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Highlights

- A two-stage pyrolysis and thermal or catalytic cracking of MSW was carried out.
- Calcined dolomite was considered as an effective catalyst for syngas production.
- A valuable syngas consisting of more than 80 vol% of CO and H_2 was produced.
- A solid refuse-derived fuel was obtained for further energy requirements.

A COMBINED TWO-STAGE PROCESS OF PYROLYSIS AND CATALYTIC CRACKING OF MUNICIPAL SOLID WASTE FOR THE PRODUCTION OF SYNGAS AND SOLID REFUSE-DERIVED FUELS

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Abstract

Pyrolysis combined to either thermal cracking or catalytic cracking of municipal solid waste was performed in a laboratory-scale facility consisting of a fixed-bed reactor followed by a tubular cracking reactor. The results showed great potential for the production of syngas. The incorporation of inexpensive and widely available dolomite in the cracking reactor (with a constant feedstock to calcined dolomite ratio of 5:1) favoured the catalytic cracking of the primary pyrolysis products towards H_2 and CO in a temperature range of 800–900 ºC. More particularly, it was possible at 900 ºC to achieve a syngas consisting of more than 80 vol% CO and H_2 with a heating value of 16 MJ/Nm^3. Additionally, a homogeneous solid fuel was obtained as a solid residue, which can be used to provide additional energy to support the process or as a refuse-derived fuel. Thus, the great potential of this process was demonstrated for turning municipal solid waste into a valuable gas fraction that can be used directly as a fuel or as a source of different value-added products.

Keywords: Municipal solid waste; pyrolysis; syngas; refuse-derived fuel; calcined dolomite.

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1. **Introduction**

Waste management has emerged as one of the present and future problems of society due to the continuous expansion in volume and complexity of urban and industrial wastes. The eco-friendly processing of municipal solid waste (MSW) will be crucial if we are to overcome the challenge of reducing its social, economic and environmental impact. MSW includes biodegradable waste (food waste, paper, etc.), waste electrical and electronics equipment, recyclable materials (plastics, glass, metals, etc.), hazardous materials (waste tyres, paints, batteries, etc.) and toxic and biomedical waste (Zhou, Long et al. 2015, Sipra, Gao et al. 2018). Currently, about 1.7–1.9 billion tonnes of MSW are generated per year worldwide. This volume is expected to increase to 2.4 billion tonnes by 2025.

Although a number of countries have significantly increased MSW recycling, reuse and energy recovery, only about a quarter of total MSW is recovered, with the remainder sent to landfills or for incineration (Malinauskaite, Jouhara et al. 2017). These traditional methods of waste disposal are becoming increasingly less viable and, in view of the European Union's Horizon 2020 programme, the amount of waste generated entails not only health hazards and negative environmental impact (greenhouse gases and leaching of waste) but also leaves significant tasks to be dealt with in the future and at great expense. In this regard, new legislation in different countries proposes banning the disposal of MSW in landfills, making the traditional options of landfilling and incineration without energy recovery unviable. Although reduction, reuse and recycling are the main and mandatory steps in the waste management hierarchy, the recovery of value-added products and energy production from thermochemical processes seems to be necessary in order to address the entire waste management process. Thus, the search for new and clean processes that are able to valorise and recover value-added chemicals

from waste is seen as a necessity. The latter entails further in-depth investigation into disposal methods and recycling, as well as into new sustainable strategies focused on the valorisation and recovery of waste materials.

In this regard, the pyrolysis of MSW is seen as an attractive alternative because it is the only thermochemical process that can produce liquid, solid and gas fractions for direct use either in different power generation facilities or for the production of value-added chemicals (Arena 2012, Chen, Yin et al. 2014). This process results in a more environmentally beneficial process than that of conventional MSW incineration systems since smaller amounts of NOx and/or SOx can be released owing to the inert atmosphere used in the process. In addition, the pyrolysis process offers the opportunity to wash the syngas prior to its application (Saffarzadeh, Shimaoka et al. 2006, Wang, Chen et al. 2017), reducing the size and cost of gas cleaning systems, particularly in comparison with state-of-the-art cleaning technology used in incineration facilities. In keeping with this approach, a number of researchers have investigated the process of MSW pyrolysis (Czajczyńska, Anguilano et al. 2017). Most of these works involved studies at laboratory scale, with the feedstock first dried and ground into very small particles and then mixed to obtain a uniform composition. These studies have concluded that temperature and particle size distribution can play a key role in product distribution and selectivity, consistently obtaining a liquid fraction with very poor characteristics. Significantly, high temperature together with small feedstock particle size can significantly enhance gas yields, leading to potential gaseous fuels with a relevant concentration of CO and H_2 and decreasing the yield to the non-valuable liquid fraction (Luo, Xiao et al. 2010, Chen, Yin et al. 2014, Dong, Chi et al. 2016). Therefore, although the pyrolysis process could be an effective waste-to-energy convertor, the low quality of the liquid fraction seems to be a very important issue to be overcome in order

78 to ensure a profitable, clean and comprehensive solution for MSW disposal. The origin
79 of this problem seems to be in the heterogeneous nature of the samples, hampering the
80 production of high quality products, specially a valuable liquid fraction, throughout the
81 optimisation of the process operational conditions.

82 Although a single pyrolysis process would be very attractive from an economical point
83 of view, pyrolysis combined with further gasification technology with air has been
84 proposed as an interesting alternative. Notably, this strategy can be used to increase the
85 yield and characteristics of the gas fraction for its further application as fuel,
86 simultaneously obtaining a homogeneous solid fraction for consideration as a refuse-
87 derived fuel and decreasing the yield of the non-valuable liquid fraction (Chen, Yin et
88 al. 2014, Manyà, García-Ceballos et al. 2015, Aluri, Syed et al. 2018).

89 On the other hand, the addition of catalysts to the process, catalytic pyrolysis, is also
90 proposed to be a very interesting solution for the production of value-added products.
91 For this purpose, several catalysts have been studied in the catalytic pyrolysis of MSW,
92 such as Y-zeolite, β-zeolite, equilibrium FCC, MoO_3, Ni–Mo catalyst, HZSM-5 and Al
93 $(OH)_3$ in a batch reactor (Ateş, Miskolczi et al. 2013). It has been demonstrated that
94 catalytic pyrolysis does not only increase the yield to the non-condensable gas but it is
95 also enhancing the percentage of valuable products (aromatic and cyclic compounds) in
96 the liquid fraction. More specifically, whilst β-zeolite and HZSM-5 catalysts favours the
97 production of benzene-derived components in the liquid fraction, Ni–Mo-catalysts
98 exhibit the most positive impact to increase H_2 production. Remarkably, although a
99 great part of this H_2 would be produced from fossil fuel derived materials included in
100 MSW, such as plastics, there is an important environmental benefit based on the use of
101 recycled carbon atoms. Though these results looks very promising, the use of low-cost
102 catalysts could be decisive for the economic feasibility of the process, since MSW

103 contains many components, which can deactivate the catalyst during the catalytic
104 pyrolysis process. The excellent performance of calcium-based sorbents for the cracking
105 and reforming of high molecular weight organic components, its widely commercial
106 availability and its relative low price, make these materials very interesting for this aim.
107 Accordingly, other authors (He, Xiao et al. 2010), have studied the catalytic pyrolysis
108 with calcined dolomite. These authors investigated syngas production from this process
109 in a bench-scale fixed-bed reactor over the temperature range of 750–950 °C. The
110 results showed that dolomite had a noteworthy influence on product yields and gas
111 composition, increasing both gas yield and CO / H_2 concentration in the final gas
112 stream. Thus, the obtained gas could be used either as a potential feedstock for Fischer–
113 Tropsch synthesis towards the production of transportation fuels, or as a gas fuel (~ 14
114 MJ/Nm^3) in reciprocating engines and gas turbines. On the other hand, O. Tursunov
115 (Tursunov 2014) studied the catalytic pyrolysis of MSW in the temperature range
116 comprised between 200 ºC and 750 °C using calcined calcite as calcium-based mineral.
117 This author found that calcined calcite also had a significant positive effect on the yield
118 and composition of the products during the pyrolysis process, particularly by increasing
119 syngas production and decreasing liquid yield. However, it is worth pointing out that
120 there is a very important drawback related to the incorporation of catalysts to the
121 pyrolysis process, since the solid fraction could not be directly commercialized as a
122 refuse-derived fuel and, hence, its use would be limited to provide additional energy to
123 support the process.

124 A very interesting alternative is proposed in this work where the use of cracking
125 catalysts in a second reactor to deal with the vapours generated during the pyrolysis
126 process is investigated. To the best of our knowledge, there is no published data related
127 to syngas production from MSW using this strategy. However, it should be pointed out

that notable results have been published by other authors using solely waste plastics (PP, PS or PE) as feedstock (Anuar Sharuddin, Abnisa et al. 2016, Saad and Williams 2016, Barbarias, Lopez et al. 2018, Lopez, Artetxe et al. 2018). Significantly, these authors found high conversion efficiencies and H_2 yields using these wastes, that can be found in great quantities in MSW and their production has been increased in late years (López, de Marco et al. 2011, Wu, Chen et al. 2014). We would like to remark that, although the use of a second gasification step of the MSW pyrolysis vapours, using either steam (He, Hu et al. 2009) or air (Chen, Yin et al. 2014), has already demonstrated to be an efficient process configuration to enhance syngas production, the process herein proposed is simpler since the addition of a gasification agent is not needed.. Therefore, this novel configuration could be an alternative thermochemical route for recovering value-added products from MSW especially syngas and refuse-derived fuels, in a simple and low-cost catalytic process using calcium-based materials. In order to accomplish this aim, a study of the influence of the temperature and the incorporation of calcined dolomite and calcined calcite to the process was analysed by a complete characterization of the non-condensable gas production.

2. Materials and methods

2.1 Feedstock

The feedstock used in the current study was obtained from MSW. The sample was provided by the company ECOHISPÁNICA S.A. The industrial pre-processing of the feedstock to make it homogeneous and biologically stable included the following treatments: a) Hydrolysis with saturated steam at 150 ºC for 15 min, b) extraction of ferric and non-ferric compounds and other impurities and c) a drying process. Finally,

152 the feedstock was transformed into pellets and used directly. Table 1 summarizes the
153 main properties of the feedstock.

154 Proximate analysis of the received feedstock was determined for moisture content
155 according to the UNE-EN ISO 18134:2016 standard, for ash content according to UNE-
156 EN ISO 18122:2016, and for volatile matter content according to UNE-EN ISO
157 18123:2016. Finally, fixed carbon was determined by balance. Ultimate analysis of the
158 feedstock was determined by Thermo flash 1112, according to the UNE EN 5104
159 standard. The higher heating value (HHV) was measured experimentally with a
160 calorimetric bomb IKA C-2000 using the standard procedure UNE 164001 EX.
161 Calcined dolomite (MgO.CaO) and calcined calcite (CaO) were used as catalysts in this
162 study. MgO.CaO (58% CaO, 36% MgO, Calcinor) and CaO (90% CaO, Calcinor) were
163 commercially available and obtained after the calcination of dolomite and calcite,
164 respectively, at 900 ºC. Particle size distribution was in the range of 300–600 μm.
165

166 **2.2. Thermogravimetric analysis**

167 Several thermogravimetric studies were performed in a Netzsch Libra F1
168 thermobalance. First, the thermal behaviour of the initial feedstock under pyrolysis
169 conditions was studied. The thermogravimetric analysis was performed, starting at room
170 temperature, until 700 ºC was reached, using heating rate of 30 ºC/min.

171 Furthermore, a semi-quantitative thermogravimetric analysis of the calcined dolomite
172 after reaction was conducted. The sample was heated (30 ºC/min) in N_2 atmosphere up
173 to 950 ºC and kept for 10 min, and the solid weight loss and temperature were recorded.
174 The sample weight used in all experiments was approximately 9 mg and the carrier gas
175 was N_2 (50 mLN/min).

176

177 **2.3 Fixed bed reactor**

178 Pyrolysis + cracking experiments were carried out in a stainless steel fixed-bed reactor
179 (52.5 cm length and 5 cm internal diameter) followed by a tubular reactor (29.5 cm
180 length and 1.5 cm internal diameter), as can be observed in Figure 1. These reactors are
181 heated externally with an electrical resistance heating system. This fixed-bed reactor has
182 the feature of incorporating a vertical mobile liner, where feedstock is deposited. As a
183 result, it is possible to preheat the reactor to the desired temperature while avoiding the
184 contact with the feedstock. Thus, once the required temperature is achieved in the
185 reactor, the liner is introduced into the reaction zone, ensuring the fast heating rates
186 needed for the devolatilisation process. Samples of 25 g were pyrolysed using N_2 as
187 carrier gas (300 ml/min) at 550 ºC. The reaction time considered to complete the
188 process was set to 30 min. A tailor-made condenser using a water reflux at 3 ºC was
189 used to collect the possible liquid fraction. Liquid fraction was directly recovered by
190 gravity from condenser. Tar fraction was considered the organic fraction deposited
191 along the different parts of the reactor that cannot be collected directly. Thus, the
192 different parts of the installation were weighted and tar was obtained by difference.
193 Finally, the non-condensable gas yield was calculated by the gas composition sampled
194 in a gas bag situated after a filter. Three runs were performed with the setting of 550 ºC
195 in the pyrolysis reactor and 700 ºC in the cracking reactor, keeping a relative standard
196 deviation (RSD) lower than 5% in product yields. For the remaining experiments, only
197 those with a mass balance of 100 ± 5% were considered valid. For thermal cracking
198 experiments, different temperatures in the cracking reactor were studied (350 ºC, 700 ºC
199 and 800 ºC) with the setting of 550 ºC considered an appropriate pyrolysis temperature.
200 In this case, silica sand was used instead of the catalyst to simulate potential cracking

due to the hot particles introduced. The performance of the catalysts was also studied at three different temperatures in the cracking reactor for calcined dolomite (700 ºC, 800 ºC and 900 ºC) and at 900 ºC for calcined CaO, keeping a constant feedstock/calcined catalyst ratio of 5:1. In addition, several catalytic pyrolysis cycles were performed in order to assess the influence of catalyst regeneration on the yields and quality of the products obtained.

2.4 Experimental procedure for cyclic operation

The lifetime activity of the catalyst was also studied. For this purpose, several tests were conducted comprising MSW pyrolysis + catalytic cracking followed by catalyst regeneration in static air (875 ºC, 2 h, 30 ºC/min). Once accomplished, the catalyst was recovered and reincorporated into the pyrolysis + cracking facility, completing one whole cycle. This process was performed three times, and product characterization was carried out after each experiment, as described in the following section.

2.5 Product characterization

After the pyrolysis + cracking process, tar, solid (char) and non-condensable gas fractions were characterized.

The char fraction was analysed by measuring its calorific value (IKA C-2000), elemental composition (Thermo flash 1112) and proximate analysis according to the previously described analytical standards.

The chemical composition of the tar fraction was analysed by GC/MS using a Varian CP-3800 gas chromatograph connected to a Saturn 2200 Ion Trap Mass Spectrometer. Firstly, the sample was diluted with 2-propanol and 1µL of sample was injected in split mode with a ratio 20:1. A low bleed capillary column, CP-Sil 8 CB: 5% phenyl, 95%

dimethylpolysiloxane (60 m x 0.25 mm i.d. x 0.25 μm film thickness) was used. An initial oven temperature of 60 ºC was maintained for 3 minutes. Then, a ramp rate of 7 ºC/min was implemented to reach a final column temperature of 300 ºC keeping this final temperature for 15.57 minutes. The carrier gas was He (BIP quality) at a constant column flow of 1 mL/min. The injector, detector and transfer line temperatures were 300 ºC, 220 ºC and 300 ºC, respectively. The MS was operated in electron ionisation mode within 35-550 m/z range. The interpretation of the mass spectra given by the GC/MS analyses was based on the automatic library search NIST 2011.

The non-condensable gases were determined by gas chromatography using a Hewlett Packard series II coupled to a TCD detector. The chromatograph was equipped with a Molsieve 5 Å column to analyse H_2, O_2, N_2 and CO, and with a HayeSep Q column to analyse CO_2 and light hydrocarbons. Both oven programmes used were isothermal at 60 ºC and 90 ºC for the Molsieve and Hayesep Q columns, respectively. Additionally, C1–C4 hydrocarbons were measured through a capillary column in a Varian GC coupled to a FID detector using a temperature programmed method (isothermal at 60 ºC for 5 minutes, followed by a heating rate of 20 ºC/min up to 120 ºC, keeping that temperature steady for 5 minutes).

3. Results and discussion

3.1 MSW fuel properties

As observed in Table 1, the feedstock was characterized by a remarkably high oxygen content (39.9 wt%) and low carbon content (34.7 wt%), implying a low HHV (13.7 MJ/kg). It is worth highlighting the relevant amount of volatile matter (53 wt%) observed in the feedstock, making it suitable for devolatilisation processes. This sample is obtained from a mixture of diverse materials such as organic matter, plastics, paper,

and metals among others. After steam treatment described in section 2.1 great part of metallic components and plastics are eliminated, whereas organic fraction and hydrolysed paper are remaining as main components. As shown in Table 1, it is worthy of mention the heterogeneous nature in the trace element composition of the stabilized MSW where RSD values ranging from 10 % to 50 % were observed.

3.2 Thermogravimetric analyses

Thermogravimetric analysis is a very useful technique to study and understand the pyrolysis behaviour of different feedstocks under well-defined conditions. It is well-known that MSW have an extreme heterogeneity, as they have components similar to organic waste that could be considered as biomass, and other components of a nature similar to what would be plastic waste. The results obtained for weight loss and rate of weight loss for the MSW sample were compiled in Figure 2A. The heterogeneity of the sample could be observed in the existence of several peaks at different temperatures. The first peak at around 100 ºC corresponded to the moisture content of the sample. The degradation of the biomass-derived component started at around 200 ºC (Navarro, Murillo et al. 2009), followed by the decomposition of plastic-derived materials between 400 ºC and 550 ºC (Sørum, Grønli et al. 2001, Zhou, Wang et al. 2006, Cabeza, Sobrón et al. 2015). Although after the steam treatment described in previous section, a great part of plastics are eliminated, several plastic-derived components can be clearly appreciated. To confirm this and to offer the reader more information about the nature of this sample several plastics models such as polystyrene or polypropylene and a lignocellulosic biomass model such as pine have been included in Figure 2B. Moreover, 550 ºC could be a suitable temperature to carry out the complete devolatilisation of this

273 particular MSW since only inert substances and fixed carbon degradation with a very
274 low reaction rate were accounted at temperatures higher than 550 ºC.

275 **3.2 Pyrolysis + cracking results**

276 **3.2.1 Product yields**

277 A summary of the product yields of liquid, tar, solid and non-condensable gas fractions
278 after the experiments were reported in Table 2. In all cases, and as expected using the
279 same pyrolysis temperature, char yields remained within the same range (50 wt%
280 approximately) where small differences can be attached to experimental error. With
281 regard to cracking temperature, it should be highlighted that low cracking temperature,
282 350 ºC, led to severe operational problems (undesirable heavy waxes formation) and a
283 remarkable proportion of a very low-quality liquid fraction was formed. This liquid
284 fraction presented negligible HHV due to the high oxygen content present (82 wt%) and
285 the low hydrogen and carbon content (6 and 10 wt% respectively). It should be pointed
286 out that, although these results were not included for brevity, experiments carried out
287 fixing up to 550 ºC in the cracking reactor produced similar yields. Fortunately, this
288 issue was prevented by using cracking temperatures higher than 750 ºC. Thus, as other
289 authors have already stated (Wang, Chen et al. 2017) the increase on the temperature
290 can promote tar cracking by means of several reactions such as decarboxylation,
291 decarbonylation, dehydrogenation, cyclization, aromatization, and polymerization
292 reactions. Under these experimental conditions, gas yield was greatly increased,
293 preventing those negative aspects associated with the production, handling, storage and
294 waste management of the low-quality liquid fraction. Accordingly, gas yield represented
295 up to 25.9 wt% when cracking temperature was set at 700 ºC, while it was possible to
296 increase the gas yield up to 35.1 wt% at 800 ºC. These results were in line with those

297 obtained by other authors in pyrolysis processes of MSW (Garcia, Font et al. 1995, Luo,
298 Xiao et al. 2010, Dong, Chi et al. 2016) where high process temperatures led to
299 remarkably higher non-condensable gas yields. In comparison with non-catalytic tests, a
300 further increase in non-condensable gases was observed by introducing calcined
301 dolomite into the catalytic cracking reactor, which was nearly 33% and 15% higher
302 when the temperature was set at 700 ºC and at 800 ºC, respectively. As expected, further
303 increases in the catalytic cracking temperature up to 900 ºC led to the highest gas yield
304 (close to 44 wt%), drastically reducing the tar production to 6.8 wt%. These findings
305 followed the general tendency observed in literature (Chen, Yin et al. 2014). After all
306 the experiments, undesirable tar deposition was found in several parts of the reactor.
307 Operational problems related to the formation of this fraction could be considered
308 inherent to reactor configuration and it would be convenient to be reduced, favouring
309 the production of more valuable products. To a better knowledge, this fraction was
310 analysed by GC/MS showing a predominant aromatic nature, where the main
311 components were styrene and benzene-derived compounds such as benzene_1,1´-(2-
312 butene,1,4-diyl)bis- and Benzene_1,1´-(3-methyl-1-propene-1,3-diyl)bis-. These results
313 were in line with TGA analysis where polystyrene could be tentatively identified as one
314 of the main components of the MSW sample. In this line, linear straight-chain alkanes
315 were also identified in tar composition. These compounds could be associated with
316 polypropylene decomposition, which was other main component tentatively identified
317 in the feedstock by TGA. Additional information about the type of compounds can be
318 found in supplementary data.

319 In addition, several pyrolysis-cracking cycles were conducted after regeneration of the
320 catalysts. The pyrolysis and cracking temperatures remained fixed at 550 ºC and 900 ºC,
321 respectively. It was observed that product yields remained steady at approximately the

same values after the cycles, and there was no evidence of catalytic deactivation. Marginal differences in yields could be associated with experimental error.

At this point, it should be noted that the cracking activity of CaO was also studied at 900 ºC (see Table 2). It was observed that the cracking effect was not so evident since there was still a remarkable amount of tar (13.1 wt%). Accordingly, lower gas yield (38.3 wt%) was obtained in comparison with that found using dolomite at the same temperature (43.6 wt%). Although both catalysts could be considered potential candidates to produce a remarkable valuable gas fraction, dolomite shows the greatest potential to enhance gas fraction reducing the operational problems due to tar formation at the same time.

3.2.2 Char characterization.

Char properties (proximate and ultimate analysis and heating value) as a mean of all samples analysed were summarised in Table 3. It can be observed that char samples presented low percentages of organic carbon and oxygen, 22.4 wt% and 2.3 wt%, respectively, and a high ash content (73.7 wt%). The low carbon content can be directly linked to the low amount of fixed carbon present in the stabilised MSW. These results entailed a poor heating value, 7.2 MJ/kg. It should be highlighted that significant RSD values were only found in those properties with marginal values. Therefore, it is possible to obtain a relative homogeneous solid fuel, which could be potentially used as an energy source to cover a part of the thermal requirements of the process. Also, given the high ash content of this by-product, its use for other applications such as refuse-derived fuel in cement plants, could be another interesting option. Recently, several researchers (Wang, Chen et al. 2017) have studied the use of the pyrolytic char from MSW as a cracking catalyst. It was demonstrated that the use of this by-product could

347 enhance gas yield and elevate carbon conversion to H_2-rich syngas in catalytic cracking
348 processes, offering another potential alternative for this product and expanding its
349 potential range of application.

350

351 **3.2.3 Non-condensable gas characterization**

352 The non-condensable gas composition was summarised in Figure 3. From that
353 composition, heating value was also calculated and was compiled in Table 4. It must
354 first be pointed out that low cracking temperatures resulted in a CO and CO_2-rich gas
355 where about 65 vol% of the gas consisted of a mixture of both components. CH_4 was
356 the next major component (15 vol%), whereas heavier hydrocarbons (calculated as C_3-
357 C_4) where found in lower proportions (5 vol%). Thus, this composition involved a
358 relatively low LHV of 15.2 MJ/Nm^3 (see Table 4). It was observed that increasing the
359 temperature in the cracking reactor up to 700 ºC and 800 ºC led to a reduction in CO_2,
360 down to 23.2 vol% and 13.9 vol%, respectively. In addition, the CO composition was
361 barely reduced, keeping within the same range of values (approximately 20 vol%). As
362 expected owing to the thermal cracking process, H_2 concentration increased with the
363 temperature, reaching values close to two-fold (33 vol%) in comparison with those
364 found at low temperature. Finally, CH_4 composition could be considered practically
365 constant (from 10.1 vol% up to 13.2 vol%), and heavier hydrocarbons suffered a
366 pronounced increase, approximately three times higher. The final component
367 distribution in non-condensable gas obtained after non-catalytic tests suggests that the
368 main reactions involved are water gas shift reaction (WGS) reaction ($CO_{(g)}$+ $H_2O_{(g)}$
369 $CO_{2(g)}$ + $H_{2(g)}$) in combination with hydrogasification (C + $2H_2$ $_4$) and
370 methanation (CO + $3H_2$ $_4$ + H_2O). These reactions were specially promoted at
371 higher temperatures (800 ºC) (Kowalski, Ludwig et al. 2007, Arena 2012, Wang, Chen

et al. 2017). These gas composition led to higher heating values, about 28 MJ/Nm^3. These values are remarkably higher than those obtained at low temperature, increasing the potential of the fuel gas to be used for power generation. These findings can be considered in line with those obtained from other authors (Chen, Yin et al. 2014). These authors used a complex mixture of feedstock such as wood, paper, polyethylene, municipal plastic waste and crushed MSW in different laboratory-scale pyrolysis plants, showing that both the addition of catalysts and the use of high temperature favoured gas production. Similarly, these authors stated that both syngas production and heating value were maximised at 900 ºC.

Different tendencies can be highlighted as regards the catalytic cracking experiments. The main tendency that could be observed in Figure 3 was the production of a non-condensable gas with a higher concentration of H_2 and CO as the temperature increased. In this sense, H_2 production increased up to 40.6 vol% and 44.5 vol% at 700 ºC and 800 ºC, respectively. These values implied an increment of more than double in comparison with the non-catalytic test at 700 ºC and an increment about 30% at 800 ºC. When the cracking temperature was increased to 900 ºC, half of the gas stream could be considered H_2 (52.3 vol%). On the other hand, CO also increased, reaching values of up to 33.1 vol% at the highest temperature. Another important parameter that monitored the quality of the product and its potential application was the H_2/CO ratio. Fortunately, H_2/CO ratios between 1.4 and 1.6 were found, which was an optimum range for further applications (Cao, Gao et al. 2008). In addition, it can be highlighted that 82 vol% of the total gas stream consisted of CO and H_2 at 900 ºC. With regard to this composition, it could be assumed that WGS reaction in combination with solid-gas reaction between CO_2 and dolomite played an important role, particularly at the highest temperature. In this sense, not only H_2 was maximized, but CO_2 was also minimised and separated from

397 the gas stream in one simple step. Moreover, although several authors have reported that
398 the activity of the Boudouard ($2CO_{(g)}$ $CO_{2(g)} + C_{(s)}$) reaction is lower than that of the
399 WGS reaction (Lim, McGregor et al. 2016), the high temperature involved in the
400 cracking reactor and the presence of CO_2 could enhance CO production through this
401 equilibrium. Indeed, several authors have showed that these two reactions are
402 considered as the main reactions occurring during the devolatilisation of MSW
403 (Kowalski, Ludwig et al. 2007, Arena 2012, Wang, Chen et al. 2017), which are
404 promoted at high temperatures. Particularly, the fact that heavier hydrocarbons are also
405 reduced in the presence of the catalyst, dry reforming ($C_nH_m + nCO_2$
406 H_2) and carbonization ($C_nH_{2n+2} \rightarrow nC + (n+1)\ H_2$) reactions seem to be taking place
407 preferentially in presence of the catalyst. These reactions prevail over above mentioned
408 hydrogasification and methanation reactions involved in the no-catalytic process.

409

410

411 A significant environmental issue could be addressed by the reduction of CO_2 and CH_4
412 with the increasing temperature. Thus, CO_2 values of 8.5 vol% and 4.3 vol% and CH_4
413 concentrations of 11.5 vol% and 7.7 vol% were found at 800 ºC and 900 ºC,
414 respectively. These results suggested that a large proportion of the vapours containing
415 high molecular weight compounds were mainly cracked into light hydrocarbons, CO
416 and H_2, leading to a significant increase in the gas fraction yield. These results were in
417 line with those obtained by *He et al*. (He, Hu et al. 2009, He, Xiao et al. 2010) where a
418 remarkable increase in H_2 and CO production was also observed as the temperature
419 increased during a catalytic pyrolysis process. Those concentrations were lower than
420 those obtained in the present work and the differences could be attributed to the

421 different nature of the feedstock, reactor design, process configuration and feedstock-to-
422 catalyst ratio.

423 From these results, the significant catalytic effect of the magnesium species in calcined
424 dolomite can be confirmed, improving CO_2 absorption to further increase the
425 concentration of H_2. Although the process is not the same, other authors have observed
426 this effect in biomass gasification (Li, Yang et al. 2017).

427 The composition of the gas fraction was also evaluated after pyrolysis-cracking cycles.
428 It was observed that approximately similar H_2 production was achieved, especially after
429 one cycle conducted, and keeping relevant values after following cycles. CO suffered
430 only a slight reduction, while CO_2 was maintained at low levels, only slightly higher in
431 comparison with the experiment performed with fresh catalyst. Finally, CH_4
432 composition evidenced the opposite trend, increasing its value as cycles were
433 performed. These facts pointed out that a slight catalyst deactivation was taking place
434 after three consecutive cycles but, fortunately, these changes barely affect in a great
435 extent to the gas composition or the heating value. In fact, the H_2/CO ratio was kept at
436 the same value (1.7) after three cycles, preserving its potential for further applications.

437 Another parameter that could be important in order to assess potential gas quality
438 together with the viability of the process is the amount of energy recovery from the
439 initial feedstock. This percentage represents the ratio between the calorific value of the
440 non-condensable gas fraction and the calorific value of the initial feedstock and it is
441 calculated as follows:

Although the energy requirements of the thermal processes should be considered, it is worth highlighting that energy recovery values up to 86.5% were obtained when dolomite was used as cracking catalyst at 900 ºC, probing that pyrolysis + catalytic cracking could be a clean and simple solution for MSW valorisation.

3.3 Thermogravimetric analysis of calcined dolomite

A semi-quantitative thermogravimetric analysis of the spent catalysts were conducted in N_2 atmosphere up to 950 ºC, see Figure 4. The thermogram plotted in Figure 4A shows the evolution of different peaks. The first peak at about 400 ºC could be related to the dehydration of the calcium hydroxide (Veses, Aznar et al. 2016) inherent to calcium-based materials. The presence of a larger second peak can be also observed with a maximum situated at approximately 750–780 ºC. This peak can be associated to the carbonation capacity of the sorbent, which is defining the CO_2 composition of the gas phase. As previously stated, CO_2 concentration seemed to exert a great influence on both WGS and Boudouard equilibriums, which was crucial for both product distribution and composition. Therefore, the evolution of the dolomite carbonation capacity could be the key parameter describing the role of calcined dolomite as cracking catalysts through cycling. Accordingly, several thermogravimetric experiments were conducted on the regenerated catalyst in order to study the CO_2 sorbent capacity of the catalyst. In order to do so, this carbonation stage was performed at 650 ºC in a CO_2/N_2 (20/80 vol%) atmosphere. As can be observed in Figure 4B, the CO_2 sorbent capacity of the regenerated catalysts remained approximately within the same range after one cycle. However, it can be observed that the carbonation capacity of the catalysts was reduced as more regeneration cycles were conducted. These features could be related to the

sintering phenomena occurring during the regeneration process associated with calcium based catalysts (Martínez, Grasa et al. 2016), decreasing the capacity for CO_2 capture of the sorbent. As expected, this CO_2 sorbent capacity evolution can be considered in line with the results obtained, since gas composition differences were more evident after cycles 2 and 3, as shown in Figure 3. In this regard, CO_2 capture, associated with the CaO contained in dolomite, which simultaneously favours H_2 production via the WGS reaction and the methane reforming reaction, was slightly reduced, and in turn, the role of the catalyst during the upgrading process could be negatively affected, reducing H_2 and increasing CO_2 in the gas stream.

3.4 Non-condensable gas applications

By focusing on the results, it is possible to distinguish two main directions. On the one hand, the gas fraction produced at higher temperatures without catalyst is characterised by a relevant heating value, reaching a maximum of 28.1 MJ/Nm^3. Thus, this gas could have a huge market, particularly in industrial and domestic boilers where fuel gas is in great demand, or it can be used in gas engines or even gas turbines. On the other hand, the gas obtained after the catalytic process can be considered a derived-syngas for which there is a broad potential market. This gas could be used as syngas for the production of methanol, hydrocarbons, ammonia or transportation liquid fuels through Fischer-Tropsch synthesis (Balat, Balat et al. 2009). Indeed, a stoichiometric H_2/CO ratio ranging from 1 to 2 is commonly utilized in the production of syngas-based chemicals (Cao, Gao et al. 2008). This gas could also be a potential source for the production of H_2, due to its significant content. Although this gas cannot be considered totally renewable, this aspect could have an important environmental impact since approximately about 95% of H_2 comes from fossil fuels, and the share of this product in the energy market is increasing due to the growing demand for zero-emission fuels.

491 Consequently, this H_2 could play a relevant role as a feedstock in the petrochemical,
492 electronics and metallurgical industries (Balat, Balat et al. 2009), as well as a transport
493 fuel. Finally, a special mention should be made of its potential use as a fuel in steam
494 boilers, where its environmental-friendly nature could allow decreasing the cost of gas
495 scrubbing devices.

496

497 **4. Conclusions**

498 A pyrolysis process coupled to either a thermal or a catalytic cracking stage of MSW,
499 was carried out in a laboratory-scale facility consisting of a fixed-bed reactor and a
500 tubular cracking reactor. The results revealed the clear potential of this process for the
501 production of value-added products, particularly that of a valuable gas fraction that can
502 be used directly as a fuel or as a source of different chemicals. The process could be
503 considered cost-effective due to the potential of the obtained char for use as a refuse-
504 derived fuel to contribute to the energy requirements of the process. Moreover, the use
505 of an inexpensive and very widely available catalyst such as calcined dolomite, together
506 with its remarkable catalytic behaviour favouring long-chain hydrocarbon cracking and
507 the formation of H_2 and CO, seems to be a promising alternative. When temperatures of
508 900 ºC are reached in the cracking reactor, a syngas is produced with more than 80
509 vol% CO and H_2 and a heating value of 16 MJ/Nm^3.

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TABLES

Table 1. Main properties of stabilized MSW as received. Left: proximate analysis, ultimate analysis and heating value. Right : trace elements.

Property	Values	RSD (%)
Proximate analysis (wt%)		
Moisture	3.7	5.9
Ash	37.1	2.6
Volatile matter	52.5	2.3
Fixed Carbon	6.6	6.3
Ultimate analysis (wt%)		
C	34.7	5.8
H	4.6	5.1
N	1.5	6.5
S	0.4	5.4
O*	39.9	10.6
LHV (MJ/kg)	12.7	3.4

*Calculated by difference

Trace elements (wt. %)	Values	RSD (%)
Al	2.61	13.4
Ca	17.9	15.8
Fe	1.46	37.5
K	3.09	41.0
Mg	1.70	28.8
Mn	0.06	35.8
Na	3.88	25.8
P	1.01	18.4
Si	18.8	15.8
Ti	0.29	17.5

Table 2. Product yields (liquid, tar, solid and non-condensable gas) after the pyrolysis + cracking of MSW.

Experimental conditions ($T_{Pyrolysis}$ - $T_{cracking}$ - Catalyst)	Yields (wt%)				
	Liquid	**Tar**	**Char**	**Non-condensable gas**	**Total**
550 ºC-350 ºC	6.1 ± 0.1	25.3± 1.2	50.1 ± 0.8	14.3 ± 0.6	95.8
550 ºC-700 ºC	0.0 ± 0.0	22.1 ± 0.9	49.3 ±1.0	25.6 ± 1.0	97.0
550 ºC-800 ºC	0.0 ± 0.0	14.5 ± 0.6	49.3± 1.0	35.6 ± 1.2	99.4
550 ºC-700 ºC-Dolomite	0.0 ± 0.0	8.7 ± 0.3	49.8 ± 0.9	39.1 ± 1.2	97.5
550 ºC-800 ºC-Dolomite	0.0 ± 0.0	8.5 ± 0.4	49.7 ± 1.0	41.0 ± 1.2	99.3
550 ºC-900 ºC-Dolomite	0.0 ± 0.0	6.8 ± 0.7	49.0 ±1.1	43.6 ± 1.4	99.4
550 ºC-900 ºC-Dolomite - Cycle 1	0.0 ± 0.0	7.7 ± 0.3	49.5 ± 0.9	42.5 ± 1.3	99.7
550 ºC-900 ºC-Dolomite - Cycle 2	0.0 ± 0.0	8.7 ± 0.4	48.1 ± 1.1	41.1 ± 1.2	98.0
550 ºC-900 ºC-Dolomite - Cycle 3	0.0 ± 0.0	7.8 ± 0.3	48.1 ± 1.1	41.8 ± 1.3	97.7
550 ºC-900 ºC-Calcined calcite	0.0 ± 0.0	13.1 ± 0.8	48.7 ± 1.0	38.3 ± 1.0	96.3

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623 **Table 3.** Proximate analyses, ultimate analyses and heating value of char after pyrolysis
624 + cracking process of MSW.

Property	Char (at 550ºC)	RSD (%)
Proximate analysis (wt%)		
Ash	73.7	0.8
Volatile matter	13.2	3.6
Fixed Carbon	10.8	4.6
Ultimate analysis (wt%)		
C	22.4	1.6
H	0.4	25.4
N	0.6	9.1
S	0.7	13.1
O	2.3	31.5
LHV (MJ/kg)	7.1	2.0

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629 **Table 4**. Heating value (MJ/Nm^3) of gas stream calculated from gas composition

Experimental conditions ($T_{Pyrolysis}$ - $T_{cracking}$ - Catalyst)	Non-condensable gas		
	LHV (MJ/Nm^3)	LHV (MJ/kg)	Energy recovery from initial feedstock (%)
550 ºC-350 ºC	15.2	11.9	12.8
550 ºC-700 ºC	26.5	23.6	45.3
550 ºC-800 ºC	28.1	31.0	80.7
550 ºC-700 ºC-Dolomite	22.5	28.4	82.3
550 ºC-800 ºC-Dolomite	17.0	24.4	74.0
550 ºC-900 ºC-Dolomite	16.1	26.8	86.4
550 ºC-900 ºC-Dolomite - Cycle 1	18.1	26.7	84.2
550 ºC-900 ºC-Dolomite - Cycle 2	16.0	25.5	77.5
550 ºC-900 ºC-Dolomite - Cycle 3	15.9	24.9	77.3

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FIGURES

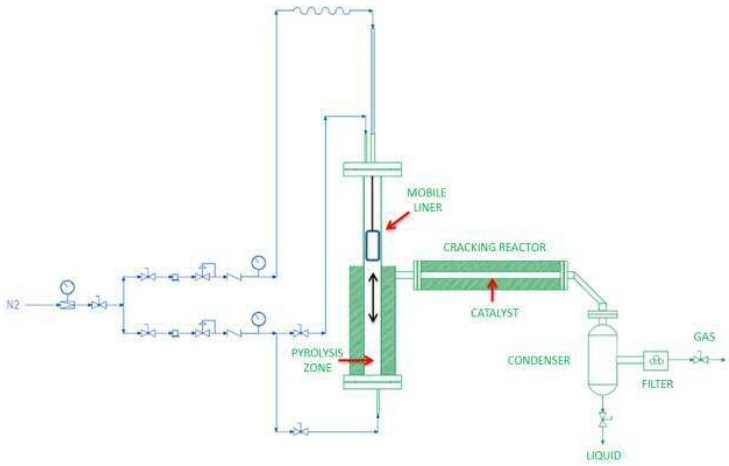

Figure 1. Schematic diagram of the fixed-bed reactor used for determining co-pyrolysis performance.

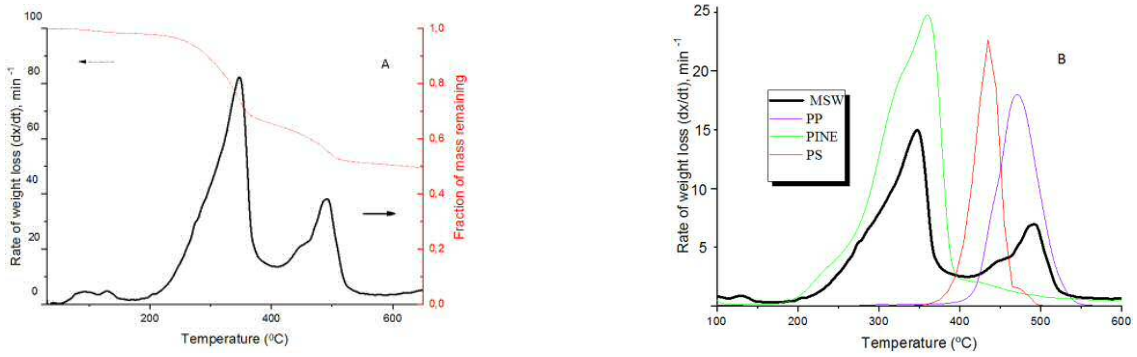

Figure 2. Thermogravimetric results of A: MSW (weight loss and rate of mass loss), and B: MSW (black), pine (green), polystyrene (red) and polypropylene (blue) at 30 °C/min.

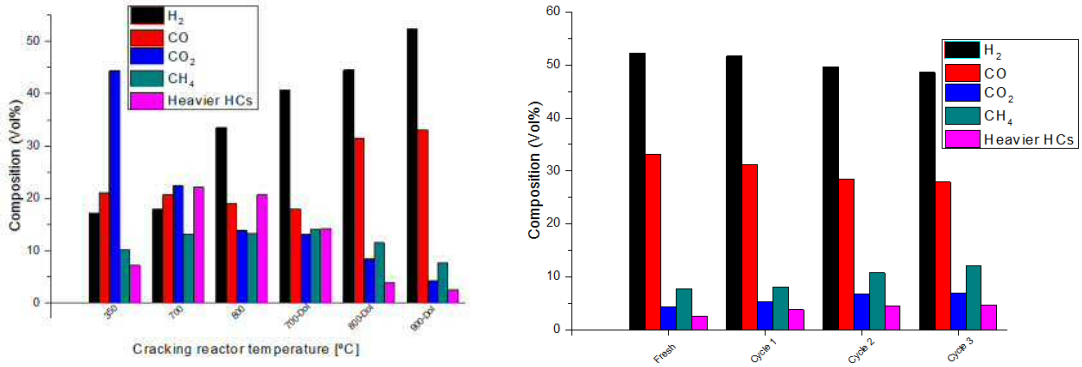

Figure 3. Left: Gas composition (vol %) after pyrolysis + cracking and catalytic cracking of MSW at different temperatures. Right: Gas composition (vol %) after several catalytic pyrolysis + cracking cycles at 900 ºC.

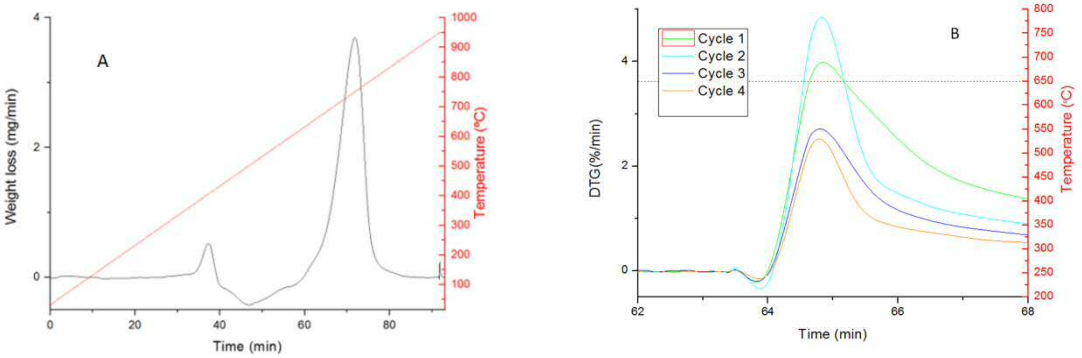

Figure 4. Thermogravimetric analysis of calcined dolomite after pyrolysis + catalytic cracking of MSW. Figure A shows the weight loss and temperature represented over time. Figure **B** shows the carbonation capacity of the catalysts after regeneration cycles.