

1 **Influence of carrier gas on microwave-induced pyrolysis**

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6

7 **Abstract**

8 Interest in microwave-induced pyrolysis has increased in recent years due to its several
9 advantages over conventional pyrolysis. Most of these advantages are related to the
10 presence of microplasmas in microwave heating, since the pyrolysis reactions that take
11 place in a plasma atmosphere generally produce light molecules, such as H₂ and CO.
12 Although the exact nature of these plasmas is as yet unknown, it is likely to be
13 dependent on the ionization of the surrounding gases. For this reason, the influence of
14 different carrier gases (N₂, He or no carrier gas) on microwave-induced pyrolysis was
15 chosen as the subject of this study. It was found that microwave-induced pyrolysis can
16 be used to obtain equally good gas compositions and yields after the reactor has been
17 inertized, without the need for a carrier gas.

18

19 **Keywords**

20 Microwave pyrolysis, Carrier, Microplasmas, Syngas

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2 **Highlights**

- 3 • The nature of the carrier gas upon syngas from microwave pyrolysis has been
4 studied
- 5 • Both N₂ and He yields similar gas compositions and yields
- 6 • Microwave pyrolysis without using a carrier gas is a promising alternative

1

2 **1. Introduction**

3 Microwave heating has attracted increasing attention as an energy source for pyrolysis
4 processes over the last decade [1]. This interest stems from the advantages that
5 microwave heating offers over conventional heating, including higher heating rates,
6 volumetric and selective heating, shorter operation times and a quick start-stop
7 capability [2,3]. In the specific case of pyrolysis, microwave heating has been
8 demonstrated to produce extraordinary gas yields, especially, of syngas [1,4,5]. This has
9 promoted interest in microwave-induced pyrolysis (MIP) as a means of converting
10 organic feedstock in biorefineries into energy, fuels or materials [6,7]. Apart from
11 parameters, such as the operating conditions or the type of feedstock used in the process
12 [1,8,9], the main reason for this high productivity seems to be the presence of
13 microplasmas during microwave heating [2,10].

14

15 These plasmas are *hot spots* that are confined to a very tiny space and last only a
16 fraction of a second. The temperature at these points is significantly higher than the
17 mean temperature of the rest of the material and high enough to cause the ionization of
18 the surrounding molecules. It is thought that these plasmas can influence the yields of
19 the different fractions (solid, liquid and gas) obtained in the pyrolysis as well as the
20 composition of the gas produced [4]. These localized higher temperatures facilitate the
21 extraction of volatiles from the matter. In addition, the plasmas enhance heterogeneous
22 reactions (such as thermal cracking or the reforming of hydrocarbons) [2,11], thus
23 modifying the composition of the evolved volatiles. Although the nature of these
24 plasmas is unknown, there is some evidence to suggest that it is dependent on the
25 gaseous molecules that are being ionized within the plasma. For example, the presence

1 of high proportions of H₂ during the microwave-assisted dry reforming of coke oven
2 gas, has allowed higher plasma temperatures than in the dry reforming of methane [12].
3 For this reason the carrier gas used in the pyrolysis can affect the microplasmas and
4 influence the distribution of the product obtained in the process. Several works have
5 been focused on the influence of the carrier gas on the pyrolysis in physical terms (i.e.,
6 contact time or dilution). However, there is a lack of studies on the influence of this
7 parameter upon the microplasmas.

8
9 The objective of the present study is to fill this gap by undertaking an analysis of the
10 yields and gas compositions obtained with N₂ and He as carrier gases and, in some
11 cases, in the absence of a carrier gas in order to determine their influence on the process
12 of microwave-induced pyrolysis.

13

14 **2. Material and methods**

15 *2.1 Waste used in pyrolysis*

16 The sample selected for this study was a dried and cleaned organic fraction from a
17 municipal solid waste, supplied by BEFESA *Gestión de Residuos Industriales* S. L.
18 (Seville, Spain). Details of the characterisation of this sample can be found elsewhere
19 [13]. The study of the influence of the carrier gas on pyrolysis was carried out using
20 nitrogen, helium and no carrier gas.

21

22 *2.2 Pyrolysis techniques and characterization of gases*

23 Microwave-induced pyrolysis was performed at 400 and 800 °C using the system shown
24 in Fig. 1a. This system consists of a microwave magnetron with a maximum output
25 power of 2 kW operating at 2450 MHz and a single mode cavity where the sample is

1 placed (approximately 4 g of waste), coupled to a condenser and a gas collecting station
2 (Fig. 1b). The temperature was controlled by means of an optical pyrometer. The gas
3 collector is fitted with a pump by means of which the resulting pyrolysis gas is fed into
4 a gas cylinder. A series of valves are so tuned as to prevent a vacuum from forming
5 inside the reactor while the evolved gas is being compressed inside the station by means
6 of a looping circuit. The valve-tuning procedure which is illustrated in Fig. 2 is as
7 follows:

8

9 a) Cylinder purge. In order to ensure the removal of all previous pyrolysis gases
10 from inside the cylinder, the pump is used to produce a vacuum inside the
11 cylinder.

12 b) Cylinder inertisation. A carrier gas (N_2 or He) is fed into the cylinder so as to
13 ensure a clean atmosphere inside.

14

15 Both steps are repeated three times. Once the cylinder has been cleaned and is in a state
16 of vacuum, the pyrolysis process is initiated and the gas passes through the system until
17 it reaches the cylinder where it is stored (step c in Fig. 2).

18

19 To study the influence of the carrier gas, the reactor was initially purged with N_2 or He
20 for 30 minutes at a flow rate of $50 \text{ mL}_{\text{STP}} \text{ min}^{-1}$. When no carrier gas was used, the
21 purge was carried out with N_2 . The flow rate was then reduced to $10 \text{ mL}_{\text{STP}} \text{ min}^{-1}$ (or
22 switched off in the event of no carrier gas being used) and the microwave irradiation
23 was switched on during 1h. The reflected power was regulated by means of tuning
24 screws until it reached zero. However, owing to the poor capacity of organic wastes to
25 absorb microwaves, it was necessary to use a microwave receptor to induce the

1 pyrolysis. The char obtained from previous pyrolysis was used for this purpose, since it
2 is a product of the process itself, does not contain any strange material that might
3 influence the composition of the fractions and is known to facilitate rapid heating and to
4 achieve the necessary pyrolysis temperature in a short time [4,6,13]. For this study, a
5 receptor-to-residue mass ratio of 0.3:1 was selected. The volatiles evolved during the
6 pyrolysis were forced to pass through a condensing system (cooled by a cryogenic
7 solution of water and NaCl) where the condensable compounds were removed from the
8 gaseous fraction. The gaseous fraction in the cylinder was then analysed by means of a
9 Varian-CP3800 gas chromatograph equipped with a TCD detector and two columns
10 connected in series. The first column was 80/100 Hayesep Q (2 m x 1/8 in. x 2mm) and
11 the second column was a 80/100 Molesieve 13X (1.5 m x 1/8 in. x 2 mm). The second
12 column was bypassed by a six-port valve for the analysis of the CO₂ and hydrocarbons.
13 The carrier gas flow (He) was 30 mL/min. The initial oven temperature was set at 40
14 °C, which was maintained for 1.2 min. It was then programmed to rise from 40 to 65 °C
15 at 50 °C/min with an isothermic step of 3.7 min. The temperature was then lowered
16 from 65 to 55 °C at 20 °C/min and held for 3.1 min. The injector and detector
17 temperatures were fixed at 150 °C. The TCD was calibrated using a standard gas
18 mixture. Both the reactor and the condensing system were weighed before and after the
19 pyrolysis experiments to measure of the solid and liquid yields. The gas yield was
20 determined by difference. Each experiment was performed by duplicate and the results
21 showed repeatability.

22

23 For purposes of comparing the influence of different carrier gas in a different heating
24 mode, conventional pyrolysis was performed in an electric furnace (EF) using the same
25 quartz reactor, temperatures, residence time and oils collector as in MIP in order to

1 determine whether the nature of the carrier gas affected the microplasmas generated
2 during MIP, and in turn the fraction yields obtained from the pyrolysis. Both
3 experimental devices are described elsewhere [4].

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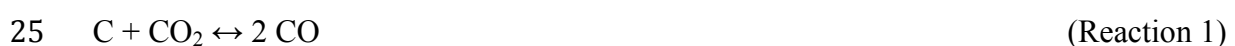
5 **3. Results and Discussion**

6 The effect of using different carrier gases during pyrolysis on the gas yield is illustrated
7 in Fig. 3. As can be seen, there are almost no differences in the yields obtained with the
8 different carrier gases (on a carrier gas free basis). The use of He enhances the gas yield
9 slightly, although this enhancement cannot be strictly attributed to the microplasma
10 phenomenon, since there is also a slight increase in the case of conventional pyrolysis at
11 800 °C, where no microplasmas are generated. Furthermore, MIP increases the gas yield
12 more than conventional pyrolysis, regardless of whether N₂ or He is used, as has been
13 reported previously [4,8].

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15 The carrier gas also influences the gas composition (Table 1). In the case of MIP, N₂
16 and He produce nearly the same composition with a syngas (H₂+CO) concentration at
17 400 °C of ca. 80 vol.%. Thus, the generated microplasmas from N₂ and He must be of
18 the same nature. Nevertheless, if no carrier gas is used, the syngas proportion is less
19 than that produced (ca. 69 vol.%), the generation of CO₂ and CH₄ in this case being
20 favoured. Consequently, it is thought that the use of a carrier gas during MIP may
21 favour gasification and methane cracking reactions (reactions 1 and 2), by allowing a
22 better contact between the solid and gas phases. At a higher temperature, 800 °C, MIP
23 provides nearly the same composition regardless of whether a carrier gas is used or not.

24





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3 In conventional heating, the absence of a carrier gas favours the generation of CO_2 ,
4 aromatics and high hydrocarbons ($> \text{C}_2$). This gives rise to a low-quality gas fraction in
5 terms of syngas production, especially at $400\text{ }^\circ\text{C}$, evidencing the superiority of MIP,
6 since at $400\text{ }^\circ\text{C}$ microwaves reduce the high hydrocarbon content from 52.36 vol.% to
7 virtually 0 vol.%. For this reason, in the case of conventional pyrolysis, it is important
8 to use a carrier gas at low temperatures. However, the differences with conventional
9 pyrolysis at high temperature ($800\text{ }^\circ\text{C}$) whether a carrier gas is used or not are not so
10 great, the gas composition being nearly the same with N_2 and He, though without a
11 carrier gas, the syngas concentration diminishes in favour of CO_2 and heavy
12 hydrocarbons. This can be attributed to a smaller conversion of tar and gases to syngas,
13 perhaps due to a poorer contact between the solid and gas phases.

14

15 Besides the composition of the gas fraction, it is also necessary to consider the energy
16 content in terms of the energy of the gas obtained both per gram of waste pyrolyzed and
17 per gram of gas, which depend on the pyrolysis yields and the composition of the gas
18 fraction, as shown in Table 2. The largest differences correspond to conventional
19 pyrolysis at low temperature. In this case the energy content per gram of gas is the
20 maximum value obtained. This is due to the large proportion of heavy hydrocarbons,
21 which are much more energetic than CH_4 , H_2 or C_2 present in the gaseous fractions
22 obtained under other experimental conditions. The large proportions of high
23 hydrocarbons may be due to the longer residence time, as has been recently reported in
24 the case of the pyrolysis of other wastes [14,15]. However, at higher temperatures, the
25 differences are not as great. The energy extracted from the waste is almost the same and

1 the energy contents of the gases are similar, the maximum value being reached in the
2 experiment with no carrier gas.

3

4 When microwave heating is used more energy is extracted from the waste than under
5 conventional heating. Both at low and high temperatures the energy extracted from the
6 waste and the energy content of the gas are very similar regardless of the carrier gas
7 used. When no carrier gas is used, the values are slightly lower than with N₂ or He.

8

9 **4. Conclusions**

10 The use of different carriers affects the yields of the fractions obtained during the
11 pyrolysis of organic residues only slightly. In the case of conventional pyrolysis, the
12 absence of a carrier gas promotes the generation of CO₂, aromatics and heavy
13 hydrocarbons, yielding a gas fraction of low quality. Nevertheless, in microwave
14 pyrolysis, and especially at high temperature, no significant differences in the gas
15 composition were observed when using different carriers, though a small increase in the
16 gas yield was obtained with helium as carrier gas. The results of this point the way to
17 the implementation of microwave pyrolysis without the need for a carrier gas.

18

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1 **Table 1.** Compositions of the gas fractions obtained at 400 and 800 °C employing
 2 different ovens and carrier gases.

	400 °C					
	EF		MW		No Carrier	
	N ₂	He	N ₂	He	N ₂	He
H ₂	0.9	1.3	0.0	46.2	46.4	38.0
CO	13.4	2.5	11.7	33.3	33.9	31.0
CO ₂	76.3	83.3	32.8	11.0	11.0	18.3
CH ₄	1.9	3.0	1.8	5.1	5.3	8.3
C ₂	1.3	2.1	1.3	4.4	3.4	4.4
Others	6.1	8.0	52.36	0.0	0.0	0.0

	800 °C					
	EF		MW		No Carrier	
	N ₂	He	N ₂	He	N ₂	He
H ₂	21.2	23.2	17.8	50.4	49.5	52.0
CO	25.3	26.4	17.1	36.2	37.6	33.9
CO ₂	25.2	22.0	31.8	8.0	6.9	8.5
CH ₄	12.6	13.6	11.0	3.3	3.7	4.3
C ₂	8.4	8.7	8.5	1.3	2.4	1.4
Others	4.2	4.0	10.1	0.0	0.0	0.0

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Table 2. Energy content of the gas fraction.

400 °C						
	N ₂	EF He	No Carrier	N ₂	MW He	No Carrier
From the waste						
J/g of waste	0.9	0.8	3.2	8.7	9.7	8.0
In the gas						
J/g of gas	6.1	6.8	27.1	18.0	17.4	15.2
800 °C						
	N ₂	EF He	No Carrier	N ₂	MW He	No Carrier
From the waste						
J/g of waste	6.9	6.8	6.9	8.6	10.2	9.3
In the gas						
J/g of gas	19.2	17.3	20.9	17.9	18.2	17.9

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1

2 **Figure captions**

3

4 **Fig. 1.** Schematic of: a) the experimental setup; b) the gas collecting station.

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6 **Fig. 2.** Schematic of the gas collecting station during: a) the cylinder purge; b) the
7 cylinder being filled with inert gas (N₂); c) the cylinder being filled with the pyrolysis
8 gas.

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10 **Fig. 3.** Gas yields of the different experiments carried out at 400 and 800 °C employing
11 different ovens, i.e. conventional pyrolysis (EF) or microwave pyrolysis (MW), and
12 carrier gases.

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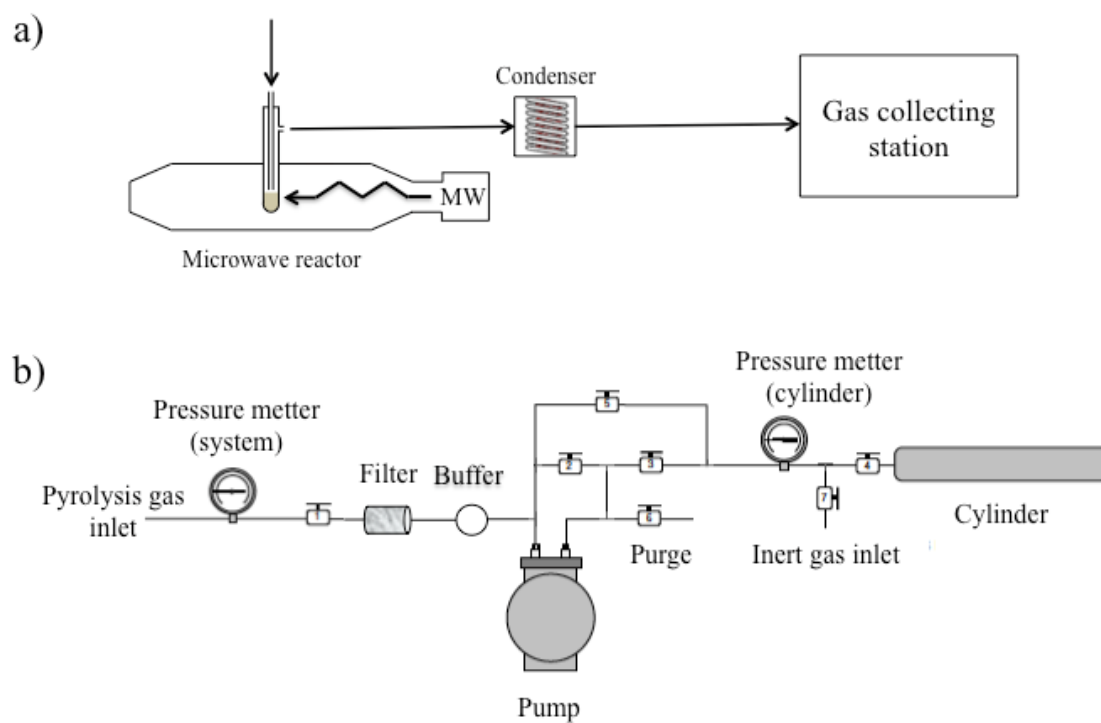


Fig. 1. Schematic of: a) the experimental setup; b) the gas collecting station

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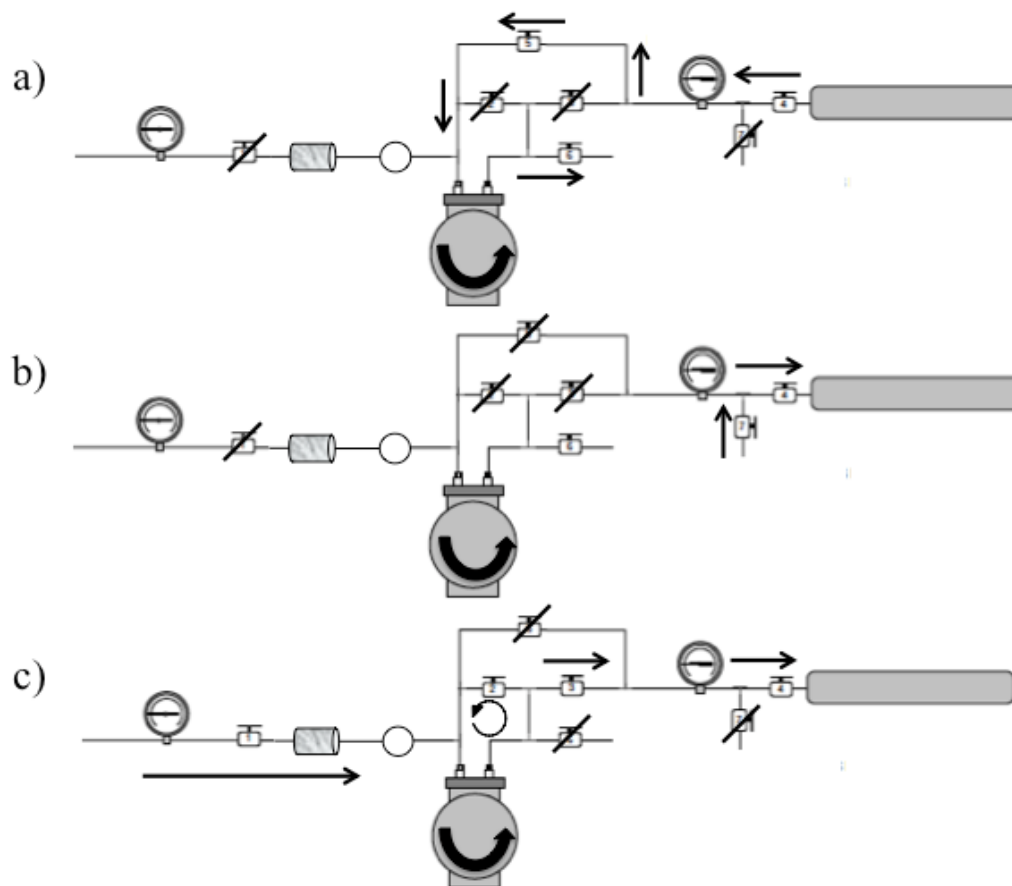
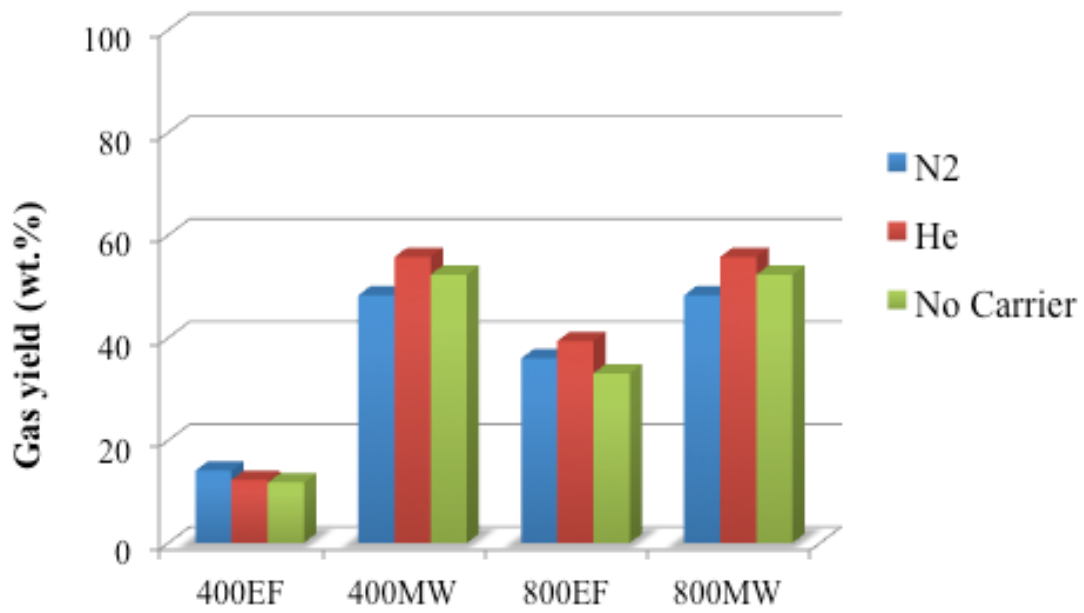


Fig. 2. Schematic of the gas collecting station during: a) the cylinder purge; b) the cylinder being filled with inert gas (N₂); c) the cylinder being filled with the pyrolysis gas.

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 2 **Fig 3.** Gas yields of the different experiments carried out at 400 and 800 °C employing
 3 different ovens, i.e. conventional pyrolysis (EF) or microwave pyrolysis (MW), and
 4 carrier gases.
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