

Thermal and catalytic pyrolysis of a mixture of plastics from small waste electrical and electronic equipment (WEEE)

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Abstract

Pyrolysis seems a promising route for recycling of heterogeneous, contaminated and additives containing plastics from waste electrical and electronic equipment (WEEE). This study deals with the thermal and catalytic pyrolysis of a synthetic mixture containing real waste plastics, representative of polymers contained in small WEEE. Two zeolite-based catalysts were used at 400 °C: HUSY and HZSM-5 with a high silica content, while three different temperatures were adopted for the thermal cracking: 400, 600 and 800 °C. The mass balance showed that the oil produced by pyrolysis is always the main product regardless the process conditions selected, with yields ranging from 83% to 93%. A higher yield was obtained when pyrolysis was carried out with HZSM-5 at 400 °C and without catalysts, but at 600 and 800 °C. Formation of a significant amount of solid residue (about 13%) is observed using HUSY. The oily liquid product of pyrolysis, analysed by GC-MS and GC-FID, as well as by elemental analysis and for energy content, appeared lighter, less viscous and with a higher concentration of monoaromatics under catalytic condition, if compared to the liquid product derived from thermal degradation at the same temperature. HZSM-5 led to the production of a high yield of styrene (17.5%), while HUSY favoured the formation of ethylbenzene (15%). Energy released by combustion of the oil was around 39 MJ/kg, thus suggesting the possibility to exploit it as a fuel, if the recovery of chemical compounds could not be realised. Elemental and proximate analysis of char and GC-TCD analysis of the gas were also performed. Finally, it was estimated to what extent these two products, showing a relevant ability to release energy, could fulfil the energy demand requested in pyrolysis.

36 *Keywords: small WEEE, plastic mixture, pyrolysis, zeolite, catalyst*

37 **1. Introduction**

38 In the last two decades a continuous growth of electronic and information technology equipment
39 has been globally observed. Consequently, a growing amount of waste from this sector, defined as
40 waste electrical and electronic equipment (WEEE), is continuously generated. In 2014 a world
41 production of 41.8 Mtons of WEEE was registered, of which 11.6 Mtons in Europe, and according
42 to forecasts the annual growth rate will achieve 4-5% (Baldé et al. 2015). The magnitude of this
43 waste stream poses an important challenge for its management. UE legislation regulated this issue
44 by setting the targets of WEEE minimum recovery (70-80% of material and energy recovery), in
45 order to reduce their landfill disposal (WEEE Directive 2012/19/EU). The achievement of this
46 target is subordinated to the recovery of all materials composing WEEE, including plastics, which
47 account for 30% wt of electronic wastes (Sodhi and Reimer, 2001).

48 Plastics contained in the WEEE result as a complex mixture of different polymers, more than 15
49 (Dimitrakakis et al. 2009) belonging to small household appliances (SHA), information
50 technologies (IT) and telecommunication equipment, according to the WEEE Directive that
51 moreover may contain additives as flame retardants. The most common WEEE plastics are, besides
52 polypropylene, styrene-based polymers, such as polystyrene (PS), acrylonitrile-butadiene-styrene
53 (ABS) and high impact polystyrene (HIPS), lower percentages of polycarbonate (PC) and polyvinyl
54 chloride (PVC) are also presents in these devices, (Dimitrakakis et al. 2009; Maris et al. 2015;
55 Martinho et al. 2012). Mechanical recycling is not always a viable option to heterogeneous and
56 contaminated materials, and, when it is, it may not result economically and environmentally
57 convenient (Panda et al. 2010). Therefore, a suitable method for recycling WEEE plastics,
58 especially when they belong to SHA and IT categories, is still a subject of research. An alternative
59 and promising route of treatment is represented by the feedstock recycling through pyrolysis, which
60 thermally breaks down the polymer chains into valuable products. This stream consists of
61 hydrocarbon chemical intermediates in the form of synthetic oil, gas and carbonaceous solid residue

62 (char). Oil can be further processed into monomers or alternative petrochemical products, while the
63 gas may be converted into a gas for the synthesis of chemicals, while char into an activated carbon
64 (Jamradloedluka and Lertsatitthanakorn, 2014). All the three products are also potential fuels
65 because of their high energy content (Sharuddin et al. 2016; Kunwar et al. 2016; Jamradloedluka
66 and Lertsatitthanakorn, 2014), referring in particular to oil, Sharma et al. (2016) showed the
67 feasibility of using liquid products from plastic waste pyrolysis as blend component for
68 conventional diesel fuel after distillation. The yields of products and their composition depend on
69 the process operating conditions and on the kind of plastic to be pyrolyzed.

70 A certain number of studies exist on pyrolysis of these plastic materials (Jung S. et al. 2013;
71 Miskolczi et al. 2008; Hall and Williams, 2008), but only a few investigated the cracking of plastics
72 recovered from real WEEE (Vasile et al. 2006; Muhammad, et al. 2015; Hall and Williams, 2006;
73 Antonakou et al., 2014) and, as far as emerged from a literature review, any of them concerning
74 mixtures of polymers representative of those contained in the WEEE categories of SHA and IT.
75 Cracking of styrene-based plastics usually results in a high yield of liquid product (Vasile et al.
76 2006; Miskolczi et al. 2008; Blazsó, 2006), consisting of different hydrocarbon compounds, with
77 particular reference to styrene and other mono and polyaromatics. The presence of monoaromatics
78 increases the economic value of the liquid product both as a fuel, thanks to the gain in the octane
79 rating (Lovink and Pine, 1990) and as a feedstock, since their ability to be exploited as chemical
80 solvents or starting materials for chemical synthesis and polymerization reactions: styrene for
81 example is commonly used to prepare new polymers. Achilias et al. (2007), investigated the direct
82 polymerization of pyrolysis oil with a high content of styrene without any oil upgrading, and
83 produced a polymer similar to PS, but with a quality lower than commercial grade. On the other
84 hand, Liu et al. (2000) obtained high purity styrene (99.6 wt%) through vacuum distillation of oil
85 derived by pyrolysis of PS, showing the feasibility of feedstock recycling from cracking of styrene-
86 based polymers. Nowadays, the most convenient solution at hand for management of pyrolysis oil
87 is to send it to refinery and process it with petroleum streams (Caballero et al. 2016), as it was

88 successfully confirmed by the experience of Kawanishi et al. (2005), who performed the upgrading
89 of liquid product from plastic waste pyrolysis in an existing refinery.

90 Catalytic pyrolysis of plastics appears as an efficient way to lower the degradation temperature and,
91 above all, to act on products composition, since the presence of a catalyst leads to the formation of
92 lighter hydrocarbons, such as monoaromatics (Panda et al. 2010). Different solid acid catalysts have
93 been tested in several studies regarding plastics pyrolysis, among them zeolites showed excellent
94 performances on products composition (Serrano et al. 2012). In particular, zeolites Y and ZSM-5
95 have been tested by different authors for catalytic pyrolysis of styrene-based polymers, obtaining an
96 increase of gas and char yield and a consequent decrease of liquid product. Furthermore, catalytic
97 pyrolysis produced higher concentrations of aliphatic and aromatics hydrocarbons with low
98 molecular weight (Hall and Williams, 2008; Muhammad et al. 2015).

99 The catalytic effect of zeolites on degradation products depends on two properties: pores dimension
100 and acidity. Zeolite Y presents a medium pore size, with a limiting dimension of 8 Å, allowing
101 molecules to enter its structure and undergo further reactions. ZSM-5 instead has a smaller pore size
102 (5÷6 Å), involving severe shape selectivity towards large molecules or branched polymeric chains.
103 This property influences the product composition and prevents the formation of coke inside the
104 catalyst, remarkably slowing down its deactivation and making the catalytic process more
105 economically convenient (Giavarini, C. 2006).

106 Acidity varies on the basis of the molar ratio between SiO₂ and Al₂O₃ present in the crystalline
107 structure of zeolites: the higher is the ratio the lower will be the acid sites number, but at the same
108 time isolated sites present a high acidity strength. In addition, zeolites with a high Si/Al molar ratio
109 present also a high thermal stability, hydrophobic character and affinity towards non polar
110 molecules (Le Febre, 1989). They are indeed employed not only as catalysts in petrochemical and
111 pyrolysis processes, but also as adsorbent material for removal of hydrocarbon pollutants in
112 wastewater treatment (patent Bagatin et al. 2011, Vignola et al. 2011a and b).

113 This research introduces two main novelties regarding the thermal degradation of plastic: the use of
114 a synthetic mixture of real plastic waste, representative of specific categories of WEEE (SHA and
115 IT), and the experimentation of a zeolite with high-silica content as catalysts for WEEE pyrolysis.
116 This study aims at providing a technology able to valorise this kind of plastic scraps, which
117 currently doesn't find a proper recycling route since the small dimension of these devices, the
118 presence of hazardous substances and the high polymeric heterogeneity make difficult to apply the
119 mechanical recycling. Two zeolites were tested, different for their crystal structure and acidity:
120 HUSY and zeolite HZSM-5 with Si/Al molar ratios equal to 30 and 1500, respectively. According
121 to our knowledge, this study represents the first attempt to understand whether the properties of
122 high-silica zeolites could be successfully exploitable for the catalytic cracking of real waste plastics
123 or virgin polymers.

124

125 **2. Experimental**

126

127 *2.1. Materials*

128 The plastic sample mixture used in this study was prepared as described—in a previous paper
129 (Cafiero et al. 2014) and it is denoted as Real WEEE. It is representative of plastics present in small
130 WEEE, as defined by Dimitrakakis (Dimitrakakis et al. 2009), and it is a mixture of three waste
131 plastics with the following composition:

- 132 – 64% wt ABS (from external housing);
- 133 – 33% wt HIPS (from external housing);
- 134 – 3% wt Polybutylene Terephthalate (PBT, from printed circuited board).

135 The three waste plastics used for the preparation of the sample were recovered from electronic
136 scraps, then milled and sieved to obtain a sample with a particle size < 0.5 mm, since size reduction
137 promotes the homogeneity of the mixture, especially when added to a catalyst. Table 1 shows the

138 elemental composition, the proximate analysis and the energetic content of the Real WEEE sample,
139 while humidity value was not reported because of it is extremely low (around 0.5% wt).

140 Plastics used for the preparation of the mixture were recovered from different WEEE with respect
141 to our previous study (e.g. ABS from a scanner casing now and from a keyboard before). This
142 different source of plastics could explain the small differences showed in the composition of the
143 two Real WEEE samples: the mixture used in this study presents slightly higher oxygen and lower
144 ashes contents. In addition, small amount of Cl and Br were found.

145 Powder commercial zeolites HUSY and HZSM-5 were used as catalysts, and their main properties
146 are summarised in Supplementary Materials (Table S1). Both zeolites were activated at 550 °C for
147 8 h under air atmosphere prior of their use.

148

149 *2.2. Pyrolysis procedure*

150 The operating conditions of pyrolysis experiments are presented in Supplementary Materials (Table
151 S2). Catalytic pyrolysis was performed with zeolites HUSY and HZSM-5 at 400 °C and the effects
152 of catalysts were compared with those obtained by thermal pyrolysis carried out at 400, 600 and
153 800 °C.

154 Thermal and catalytic pyrolysis was studied carrying out all the experiments in a bench scale semi-
155 batch reactor, where each sample was loaded before the experiment, whereas the gaseous products
156 were removed progressively as they were formed. The pyrolysis system is shown in Fig. 1, where
157 the reactor is a quartz tube with an internal diameter of 14 mm, 450 mm long, heated by an external
158 electrical furnace. The inert atmosphere was guaranteed by a continuous flow of N₂, also used as
159 carrier for gases and vapours evolved during the degradation. The reactor loaded with the sample
160 was inserted in the furnace once the desired temperature was achieved, carrying out an isothermal
161 pyrolysis. The vapours evolved during the degradation were condensed at 0 or -20 °C in a cold trap,
162 equipped with an ice bath or a bath of a freezing mixture, consisting of a saturated aqueous solution
163 of NaCl, respectively. This second option was chosen to ensure the condensation of the hotter

164 vapours produced from pyrolysis at 600 and 800 °C. Non-condensed gases coming out from the
165 cold trap were collected in a gas sample bag to be analysed. Degradation was considered completed
166 when no detectable vapours could be observed to come out from the reactor and the two
167 flowmeters, placed before and after the reactor, displayed the same flow value.
168 For each experiment a Real WEEE sample of 6 to 8 g was loaded in the reactor. In literature we
169 found polymer/catalyst weight ratios of 1:1 or 1:3 (Supplementary Materials, Table S3). However,
170 since preliminary runs with ABS plastic (data not shown in this study) revealed to be satisfying in
171 terms of oil yield using a polymer/catalyst weight ratio of 3:1, we decided to use the same weight
172 ratio for catalytic pyrolysis of Real WEEE, aiming at avoiding significant consumption of catalysts.
173 Catalysts were used in the liquid phase contact mode: zeolites and plastic were mixed together,
174 loaded in the reactor and then inserted in the hot furnace. Each experiment was repeated at least
175 three times to check its reproducibility.

176

177 *2.3. Mass Balance*

178 The mass balance was calculated by weighing the oil collected in the cold trap, the residue oil
179 adhered to the reactor's walls, and the char. The gas yield was calculated by difference from the
180 weight of the starting Real WEEE sample, as often made for bench scale pyrolysis tests (Adrados et
181 al. 2012; Sakata et. al. 1999; Seo et al. 2003).

182 In order to determine the weight of the oil traces in the reactor and that of the char, a second
183 pyrolysis was carried out under nitrogen flow in a muffle furnace at the same temperature of the
184 first pyrolysis. During this second degradation the oil residue volatilised and only the char remained
185 in the reactor. Weighing the reactor before and after the second pyrolysis allowed to determine the
186 weight of the char produced and that of the oil adhered to the reactor's walls.

187

188 *2.4. Products Characterization*

189 All the analyses were conducted separately on all the substances produced from each pyrolysis run
190 in three replicates, and the results presented are average values for the different pyrolysis conditions
191 (temperature and catalyst used).

192

193 *2.4.1 Liquid Product*

194 All the analyses were carried out on the oil collected in the cold trap, while the small portion of the
195 residue oil adhered to the reactor walls volatilized completely during the second pyrolysis and then
196 it couldn't be analysed.

197 The liquid mixture produced by pyrolysis at 400 °C were qualitatively analysed by gas
198 chromatography coupled with a mass spectrometry detector (GC-MS) to individuate the
199 components. The GC-MS used was a Shimadzu 2010 Plus GC Ultra QP2010 MSD (electron energy
200 70 eV, ion source and transfer line temperature 230 °C, 280 °C, mass scan range: 45–500 amu),
201 equipped with a Restech RTX-5MS, capillary column (30 m x 0.25 mm x 0.25 µm), with helium
202 used as carrier gas (50:1 split ratio). The injector temperature was kept at 300 °C and the oven was
203 held at 45 °C for 10 min, then ramped to 280 °C at 30 °C/min and held at this temperature for 5
204 min. Finally, the temperature of the oven was ramped to 320 °C at 50 °C/min with a final
205 isothermal step of 10 min.

206 Furthermore, for the oil derived from catalytic and thermal experiments at each degradation
207 temperature, the presence of four aromatic hydrocarbons was detected (styrene, benzene, toluene
208 and ethylbenzene). These substances are known to be the main components found in the oil
209 obtained by pyrolysis of styrene-based polymers (Jung et al. 2013; Bozi et al. 2008; Pinto et al.
210 1999), and represent a potential feedstock for chemical processes. Oil samples spiked with an
211 internal standard were analysed by a Perkin Elmer 8700 gas chromatograph, equipped with a flame
212 ionization detector (FID), a split/splitless injection port, a SE-54 capillary column (30 m x 0.25 mm
213 x 0.25 µm) and helium as carrier gas with a split flow of 30 mL/min. The injector and FID

214 temperatures were both 300 °C, while the GC oven was programmed to hold at 40 °C for 10 min,
215 then ramp to 280 °C at 30 °C/min, and hold at this temperature for 5 min. The oil samples were
216 injected after dilution in hexane at 1%.

217 A Macro VARIO Cube Elemental Analyser was used to determine the weight percentages of
218 carbon, nitrogen, hydrogen and sulphur. 10-20 mg of each oil sample were placed in a crucible with
219 an equal amount of an inert adsorbent material (Chromosorb, Thermo Electron) and tested for
220 analysis. The Low Heating Value (LHV) was calculated according to the methodology described in
221 previous studies (Cafiero et al. 2014; Cafiero et al. and 2015).

222

223 *2.4.2. Solid Residue*

224 Characterization of the solid residue consisted in the following measurements: proximate and
225 elemental analysis, according to what previously explained in previous studies (Cafiero et al. 2014;
226 Cafiero et al. and 2015). In the case of catalytic pyrolysis product, analyses were performed on a
227 sample of char mixed with the zeolite catalysts, once they were extracted from the reactor after the
228 pyrolysis experiment. The LHV was estimated by the Dulong-Petit expression (Petit and Dulong,
229 1819) and not by direct measurement because of the scarce amount of char.

230

231 *2.4.3. Gases*

232 In order to have an estimate of the LHV, the gases collected in the gas sample bag during the
233 experiment were analyzed using a Thermo Scientific Trace GC Ultra gas chromatograph, coupled
234 with a thermal conductivity detector (TCD). The column used was a CARBOXEN 1010 PLOT
235 packed with silica, able to separate CO₂, CO, H₂, N₂, O₂, CH₄, C₂H₄, C₂H₆, being helium the carrier
236 gas. The GC oven temperature was kept at 40 °C for 7.5 min, and programmed to reach 200 °C at a
237 rate of 50 °C/min, and keeping this temperature for 10 min. The LHV of the gas mixture was
238 calculated according to its composition resulting from the GC analysis, by considering the LHV of

239 each compound taken from literature (Guadagni, 2010) and converting its units in MJ/kg, taking
240 into account the standard conditions (P = 1 bar, T = 298 K).

241

242

243 **3. Results and discussion**

244 *3.1. Product yields*

245 Table 2 shows the results of the mass balance for the thermal and catalytic pyrolysis investigated.
246 Oil resulted always the main product, with the highest yields obtained at higher temperatures (about
247 94% wt at 600 and 800 °C). Similarly, HZSM-5 favoured the oil production with an increase of 5%
248 wt at 400 °C with respect to that obtained by thermal pyrolysis, and close to the yields observed at
249 600 and 800 °C. Previous studies (Vasile et al. 2006; Hall and Williams, 2006; Miskolczi et al.
250 2008) confirmed the prevalence of the liquid products from pyrolysis of styrene-based polymers.

251 The mass balances regarding the pyrolysis of virgins or WEEE styrene-based plastics taken from
252 different studies reported in literature (Williams and Bagri, 2004; Vasile et al. 2006; Hall and
253 Williams, 2006; Miskolczi et al. 2008; Hall and Williams, 2008; Jung et al. 2013; Muhammad et al.
254 2015) are compared in Table S3 (Supplementary Material). The high oil and the low gas yields are
255 both ascribed to the presence of intermediate radicals (with high molecular weights and an aromatic
256 structure) produced during the occurrence of the reaction (Pinto F. et al. 1999).

257 The gas yield from both thermal and catalytic pyrolysis resulted always $\leq 3\%$ wt of the Real WEEE
258 sample decomposed. This result was unexpected because it has not been observed in previous
259 studies, where in the presence of catalysts (*i.e.*, zeolites HUSY and HZSM-5) an increase of the
260 gaseous product was observed with respect to the findings obtained by thermal pyrolysis at the
261 same temperature. Two main factors could have led to this result: the contact mode between the
262 plastic sample and the catalysts and the weight ratio polymers/catalyst. Sakata and co-workers
263 (Sakata et al. 1999) investigated the influence of the contact mode between the plastic and the
264 catalysts on the products yield. They tested the pyrolysis of polypropylene in a batch reactor

265 catalysed by a commercial silica-alumina, both in the vapour phase and liquid phase contact. They
266 found that in the case of the liquid phase contact the gas yield did not differ much from that of
267 thermal pyrolysis and, on the other hand, for the vapour phase contact mode the gas yield increased
268 with a consequent decrease of the oil production. The high weight ratio between the plastics sample
269 and the catalyst is the second factor affecting the products distribution. In fact, the yield of gaseous
270 product seems to be directly proportional to the amount of catalyst (Williams and Bagri, 2004). This
271 result suggests that if the oil is the desired product, a lower amount of catalyst is required to
272 optimise its yield, with a consequent economic advantage. The char produced under the tested
273 conditions ranged from 3 to 13% wt, with the highest content observed in the pyrolysis catalysed by
274 HUSY. This result, confirmed by previous studies (Hall and Williams, W. et al. 2008; Williams P.
275 et al. and Bagri, 2004), is due to the characteristics of the catalyst: HUSY presents a low Si/Al
276 molar ratio, which implies a significant number of acid sites, and a larger pore dimension in
277 comparison to HZSM-5 used in this work, being both these features responsible of char formation
278 (Giavarini, C. 2006). With HZSM-5 the char decreased with a consequent increase of the oil
279 production compared to what has been produced by thermal pyrolysis at 400 °C. In other studies
280 (Hall and Williams, 2008; Williams and Bagri, 2004) the same catalyst caused a decrease of the oil
281 yield and an increase of char and gas. HZSM-5 used in this work is characterised by a very high
282 Si/Al molar ratio, never used in previous studies on pyrolysis of plastics. Since high silica content
283 in zeolites results in high hydrophobicity, they show high affinity towards hydrocarbons. This
284 feature probably promotes the interaction between molecules produced by polymer thermal
285 breakdown and zeolite surface. Taking into account also the high strength of HZSM-5 acid sites, the
286 cracking effect leading to a higher oil yield resulted enhanced.

287 In addition, the medium pore diameters of HZSM-5 promote a particular shape selectivity
288 (transition state selectivity), which occurs when certain reactions are prevented because the
289 corresponding transition state would require a greater volume than the one available in the cavities.
290 This kind of shape selectivity prevents char formation (Csicsery, 1986) and this implies that HZSM-

291 5 deactivates more slowly than HUSY, conferring to the catalyst a longer life. Zeolites reuse seems
292 actually feasible in this case, also for the low ashes content of the Real WEEE sample, which
293 remains mixed to the catalysts once that char is burnt off, as it was also found by Lopez et al. (2011)
294 in their study on pyrolysis of packaging plastic waste.
295 In terms of product yields HZSM-5 at 400 °C allowed to provide the same results obtained at 600
296 and 800 °C for thermal pyrolysis, thus suggesting that the catalyst had the same effect of cracking
297 enhanced performance usually achieved by increasing the temperature.

298

299 *3.2. Product Characterization*

300 *3.2.1. Liquid Product*

301 Results of elemental analysis show the same element distribution for all the oil samples, being
302 carbon the prevalent element (around 86%), and hydrogen and nitrogen concentrations at 7% and 3-
303 4%, respectively.

304 Oil appears mainly composed by two different fractions: the first one condensed in the cold trap to
305 produce a fair yellow coloured and less viscous oil, while the second one consists of a dark brown
306 coloured oil condensed before entering the cold trap, which tends to adhere to the reactor's inner
307 walls because of its high viscosity, being this fraction supposed to be composed of compounds with
308 high molecular weight. Fig. 2 shows how the liquid product is distributed, for thermal and catalytic
309 pyrolysis, partly in the fraction collected in the flask (lighter), partly in the one adhered to the
310 reactor (heavier). The highest amount of viscous oil was found for pyrolysis at 400 °C in absence of
311 catalyst, because of the presence of compounds with high molecular weight and with a lower
312 cracking effect on the polymeric chains. With the use of zeolites the heavier fraction almost
313 disappeared from the reactor (Supplementary Material, Fig. S1), consequently the oil condensed in
314 the cold trap significantly increased. The latter appeared of a fairer colouration (Supplementary
315 Material, Fig. S2) and less viscous, if compared to the oil produced by thermal pyrolysis at 400 °C.

316 In addition, the oil derived by catalytic pyrolysis resulted almost completely soluble in hexane,
317 while the oil obtained by thermal degradation presented an insoluble residue.

318 High temperature conditions causes the breakage of C-C bonds in the polymeric chains, and the
319 consequent production of a less viscous oil made up of small molecules, as already reported in other
320 studies (Yang et al. 2013; Onwudili et al. 2009; Miskolczi et al. 2008). In this investigation similar
321 results were found for thermal pyrolysis at 600 and 800 °C and for pyrolysis at 400 °C with the use
322 of zeolites, thus demonstrating that these catalysts cause the same cracking effect on polymers
323 structure when it is subjected to higher temperatures.

324 Compounds detected by an explorative analysis with GC-MS on oil from pyrolysis at 400 °C,
325 thermal and catalytic, are listed in Table 3 as agreed with results reported in literature (Hall and
326 Williams, 2006; Jung et al. 2013). Oil resulted mostly composed of aromatic hydrocarbons, which
327 are typical products of styrene-based plastics, but also compounds containing nitrogen are still
328 present, deriving from acrylonitrile unit of ABS polymer. A lower number of compounds was
329 detected from the oil, deriving from catalytic pyrolysis and lighter products, such as toluene,
330 ethylbenzene and styrene monomer, presented a higher relative area value, compared to the oil from
331 thermal pyrolysis, suggesting that zeolites influence liquid product composition in favour of lighter
332 compounds. Oil obtained in the presence of HUSY contains hydrocarbons not detected in other oil
333 samples: mainly indane (the formation of which will be discussed later), naphthalene and their
334 derivatives. The presence of naphthalene and its derivatives could be related to the tendency of
335 HUSY to form solid residue. Furthermore, char is obtained from reaction of cyclisation and
336 condensation that could lead also to the formation of these cyclic compounds (Giavarini, 2006).

337 A GC-FID analysis was performed, focusing the attention on the concentration of styrene, benzene,
338 ethylbenzene and toluene. Fig. 3 shows chromatograms obtained by the liquid product of pyrolysis
339 at 400 °C, with or without catalysts. Amount of benzene, ethylbenzene, toluene and styrene
340 contained in the oil produced in all the experimental conditions, and their yields expressed as

341 weight percentages with respect to the weight of the real WEEE decomposed are reported in Table
342 4.

343 Thermal pyrolysis carried out at 400 °C produced the lowest yield of aromatic hydrocarbons, while
344 the use of the two zeolites at the same temperature is responsible of a remarkable increase of the
345 total amount of the compounds, which exceeds the 20% of the plastic sample, but with different
346 results depending on the catalyst adopted.

347 In particular, HUSY favoured the formation of benzene, toluene and, above all, of ethylbenzene,
348 being the latter the 15% of the weight of the Real WEEE. The amount of styrene produced at 400
349 °C in the presence of HUSY is substantially the same derived by thermal pyrolysis. The wide cages
350 characterizing the HUSY structure allow the molecules generated during the thermal cracking
351 entering the zeolite pores, where they are exposed to further reactions enhanced also by the acid
352 strength of the catalyst: styrene is subjected to hydrogenation reaction producing ethylbenzene, as
353 confirmed by previous studies on pyrolysis of styrene-based plastics catalysed by HUSY
354 (Muhammad et al. 2015; Bozi et al. 2008; Jung et al. 2013; Pinto et al. 1999).

355 In addition, HUSY influenced also the production of benzene with concentrations significantly
356 higher than those obtained for pyrolysis with HZSM-5 and thermal pyrolysis at 400 and 600 °C (>1
357 mg/g), as well as for thermal pyrolysis at 800 °C (around 3 mg/g). This can be explained by the fact
358 that the bonds cracking in the polystyrene chains, which lead to the formation of benzene is less
359 energetically favoured with respect to the cracking of other bonds responsible of the production of
360 toluene and ethylbenzene (Pinto et al. 1999).

361 This so high concentration of benzene in the liquid product in the presence of HUSY (19 mg/g)
362 seems to be favoured by acid catalysts with a low Si/Al molar ratio, as suggested by Zhang et al.
363 (1995), thus promoting a reaction mechanism that involves also the formation of indane and its
364 derivatives, detected by GC-MS only for pyrolysis with HUSY.

365 HZSM-5 showed the best result in terms of the total yield of monoaromatic compounds. The high
366 yield of styrene and other aromatic hydrocarbons produced compared to the ones obtained by

367 thermal pyrolysis can be ascribed to the high strength of the acid sites of this zeolite. Furthermore,
368 HZSM-5 had effects completely different on hydrocarbons distribution if compared to zeolite
369 HUSY, and, on the other hand, similar to those obtained for thermal pyrolysis at 600 and 800 °C,
370 but with a higher total yield of monoaromatic hydrocarbons. The most significant effect was
371 registered for styrene monomer, which reached about the 18% of the Real WEEE decomposed.
372 According to the obtained results, pyrolysis carried out in the presence of HZSM-5 is supposed to
373 follow the degradation mechanism of thermal cracking proceeding via a β scission of the C-C bonds
374 of the polystyrene chains (Tae et al. 2004), which favours the production of styrene at higher
375 temperature, rather than that of other hydrocarbons. The high production of styrene could also be
376 ascribable to the pores dimension of HZSM-5, comparable to benzene ring diameter (Olson et al.
377 1981): styrene molecule, unable to enter the zeolite structure, is not exposed to further reactions and
378 it is not converted in other compounds.

379 Finally, high silica HZSM-5 used at 400 °C showed a strong cracking effect, and seems to be
380 promisingly attractive to recover styrene monomer, while HUSY enabled to obtain high yield of
381 ethylbenzene, whose main application is as intermediate for preparation of styrene through catalytic
382 dehydrogenation. The use of HZSM-5 seems to be more convenient due to the possibility to obtain
383 directly the final product.

384 Oil produced by thermal and catalytic pyrolysis shows a high energy content with a LHV of $38.8 \pm$
385 0.2 MJ/kg, which is comparable to those of petroleum and its derivatives, slightly over 40 MJ/kg.
386 This important result makes the energy recovery a possible valuable alternative for oil employment,
387 if the feedstock recycling could not be feasible.

388

389 3.2.2. *Solid Residue*

390 Elemental, proximate analysis and energy content of char are presented in Table 5. As it can be
391 expected the most abundant element of this product is carbon. Organic matter (volatile matter plus
392 fixed carbon) seems to decrease with increasing the pyrolysis temperature and in the presence of a

393 catalyst, while ashes content increases. This result is ascribed to the higher volatilization rate
394 measurable at higher temperatures (Imam and Capareda, 2012; Murzin, 2013) and to the catalytic
395 effect of zeolites. The low values of the elements concentration determined in the solid residue from
396 the catalytic cracking (but also the volatile matter, fixed carbon and humidity) are due to the
397 presence of zeolites in the samples subjected to analysis: the values are expressed as weight
398 percentages of the total amount of char and catalyst analysed. As a confirmation, carbon content,
399 volatile matter, fixed carbon and humidity were calculated excluding the weight of zeolites, thus
400 showing higher values: e.g. carbon content: 58.0% and 37.1% for the residue derived by pyrolysis
401 with HUSY and HZSM-5, respectively. Furthermore, elemental composition determined without
402 the contribution of zeolites and ashes content shows similar values of the char regardless the
403 pyrolysis conditions: carbon, nitrogen and oxygen percentage contents around 82, between 2 and 3,
404 and around 10%, respectively. By contrast, the hydrogen percentage decreases with increasing the
405 temperature (in accordance with the results shown in Table 6, where gaseous hydrogen was
406 detected at 600 and 800 °C). This trend is explained by the breaking of the weaker bonds found in
407 the structure of char (Imam and Capareda 2012).

408 The energy released by char varies with the elemental composition, showing high values of LHV.
409 So, this solid residue could be used as a fuel, possibly to supply the heat necessary to the pyrolysis
410 process.

411

412 3.2.3. Gas

413 As shown in Table 6, the gaseous product was found to be a mixture of CH₄, CO₂, C₂H₄ and C₂H₆,
414 while H₂ and CO were found in low concentration only in the case of thermal pyrolysis at 600 and
415 800 °C. The use of HZSM-5 did not affect gas composition, which was substantially the same in
416 absence of the catalysts at 400 °C. On the other hand, in the presence of HUSY the CO₂ content
417 decreased with respect to hydrocarbons, thus producing an increase in the energy content
418 corresponding to a LHV of 30 MJ/kg. Similar results were obtained for the gaseous product derived

419 by thermal pyrolysis at 600 and 800 °C. Either way, the LHV of the gaseous product derived by
420 each pyrolysis test with or without the presence of a catalyst was found to be high enough to
421 consider this product actually exploitable as a fuel.

422

423 *3.3. Energy balance*

424 The amount of heat required for the thermal degradation of Real WEEE was calculated in a
425 previous work (Cafiero et al., 2015). It was estimated that about 1.6 MJ/kg (corresponding to 4.9%
426 of the energy content of the plastic sample) is necessary for completing the reaction (heating, PBT
427 melting and degradation). Considering the LHV calculated for both char and gas and their yields
428 obtained from thermal and catalytic pyrolysis, it was possible to estimate how these products could
429 contribute as fuels for the self-sustaining the process. As it can be seen in Table 7, the char and gas
430 derived by thermal pyrolysis at 400 °C and catalytic pyrolysis in the presence of HUSY could
431 completely cover the heating degradation demand. In all the other cases, combustion of both the
432 char and gas products generates an amount of heat not much lower than the energy requested for
433 pyrolysis. It must be specified that the energy required for pyrolysis of Real WEEE was determined
434 for the occurrence of degradation without zeolites. As a consequence, the energy balance doesn't
435 take into account the effect of the presence of catalysts on the degradation temperature. Since it is
436 reasonably to expect that catalysts lower the degradation temperature of a process (Williams and
437 Bagri 2004; Bozi et al. 2008), it was supposed that in the presence of zeolites the energy demand
438 could be lower, or at least not higher than that estimated. In any case, the presence of halogenated
439 compounds may be of concern during a combustion, and a treatment of the flue gas released by
440 scrubbing coupled with active carbon adsorption can be foreseen. For the liquid product, its
441 upgrading via catalytic hydrodehalogenation seems to be an efficient treatment to remove halogen
442 substituent in aromatics (Yang et al., 2013). Moreover, Hall and Williams (2008) found that zeolites
443 Y and ZSM-5 used to catalyse pyrolysis of flame retarded HIPS and ABS allowed removing
444 volatile organobromines.

445

446

447 **4. Conclusions**

448 Thermal and catalytic pyrolysis of plastics recovered from small WEEE has been investigated to
449 study variations of products yields and composition. Both zeolites HUSY and high-silica HZSM-5,
450 employed at 400 °C, showed a strong cracking effect, involving a decrease of the viscous fraction
451 and an increase of light hydrocarbons content in the oil. HUSY enhanced particularly the
452 production of ethylbenzene, while HZSM-5 was able to produce a high concentration of monomer
453 styrene. Moreover, HZSM-5 showed the best performance in terms of the oil yield, comparable to
454 the ones obtained at higher temperatures without catalysts. A subject that is currently under study is
455 the actual possibility to extract aromatic monomers from the hydrocarbons complex mixture
456 obtained from pyrolysis. This could be an interesting development for future investigations. If this
457 route could not be viable the liquid product could be exploited, for example, as bunker fuel for
458 vessels engines. Since char and gas produced showed high LHV, their possible use as fuels could
459 satisfy completely or almost completely the energy demand for degradation. Taking into account
460 the results obtained in this study, further developments will be focused on testing several HZSM-5
461 zeolites, in order to find a possible relation between their Si/Al molar ratio and their performances
462 in the catalytic pyrolysis of plastics from WEEE.

463

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598

599 **Table 1 - Elemental analysis, proximate analysis and energetic content of Real WEEE.**

C (%)	H (%)	N (%)	S (%)	O (%)	Cl (%)	Br (%)	Volatile matter (%)	Fixed Carbon (%)	Ash (%)	LHV (MJ/kg)
85.3 ± 0.7	7.8 ± 0.1	3.4 ± 0.1	n.d.	0.98 ± 0.04	0.02 ± 0.01	0.13 ± 0.03	97.0 ± 0.9	1.7 ± 0.2	1.9	37.7 ± 0.2

600 n.d. = not detected

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Table 2 – Thermal and catalytic pyrolysis product yields

Catalyst	Pyrolysis temperature (°C)	Oil (wt%)	Char (wt%)	Gas (wt%)
-	400	86 ± 1	10.9 ± 0.1	3 ± 1
HUSY	400	83 ± 1	13.2 ± 0.3	3 ± 1
HZSM-5	400	91 ± 1	7.1 ± 0.3	2 ± 1
-	600	94 ± 1	3.3 ± 0.9	2 ± 1
-	800	93.2 ± 0.6	3.5 ± 0.3	3.2 ± 0.1

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608 **Table 3 - Detected compounds by GC-MS in liquid product of pyrolysis at 400 °C without**
 609 **zeolites, with zeolite HUSY and with zeolite HZSM-5 at 400°C, with relative area%≥0.1.**

Retention Time (min)	Attribution	Formula	400 °C (%)	HUSY (%)	HZSM5 (%)
2.48	toluene	C ₇ H ₈	0.5	6.9	6.9
4.58	ethylbenzene	C ₈ H ₁₀	2.3	31.9	10.4
4.89	o-xylene	C ₈ H ₁₀	--	0.3	--
5.62	styrene	C ₈ H ₈	5.9	20.7	38.9
7.32	benzene,(1-methylethyl)-	C ₉ H ₁₂	1.1	5.5	1.8
10.84	α-methylstyrene	C ₉ H ₁₀	2.0	4.4	5.7
11.95	indane	C ₉ H ₁₀	--	0.5	--
12.65	benzene,1-ethenyl-4-ethyl-	C ₁₀ H ₁₂	--	0.4	--
13.28	2-methylindene	C ₁₀ H ₁₀	--	0.3	--
13.47	benzeneacetonitrile,α-methyl-	C ₉ H ₉ N	0.6	--	--
13.54	1H-Indene,2,3-dimethyl-	C ₁₁ H ₁₂	--	0.3	--
13.58	naphthalene	C ₁₀ H ₈	--	0.7	--
14.14	1,4-dicyanobenzene	C ₈ H ₄ N ₂	1.5	--	1.0
14.46	naphthalene,2-methyl-	C ₁₁ H ₁₀	--	1.0	--
14.56	benzenebutanenitrile	C ₁₀ H ₁₁ N	40.2	13.3	15.9
14.76	NA		--	0.4	--
14.79	benzene,(1,3-dimethyl-3-butenyl)-	C ₁₂ H ₁₆	5.0	1.8	1.6
14.90	NA		0.2	--	--
15.02	1,2-Dihydrobenzocyclobutene, 7-(3-butenyl)-	C ₁₂ H ₁₈	1.2	--	0.3
15.11	diphenylmethane	C ₁₃ H ₁₂	0.1	0.1	--
15.18	naphthalene-based structure	C ₁₂ H ₁₂	--	0.1	--
15.40	1,1-diphenylethane	C ₁₄ H ₁₄	--	0.3	--
15.56	bibenzyl	C ₁₄ H ₁₄	0.4	--	--
15.71	diphenyl-based structure	C ₁₆ H ₁₈	0.2	--	--

15.96	benzene-based structure with cyano and carbonyl group	$C_{12}H_8N_2O$ 4	0.2	--	--
16.13	1,3-diphenylpropane	$C_{15}H_{16}$	20.1	6.9	8.5
16.18	1-naphthaleneacetonitrile	$C_{12}H_9N$	1.8	--	0.5
16.26	1,3-diphenylbutane	$C_{16}H_{18}$	1.4	--	0.4
16.36	NA		--	0.2	--
16.42	diphenyl-based structure with cyano group	$C_{15}H_{15}N$	4.7	--	2.1
16.47	diphenyl-based structure	$C_{15}H_{14}$	--	0.4	--
16.53	diphenyl-based structure	$C_{17}H_{16}$	--	0.2	--
16.65	1H-Indene,2-phenyl-	$C_{15}H_{12}$		0.5	
16.67	naphthalene-based structure	$C_{16}H_{16}$	0.2	--	--
16.73	1,3-diphenyl-1-butene	$C_{16}H_{16}$	0.7	0.4	1.1
16.85	NA		0.8		
16.93	NA		0.2	--	0.3
16.98	benzene,1,1'-(1-ethyl-1,3-propanediyl)bis-	$C_{16}H_{18}$	0.7	0.2	0.3
17.02	anthracene-based structure	$C_{17}H_{16}$	--	0.3	--
17.03	pentadecanenitrile	$C_{15}H_{29}N$	0.5	--	0.1
17.08	diphenyl -based structure	$C_{18}H_{22}$	0.4	--	--
17.17	indene-based structure	$C_{16}H_{14}$	--	0.2	--
17.25	NA		--	--	0.1
17.7	heptadecanenitrile	$C_{17}H_{33}N$	0.5	--	--
17.87	benzene,(4-chlorobutyl)-	$C_{10}H_{13}Cl$	2.2	--	1.4
17.90	phenanthrene-based structure	$C_{17}H_{14}$	--	--	0.6
19.29	anthracene-based structure	$C_{19}H_{13}N$	0.6	--	--
18.86	diphenyl -based structure	$C_{21}H_{22}$	2.5	0.3	1.3
19.79	NA		0.2	--	--
20.59	NA		0.1	--	--
22.58	NA		0.4	0.3	0.3

610 NA: not attributed

Table 4 - Content of benzene, toluene, ethylbenzene and styrene in liquid product, expressed as mg of hydrocarbon/g of oil, and their yields respect to the weight of Real WEEE pyrolysed.

Catalyst	Pyrolysis temperature (°C)	Benzene		Toluene		Ethylbenzene		Styrene		Total monoaromatics yields (%wt)
		(mg/g)	yield (%wt)	(mg/g)	yield (%wt)	(mg/g)	yield (%wt)	(mg/g)	yield (%wt)	
-	400	0.7 ± 0.3	0.04 ± 0.02	10 ± 1	0.59 ± 0.06	24 ± 1	1.40 ± 0.08	45 ± 4	2.6 ± 0.1	4.6 ± 0.1
HUSY	400	19.6 ± 0.8	1.51 ± 0.03	53 ± 1	4.1 ± 0.1	193 ± 9	14.9 ± 0.4	46 ± 10	3.5 ± 0.8	24 ± 1
HZSM-5	400	0.5 ± 0.2	0.05 ± 0.02	41 ± 2	3.5 ± 0.1	50 ± 2	4.2 ± 0.2	207 ± 13	17 ± 1	25 ± 2
-	600	0.70 ± 0.02	0.064 ± 0.003	20.03 ± 0.08	1.84 ± 0.04	19 ± 1	1.77 ± 0.08	160 ± 2	14.7 ± 0.2	18.4 ± 0.2
-	800	2.7 ± 0.7	0.2 ± 0.1	23 ± 3	2.2 ± 0.2	16.8 ± 0.2	1.54 ± 0.01	210 ± 43	19 ± 4	23 ± 4

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Table 5 - Elemental analysis, proximate analysis and energy content of pyrolysis char

Catalyst	Pyrolysis temperature (°C)	C (%)	H (%)	N (%)	O (%)	Humidity (%)	Volatile matter (%)	Fixed Carbon (%)	Ash (%)	LHV (MJ/kg)
-	400	74.9 ± 0.8	1.70 ± 0.1	2.78 ± 0.04	8.6 ± 0.8	5.6 ± 0.2	17.5 ± 0.9	65 ± 1	12 ± 1	25 ± 1
HUSY	400	27.2 ± 0.2	1.22 ± 0.02	0.96 ± 0.03	3.00 ± 0.02	1.2 ± 0.1	10 ± 1	20.0 ± 0.7	69.3 ± 0.6*	10.2 ± 0.2
HZSM-5	400	18.3 ± 0.9	0.83 ± 0.06	0.82 ± 0.08	2.4 ± 0.2	1.3 ± 0.4	7 ± 1	14 ± 1	78 ± 1*	7 ± 1
-	600	50 ± 6	0.6 ± 0.1	1.7 ± 0.1	9 ± 3	6.2 ± 0.9	18 ± 5	38 ± 2	38 ± 7	16 ± 4
-	800	42 ± 2	n.d.	1.2 ± 0.1	7.8 ± 2	5 ± 1	14 ± 3	33 ± 5	49 ± 3	12 ± 3

n.d.=not detected

*Percentage of ashes and zeolites in the solid residue sample.

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Table 6 - Gas composition and energy content of gaseous mixture

Catalyst	Pyrolysis temperature (°C)	H ₂ (%v)	CO (%v)	CH ₄ (%v)	CO ₂ (%v)	C ₂ H ₄ (%v)	C ₂ H ₆ (%v)	LHV (MJ/kg)
-	400	n.d.	n.d.	28 ± 1	42 ± 3	18 ± 3	13 ± 3	20 ± 4
HUSY	400	n.d.	n.d.	28 ± 1	38 ± 2	17 ± 1	16 ± 3	22 ± 3
HZSM-5	400	n.d.	n.d.	24.2 ± 0.5	47 ± 3	14 ± 1	13.8 ± 0.3	18 ± 1
-	600	0.5 ± 0.1	3.9 ± 0.1	30.6 ± 0.6	25.8 ± 0.2	24.9 ± 0.1	14.3 ± 0.2	27.6 ± 0.7
-	800	0.6 ± 0.1	6.0 ± 0.9	32.6 ± 0.7	18.0 ± 0.3	31.1 ± 0.1	11.8 ± 0.1	32 ± 1

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622 **Table 7 - Combustion energy of char and gas produced from 1 kg of Real WEEE pyrolysed**

Catalyst	Pyrolysis temperature (°C)	Char energy (MJ)	Gas energy (MJ)	Total energy (MJ)
-	400	2.7 ± 0.1	0.5 ± 0.2	3.2 ± 0.2
HUSY	400	1.34 ± 0.04	0.8 ± 0.2	2.1 ± 0.2
HZSM-5	400	0.48 ± 0.07	0.3 ± 0.2	0.8 ± 0.2
-	600	0.5 ± 0.2	0.7 ± 0.3	1.2 ± 0.4
-	800	0.4 ± 0.1	1.01 ± 0.05	1.4 ± 0.1

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633 **Captions to the figures**

634 **Figure 1 - Pyrolysis system. a. N₂ cylinder, b. flowmeter, c. manometer, d. electric furnace, e.**
 635 **reactor, f. flask for condensed products collection, g. cold trap, h. filter, i. flowmeter, j. gas**
 636 **sample bag.**

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638 **Figure 2 - Distribution of liquid product from thermal and catalytic pyrolysis between oil**
 639 **condensed in the flask and oil adhered to the reactor's walls.**

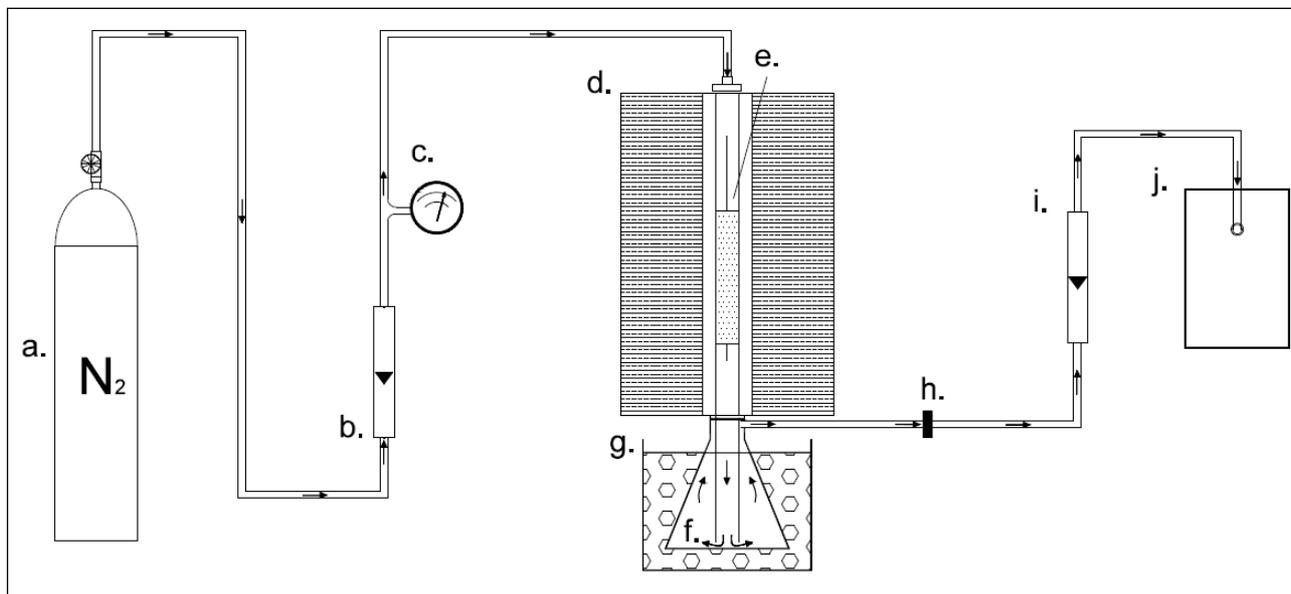
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641 **Figure 3 - Gas chromatograms for oil produced from pyrolysis at 400 °C without catalyst (a),**
 642 **with zeolite HUSY (b) and with zeolite HZSM-5 (c).**

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644 **Figures**

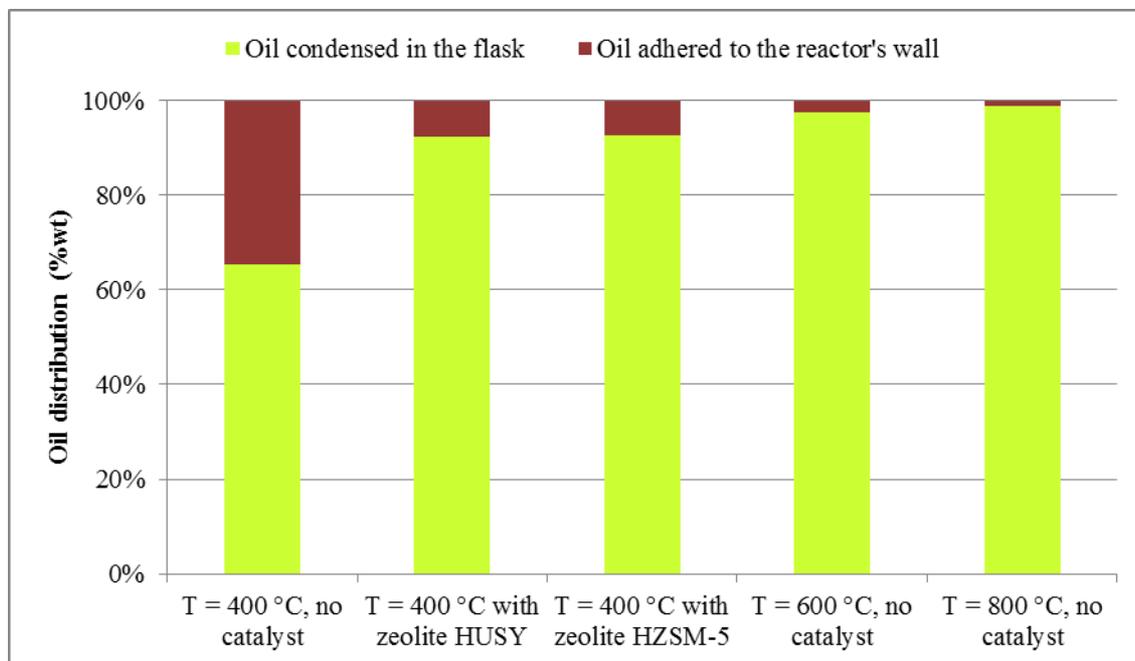
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647 **Fig. 1**

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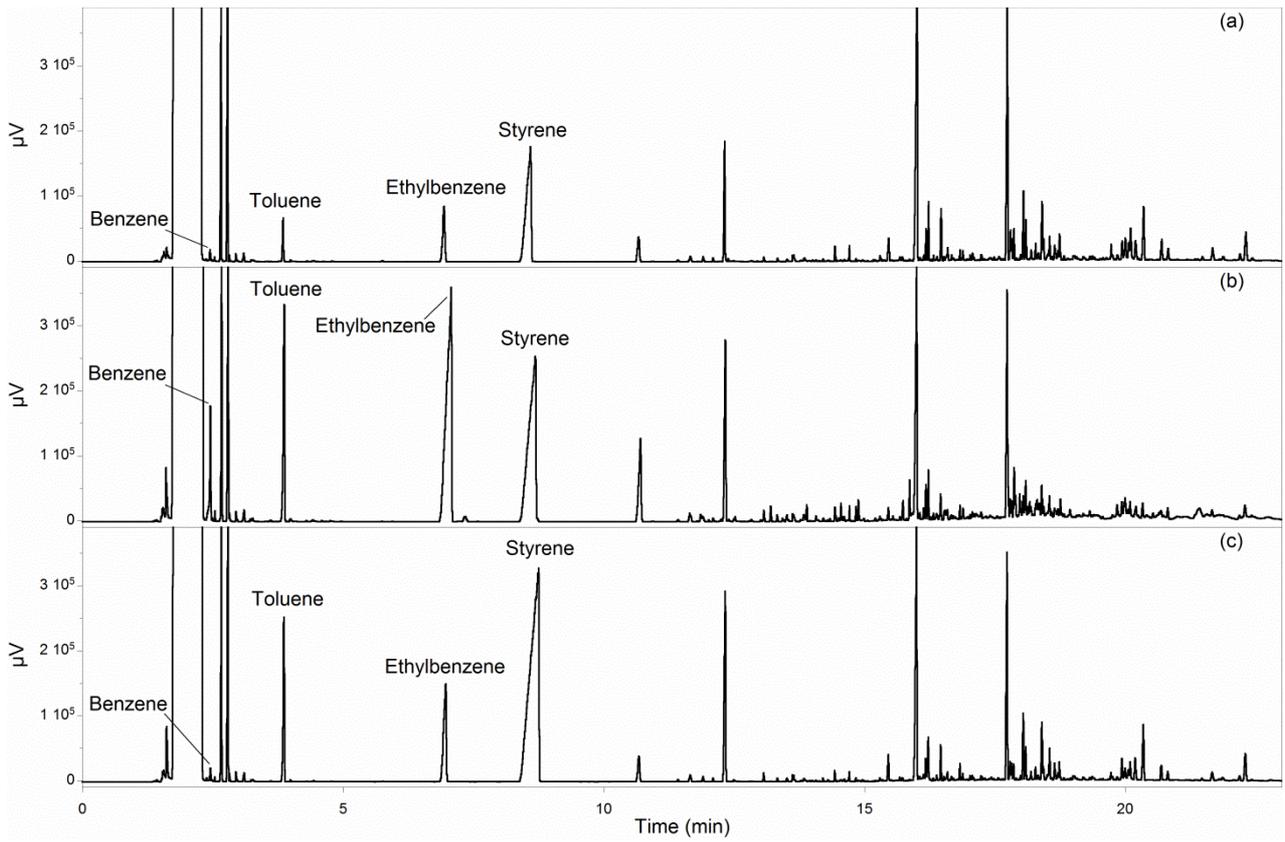


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650 **Fig. 2**

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654 **Fig. 3**