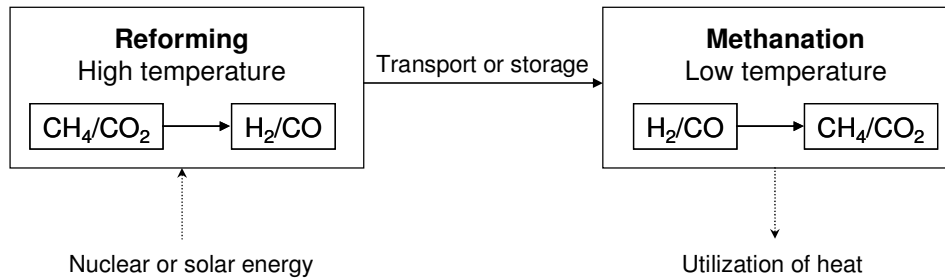


Figure 5.2. Schematic diagram of the chemical energy transmission system.

Dry reforming of methane constitutes a promising option for the conversion of natural gas into syngas mainly due to the environmental benefits that it offers. The dry reforming reaction turns two greenhouse gases ( $\text{CH}_4$  and mainly  $\text{CO}_2$ ) into a valuable feedstock and may lead to the reduction of  $\text{CO}_2$  emissions [2,9,10,18-20]. Unless the required energy is supplied from renewable or non-fossil sources, it is unlikely that  $\text{CO}_2$  emissions will be completely eliminated since dry reforming is an endothermic process. Nevertheless, if the heat supply is provided by the combustion of part of the methane feedstock,  $\text{CO}_2$  emissions will be around  $0.2 \text{ m}^3$  of  $\text{CO}_2$  per  $\text{m}^3$  of  $\text{H}_2$  produced, which is lower than the quantity emitted by steam methane reforming [4,22].

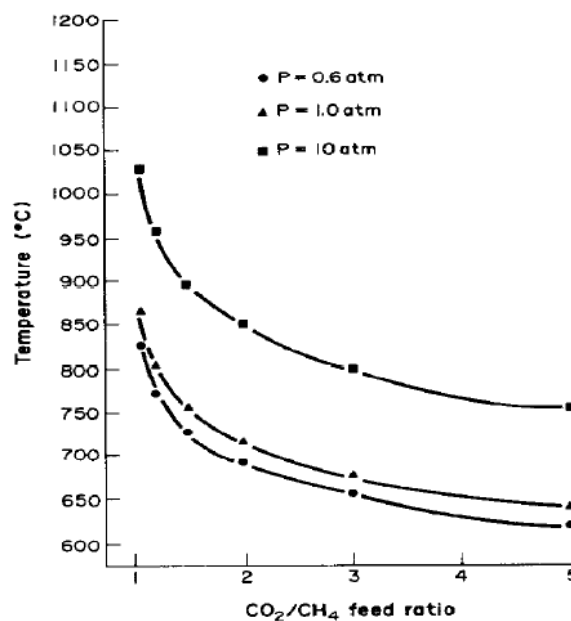
Because of the high endothermicity of  $\text{CO}_2$  reforming of  $\text{CH}_4$ , which exceeds that of steam methane reforming, this reaction has also been tested for viability in energy transmission systems (from solar energy to chemical energy), in energy storage in the form of syngas and in transportation of nuclear energy [9,18,21]. Figure 5.2 shows a schematic diagram of the chemical energy transmission system. The  $\text{CO}_2$  reforming of  $\text{CH}_4$  is carried out by supplying nuclear or solar energy, so that the  $\text{H}_2$  and  $\text{CO}$  produced stores the incident energy. Syngas is saved for later or transported through pipelines to distant locations, where the energy is released by the reverse reaction.

The dry reforming reaction can be carried out with natural gas obtained from remote fields that contains large amounts of  $\text{CO}_2$ , without the need to separate carbon dioxide from the feed, and from petroleum fields where natural gas is flared [10,18,22,23]. In general, the dry reforming of methane may be the most effective process wherever carbon dioxide is a byproduct and available for utilization, for instance, in power plants, which emit a large amount of  $\text{CO}_2$  at relatively high temperature, and in petrochemical industries, where effluents of light gases can be processed with waste streams of  $\text{CO}_2$  [9,23]. In the metallurgical industry, the excess coke oven gases (GOG), consisting mainly of  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{CO}$  and  $\text{N}_2$ , may be turned into synthesis gas by means of dry reforming. The syngas can then be used to produce a variety of compounds but mainly methanol [24,25]. Dry reforming is also an interesting alternative for the valorisation of landfill gas or biogas from the digestion of industrial and municipal waste. Biogas is a renewable, local and low-cost raw material and it consists of approximately 55-75% of  $\text{CH}_4$  and 25-45% of  $\text{CO}_2$ , as well as small amounts of  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{H}_2\text{S}$  or  $\text{CO}$ . The dry reforming of biogas to syngas for the subsequent production of hydrogen would seem to be a more efficient option than the combustion of the biogas in a turbine to produce electricity for the electrolysis of water, or the separation of methane from the biogas to turn it into hydrogen via steam reforming [20,26,27]. In addition, methane

reforming with CO<sub>2</sub>, rather than steam, is an attractive alternative in areas where water is restricted [22].

Despite the advantages afforded by the dry reforming of methane, few industrial processes utilize this reaction [9,18]. One of such processes, the SPARG process, was implemented by Sterling Chemicals Inc. in 1987 [28]. This process produces a syngas with low H<sub>2</sub>/CO ratio by using a partially sulphur-passivated nickel catalyst. The sulphur blocks the sites for carbon nucleation while sufficient sites for the CO<sub>2</sub> reforming reaction are maintained. Another process, the Calcor process, was implemented by Caloric for the production of CO [29]. This is a catalytic reforming process designed to operate under low pressure and at high temperature to treat a desulphurized and CO<sub>2</sub>-rich feedstock.

The main obstacle to the industrial implementation of CO<sub>2</sub> reforming of CH<sub>4</sub> is that there are no commercial catalysts that can operate without undergoing deactivation due to carbon deposition [9,10,19-22]. Therefore, the principal objective of CO<sub>2</sub> reforming studies has been to develop suitable catalysts with good lifetime stability. The catalytic activity of several metals (Cu, Fe, Co, Ni, Ru, Rh, Pd, Ir or Pt) over different supports (Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, MgO, C, ZnO, SiC, La<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, CeO<sub>2</sub> or zeolites) has been studied. The CO<sub>2</sub> reforming of CH<sub>4</sub> over noble metals was found to yield no carbon but their high cost and limited availability prevent them from being used commercially. Although the use of nickel catalysts is more feasible for industrial purposes, they deactivate more easily due to carbon deposition [8,18-20,30]. Moreover, carbon catalysts have been proposed as an alternative to metal catalysts because of their low cost, high temperature resistance and the absence of sulphur poisoning. Moreover, they have showed good catalytic activity [13,19-21,31].



Note: The picture was obtained from Ref. [23] with the permission of Elsevier.

Figure 5.3. Effect of the CO<sub>2</sub>/CH<sub>4</sub> feed ratio on the temperature below which carbon deposits form at various pressures.

In addition to the search for new catalysts, changes to the process are also being investigated in order to achieve high and steady conversions. Thus, high temperatures and  $\text{CO}_2/\text{CH}_4$  ratios higher than unity can be used to avoid carbon deposition. Figure 5.3 shows, for different  $\text{CO}_2/\text{CH}_4$  ratios, the temperatures above which the carbon deposition is avoided. Nevertheless, low temperatures and  $\text{CO}_2/\text{CH}_4$  ratios of 1:1 are preferred in industrial processes in order to maintain a high selectivity towards syngas [4,9,10,22]. In certain circumstances, the simultaneous reforming of methane with  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{O}_2$  may be advantageous. The combination of dry reforming with steam reforming and/or partial oxidation (partial combustion of  $\text{CH}_4$  with oxygen) offers several advantages compared to the individual processes: (i) the  $\text{H}_2/\text{CO}$  ratio can be adjusted by varying the  $\text{CO}_2/\text{H}_2\text{O}/\text{O}_2$  ratio in the feed; (ii) the presence of oxidant agents, such as  $\text{H}_2\text{O}$  and  $\text{O}_2$ , inhibits the process of carbon deposition; and, (iii) as partial oxidation is an exothermic reaction, the energy requirement of the process is reduced when  $\text{O}_2$  is introduced [9,22]. In addition, alternatives to the conventional heating used in the process are being evaluated, such as, the direct conversion of  $\text{CH}_4$  and  $\text{CO}_2$  by using plasma [32,33] or the microwave-assisted dry reforming of methane [19,20,34], which is discussed in detail in this Chapter.

## MICROWAVE HEATING IN HETEROGENEOUS GAS-PHASE CATALYTIC REACTIONS

### Fundamentals of Microwave Heating

Microwaves are a non-ionizing electromagnetic radiation that lies in the range of the electromagnetic spectrum limited by the frequencies between 300 MHz and 300 GHz (wavelength between 1 m and 1 mm). Domestic and industrial microwave applications generally operate at a frequency of 2.45 GHz in order to avoid interference with radar and telecommunication frequencies [35-39].

Dielectric heating is caused by high frequency electromagnetic radiation, i.e., radio and microwaves. The electric field component of the electromagnetic radiation interacts with the charged particles of a material. A current is induced when these particles are free to move. However, when the particles are linked to the material, they try to align themselves with the alternating field, as a consequence of which, the material heats up (dielectric polarization) [40]. As microwave heating is the result of the transformation of microwave energy into thermal energy, due to a molecular interaction with an electromagnetic field, it is in actual fact a question of energy conversion rather than heat transfer. Two principal dielectric polarizations, which are represented in Figure 5.4, are involved in microwave radiation [35,41]: (i) dipolar polarization, which occurs in dielectrics that have induced or permanent dipoles, such as water; and, (ii) space charge polarization, which occurs mainly in dielectric solid materials with charged particles which are free to move in a delimited region (Maxwell-Wagner polarization).

The materials which interact with microwave radiation to produce heat are called dielectrics or microwave absorbers. The ability of a material to be heated in the presence of a microwave field is described by its dielectric loss tangent  $\tan\delta = \varepsilon'' / \varepsilon'$ . The dielectric loss tangent is composed of two parameters: the dielectric constant (or real permittivity),  $\varepsilon'$ , which

measures the ability to propagate microwaves into the material, and the dielectric loss factor (or imaginary permittivity),  $\epsilon''$ , which measures the ability of the material to dissipate the energy in the form of heat [35-38]. Materials which reflect microwaves from the surface and do not heat are called conductors, and materials which are transparent to microwaves are classed as insulators.

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. In Figure 5.5 temperature gradients caused by microwave and conventional heating are compared. Microwave heating offers a number of advantages over conventional heating, such as: (i) non-contacting heating; (ii) rapid heating; (iii) selective heating of materials; (iv) quick start-up and stoppage; (v) a higher level of safety and automation; (vi) a reduction in the size of equipment and higher flexibility; and, (vii) reduced processing time [35,37,38,42].

In recent years, the industrial applications of microwave radiation have increased significantly. Microwave heating is mainly used in food processing, wood drying and rubber vulcanization. Microwave heating is also applied to organic synthesis and analytical chemistry processes, such as, drying, extractions, acid solution, decomposition or hydrolysis [43]. In addition, there is increasing interest in the use of microwaves in a wide range of areas, such as, waste management [37,44], ceramic and polymer processing [39], environmental applications [42,43], metallurgy and mineral processing [35,37,38], carbon-related processes [35], or heterogeneous gas-phase catalytic systems [34-36,41,42].

Various heterogeneous gas-phase catalytic reactions have been studied under microwave heating, such as CH<sub>4</sub> decomposition, CO<sub>2</sub> reforming of CH<sub>4</sub>, H<sub>2</sub>S decomposition, NO<sub>x</sub> and SO<sub>2</sub> reduction or CH<sub>4</sub> oxidative coupling [14,19,20,34,36,41,42]. In general, in a catalytic heterogeneous system, the microwave radiation is selectively absorbed by the solid catalyst. Therefore, the catalyst should be a dielectric material and act not only as a catalyst but also as a microwave receptor [19,35]. However, some catalysts are insulator materials and, consequently, they must be used in conjunction with microwave receptors, such as carbons and certain oxides, in order to be heated easily [35,40]. Carbon materials are usually very good microwave absorbers so they can indirectly heat materials that are transparent to microwaves.

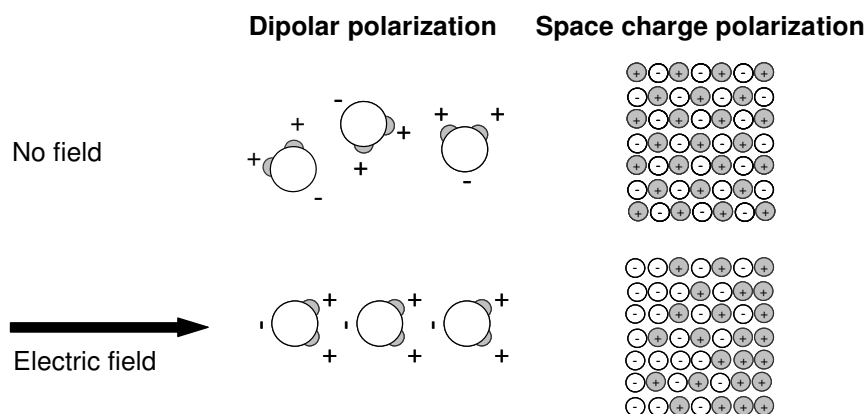


Figure 5.4. Mechanisms of dielectric polarization present under microwave heating.

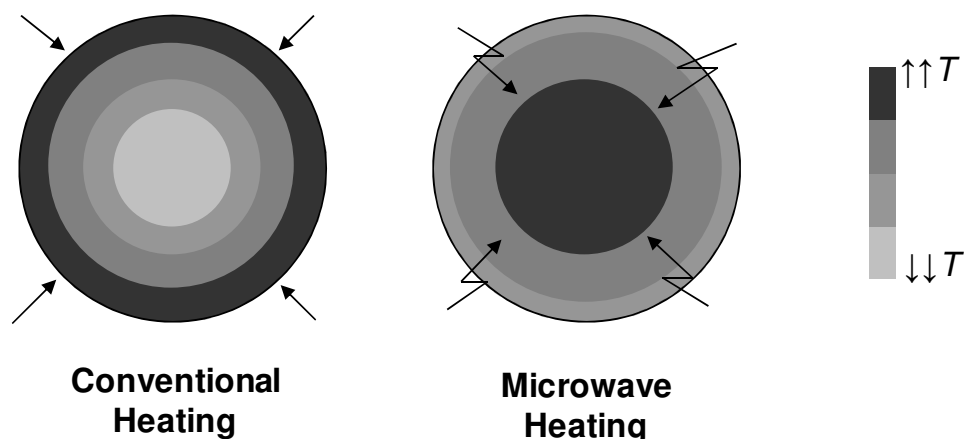


Figure 5.5. Qualitative comparison of the temperature gradients produced by microwave and conventional heating.

Microwave radiation is known to have the potential to increase the rate of reaction, selectivity and yield of catalytic heterogeneous reactions [14,34-36,41,42]. The improvement observed under microwave heating is normally attributed to various thermal effects [42], although the presence of hot spots within the catalyst bed, which are at higher temperature than the average temperature, may be the main reason for the improvement in gas-solid reactions. Hot spots are electric arcs which are caused by an uneven distribution of the electromagnetic fields and preferential heating, due to differences in dielectric properties, impurities or geometric defects within the catalyst. The electric arcs may cause the ignition of the surrounding atmosphere. Moreover, in the case of carbons, the increase in the kinetic energy of the delocalized  $\pi$ -electrons, which are free to move in relatively broad regions and which try to align themselves with the alternating electric component of the microwave field, may give rise to the ionization of the surrounding atmosphere. These hot spots can be therefore considered as microplasmas both from the point of view of space and time, since they are confined to a tiny region of space and last for just a fraction of a second [35,45].

### Microwave Heating Technologies in Gas-Solid Systems

Various microwave technologies can be used in order to carry out gas-solid reactions. In general, microwave heating systems are made up of four basic components: (i) the power supply; (ii) the magnetron, which turns the electric energy into electromagnetic energy; (iii) the applicator or cavity for the heating of the catalyst; and, (iv) the waveguide for transporting microwaves from the magnetron to the applicator. Nevertheless, the main differences among the microwave devices arise from the method used to control the average power output of the magnetron (on/off or variable control) and the design of the applicators (unimode or multimode) [38].

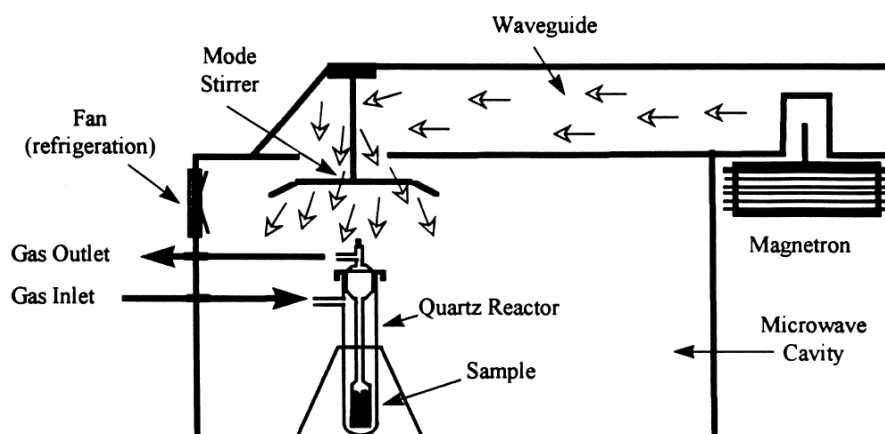
The magnetrons with an on/off control operate at full power but the current is turned on and off in order to reduce the average power. The output power of the magnetrons with variable control can be altered by changing the current amplitude or the intensity of the



magnetic field. Variable control is useful when continuous microwave power is required [36,39].

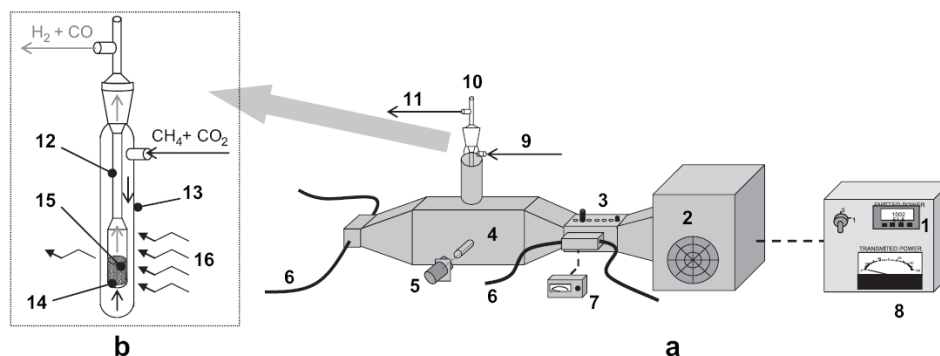
On the other hand, the type of applicator used in a microwave system usually depends on the materials to be processed. Common microwave applicators include unimode and multimode cavities. The unimode applicators, which have one resonant mode, display interesting features, such as precise energy input, predictable electromagnetic field distribution and the possibility of focusing the microwave field at a given location. In addition, it is possible to work with small amounts of catalyst, to determine the dielectric properties of substances and to obtain good reproducibility in the results. For these reasons, unimode cavities are preferred for most experimental set-ups, despite the fact that the effective space for the catalyst tested is limited because the applicator normally forms part of the waveguide. Multimode applicators are capable of sustaining several modes at the same time, as a result of multiple reflections from the oven walls. As multiple maxima of the electromagnetic field within the cavity are found, uniform field distribution can be achieved through changes in geometry and the use of mode stirrers. Multimode microwave ovens are usually more versatile than unimode ovens and, consequently, they are by far the most common processing devices used in industrial applications [36,39].

Temperature measurement inside microwave devices is not a straightforward issue. In order to avoid interactions with microwaves, common thermocouples can be used only when they are shielded and earthed or, in the case of fixed electric field distribution, when they are arranged perpendicular to the field. As an alternative to thermocouples, fiber optic sensors and IR-pyrometers can be employed. Fiber optics usually measure temperatures up to 400°C and are too fragile for most industrial applications. IR-pyrometers can measure higher temperatures and only record the surface temperature, which may differ from the temperature of the interior of the catalyst. Therefore, it is possible to obtain average temperatures but difficult to measure the temperature of hot spots. The use of ultrasonic temperature sensors for covering temperatures up to 1500°C has also been proposed [36,38,41,46].



Note: The picture is obtained from Ref. [47] with the permission of Elsevier.

Figure 5.6. Schematic diagram of a commercial microwave oven adapted for modifying the chemistry of active carbons.



Note: The picture was obtained from Ref. [19] with the permission of Elsevier. 1. Input power control; 2. Air-cooled microwave generator or magnetron; 3. Manual 2-stub unit; 4. Waveguide; 5. Optical pyrometer; 6. Water sink; 7. Reflected power control; 8. Transmitted power control; 9. Inflow gas line; 10. Set quartz reactor-jacket and catalyst/microwave receptor (C/MR); 11. Outflow gas line. 12. Quartz reactor; 13. Quartz jacket; 14. Porous plate; 15. C/MR bed; 16. Microwave radiation.

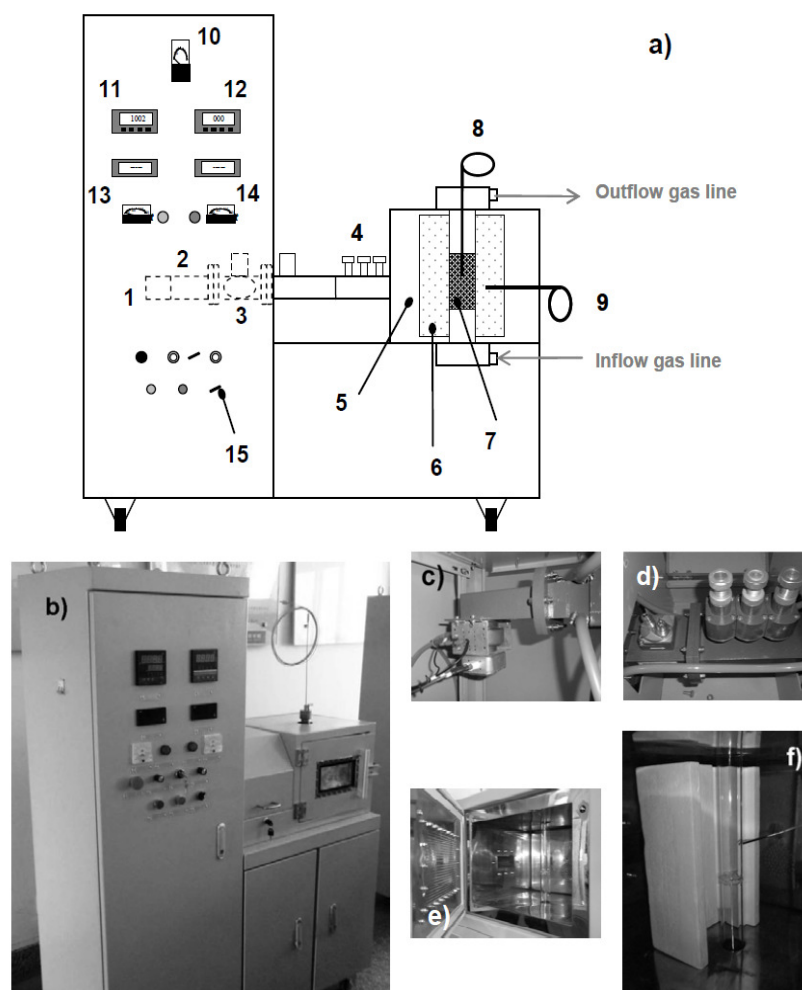
Figure 5.7. (a) Schematic diagram of the single mode microwave device. (b) Close-up view of the set quartz reactor-jacket.

The household microwave oven represents the simplest and least expensive type of multimode on/off control device. Home microwave ovens can be modified by drilling holes on appropriate positions and simple experiments can be performed [36,43]. Figure 5.6 shows a diagram of a commercial microwave oven adapted in order to modify the surface chemistry of active carbons [47]. Microwave devices must be specially design for most applications because proper safety precautions must be taken in order to avoid radiation leaks. These modified ovens cannot be used under explosive conditions or aggressive media.

Unimode microwave ovens have been employed for the in-lab study of various gas-solid reactions [14,19,20,34,48-50]. Figure 5.7 shows a diagram of a possible set-up for a unimode microwave device to carry out experiments of the decomposition and  $\text{CO}_2$  reforming of methane over carbon catalysts [14,19,20]. In this case, the microwave oven can operate at a variable power from 0 to 1860 W and at a fixed frequency of 2.45 GHz. The catalyst sample is placed inside a quartz reactor, which is housed in the centre of the rectangular microwave guide that directs the microwaves from the magnetron into the sample. The non-absorbed radiation is dissipated by a water sink. The power reflected back towards the magnetron is minimized by adjusting the manual 2-stub unit in the waveguide. The catalyst temperature is measured with an IR-pyrometer. Other unimode microwave ovens with variable output power have been described elsewhere [46,48-50]. They can be illustrated by means of a similar schematic diagram to that shown in Figure 5.7, although some differences in the set-ups have been pointed out. Examples of such differences include different maximum operating powers, the use of co-axial cable instead of a rectangular microwave guide, the measurement of temperature with optic fiber and the use of mobile piston, short circuits, apertures, irises or posts, instead of stub units.

Although multimode microwaves are widely used in industrial applications, there are few examples of the use of lab-scale multimode microwave ovens in gas-solid reactions [41,51]. Figure 5.8 shows an experimental set-up used to investigate the microwave-assisted  $\text{CO}_2$  reforming of  $\text{CH}_4$  over carbon-based catalysts. This lab-scale pilot plant is a multimode

microwave device, which operates at a frequency of 2450 MHz over a power range of 0 - 1500 W. Microwaves are generated in a magnetron and directed through a rectangular waveguide to the multimode applicator, which houses the reactor charged with the catalyst. The reactor is isolated by an insulator, which is transparent to microwaves. The catalyst temperature is measured by means of a thermocouple placed inside the catalyst bed. The insulator temperature is measured by means of another thermocouple. The power reflected back to the magnetron is minimized by adjusting a manual 3-stub unit, situated inside the waveguide.



Note: 1. Magnetron; 2. Waveguide; 3. Circulator, detector of reflected power and water sink; 4. Manual 3-stub unit; 5. Multimode microwave applicator; 6. Insulator; 7. Reactor loaded with a catalyst/microwave receptor; 8. Sample thermocouple; 9. Insulator thermocouple; 10. Meter of energy consumption; 11. Controller/display of sample temperature; 12. Display of insulator temperature; 13. Display of emitted power; 14. Display of reflected power; 15. Manual/automatic mode.

Figure 5.8. (a) Schematic diagram of the multimode microwave pilot plant. (b) Multimode microwave pilot plant. (c) Microwave generator, circulator and water sink. (d) 3-stub unit. (e) Multimode applicator and reactor. (f) Reactor and insulator.

A circulator prevents the reflected microwaves from reaching and damaging the magnetron. The reflected power is measured by a detector and dissipated by a water sink. The power needed to generate microwaves during the CO<sub>2</sub> reforming of CH<sub>4</sub> is recorded by an energy consumption meter. The instantaneous electric current and voltage are displayed on a control panel, so that the power required at any one moment can be known. In addition, the microwave pilot plant can operate in manual mode (the operating power is fixed and the C/MR is heated up to the maximum possible temperature under these conditions) and in automatic mode (the operating temperature is fixed at the desired value and controlled by a PID, which adjusts the power emitted by the magnetron in order to keep the sample temperature constant).

Another multimode microwave oven has been described to investigate the microwave-assisted heterogeneous catalytic gas-phase oxidation of hydrocarbons [41]. In this case, a commercial microwave oven with two magnetrons of 900W and rotating antennas was modified using two independent switched-mode power supplies, two metallic flanges for supporting the quartz reactor where the catalyst sample is placed and another metallic flange to support an IR-pyrometer for measuring the temperature. A thermocouple is also used to measure the catalyst temperature after the microwave power has been turned off.

The design of a microwave oven for industrial applications is very much dependent on each specific process and it must take into account critical issues such as power efficiency, uniform power distribution and consistent and reliable performance over the expected range of process conditions [38,41].

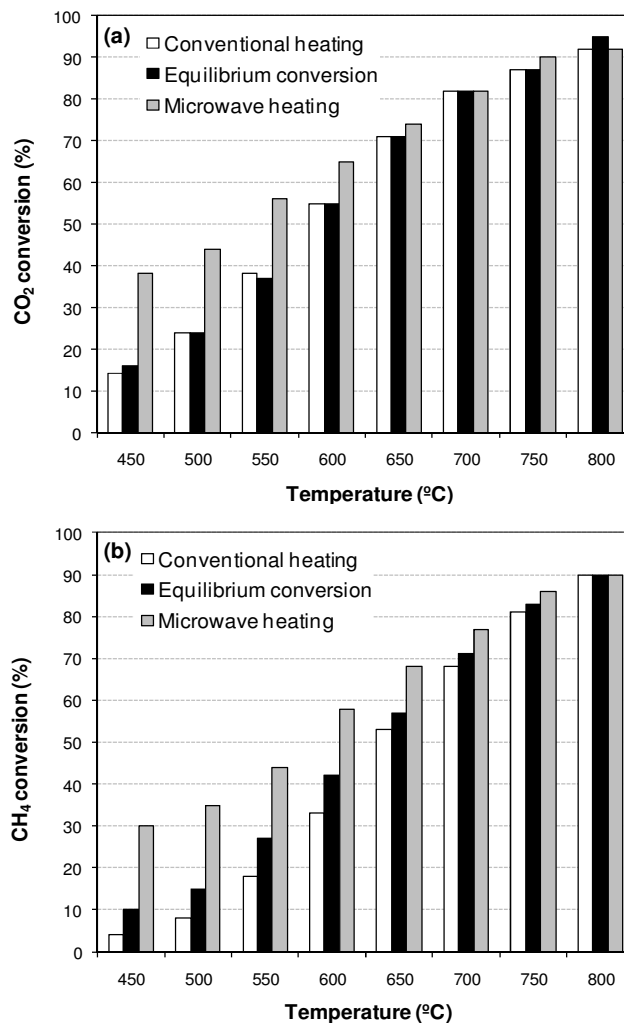
## MICROWAVE-ASSISTED CO<sub>2</sub> REFORMING OF CH<sub>4</sub>

Microwave heating has been applied to the heterogeneous catalytic reaction of CO<sub>2</sub> reforming of CH<sub>4</sub> over carbon catalysts [19,20,52] and metal catalysts [34,42,53]. Carbon catalysts are usually good microwave absorbers and, consequently, heat more easily than metal catalysts, which normally need to be mixed with microwave receptors. However, the catalytic activity of metal-based catalysts is as a rule higher, which makes it possible to work under more severe operating conditions. The operating conditions (temperature, feed gas composition or space velocity) required to ensure a good performance of microwave-assisted dry reforming may depend on the type of catalyst used.

### Operating Conditions

Microwave-assisted dry reforming is an endothermic reaction and, for that reason, CO<sub>2</sub> and CH<sub>4</sub> conversions improve as the temperature increases. Normally, the H<sub>2</sub>/CO ratio of the resulting syngas also increases when the temperature rises. An example of the evolution of the CO<sub>2</sub> and CH<sub>4</sub> conversions as a function of temperature for a series of experiments of dry reforming over a Pt-based catalyst with both microwave and conventional heating is shown in Figure 5.9. In addition, the equilibrium conversions of CO<sub>2</sub> and CH<sub>4</sub>, established according to a mechanism which considers RWGS (reaction 5.4) as secondary reaction, are plotted. As well as the increase in conversion with temperature, the microwave enhancement in the dry

reforming reaction is corroborated by the higher CO<sub>2</sub> and CH<sub>4</sub> conversions obtained under microwave heating compared to conventional heating, mainly below 700 °C. Moreover, under microwave heating, conversions higher than the thermodynamic equilibrium values are achieved due to the formation of random hot spots where temperatures are higher than the average temperature in a bulk metal-based catalyst [34,42]. Microwave enhancement in the CO<sub>2</sub> reforming of CH<sub>4</sub> is also observed over carbon catalysts, the CO<sub>2</sub> and CH<sub>4</sub> conversions being clearly higher under microwave heating than under conventional heating, due to the differences between the heating mechanisms and the presence of hot spots throughout the carbonaceous bed [19].



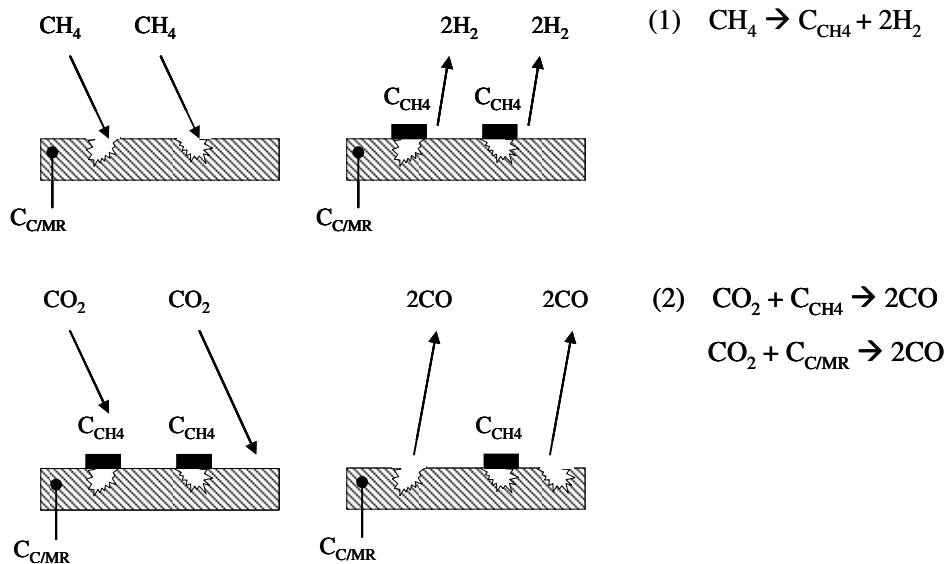
Note: Adapted from Ref. [34].

Figure 5.9. Influence of temperature on the microwave-assisted CO<sub>2</sub> reforming of CH<sub>4</sub> over catalyst Pt (8 wt.%)/CeO<sub>2</sub> (20 wt.%)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at a CH<sub>4</sub>/CO<sub>2</sub> ratio of 1: (a) CO<sub>2</sub> conversion and (b) CH<sub>4</sub> conversion.

Microwave-assisted dry reforming over carbon catalyst is believed to be a combination of catalytic methane decomposition (reaction 5.7) and CO<sub>2</sub> gasification (reaction 5.6), as it is shown in Figure 5.10 [19,20]. Thus, the decomposition of CH<sub>4</sub> takes place in the active centres of the C/MR and, consequently, these are blocked by the carbonaceous deposits from methane. The nature and reactivity towards CO<sub>2</sub> of these carbon deposits is very heterogeneous [20,54]. Most of them are discrete deposits of irregular shape and different size that tend to physically cover the active surface. However, under microwave heating, groups of nanofilaments scattered all over the catalyst surface are formed along with the other deposits (see Figure 5.11). As a result, the highly reactive carbonaceous deposits are gasified by the CO<sub>2</sub>, giving rise to the in situ regeneration of the active centres. Ideally, the catalytic activity of the carbon catalysts is maintained with time.

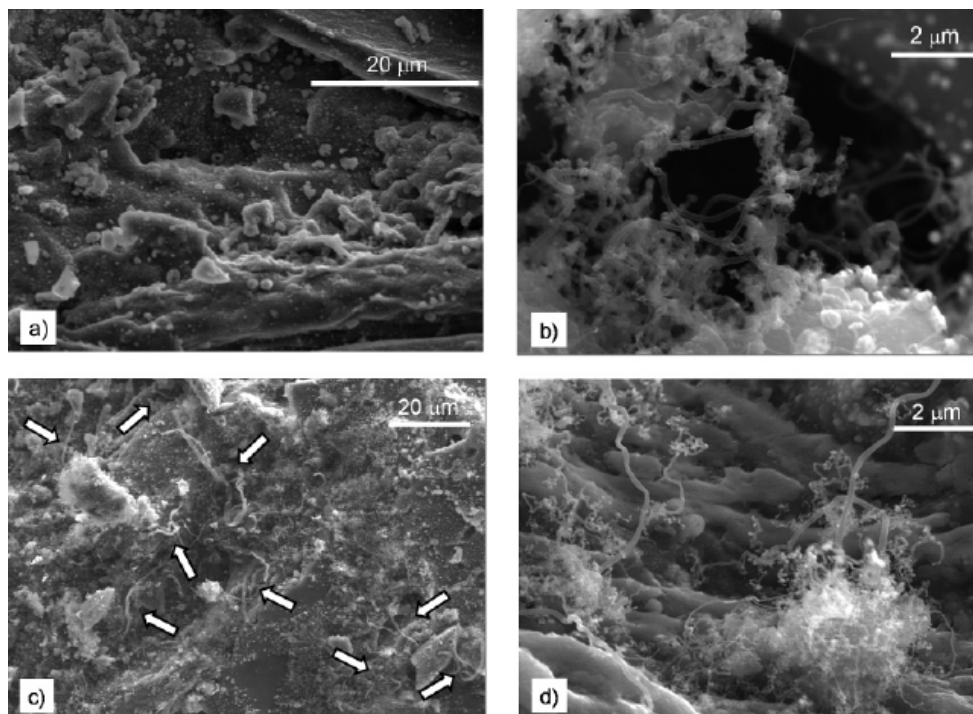
However, the conversion of CH<sub>4</sub> to H<sub>2</sub> may be partially impeded with time due to the existence of non-recovered active centres that are blocked by refractory carbon deposits. CO production is less restricted since CO<sub>2</sub> is able to react with some carbon from the original catalyst. However, the conversion of CO<sub>2</sub> may eventually decrease due to the fact that blockage of the pores by the refractory carbonaceous deposits may impede the access of CO<sub>2</sub> to the highly reactive carbon.

The mechanism proposed is verified between 700 and 800°C, which is therefore the optimum temperature range for carrying out microwave-assisted dry reforming over carbon catalysts [19]. Temperatures of around 900°C and above are discarded because they may favour the formation of a thin film of a pyrolytic carbon deposit on the outside wall of the reactor, which is shown in Figure 5.12a. This pyrolytic deposit is a mixture of non-graphitic/graphitic carbon, the latter being predominant ( $I_D/I_G = 0.69$ , according to the Raman spectrum shown in Figure 5.12b).



Note: C<sub>CH<sub>4</sub></sub>, carbonaceous deposits from the decomposition of CH<sub>4</sub> and C<sub>C/MR</sub>, carbon of catalyst/microwave receptor.

Figure 5.10. Mechanism for the microwave-assisted CO<sub>2</sub> reforming of CH<sub>4</sub> over carbon catalysts.



Note: Ref. [20] with the permission of ACS Publications.

Figure 5.11. SEM images of the deposits obtained after reactions at 800 °C for 2 h: (a) carbon deposits on the carbon catalyst surface, obtained after the decomposition of CH<sub>4</sub> under conventional heating; (b) close-up of the nanofibers obtained after the decomposition of CH<sub>4</sub> under microwave heating; (c) carbon catalyst surface after the CO<sub>2</sub> reforming of CH<sub>4</sub> under microwave heating (arrows indicate the location of groups of nanofibers); and (d) close-up of the nanofibers obtained after the CO<sub>2</sub> reforming of CH<sub>4</sub> under microwave heating.

Because of its graphitic nature, the deposit reflects the microwaves and prevents the C/MR from absorbing radiation, which may cause the experimental device to fail. At lower temperatures, of around 600°C, a mechanism that assumes the occurrence of the RWGS reaction as a side reaction, as in the case of microwave-assisted dry reforming over metal catalysts, is proposed, instead of the one proposed previously.

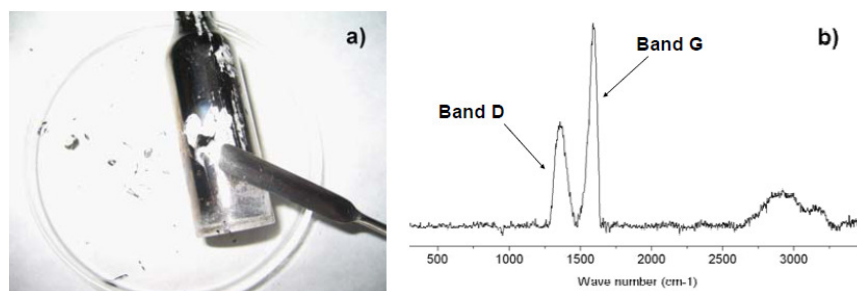
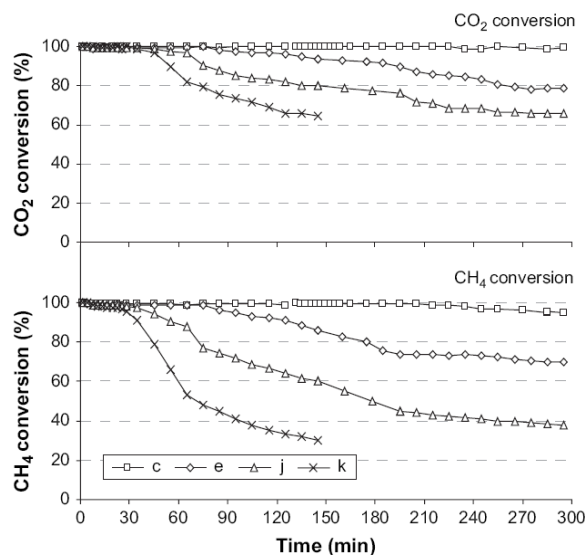


Figure 5.12. (a) Pyrolytic carbon deposits formed on the outside wall of the reactor during microwave-assisted CO<sub>2</sub> reforming of CH<sub>4</sub> at 900 °C; and, (b) Raman spectrum of the pyrolytic carbon deposits.

Apart from temperature, other operating conditions influence the performance of the dry reforming reaction. Thus, in the case of microwave-assisted reforming over carbon catalysts, an increase in volumetric hourly space velocity (VHSV, defined as the ratio between the feed flow rate and the catalyst charge [55]) leads to a decrease in the conversions of  $\text{CO}_2$  and  $\text{CH}_4$ , since the contact time between the reactant gases and the catalyst is reduced. However, the changes in VHSV may not affect the  $\text{H}_2/\text{CO}$  ratio of the synthesis gas produced [19]. The values of VHSV needed in order to achieve acceptable  $\text{CH}_4$  and  $\text{CO}_2$  conversions depend on the type of catalyst. For example, in the case of carbon catalysts, conversions of 80% or above may be obtained with a volumetric hourly space velocity of around  $0.3 \text{ L}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$  [19,20].

The feed gas composition, i.e. the  $\text{CO}_2/\text{CH}_4$  ratio, also influences the microwave-assisted  $\text{CO}_2$  reforming of  $\text{CH}_4$  performance. In the case of carbon catalysts, the quantity of  $\text{CO}_2$  introduced also has a key influence on the conversions achieved. Thus, as is illustrated in Figure 5.13, when the  $\text{CO}_2/\text{CH}_4$  feed ratio is raised, the  $\text{CO}_2$  and  $\text{CH}_4$  conversions increase, especially in the case of  $\text{CH}_4$ . Thus, according to the mechanism explained above, when the proportion of  $\text{CO}_2$  increases, the capacity of  $\text{CO}_2$  for regenerating active centres increases, since there is more  $\text{CO}_2$  available for gasifying the carbonaceous deposits which are blocking the active centres. Consequently, the conversion of  $\text{CH}_4$  increases. At the same time,  $\text{CO}_2$  conversion increases because there is access to the highly reactive carbon deposits and carbon of the catalyst [19]. Interestingly, in the case of the metal-based catalysts, as the ratio of  $\text{CO}_2/\text{CH}_4$  increases,  $\text{CH}_4$  conversion does increase whereas  $\text{CO}_2$  decreases due to the occurrence of the secondary reaction between  $\text{CO}_2$  and  $\text{H}_2$  (RWGS reaction) [34]. Nevertheless, independently of the type of catalyst used, an increase in the  $\text{CO}_2/\text{CH}_4$  ratio introduced causes the  $\text{H}_2/\text{CO}$  ratio of the resulting syngas to decrease. Thus, a  $\text{H}_2/\text{CO}$  ratio of approximately 1.4 can be obtained at a  $\text{CO}_2/\text{CH}_4$  ratio of 0.5, while the  $\text{H}_2/\text{CO}$  ratio may diminish to 0.5 at a  $\text{CO}_2/\text{CH}_4$  ratio of 3.0 [19,34].



Note: The picture is obtained from Ref. [19] with the permission of Elsevier.

Figure 5.13. Influence of the proportion of  $\text{CO}_2$  introduced on the microwave-assisted  $\text{CO}_2$  reforming of  $\text{CH}_4$  over activated carbon at  $800^\circ\text{C}$ .  $\text{CO}_2/\text{CH}_4$  ratio: (c) 1.5, (e) 1.0, (j) 0.8 and (k) 0.5.

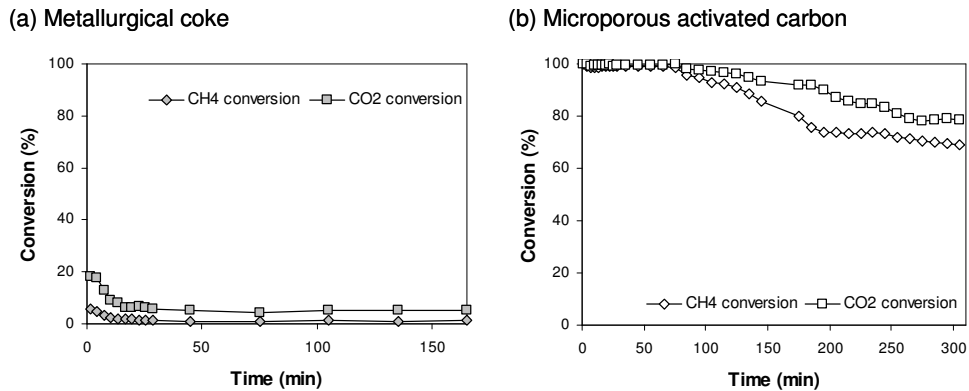


## Catalysts

Since one of the main obstacles for the industrial application of the dry reforming process is that there are no effective catalysts that do not undergo deactivation due to carbon deposition, numerous investigations have been carried out in order to find new catalysts. Nearly all the metals in group VIII over different supports have been studied under conventional heating, resulting in a good catalytic activity [9,10,18]. Noble metals like Rh, Pt, Ru or Ir show the best catalytic activity and the lowest susceptibility to coke formation. However, their high cost and low availability make them unattractive for implementation on an industrial scale. Ni-based catalysts are preferred since they are cheaper and, although they are more susceptible to coke formation, they exhibit a high activity in dry reforming [9,18]. In addition, the type of support used can have a big influence on the catalytic activity and deactivation of metal catalysts. As it is shown in Table 5.2, the activity, selectivity and stability of a metal catalyst can vary with the support. For this reason, several materials have been evaluated as supports, including inorganic oxides [9,10,18,23] and carbon materials [18,56,57]. Ni/Al<sub>2</sub>O<sub>3</sub> is one of the catalysts that give rise to the best results [18]. To a lesser extent, the conventionally-heated CO<sub>2</sub> reforming of CH<sub>4</sub> over carbon catalysts has also been studied [19-21,31] and although they show an acceptable catalytic activity, in general, it is worse than that of metal-based catalyst. On the other hand, microwave-assisted CO<sub>2</sub> reforming of CH<sub>4</sub> has been mainly studied over carbon catalysts [19,20,52], although the catalytic activity of some metal-based catalysts has also been investigated [34,42,58]. Carbon materials are mainly used because they are usually good microwave absorbers, which make them suitable catalysts/microwave receptors for the dry reforming reaction under microwave heating [35,52]. However, many metal-based catalysts are not heated by microwave radiation because, in general, metals reflect microwaves and supports are insulators [38]. Therefore, most of the metal catalysts that exhibit good catalytic activity under conventional heating (e.g. Ni/Al<sub>2</sub>O<sub>3</sub>) cannot be used directly for the microwave-assisted dry reforming, they have to be mixed with or supported on microwave receptors (carbons and certain oxides) for them to be heated by microwaves [40,53,58].

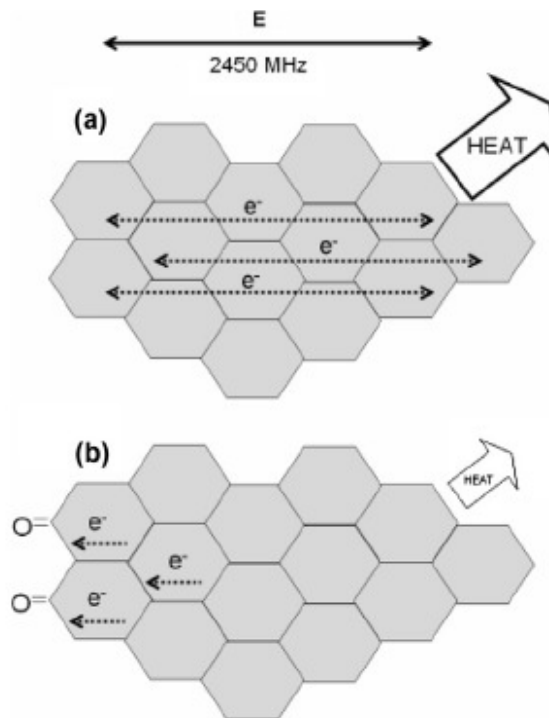
**Table 5.2. Catalytic activity of metals on various supports**

Metal activity	<i>T</i> (°C)	Metal loading (wt. %)
<b>Ru</b>		
Al <sub>2</sub> O <sub>3</sub> > TiO <sub>2</sub> > SiO <sub>2</sub>	620	0.5
<b>Pd</b>		
TiO <sub>2</sub> > Al <sub>2</sub> O <sub>3</sub> > NaY > SiO <sub>2</sub> > MgO	500	5.0
TiO <sub>2</sub> > Al <sub>2</sub> O <sub>3</sub> > SiO <sub>2</sub> > MgO	500	1.0
<b>Rh</b>		
YSZ > Al <sub>2</sub> O <sub>3</sub> > TiO <sub>2</sub> > SiO <sub>2</sub> >> MgO	650	0.5
Al <sub>2</sub> O <sub>3</sub> > SiO <sub>2</sub> > TiO <sub>2</sub> > MgO	500	1.0
<b>Ni</b>		
Al <sub>2</sub> O <sub>3</sub> > SiO <sub>2</sub>	525-725	40
Al <sub>2</sub> O <sub>3</sub> > SiO <sub>2</sub>	600	10
NaY > Al <sub>2</sub> O <sub>3</sub> > SiO <sub>2</sub>	600	2
SiO <sub>2</sub> > ZrO <sub>2</sub> > La <sub>2</sub> O <sub>3</sub> > MgO > TiO <sub>2</sub>	550	4



Note: Adapted from Ref. [52].

Figure 5.14. Influence of the textural properties of carbons on their catalytic activity for the microwave-assisted  $\text{CO}_2$  reforming of  $\text{CH}_4$ : (a) Metallurgical coke – no textural development and (b) Microporous activated carbon –  $S_{BET} = 821 \text{ m}^2 \cdot \text{g}^{-1}$ ,  $V_{mic} = 0.323 \text{ cm}^3 \cdot \text{g}^{-1}$ .



Note: The picture is obtained from Ref. [52] with the permission of Elsevier.

Figure 5.15. Schematic representation of some of the effects involved in the microwave heating of carbons: (a) When microwave heating is caused by the Maxwell–Wagner effect (Interfacial polarization), the delocalized  $\pi$ -electrons try to couple the changes of phase of the electric component of the electromagnetic field dissipating heat and (b) Oxygen-containing surface groups are electron-withdrawing, limiting the mobility of some of the  $\pi$ -electrons of the basal planes and therefore restricting the heat released.

The catalytic activity of carbons in the microwave-assisted CO<sub>2</sub> reforming of CH<sub>4</sub> is considered to be determined by their structural and surface properties [59], as in the case of the decomposition of CH<sub>4</sub>, which has been widely evaluated over various carbonaceous materials (including carbon blacks, activated carbons or chars from biomass residues), mainly under conventional heating but also under microwave heating [14,17,55,60-65].

The catalytic activity of the carbons used as catalysts for microwave-assisted dry reforming of CH<sub>4</sub> is related to their micropores volume [52]. Carbons with a large microporosity are necessary in order to obtain acceptable CH<sub>4</sub> and CO<sub>2</sub> conversions. This is illustrated in Figure 5.14, where the negligible conversions achieved over a metallurgical coke with no textural development are compared with the high conversions obtained over a microporous activated carbon.

Moreover, as microporosity is prevented from being blocked and the catalytic activity of carbons is maintained by the CO<sub>2</sub> gasification of the carbon deposits (according to the mechanism described in Figure 5.10), carbon catalysts need to show good reactivity towards CO<sub>2</sub> [52,59]. Carbons with a low CO<sub>2</sub> reactivity are usually bad catalysts for the microwave-assisted CO<sub>2</sub> reforming of CH<sub>4</sub>. Carbons with a high content in oxygen surface groups show a poor catalytic activity, possibly due to the fact that oxidized carbons show a lower reactivity towards CO<sub>2</sub> and because they are difficult to heat up [52].

Indeed, oxidized carbons heat up with difficulty under microwave radiation and the generation of microplasmas is also more difficult because oxygen, which is electronegative, shows an affinity towards electrons [66]. In other words, oxygenated functionalities are electron-withdrawing, their mobility is limited and, therefore, less density of delocalized  $\pi$ -electrons is available for promoting microwave heating [52,67,68]. This phenomenon is schematically represented in Figure 5.15.

Microwave-assisted dry reforming over suitable carbon catalysts can give rise to high CO<sub>2</sub> and CH<sub>4</sub> conversions for a long period of time. However, as mentioned above, this requires the use of a high CO<sub>2</sub>/CH<sub>4</sub> ratio and a low VHSV, which results in a low production of synthesis gas with a H<sub>2</sub>/CO ratio lower than unity.

Consequently, carbon-supported nickel catalysts have been investigated as alternatives to carbonaceous catalysts. They have the advantages of the carbon catalysts (i.e. they heat up under microwave radiation) and the advantages of the metal catalysts (i.e. a higher catalytic activity). CO<sub>2</sub> and CH<sub>4</sub> conversions achieved over carbon-supported nickel catalysts are higher and steadier than those obtained over the non-impregnated carbons because of the good catalytic activity of metal.

Moreover, higher conversions over carbon-supported nickel catalysts can be obtained by using higher operating times and space velocities, which gives rise to a larger syngas production. For example, as can be seen in Figure 5.16, by using Ni/activated carbon, a CO<sub>2</sub> conversion of 100% and a CH<sub>4</sub> conversion of 60% were obtained after 300 min at a VHSV of 1.50 L·h<sup>-1</sup>g<sup>-1</sup>, whereas a CO<sub>2</sub> conversion of 80% and a CH<sub>4</sub> conversion of 70% were obtained over the non-impregnated activated carbon at a much lower VHSV (around 0.30 L·h<sup>-1</sup>g<sup>-1</sup>). However, syngas production over Ni/activated carbon is limited by the catalyst deactivation, which is probably due to the agglomeration of Ni particles by sintering and due to the blockage of active sites by carbonaceous deposits as in the case of carbon catalysts [2,18].

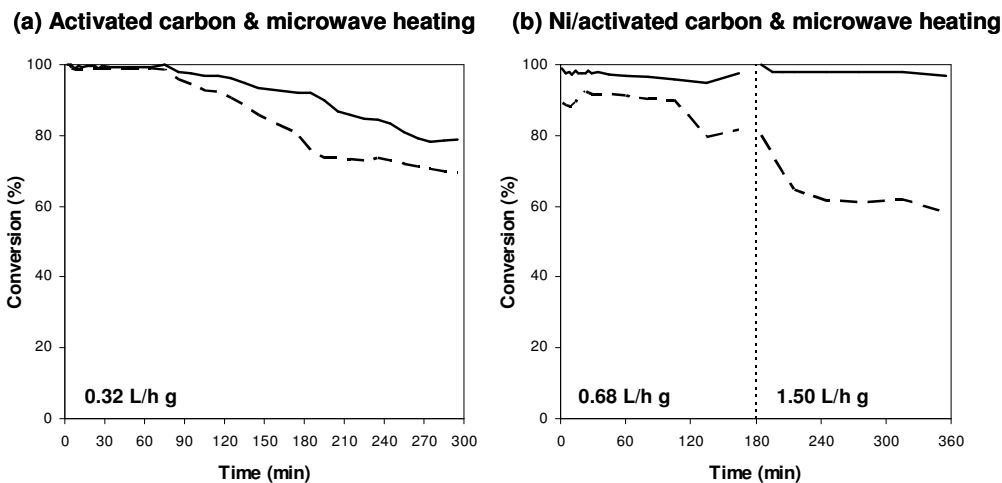


Figure 5.16. CO<sub>2</sub> conversion (solid line) and CH<sub>4</sub> conversion (dotted line) obtained by the microwave-assisted CO<sub>2</sub> reforming of CH<sub>4</sub> over different catalysts: (a) Carbon catalyst (activated carbon) and VHSV of 0.32 L·h<sup>-1</sup>·g<sup>-1</sup>, and (b) Carbon-based Ni catalyst (Ni/activated carbon) and VHSV of 0.68 and 1.50 L·h<sup>-1</sup>·g<sup>-1</sup>.

As well as carbon-supported nickel catalysts, heterogeneous mixtures of carbonaceous materials and metal catalysts can be used in order to catalyze the microwave-assisted CO<sub>2</sub> reforming of CH<sub>4</sub>. As in the case of carbon-supported Ni catalysts, the catalytic mixture combines the characteristics of a good microwave receptor and catalyst. In the light of previous results, the chosen carbon material needs to be microporous and have good reactivity towards CO<sub>2</sub>, and alumina-supported nickel catalyst (Ni/Al<sub>2</sub>O<sub>3</sub>) is one of the preferred metal components [18,52,53]. When a heterogeneous mixture of carbon and Ni/Al<sub>2</sub>O<sub>3</sub> is used as catalyst for the dry reforming reaction, the mechanism of reaction described above (Figure 5.10) is slightly modified. Thus, CH<sub>4</sub> decomposition tends to occur preferentially over the Ni-based fraction, whereas the CO<sub>2</sub> tends to gasify the carbon deposits from methane (active sites for methane decomposition are continuously being regenerated) and part of the initial carbonaceous fraction [53]. Therefore, choosing a suitable carbonaceous material for the blend is no trivial matter. Indeed, this may influence the catalytic activity of the resulting mixture of carbon fraction and metal-based fraction and the regeneration of the active centres by CO<sub>2</sub> gasification, since reactivity towards CO<sub>2</sub> varies for different carbonaceous materials [52]. In addition, the microwave heating capacity of the mixture is determined by the dielectric properties of the carbonaceous fraction, which may differ depending on the material used [35]. Figure 5.17 shows the profiles of the CO<sub>2</sub> and CH<sub>4</sub> conversions during microwave-assisted dry reforming over a catalytic mixture of activated carbon and Ni/Al<sub>2</sub>O<sub>3</sub>. Conversions close to 100% are obtained during at least 15 hours at a VHSV of 3 L/h g. This catalytic mixture therefore is preferable Ni/activated carbon, since higher conversions are obtained at a higher VHSV (see Figure 5.16b).

According to the results presented in Figure 5.17, CO<sub>2</sub> and CH<sub>4</sub> conversions can increase with time, which may be due to the fact that the carbon deposits from the decomposition of CH<sub>4</sub> are more reactive than the initial activated carbon [62,69], or possibly, because the carbonaceous deposits favour changes in the metal-based fraction of the catalyst.

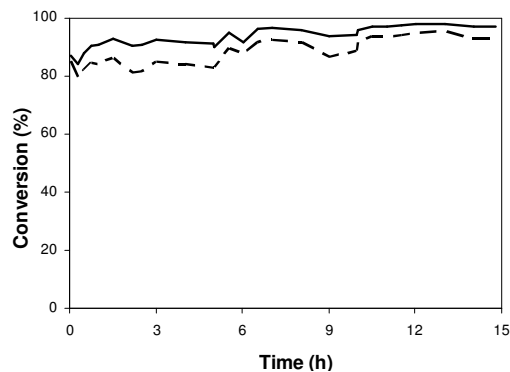
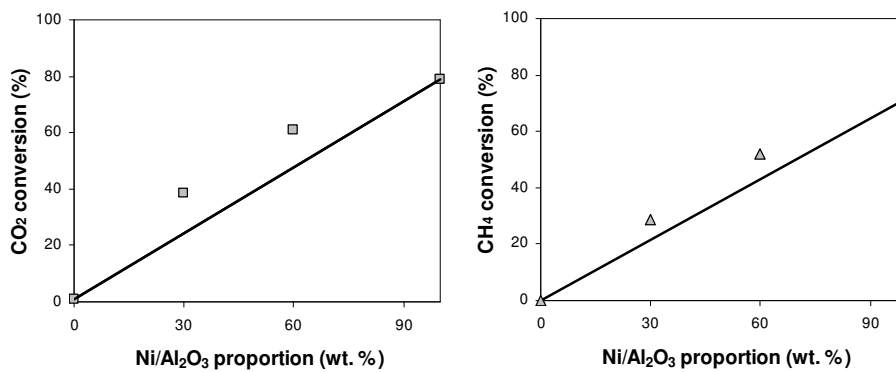


Figure 5.17. CO<sub>2</sub> conversion (solid line) and CH<sub>4</sub> conversion (dotted line) obtained by the microwave-assisted CO<sub>2</sub> reforming of CH<sub>4</sub> over a catalytic mixture of activated carbon and Ni/Al<sub>2</sub>O<sub>3</sub>, 800 °C, 50 vol.% CH<sub>4</sub> – 50 vol.% CO<sub>2</sub> and 3 L·h<sup>-1</sup>g<sup>-1</sup>.

In addition, reduced Ni may interact with the alumina during the heating up to operating temperature (around 800°C) and under inert atmosphere, previous to the dry reforming reaction, leading to the formation of the spinel NiAl<sub>2</sub>O<sub>4</sub> [53,70,71]. In actual fact, NiAl<sub>2</sub>O<sub>4</sub> is not active in the dry reforming reaction, but in its reduced form, which may be continuously produced under the reaction atmosphere, it tends to inhibit the formation of carbonaceous deposits and it shows a good stability, since reduced Ni from spinel tends to be disperse, making sintering more difficult. Therefore, the interaction between the metal and the support may favour the steady conversions obtained over the catalytic mixture, although the blockage of Ni by carbon deposition and the sinterization of Ni particles may eventually lead to the deactivation of Ni/Al<sub>2</sub>O<sub>3</sub> [70,71]. Moreover, a synergetic effect exists between the carbonaceous fraction and the metal-based fraction, which means that the experimental CO<sub>2</sub> and CH<sub>4</sub> conversions obtained over the mixtures of carbonaceous materials and metal-based catalysts are higher than the conversions calculated by means of the law of mixtures (i.e. by adding the weighed individual conversions) [53], as is illustrated in Figure 5.18.



Note: Adapted from Ref. [53]. Operating conditions: conventional heating at 800°C, 50 vol.% CH<sub>4</sub> – 50 vol.% CO<sub>2</sub> and 3 L·h<sup>-1</sup>g<sup>-1</sup>.

Figure 5.18. Comparison between the CO<sub>2</sub> and CH<sub>4</sub> conversions expected by the law of mixtures (solid lines) with the experimental conversions of CO<sub>2</sub> (squares) and CH<sub>4</sub> (triangle) attained during dry reforming over different catalytic mixtures of activated carbon and Ni/Al<sub>2</sub>O<sub>3</sub>.

The existence of a synergetic effect facilitates a compromise between the catalytic activity and the cost of the catalyst. Thus, the replacement of part of the metal-based fraction, which is probably a better catalyst for the CO<sub>2</sub> reforming of methane, by a carbonaceous material, which is cheaper [61], leads to a decrease in the conversions lower than that expected if there were no synergetic effect. The synergetic effect is especially advantageous in the microwave-assisted dry reforming process because, as mentioned above, part of the metal-based catalyst, which does not absorb microwaves, must be replaced by the carbonaceous material in order to be heated by microwave radiation. Due to the synergetic effect, this substitution does not involve any significant loss of catalytic activity. Moreover, any loss of catalytic activity from the use of catalytic mixtures instead of metal-based catalysts may be offset by the enhancement of the CO<sub>2</sub> and CH<sub>4</sub> conversions due to microwave heating.

The production of synthesis gas depends on the type of catalyst used. Thus, larger quantities of methane can be treated with CO<sub>2</sub> over the catalytic mixtures than over carbon catalysts, as a consequence of which more syngas can be produced. However, syngas composition seems to depend on the operating conditions, mainly the CH<sub>4</sub>/CO<sub>2</sub> ratio and the heating device, rather than on the type of catalyst used. Thus, under similar operating conditions, the microwave-assisted dry reforming of methane produces syngas with a similar H<sub>2</sub>/CO ratio irrespective of the carbon-based catalyst used [53].

For example, at 800 °C and 50 vol.% CH<sub>4</sub> – 50 vol.% CO<sub>2</sub>, syngas with a H<sub>2</sub>/CO ratio of 0.8 is obtained over Ni/activated carbon and of 0.9 over a mixture of activated carbon and Ni/Al<sub>2</sub>O<sub>3</sub>. These values are very close to the stoichiometric H<sub>2</sub>/CO ratio of 1 and considerably higher than the values obtained from conventional dry reforming over metal catalysts, where the reverse water gas shift takes place as a side reaction (H<sub>2</sub>/CO ratio around 0.5 or even lower) [72].

## ENERGY CONSUMPTION

In this Section, preliminary estimations of energy consumption during the microwave-assisted CO<sub>2</sub> reforming of CH<sub>4</sub> over carbon-based catalysts are shown and compared with bibliographic values of energy consumption for the steam methane reforming reaction over metal catalysts in two industrial-based H<sub>2</sub> production processes [73,74]. Table 5.3 summarizes the values of energy consumption estimated for the different processes.

In their work, Carrara et al. [73] developed a simulation tool for performance prediction in a steam reforming hydrogen production plant. A 1500 m<sup>3</sup>/h hydrogen production plant is simulated and, although the investigation is a theoretical one, field data from an industrial plant were used to validate the model.

According to these data, the energy consumption for the steam reforming reaction over metal-based catalysts is 3.4 kW·h per m<sup>3</sup> of CH<sub>4</sub> introduced or 1.2 kW·h per m<sup>3</sup> of H<sub>2</sub> produced. The reactor outflow gases include CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub> and CO, at a H<sub>2</sub>/CO ratio of 5:1. Only the energy consumed in the reaction stage is taken into consideration in order to compare the dry and steam reforming reactions. In other words, the other stages of the global process, such as heat exchangers, WGS reactor or separation units are not taken into account.

**Table 5.3. Energy consumption for the steam reforming and microwave-assisted CO<sub>2</sub> reforming of methane**

STEAM REFORMING OF METHANE		
Reference	Carrara, 2010 [73]	Seo, 2002 [74]
Calculation basis *	H <sub>2</sub> production of 1500 m <sup>3</sup> ·h <sup>-1</sup>	H <sub>2</sub> production of 1 mol·s <sup>-1</sup>
Syngas H <sub>2</sub> /CO ratio	5:1	4:1
Supplied power to reforming reactor	2094.5 kW	78.8 kW
Energy consumption respect to introduced CH <sub>4</sub>	3.4 kW·h per m <sup>3</sup> of CH <sub>4</sub>	3.9 kW·h per m <sup>3</sup> of CH <sub>4</sub>
Energy consumption respect to produced H <sub>2</sub>	1.2 kW·h per m <sup>3</sup> of H <sub>2</sub>	1.2 kW·h per m <sup>3</sup> of H <sub>2</sub>
MICROWAVE-ASSISTED CO <sub>2</sub> REFORMING OF METHANE		
Reference	activated carbon	Ni/Al <sub>2</sub> O <sub>3</sub> + activated carbon
Calculation basis	1 m <sup>3</sup> ·h <sup>-1</sup> of introduced CH <sub>4</sub>	1 m <sup>3</sup> ·h <sup>-1</sup> of introduced CH <sub>4</sub>
Syngas H <sub>2</sub> /CO ratio	2:3	1:1
Supplied power to reforming reactor	84.4 kW	8.3 kW
Energy consumption respect to introduced CH <sub>4</sub>	84.4 kW·h per m <sup>3</sup> of CH <sub>4</sub>	8.3 kW·h per m <sup>3</sup> of CH <sub>4</sub>
Energy consumption respect to produced H <sub>2</sub>	44.4 kW·h per m <sup>3</sup> of H <sub>2</sub>	4.6 kW·h per m <sup>3</sup> of H <sub>2</sub>

Note: \* Final H<sub>2</sub> production, after the reforming, water gas shift and purification stages.

On the other hand, Seo et al. [74] developed simulation models for the steam methane reforming, partial oxidation and autothermal reforming processes, using as a basis of calculation 1 mol s<sup>-1</sup> of H<sub>2</sub> produced. The thermal energy required by each stage of the reforming process is evaluated. These stages comprise a reforming reactor, a water gas shift reactor, a steam generator and a heat exchanger, but only the energy consumed in the reaction stage is taken into consideration for comparison purposes. According to this work, energy consumption for the steam reforming reaction is approximately 3.9 kW·h per m<sup>3</sup> of CH<sub>4</sub> introduced or 1.2 kW·h per m<sup>3</sup> of H<sub>2</sub> produced. The reactor outflow gases are composed of CO<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub> and CO, at a H<sub>2</sub>/CO ratio of 4:1.

The energy consumption values of the microwave-assisted CO<sub>2</sub> reforming of CH<sub>4</sub> are estimated by scaling up the experimental data obtained from the multimode device described in Figure 5.8 and using a flow rate of 1 m<sup>3</sup>/h of CH<sub>4</sub> as a basis of calculation. In addition, experiments over two different catalysts, an activated carbon and a mixture of activated carbon and Ni/Al<sub>2</sub>O<sub>3</sub>, are carried out. As can be seen in Table 5.3, the estimated energy consumption for the microwave-assisted CO<sub>2</sub> reforming of CH<sub>4</sub> over activated carbon is 84.4 kW·h per m<sup>3</sup> of CH<sub>4</sub> introduced, 44.4 kW·h per m<sup>3</sup> of H<sub>2</sub> produced or 17.6 kW·h per m<sup>3</sup> of syngas produced, the ratio of the syngas being H<sub>2</sub>/CO ≈ 2:3. In the case of microwave-

assisted CO<sub>2</sub> reforming of CH<sub>4</sub> over a mixture of activated carbon and Ni/Al<sub>2</sub>O<sub>3</sub>, energy consumption is estimated as 8.3 kW·h per m<sup>3</sup> of CH<sub>4</sub> introduced, 4.6 kW·h per m<sup>3</sup> of H<sub>2</sub> produced or 2.2 kW·h per m<sup>3</sup> of syngas produced at a H<sub>2</sub>/CO ratio of 1:1. In effect, energy consumption during microwave-assisted dry reforming is nearly ten times lower when the catalytic mixture is used as catalyst instead of only the activated carbon. In the case of the catalytic mixture, only the carbonaceous fraction is heated by microwave radiation (the metal-based fraction cannot be heated by microwaves and is presumably heated by conduction from the particles of the carbonaceous material). However, the much lower energy consumption estimated over the catalytic mixture may be due to the fact that the reforming reaction can operate at a large volumetric hourly space velocity and still achieve high conversions, which is reflected directly in a larger syngas (or hydrogen) production per mass of catalyst.

The energy consumption value of 44.4 kW·h per m<sup>3</sup> of H<sub>2</sub> produced estimated from the microwave-assisted CO<sub>2</sub> reforming of CH<sub>4</sub> over an activated carbon was found to be too high compared to the value of 1.2 kW·h per m<sup>3</sup> of H<sub>2</sub> produced, obtained from the bibliographic data for the steam reforming reaction over metal-based catalysts. Under adequate operating conditions, high conversions can be obtained when the use of carbon catalysts and microwave heating are combined. However, from an energy point of view, dry reforming must be optimized for it to be able to rival the industrial process of steam methane reforming.

The energy consumption value of 4.6 kW·h per m<sup>3</sup> of H<sub>2</sub> produced estimated from the microwave-assisted CO<sub>2</sub> reforming of CH<sub>4</sub> over a catalytic mixture was also higher than the value of 1.2 kW·h per m<sup>3</sup> of H<sub>2</sub> produced from steam reforming. However, various premises need to be considered when comparing the two reforming processes. First, the given values of energy consumption for the microwave-assisted dry reforming are estimated from experimental data obtained in a lab pilot plant, whereas the consumption values for steam reforming are established on the basis of data obtained from industrial plants of H<sub>2</sub> production. Presumably, energy consumption during the dry reforming would be lower with a larger scaling up and energy integration of the global process. Secondly, the dry reforming reaction is more endothermic than the steam reforming reaction (+247 kJ·mol<sup>-1</sup> and +206 kJ·mol<sup>-1</sup>, respectively). What is more, energy consumption during the dry reforming reaction stage could be higher than consumption during the steam reforming stage whereas consumption in the global process of microwave-assisted CO<sub>2</sub> reforming of CH<sub>4</sub> could be lower than that of the steam reforming process. For example, the dry reforming of CO<sub>2</sub>-rich natural gas, biogas and CO<sub>2</sub>-rich industrial residual streams can be carried out without the need for other condition stages [9,10,18,20,25]. However, previous methane separation stages would be needed in the case of the industrial steam reforming process. The same could occur with the subsequent stages. Besides, in the case of microwave-assisted dry reforming, the high CH<sub>4</sub> and CO<sub>2</sub> conversions achieved may eliminate the need for purification stages and, depending on the desired byproduct, additional stages to adjust the H<sub>2</sub>/CO ratio could be avoided. CO<sub>2</sub> emissions from each process should also be taken into consideration. According to the bibliographic data, global CO<sub>2</sub> emissions for steam reforming are usually in the range of 0.35 to 0.42 m<sup>3</sup> of CO<sub>2</sub> per m<sup>3</sup> of H<sub>2</sub> produced [12], whereas CO<sub>2</sub> emissions for the dry reforming reaction can be as low as 0.2 m<sup>3</sup> of CO<sub>2</sub> per m<sup>3</sup> of H<sub>2</sub> produced [4]. Moreover, CO<sub>2</sub> emissions could hypothetically be zero or even negative if the electricity consumed for the generation of microwave energy in the dry reforming process were produced from renewable sources. All in all, energy consumption during the microwave-assisted dry reforming of



methane over a mixture of carbon and Ni/Al<sub>2</sub>O<sub>3</sub>, estimated at 4.6 kW·h per m<sup>3</sup> of H<sub>2</sub> produced, can be considered a promising result compared to the value of 1.2 kW·h per m<sup>3</sup> of H<sub>2</sub> produced in the industrial steam reforming process. Moreover, the microwave-assisted CO<sub>2</sub> reforming of CH<sub>4</sub> over catalytic mixtures may be able to rival the steam reforming alternative, both from a point of view of conversion and energy consumption.

## CHALLENGES AND OPPORTUNITIES

The microwave-assisted CO<sub>2</sub> reforming of CH<sub>4</sub> offers an alternative to the well-established process of steam reforming of natural gas for the production of synthesis gas and its resulting byproducts. Dry reforming has clear environmental benefits since it turns two greenhouse gases (CH<sub>4</sub> and mainly CO<sub>2</sub>) into a valuable feedstock. Moreover, microwave-assisted dry reforming could lead to the reduction of CO<sub>2</sub> emissions or even to their complete elimination if the electricity consumed in the generation of microwave energy in the dry reforming process were produced from renewable sources. In addition, the dry reforming of CO<sub>2</sub>-rich natural gas, biogas and CO<sub>2</sub>-rich industrial residual streams can be carried out without the need for previous condition stages. Also, CO<sub>2</sub> reforming of CH<sub>4</sub> yields syngas with a H<sub>2</sub>/CO ratio of 1:1 for a complete conversion, which could eliminate the need to adjust H<sub>2</sub>/CO ratio by means of subsequent stages, such as the WGS reaction.

One of the main challenges to the industrial implementation of CO<sub>2</sub> reforming of CH<sub>4</sub> is that there are no commercial catalysts that can operate without undergoing deactivation due to carbon deposition. The microwave-assisted CO<sub>2</sub> reforming of CH<sub>4</sub> over carbon-based catalysts, which combines the catalytic and dielectric properties of the carbonaceous catalysts with microwave heating, which is known to have the potential to increase the rate of reaction, selectivity and yield of the catalytic heterogeneous reactions, has given rise to promising conversion results. However, the energy consumption during dry reforming needs to be reduced in order to be able to rival the steam reforming process. A reduction in energy consumption can be achieved by the improvement of the catalysts in order to operate at large volumetric hourly space velocity but still maintain high conversions, which would yield larger syngas production per mass of catalyst. A scaling up of the process would also enhance the energetic yield. Scaling up is in itself a considerable challenge as it entails the designing of new microwave equipment able to satisfy the requirements of a large scale process, but also it is the opportunity of implementing this type of heating in this and other analogous processes at industrial scale.

## NOMENCLATURE

$\Delta H_{298}$	Enthalpy of reaction at 298K, kJ·mol <sup>-1</sup>
$\varepsilon'$	Dielectric constant or real permittivity
$\varepsilon''$	Dielectric loss factor or imaginary permittivity
$E$	Electromagnetic field, V·m <sup>-1</sup>
$I_D$	D-band intensity in Raman spectrum
$I_G$	G-band intensity in Raman spectrum

RWGS	Reverse Water Gas Shift
$S_{BET}$	Specific BET surface area, $m^2 \cdot g^{-1}$
$T$	Temperature, $^{\circ}C$
$\tan \delta$	Dielectric loss tangent
VHSV	Volumetric Hourly Space Velocity, $L \cdot g^{-1} h^{-1}$
$V_{mic}$	Micropores volume, $cm^3 \cdot g^{-1}$
vol. %	Percentage in volume
WGS	Water Gas Shift
wt. %	Percentage in weight

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