

24 **1. Introduction**

25 Municipal solid waste (MSW) consists mainly of waste from households (60-90%),
26 though similar wastes from other sources such as commerce or public institutions are
27 also included. According to Eurostat, which is the statistical body of the EU, MSW
28 generation in Europe has remained stable at about 260 Mt per year since 2002 [1].
29 Various management alternatives are available for the treatment of MSW such as
30 landfilling, incineration, recycling or composting. In recent years, recycling has
31 increased, although landfilling still remains the most widely used method of disposal, in
32 spite of its several drawbacks, such as the leaching of dangerous chemicals into the soil
33 and the release of methane to the air. However, this gap has narrowed in the last few
34 years. In the EU the landfill/recycling MSW weight ratio was 56/17 in 2001 compared
35 to 37/25 in 2011 [2].

36 Pyrolysis technology has emerged not only as a very effective way of MSW disposal
37 but also as an attractive technology for valorising these residues by producing fuels or
38 precursors of valuable chemicals, such as syngas ($\text{CO} + \text{H}_2$). As an example, the
39 SYNPOL project [3] aims to produce new biopolymers via the fermentation of syngas
40 from waste materials.

41 Several studies have been carried out on MSW pyrolysis [4-7]. In general, the syngas
42 content of the gas fraction produced in pyrolysis processes is not very high, since it is
43 mixed with large amounts of CO_2 , CH_4 and light hydrocarbons. As a way to improve
44 the syngas concentration and, especially, the H_2 content, several researchers have
45 proposed catalytic pyrolysis. In such cases, the role of the catalyst, such as dolomite [4],
46 is to crack the heavy compounds in order to obtain lighter gases. However, the same
47 effect can be achieved by means of microwave irradiation, without the need to add a

48 catalyst to the system, as demonstrated in previous studies [8-10]. Microwaves are able
49 to generate microplasmas, which promote heterogeneous catalytic reactions, but not all
50 materials can be heated by means of microwave irradiation, since some materials are
51 transparent to microwaves. To solve this problem, the addition of carbon-rich materials
52 has been proposed to absorb microwaves [11-14]. The material to be pyrolysed is then
53 heated by conduction. Use of the char obtained from MSW pyrolysis process as
54 microwave absorbent is an attractive solution since it avoids the addition of materials
55 that might increase the cost of the process.

56 The microwave pyrolysis of MSW has been performed previously by Gedam and
57 Regupathi [15], but it is still at an early stage of development. In the study of Gedam
58 and Regupathi, both the microwave power and irradiation time were varied. Although a
59 minimum value of power was required to carry out the pyrolysis of MSW, the addition
60 of different carbon materials that served as microwave absorbents allowed the pyrolysis
61 to proceed at a lower microwave power. Surprisingly, no hydrogen was produced other
62 than trace concentrations, providing a gas rich in CO, CO₂ and CH₄. So far the effect of
63 the amount of microwave absorbent on MSW pyrolysis has not received much attention.
64 However, this parameter has been studied in relation to other materials. The microwave
65 induced pyrolysis (MIP) of microalgae with various microwave absorbents, such as
66 activated carbon, CaO, SiC or microalgae char has been carried out by Hu *et al.* [16].
67 These authors found that there was a specific proportion of absorbent-to-microalga at
68 which the liquid fraction was maximised, depending on the absorbent used. Oil palm
69 shell biomass was recently subjected to MIP in a study by Salema and Ani [17], which
70 showed the importance of the quantity of microwave absorbent added to the oil palm
71 shell as a method of controlling the pyrolysis temperature in an overhead stirrer reactor.
72 The authors reported that an increase in microwave absorbent led to a decrease in the

73 pyrolysis temperature and in turn in to higher solid fraction yields. All of these studies
74 were focused on maximising the liquid fraction yield. However, to the best of our
75 knowledge, no studies have been aimed at maximising the gas fraction yield.

76 Herein, we report for the first time on a statistical model based on Response Surface
77 Methodology (RSM) designed to assess the combined effect of microwave power and
78 ratio of microwave absorbent-to-waste upon the amount and characteristics of the
79 syngas generated from MIP. In addition, the effect of moisture content of the MSW is
80 evaluated.

81 **2. Materials and Methods**

82 2.1. Materials

83 The sample selected for this study was an organic fraction from a municipal solid waste,
84 supplied by BEFESA *Gestión de Residuos Industriales* S. L. (Seville, Spain) in two
85 forms: wet (with a moisture content of c.a. 45 wt.%) and dry (with a moisture content of
86 c.a. 1.5 wt.%). The dry and wet fractions will be labelled as D and W respectively.

87 Proximate and ultimate analyses were performed to characterise the composition of the
88 feedstock samples. The moisture, ash content and volatile matter data (from a LECO
89 TGA-601) are summarised in Table 1 together with the ultimate analysis results (a
90 LECO-CHNS-932 micro-analyser and LECO-TF-900 furnace were used). Metallic
91 content of the ashes from the organic MSW was determined by means of atomic
92 absorption spectroscopy.

93 The gases were analysed in a Varian-CP3800 gas-chromatograph equipped with a TCD
94 detector and two columns connected in series. The first column was 80/100 Hayesep Q
95 (2 m x 1/8 in. x 2mm) and the second column was a 80/100 Molesieve 13X (1.5 m x 1/8

96 in. x 2 mm). The second column was bypassed by a six-port valve for the analysis of
 97 CO₂ and hydrocarbons. The TCD was calibrated with a standard gas mixture.

98

99 **Table 1.** Proximate and ultimate analyses of the organic fraction from MSW and metal
 100 content of the ashes.

Proximate Analysis (wt.%)			Ultimate Analysis (wt.%) ^a					
Moisture	Ash ^a	Volatile matter ^a	C	H	N	S	Cl	O ^c
1.5 ^b	30.3	61.1	39.4	5.2	1.5	0.4	0.9	22.3
Metal content of ashes (mg _{metal} / kg _{MSW})								
Fe	Zn	Mn	Cr	Cu	Pb	Ni		
8896	183	83	59	45	31	18		

101

102 ^a Dry basis

103 ^b Moisture content of D. In the case of W, moisture content is 45 wt.%

104 ^c Calculated by difference

105

106 2.2 Microwave induced pyrolysis

107 The pyrolysis of D and W was carried out in a microwave oven which consisted
 108 basically of a microwave magnetron with a maximum output power of 2 kW operating
 109 at 2450 MHz and a single mode cavity where the sample was irradiated using powers
 110 ranging from 150 to 450 W. The single mode cavity allows a well-defined electric field
 111 in a relatively small volume due to the superposition of incident and reflected waves,
 112 and causes the microwave field to focus on a given location [18]. The reflected power is
 113 regulated until it is reduced to zero by means of stub tuners. About 3 g of sample (on a
 114 dry basis) was placed on an inert bed inside a quartz reactor. The reactor was purged
 115 with N₂ for 30 minutes at a flow rate of 50 mL_{STP} min⁻¹. The N₂ flow rate was then set
 116 to 10 mL_{STP} min⁻¹ for the pyrolysis experiments in order to ensure an oxygen-free
 117 atmosphere.

118 As mentioned in previous studies on microwave induced pyrolysis of biomass, it is also
119 necessary to mix the MSW fraction with an appropriate microwave absorbent to achieve
120 the high temperatures required for pyrolysis [11-14]. The char obtained from the prior
121 pyrolysis of D and W at 800 °C in an electrical furnace was used as microwave
122 absorbent in different absorbent-to-waste ratios (0.2:1, 0.4:1 and 1:1), in order to
123 evaluate the influence of this parameter on the characteristics of the syngas. Preliminary
124 experiments showed that lower values of absorbent-to-waste ratio prevented the
125 pyrolysis of the MSW fraction.

126 The experiments lasted 1 hour, but the time chosen for the calculation of the parameters
127 was 40 minutes, since by this time all the MIP experiments would have reached 90% of
128 total syngas production.

129 The volatiles released from the pyrolysis of both organic fractions were passed through
130 a condensing system cooled by a cryogenic solution of water and NaCl. The liquid
131 fraction was recovered from the condensing system by dissolving it in CH₂Cl₂. It was
132 then subjected to further evaporation to remove the solvent at 40 °C. The non-
133 condensable gases were collected at intervals of 10 minutes in Tedlar sample bags and
134 then analysed by gas chromatography. The composition of the gaseous fraction was
135 determined from the composition of each bag and the N₂ flow rate.

136 2.3 Statistical model

137 RSM is a widely used technique for the optimisation of a set of parameters. This
138 methodology assesses the combined effect of a set of independent variables on response
139 variables by means of three-dimensional surface plots. The experimental response
140 variables are fitted to a mathematical model by multiple regression analysis, which is
141 then subjected to statistical evaluation by means of the analysis of variance (ANOVA)

142 in order to determine whether the model and model parameters are significant on the
 143 basis of the p -value to within a certain level of confidence, e.g. at 95%. In the field of
 144 MIP, only a few studies employ RSM [19,20], but none of them are focused on the
 145 influence of the microwave power or on the effect of the microwave absorbent on the
 146 syngas produced.

147 As mentioned at the end of Section 1, three factors were selected as the independent
 148 variables used to model the characteristics of the gas obtained from the MIP of the
 149 organic fraction of municipal solid waste: the microwave power (P , expressed in watts),
 150 the absorbent-to-waste ratio (A , wt.% : wt.%) and the moisture content (M , wt.%). The
 151 values of P ranged from 150 W to 450 W and those of A from 0.2:1 to 1:1. Additional
 152 experiments were performed on the W fraction (45 wt.% of moisture) to evaluate the
 153 influence of the water content on the pyrolysis process.

154 In order to model the gas fraction evolved during the MIP, the following response
 155 variables were characterised: the syngas concentration, i.e. CO + H₂ concentration in the
 156 pyrolysis gases (S , vol.%); the syngas production (SP, L_{STP} g_{MSW}⁻¹) and the H₂, CO,
 157 CO₂ and CH₄ concentrations in the gas fraction (vol.%). The experimental design is
 158 shown in Table 2.

159 The experimental results for D and W were fitted using a polynomial quadratic equation
 160 (Eq. (2.1)) by means of Design Expert® software to correlate the response variables
 161 $R(P,A)$ to the independent variables P and A within the model parameters: the offset
 162 term (α), the linear effects (β, γ) the squared effects (δ, ε) and the interaction term (ζ):

163

$$164 \quad R(P, A) = \alpha + \beta P + \gamma A + \delta P^2 + \varepsilon A^2 + \zeta PA \quad (2.1)$$

165

166

167 **Table 2.** Experimental design for the MIP of organic MSW.

Experiment	<i>P</i> (W)	<i>A</i> (wt.% absorbent : wt.% residue)	<i>M</i> (wt.%)
1	150	0.2:1	1.5
2	150	0.4:1	1.5
3	150	1:1	1.5
4	250	0.2:1	1.5
5	250	0.4:1	1.5
6	250	1:1	1.5
7	350	0.2:1	1.5
8	350	0.4:1	1.5
9	350	1:1	1.5
10	450	0.2:1	1.5
11	450	0.4:1	1.5
12	450	1:1	1.5
13	150	0.2:1	45
14	150	1:1	45
15	450	0.2:1	45
16	450	1:1	45

168

169

170 **3. Results and Discussion**

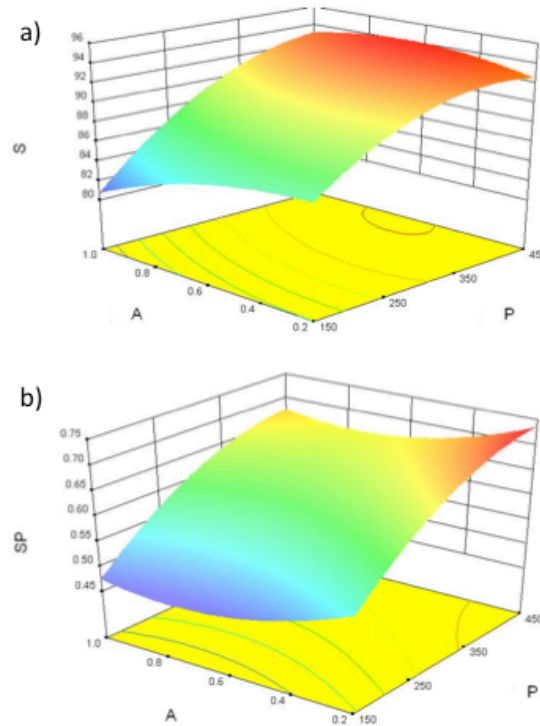
171 3.1 Syngas production models

172 The main objective of this study is to characterise the syngas generated by the
173 microwave induced pyrolysis of municipal solid waste and determine its composition
174 and production. The relationships between the factors *P* and *A* and the responses *S* and
175 *SP* are illustrated Fig. 1(a)-(b). Qualitatively, an increase in the microwave power
176 directed at the sample leads to a higher syngas concentration and production. Factor *A*
177 seems to have only a slight effect on the responses studied. The regression models
178 calculated to predict *S* (vol.%) and *SP* ($L_{STP} g_{MSW}^{-1}$) are expressed as follows:

179

$$180 \quad S = 75.247 + 0.087P - 0.787A + 0.024PA - 1.171 \cdot 10^{-4}P^2 - 7.885A^2 \quad (3.1)$$

$$181 \quad SP = 0.039 + 1.765P - 0.393A + 3.395 \cdot 10^{-5}PA - 1.870 \cdot 10^{-6}P^2 + 0.253A^2 \quad (3.2)$$



182

183 **Figure 1.** Response surface plots based on syngas concentration (S, vol.%) (a), and
 184 syngas production ($SP, L_{STP} g_{MSW}^{-1}$) (b), as a function of microwave power (P) and
 185 absorbent-to-waste ratio (A).

186

187 To statistically quantify the influences of the P and A factors, ANOVA tests were
 188 performed. In Table 3, the model p -values $\ll 0.05$ suggest that both models are
 189 significant to within a 95% confidence level. In the case of the syngas concentration
 190 model (Eq. 3.1), the linear term for microwave power (P) has the greatest effect on the
 191 $H_2 + CO$ content due to the extremely low p -value (<0.0001). In contrast, the influence
 192 of the microwave absorbent quantity, although significant, is not as great. The term for
 193 the absorbent-to-waste ratio (A) has a significant effect on S with a p -value of 0.0012. In
 194 the case of the syngas production model, the terms P and A were found to be significant
 195 factors too.

196

197 **Table 3.** ANOVA for the syngas models (*S* and *SP*).

Source	Sum of squares	Degree of freedom	Mean Square	F value	p-value	Significance (to within a 95% confidence level)	R^2 $Adj-R^2$
<i>Response: Syngas composition (S, vol.%)</i>							
Model	179.697	5	35.939	109.125	<0.0001	Significant	0.989 0.980
<i>P</i>	145.264	1	145.264	441.072	<0.0001	Significant	
<i>A</i>	10.904	1	10.904	33.109	0.0012	Significant	
<i>PA</i>	10.359	1	10.349	31.423	0.0014	Significant	
<i>P</i> ²	16.450	1	16.450	49.948	0.0004	Significant	
<i>A</i> ²	2.204	1	2.204	6.692	0.0414	Significant	
<i>Response: Syngas production (SP, $L_{STP} g_{MSW}^{-1}$)</i>							
Model	0.068	5	0.014	52.400	0.0010	Significant	0.985 0.966
<i>P</i>	0.062	1	0.062	235.94	<0.0001	Significant	
<i>A</i>	0.005	1	0.005	17.78	0.014	Significant	
<i>PA</i>	$1.932 \cdot 10^{-5}$	1	$1.932 \cdot 10^{-5}$	0.074	0.799	Not significant	
<i>P</i> ²	0.003	1	0.003	10.770	0.031	Significant	
<i>A</i> ²	0.001	1	0.001	5.700	0.075	Not significant	

198

199 From the surface plots of the regression models (Fig. 1(a)-(b)), it is possible to
200 determine the effect exerted by *P* and *A* on the response variables in the experimental
201 space studied. At a low microwave power (150, 250 and 350 W), a high *A* leads to a
202 decrease in both the syngas concentration and production, although at 450 W the trend
203 of *S* seems to change, since a maximum appears at $A = 0.4:1$. Anyway, the
204 concentration of syngas in the gas fraction obtained over the entire range of
205 experimental conditions studied is considerable (>80 vol.% in all the cases). In short,
206 the MIP of MSW is very selective towards syngas.

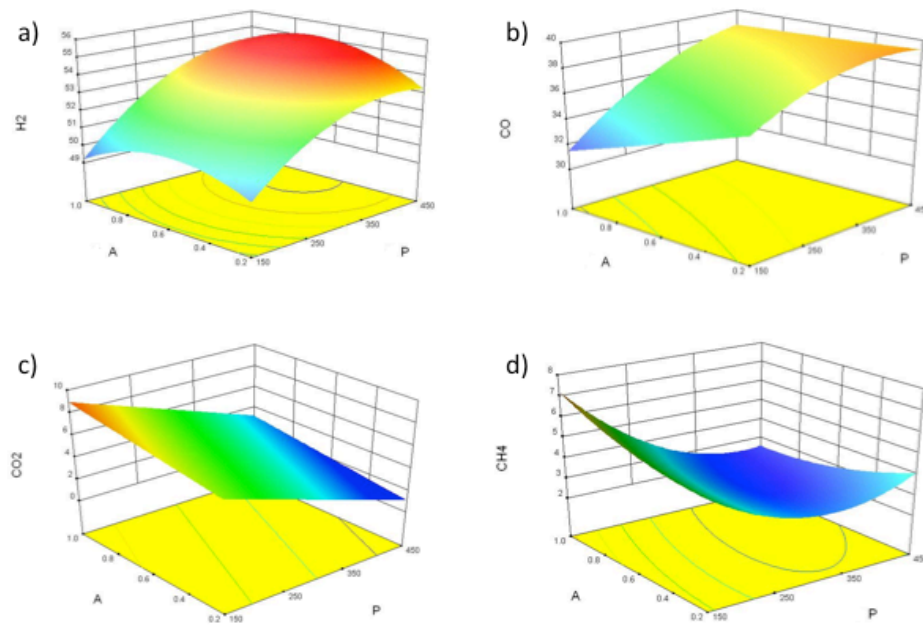
207 To investigate the fit of the model, the *R*-squared and Adjusted *R*-squared values were
208 evaluated. As can be observed in Table 3, the *S* model has an R^2 value of 0.989,
209 indicating that the model variation of 98.9% for the syngas concentration is attributable
210 to the independent variables and only 1.1% of the total variation could not be explained
211 by the model. The value of $Adj-R^2$ is also very high, lending further support to the high
212 significance of the model proposed. In the case of the *SP* model, similar conclusions can
213 be drawn.

214 Of the two factors (i.e. microwave power and the absorbent-to-waste ratio), microwave
215 power plays the more important role in MIP. Nevertheless, it is important to emphasize
216 that without the presence of a microwave absorbent, it would be impossible to carry out
217 the MIP experiments and that its presence allows the microwave power to be reduced,
218 as mentioned by Gedam and Regupathi [15]. These authors found that with a single
219 mode cavity, the MIP of MSW was not possible without the addition of a microwave
220 absorbent, unless the microwave power was higher than 450 W. However, the addition
221 of carbonaceous absorbents such as charcoal with an A value of 0.5:1 allowed MSW to
222 be pyrolysed even at 100 W. In a more recent study by Hu *et al.* [16], the authors
223 performed the MIP of microalgae without any absorbents but at powers higher than 750
224 W. They also found that the addition of small amounts of solid residue obtained from
225 the microalgae promoted gas production.

226 3.2 Gas component models

227 The response surface models corresponding to the major components of the gas fraction
228 (i.e. H₂, CO, CO₂ and CH₄) are shown in Fig. 2(a)-(d). From the trends of these models,
229 it can be seen that the concentrations of the most valuable components (H₂ and CO)
230 were favoured by the power irradiated at the sample. As observed by Hu *et al.* [16], the
231 higher the microwave power is, the higher the temperature reached inside the bulk,
232 since both the microwave density and the microwave energy absorbed by the bulk
233 increase. As a consequence, the endothermic reactions leading to the formation of
234 syngas are favoured [9]. On the other hand, the addition of absorbent to MSW seems to
235 have little effect on the gas concentrations. To assess the effects of both factors more
236 effectively, the following regression models for H₂, CO, CO₂ and CH₄ (vol.%) were
237 obtained:

238



239

240 **Figure 2.** Response surface plots based on H₂ (a), CO (b), CO₂ (c) and CH₄ (d)
 241 concentrations (vol.%) in the gas fraction as a function of microwave power (P) and
 242 absorbent-to-waste ratio (A).

243

$$244 \quad H_2 = 42.367 + 0.048P + 8.242A + 6.475 \cdot 10^{-3}PA - 6.183 \cdot 10^{-5}P^2 - 8.162A^2 \quad (3.3)$$

$$245 \quad CO = 32.870 + 0.039P - 9.013A + 0.018PA - 5.533 \cdot 10^{-5}P^2 + 0.271A^2 \quad (3.4)$$

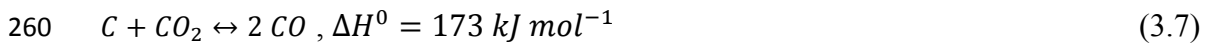
$$246 \quad CO_2 = 9.114 - 0.019P + 2.693A \quad (3.5)$$

$$247 \quad CH_4 = 9.768 - 0.039P + 1.524A - 0.015PA + 6.508 \cdot 10^{-5}P^2 + 2.667A^2 \quad (3.6)$$

248

249 ANOVA tests were carried out as in Section 3.2. The model *p*-values $\ll 0.05$ (Table 4)
 250 imply that all the models are significant to within a confidence level of 95%. In the case
 251 of the hydrogen concentration model (Eq. 3.3), the only significant term is the
 252 microwave power linear term (*P*) since its *p*-value is 0.0029. No significance was found
 253 for the other terms. In the case of the CO model (Eq. 3.4), both the *P* and the *A* terms

254 have significance, their p -values 0.0028 and 0.0310 being respectively. For CO₂, a
 255 linear model was found to be the most accurate (Eq. 3.5). Both linear terms were found
 256 to be significant for the CO₂ model. However, the trend of the CO₂ model was the
 257 opposite to that of the CO model. This is because CO and CO₂ are related by
 258 *Boudouard's* equilibrium (Eq. 3.7):



260
 261
 262 **Table 4.** ANOVA for the gas fraction component models.

Source	Sum of squares	Degree of freedom	Mean Square	F value	p-value	Significance (to within a 95% confidence level)	R^2 $Adj-R^2$
<i>Response: Hydrogen concentration (H₂, vol.%)</i>							
Model	37.809	5	7.562	5.726	0.0277	Significant	0.827 0.682
<i>P</i>	30.811	1	30.811	23.330	0.0029	Significant	
<i>A</i>	0.195	1	0.195	0.148	0.7138	Not significant	
<i>PA</i>	0.727	1	0.727	0.550	0.4862	Not significant	
<i>P</i> ²	4.588	1	4.588	3.474	0.1116	Not significant	
<i>A</i> ²	2.361	1	2.361	1.788	0.2297	Not significant	
<i>Response: Carbon monoxide concentration (CO, vol.%)</i>							
Model	62.265	5	12.453	6.967	0.0175	Significant	0.853 0.731
<i>P</i>	42.210	1	42.210	23.615	0.0028	Significant	
<i>A</i>	14.045	1	14.045	7.857	0.0310	Significant	
<i>PA</i>	5.566	1	5.566	3.114	0.1281	Not significant	
<i>P</i> ²	3.674	1	3.674	2.055	0.2016	Not significant	
<i>A</i> ²	0.003	1	0.003	0.002	0.9708	Not significant	
<i>Response: Carbon dioxide concentration (CO₂, vol.%)</i>							
Model	63.830	2	31.910	50.230	<0.0001	Significant	0.918 0.899
<i>P</i>	53.770	1	53.770	84.640	<0.0001	Significant	
<i>A</i>	10.050	1	10.050	15.830	0.0032	Significant	
<i>Response: Methane concentration (CH₄, vol.%)</i>							
Model	20.628	5	4.126	6.032	0.0246	Significant	0.834 0.695
<i>P</i>	13.455	1	13.455	19.672	0.0044	Significant	
<i>A</i>	0.146	1	0.146	0.213	0.6606	Not significant	
<i>PA</i>	3.706	1	3.706	5.419	0.0588	Not significant	
<i>P</i> ²	5.083	1	5.083	7.431	0.0344	Significant	
<i>A</i> ²	0.252	1	0.252	0.369	0.5661	Not significant	

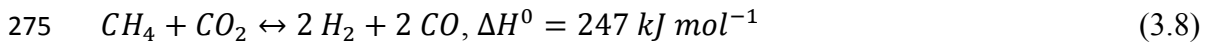
263

264

265 From Fig. 2(b)-(c) it can be observed that the maximum CO₂ concentration corresponds
 266 to the conditions at which the CO concentration is minimised (low power and a high

267 quantity of microwave absorbent) and vice versa. This behaviour could be due to the
268 fact that, as A increases, the bulk temperature decreases as stated in another study by
269 Salema and Ani [17] and that the lower power leads to lower temperatures, shifting Eq.
270 3.7 to the side of reactants since it has an endothermic enthalpy (173 kJ mol^{-1}).

271 Finally, in the CH_4 model (Eq. 3.6), P is the only significant factor since it has p -value
272 of 0.0044, and its trend is similar to that of the CO_2 model. Endothermic reforming
273 reaction of methane (Eq. 3.8) is favoured at high power and so CO and H_2 production
274 from these reactions is greater.



276 From the mathematical models presented above (Eqs. 3.3-3.6), it can be seen that the
277 microwave power has a positive effect on H_2 and CO production, but a negative effect
278 on the production of CO_2 and CH_4 . Moreover, the addition of larger quantities of
279 absorbent to MSW inhibits the production of CO but favours the production of CO_2 .
280 Table 4 shows that factor A has no significance for the H_2 and CH_4 response variables in
281 the experimental set-up employed in this study. Anyway, it would seem that the
282 hydrogen model would not represent the physical process very well since the absorbent
283 would modify the pyrolysis temperature and, hence, affect the production of hydrogen.
284 As scale-effects may be masking this point, larger scale experiments are being carried
285 out by our research group.

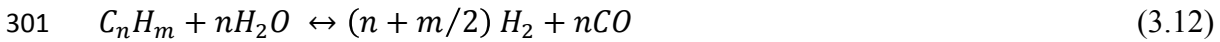
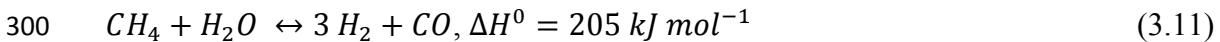
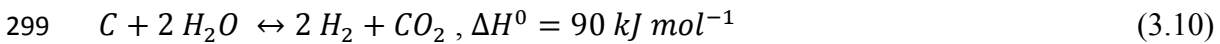
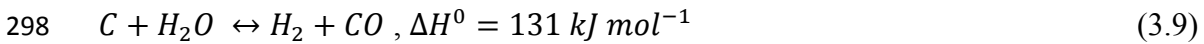
286 An interesting point in relation to the quality of the syngas produced is the H_2/CO ratio,
287 especially in regard to its future use. For example, in the case of methanol synthesis
288 from syngas, a H_2/CO ratio of around 2 would be the ideal [21]. In this work, it was
289 found that from the microwave pyrolysis of MSW, this parameter does not vary

290 appreciably. H₂/CO ratios between 1.3-1.5 were obtained over the entire experimental
 291 space analysed.

292

293 3.3 Effect of the moisture content of the MSW

294 Since the wet fraction has a large moisture content (*M*), H₂O might be expected to play
 295 an important role in the pyrolysis process via the gasification reactions of the char (Eq.
 296 3.9-3.10) and the reforming reactions (Eq. 3.11-3.12), leading to an enrichment in H₂,
 297 CO or CO₂ depending on the experimental conditions.



302 The MIP experiments on W were conducted at both low and high power (150 W and
 303 450 W). In addition, the quantity of microwave absorbent was evaluated along with *M*,
 304 using *A* ratios of 0.2:1 and 1:1, as shown in Table 2. The results of the analysis of the
 305 gas fraction for these cases are reported in Table 5. As might be expected from Eq. 3.10,
 306 the H₂ and CO₂ concentrations obtained from the wet fraction at 150 W are greater than
 307 those obtained from the dry fraction. In fact, water condenses at the top of the reactor,
 308 which is at a much lower temperature than the sample. In other words, there is a water
 309 reflux effect which favours a vapour-rich atmosphere and the gasification of the char.
 310 However, when the power is increased to 450 W, there are no appreciable differences in
 311 the gas composition of W and D. Therefore, Eq. 3.9 might be taking place to a much
 312 greater extent than Eq. 3.10, since the endothermic character of Eq. 3.9 is favoured by

313 the higher temperatures. Moreover, M also affects the CH_4 concentration in the gas
 314 fraction by reducing its content. This may be due to the steam reforming reaction of
 315 methane (Eq. 3.11). At 450 W the higher temperature would favour the thermal
 316 cracking and the steam reforming reaction of CH_4 much more than at 150 W. Finally, it
 317 could be remarkable that the percentage of syngas within the gas fractions seems to be
 318 similar regardless the moisture content. However, this behaviour might not be
 319 generalised yet.

320 **Table 5.** Comparison of the gas fraction from the MIP of the dry fraction (D) and the
 321 wet fraction (W) with different A ratios (0.2:1 and 1:1) at 150 W and 450 W.

$P = 150\text{ W}$				
	$A = 0.2:1$		$A = 1:1$	
	D	W	D	W
H_2 (vol.%)	49.37	53.40	48.94	57.03
CO (vol.%)	36.89	33.72	31.46	23.45
CO_2 (vol.%)	6.52	7.62	9.59	15.33
CH_4 (vol.%)	5.43	3.99	7.70	3.05
S (vol.%)	86.26	87.12	80.40	80.48
Gas production (L_{STP}/g_{MSW})[*]	0.64	0.92	0.58	1.06
SP (L_{STP}/g_{MSW}) [*]	0.55	0.73	0.47	0.85
$P = 450\text{ W}$				
	$A = 0.2:1$		$A = 1:1$	
	D	W	D	W
H_2 (vol.%)	53.54	53.10	54.30	53.61
CO (vol.%)	38.60	37.42	38.66	41.13
CO_2 (vol.%)	2.17	5.17	3.50	3.77
CH_4 (vol.%)	4.22	2.50	2.50	1.01
S (vol.%)	92.14	90.52	92.96	94.74
Gas production (L_{STP}/g_{MSW})[*]	0.79	0.94	0.73	1.10
SP (L_{STP}/g_{MSW}) [*]	0.73	0.85	0.68	1.05

322

323 * Calculated on a dry basis

324

325 Also important is the effect of moisture on syngas production. At 450 W, the W fraction
 326 produces 35% more syngas than the D fraction when a ratio 1:1 is employed, but their
 327 values converge at a ratio of 0.2:1, there being a difference in this case of around 15%.
 328 There is also a marked difference between these values at 150 W, since the W fraction

329 produces much more syngas than fraction D (45% higher) when a 1:1 ratio is employed.
330 Once more, these values converge at a ratio of 0.2:1, the wet fraction producing 25%
331 more syngas than the dry fraction. This suggests that moisture content favours the
332 production of a greater amount of gas, an impression that is confirmed by the results in
333 Table 5. This is an interesting point since it implies that the drying and pyrolysis
334 processes of MSW could be integrated in the MIP process to increase the production of
335 gas.

336 Both the quantity of absorbent and the moisture content influence the gas composition.
337 However, in the case of the wet fraction the amount of absorbent added has a much
338 greater influence. Hence gasification of the char from the wet fraction is bound to occur.
339 At 150 W, a greater increase in H₂ and CO₂ is observed at a ratio of 1:1 than at 0.2:1.
340 However, at 450 W the CO₂ concentration decreases as CO is produced due to the
341 increase in the quantity of absorbent. Thus, it may be assumed that the *Boudouard*
342 equilibrium (Eq. 3.7) is controlling the process in these conditions. In contrast, the
343 syngas production results reported in the above paragraph suggest that the addition of
344 more microwave absorbent to the wet fraction improves the production of syngas,
345 which is not the case with the dry fraction. Once more, this evidences the importance of
346 the char gasification reactions.

347 **4. Conclusions**

348 This study has demonstrated the possibility of recycling the char obtained from
349 municipal solid wastes for use as microwave absorbent in the microwave pyrolysis
350 process. Although microwave power is the most important factor for controlling the
351 pyrolysis, since higher power allows better conversion to syngas and syngas production,
352 the presence of the char in the material subjected to microwave pyrolysis is of

353 overwhelming importance. This allows a rich syngas (CO + H₂) fraction (c.a. 80-94
354 vol.% of the gas fraction) to be obtained with a low microwave power. A minimum *A*
355 ratio of 0.2:1 was found to be necessary to induce the microwave pyrolysis process. In
356 addition, low ratios seem to be more suitable for obtaining a higher concentration and
357 production of syngas. Moisture also plays an important role, as it favours H₂ and CO₂
358 production, especially at low power, in addition to improving the syngas production
359 process.

360

361 **List of abbreviations**

362 *A*: absorbent-to-waste ratio (kg:kg)

363 ANOVA: Analysis of variance

364 *D*: Dry fraction from organic municipal solid waste

365 MIP: Microwave induced pyrolysis

366 MSW: Municipal solid waste

367 *P*: Microwave power (watts)

368 RSM: Response surface methodology

369 *S*: Syngas concentration (vol.%)

370 *SP*: Syngas production (L_{STP} g_{MSW}⁻¹)

371 *W*: Wet fraction from organic municipal solid waste

372

373 **Acknowledgments**

374 The research leading to these results has received funding from the European Union
375 Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 311815
376 (SYNPOL project).

References

- [1] http://epp.eurostat.ec.europa.eu/cache/ITY_OFFPUB/KS-SF-11-031/EN/KS-SF-11-031-EN.PDF, (Last access 28.10.2013).
- [2] http://epp.eurostat.ec.europa.eu/cache/ITY_PUBLIC/8-04032013-BP/EN/8-04032013-BP-EN.PDF, (Last access 28.10.2013).
- [3] <http://www.synpol.org/>, (Last access 28.10.2013).
- [4] M. He, B. Xiao, S. Liu, Z. Hu, X. Guo, S. Luo and F. Yang, Syngas production from pyrolysis of municipal solid waste (MSW) with dolomite as downstream catalysts, *J. Anal. Appl. Pyrol.* 87 (2010) 181-187.
- [5] F. Ateş, N. Miskolczi and N. Borsodi, Comparison of real waste (MSW and MPW) pyrolysis in batch reactor over different catalysts. Part I: Product yields, gas and pyrolysis oil properties, *Bioresour. Technol.* 133 (2013) 443-454.
- [6] I. Velghe, R. Carleer, J. Yperman and S. Schreurs, Study of the pyrolysis of municipal solid waste for the production of valuable products, *J. Anal. Appl. Pyrol.* 92 (2011) 366-375.
- [7] W.K. Buah, A.M. Cunliffe and P.T. Williams, Characterization of Products from the Pyrolysis of Municipal Solid Waste, *Process Saf. Environ.* 85 (2007) 450-457.
- [8] D. Beneroso, J.M. Bermúdez, A. Arenillas and J.A. Menéndez, Microwave pyrolysis of microalgae for high syngas production, *Bioresour. Technol.* 144 (2013) 240-246.
- [9] A. Domínguez, J.A. Menéndez, Y. Fernández, J.J. Pis, J.M.V. Nabais, P.J.M. Carrott and M.M.L.R. Carrott, Conventional and microwave induced pyrolysis of coffee hulls for the production of a hydrogen rich fuel gas, *J. Anal. Appl. Pyrol.* 79 (2007) 128-135.
- [10] Y.F. Huang, W.H. Kuan, S.L. Lo and C.F. Lin, Hydrogen-rich fuel gas from rice straw via microwave-induced pyrolysis, *Bioresour. Technol.* 101 (2010) 1968-1973.
- [11] J.A. Menéndez, E.J. Juárez-Pérez, E. Ruisánchez, J.M. Bermúdez and A. Arenillas, Ball lightning plasma and plasma arc formation during the microwave heating of carbons, *Carbon.* 49 (2011) 346-349.
- [12] J.A. Menéndez, A. Arenillas, B. Fidalgo, Y. Fernández, L. Zubizarreta, E.G. Calvo and J.M. Bermúdez, Microwave heating processes involving carbon materials, *Fuel Process. Technol.* 91 (2010) 1-8.
- [13] A. Domínguez, J.A. Menéndez, M. Inguanzo and J.J. Pis, Investigations into the characteristics of oils produced from microwave pyrolysis of sewage sludge, *Fuel Process. Technol.* 86 (2005) 1007-1020.
- [14] Y. Fernández, A. Arenillas, M.A. Díez, J.J. Pis and J.A. Menéndez, Pyrolysis of glycerol over activated carbons for syngas production, *J. Anal. Appl. Pyrol.* 84 (2009) 145-150.
- [15] V. Gedam and I. Regupathi, Pyrolysis of Municipal Solid Waste for Syngas Production by Microwave Irradiation, *Nat. Resour. Res.* 21 (2012) 75-82.
- [16] Z. Hu, X. Ma and C. Chen, A study on experimental characteristic of microwave-assisted pyrolysis of microalgae, *Bioresour. Technol.* 107 (2012) 487-493.
- [17] A.A. Salema and F.N. Ani, Microwave-assisted pyrolysis of oil palm shell biomass using an overhead stirrer, *J. Anal. Appl. Pyrol.* 96 (2012) 162-172.
- [18] E.T. Thostenson and T.W. Chou, Microwave processing: fundamentals and applications, *Composites Part A: Applied Science and Manufacturing.* 30 (1999) 1055-1071.
- [19] M.A. Jamaluddin, K. Ismail, M.A. Mohd Ishak, Z. Ab Ghani, M.F. Abdullah, M.T.-u. Safian, S.S. Idris, S. Tahiruddin, M.F. Mohammed Yunus and N.I.N. Mohd Hakimi, Microwave-assisted pyrolysis of palm kernel shell: Optimization using response surface methodology (RSM), *Renewable Energy.* 55 (2013) 357-365.
- [20] R. Zhou, H. Lei and J. Julson, The effects of pyrolytic conditions on microwave pyrolysis of prairie cordgrass and kinetics, *J. Anal. Appl. Pyrol.* 101 (2013) 172-176.

- [21] X. Yin, D.Y.C. Leung, J. Chang, J. Wang, Y. Fu and C. Wu, Characteristics of the Synthesis of Methanol Using Biomass-Derived Syngas, *Energy Fuels*. 19 (2004) 305-310.