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26 **Chemical recycling of waste polystyrene by thermo-catalytic pyrolysis: A description for**
27 **different feedstocks, catalysts and operation modes**

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37 **Abstract**

38 Chemical recycling by thermo-catalytic pyrolysis/degradation offers the possibility of
39 converting waste plastics into their original monomers or other valuable chemicals which
40 can be used as feedstocks in chemical and petrochemical industries. Plastic wastes of
41 polystyrene (PS) based materials can be a good source of styrene as well as mono-aromatic
42 (BTEX: benzene, toluene, ethylbenzene, xylenes) compounds. The selectivity of pyrolysis
43 products can be tuned by choosing the right catalyst as well as appropriate operating
44 conditions/operation modes. In this regard, the focus of the present work was to perform
45 thermo-catalytic pyrolysis of different waste polystyrene (WPS) feedstocks over acid and
46 base catalysts employed in *ex-situ* and *in-situ* modes. The main goal was to compare the
47 compositions of pyrolysis products obtained by changing feedstocks, catalysts and
48 operation modes. A further goal was to discuss the suitability of the catalysts employed for
49 the enhanced recovery of desired products from WPS pyrolysis. It was demonstrated that

50 expanded polystyrene gives very similar product distribution as compared to virgin PS, both
51 giving high styrene content. Likewise, hard PS-based random packing materials produce
52 similar results as compared to high impact polystyrene (HIPS). Moreover, it was shown that
53 solid base catalysts influence the composition of the pyrolysis products only slightly as
54 compared to thermolysis. Solid acid catalyst however, showed significant impact on the
55 composition of the pyrolysis products as compared to non-catalytic pyrolysis. These results
56 may provide new insights for the chemical recycling of plastic wastes.

57 Keywords: Chemical recycling, pyrolysis, polymer degradation, thermo-catalytic process,
58 plastic recycling

59 **1. Introduction**

60 Waste polymeric substrates are potential sources of important raw materials that can be used
61 as feedstocks for the production of new/virgin polymers, fuels and/or other valuable
62 chemicals. Chemical recycling offers the possibility of transforming waste plastics into
63 useful chemicals, and hence it is considered as a promising approach towards resource
64 conservation and waste minimization (Ignatyev et al., 2014; Lee et al., 2021). During
65 chemical recycling process of waste plastics, the type or nature of the polymeric material
66 can play a major role in defining the product distribution. For example, one can expect
67 different types of products during pyrolysis of condensation and addition polymers. The
68 condensation polymers *e.g.* PLA (Polylactic acid) and PET (Polyethylene terephthalate)
69 have an appreciable tendency to depolymerize and give original monomers as a major
70 product. Whereas, addition polymers *e.g.* PE (Polyethylene) and PP (Polypropylene) tend
71 to give diverse products during pyrolysis process, where respective monomers are not the
72 major ones (Brems et al., 2012; Ignatyev et al., 2014). In contrast to most addition polymers

73 however, polystyrene (PS) shows a different behavior during pyrolysis by giving styrene
74 monomers as major product. The other products include BTEX (benzene, toluene,
75 ethylbenzene, xylenes) compounds (Achilias et al., 2007; Jaafar et al., 2022; Mo et al., 2014;
76 Verma et al., 2021; Zayoud et al., 2022). Thus, polystyrene-based plastic wastes are a good
77 source of styrene monomers as well as BTEX compounds. In literature, there have been
78 several investigations on the thermal and thermo-catalytic pyrolysis of virgin polystyrene
79 (VPS) and waste polystyrene (WPS). The authors used different catalysts (including solid
80 acids and solid bases) and reactor configuration in order to tune the product selectivity. Solid
81 acid catalysts (*e.g.* zeolites) have been employed by several authors for the thermo-catalytic
82 pyrolysis of both polyolefin-based (Gaurh and Pramanik, 2018; Ratnasari et al., 2017;
83 Santos et al., 2019) and PS-based (Ma et al., 2017b, 2017a; Sul Jung et al., 2021; Xue et al.,
84 2017) plastics. Whereas, solid base catalysts (*e.g.* MgO) were mainly used for the PS-based
85 plastics (Antonakou et al., 2014; Shah et al., 2014; Ukei et al., 2000). The details of reaction
86 mechanism for acid and base catalysis can be found in (Marczewski et al., 2013; Ojha and
87 Vinu, 2015; Ukei et al., 2000).

88 A recent study of the literature on the pyrolysis of PS-based materials reveals that despite
89 some comprehensive reports that have been presented, systematic studies showing the
90 influence of process parameters (in conjunction with different WPS materials and catalysts)
91 are rather scarce. A brief overview of literature studies is given in Table 1. From Table 1, it
92 can be observed that the data of product yields are somewhat scattered and lacking a
93 correlation. Moreover, most authors have used only one type of feedstock. When dealing
94 with PS-based plastic wastes, however, one must confront different types of materials *e.g.*
95 expanded PS, high impact polystyrene (HIPS) or hard PS-based random packing materials.

96 Table 1. An overview of literature studies on the pyrolysis of PS-based feedstocks.

Reference	Feedstock	T (°C)	Catalyst	Catalyst placement	Operation	Styrene Yield (wt%)	BTEX Yield (wt%)
(Ukei et al., 2000)	Virgin PS	600	None	-	Semi-batch	56.10	7.50
		350	Powder MgO	Above the feedstock	in-situ gas phase/ Semi-batch	62.96	4.60
		350	Powder HZSM-5			50.36	11.50
(Kijeński and Kaczorek, 2005)	Virgin PS	400	None	-	Semi-batch	57.90	3.10
		375	MgO	Mixed with feedstock	in-situ liquid phase/ semi-batch	59.60	4.50
		400	(particle size: 1.25 mm)			57.80	3.80
(Mo et al., 2014)	Container PS + Expanded PS	470-505	None	-	Semi-batch	64.52	Not given
(Artetxe et al., 2015)	Virgin PS	450	None	-	Continuous/ Conical spouted bed reactor	55.86	3.06
		500				70.57	5.26
		550				67.10	8.29
		600				66.80	7.88
(Verma et al., 2021)	Expanded PS	650	None	-	Semi-batch	84.74	11.38
		600	HZSM-5	Mixed with feedstock	in-situ liquid phase/ Semi-batch	55.78	18.98
		550		Above the feedstock	in-situ gas phase/ Semi-batch	46.42	24.27
		550		Above and mixed with the feedstock	in-situ multiphase/ Semi-batch	46.30	28.12
(Zayoud et al., 2022)	Expanded PS: 94.20%	450	None	-	Continuous stirred tank reactor (CSTR) at 1 bar	35.70	16.70
		550				41.20	15.10
		600				43.20	15.30

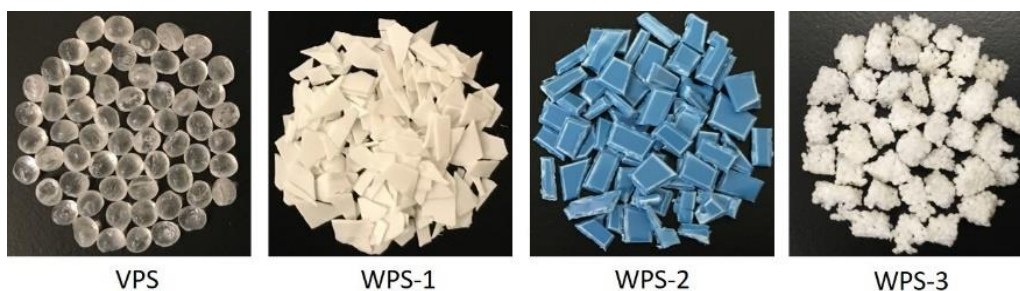
98 Due to differences in the overall compositions, these materials are expected to give different
99 product distributions during pyrolysis process. Furthermore, the use of different operating
100 conditions, catalysts, as well as operation modes can also affect the yields and compositions
101 of the pyrolysis products to a great extent.

102 Considering the facts described in the above paragraphs, it becomes clear that systematic
103 studies on thermal and thermo-catalytic pyrolysis are essential with regard to providing the
104 data which in turn are required for designing efficient and selective pyrolysis processes.
105 Therefore, the focus of the present investigation was to perform thermo-catalytic pyrolysis
106 of different WPS feedstocks over acid and base catalysts employed in *in-situ* and *ex-situ*
107 modus. The aim was to compare the compositions of pyrolysis oils obtained and to discuss
108 the suitability of employed catalysts as well as operation modes in order to tune the product
109 selectivity during pyrolysis of different PS-based plastic wastes.

110 **2. Materials and Methods**

111 **2.1 Feedstocks and catalysts**

112 Three types of WPS materials along with VPS were used as feedstocks (Fig. 1). VPS (3–4
113 mm diameter spheres) with an average molecular weight of $192000 \text{ g}\cdot\text{mol}^{-1}$ was purchased
114 from the company Sigma-Aldrich, Germany. The sample WPS-1 (HIPS, produced by
115 recycling of cups used for dairy products) was purchased from the company SOLLAU,
116 Czech Republic. The samples WPS-2 (hard PS-based material used in the packing of
117 KONICA toner cartridge) and WPS-3 (expanded PS) were random packing materials.



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Fig. 1 Polystyrene samples used as feedstocks.

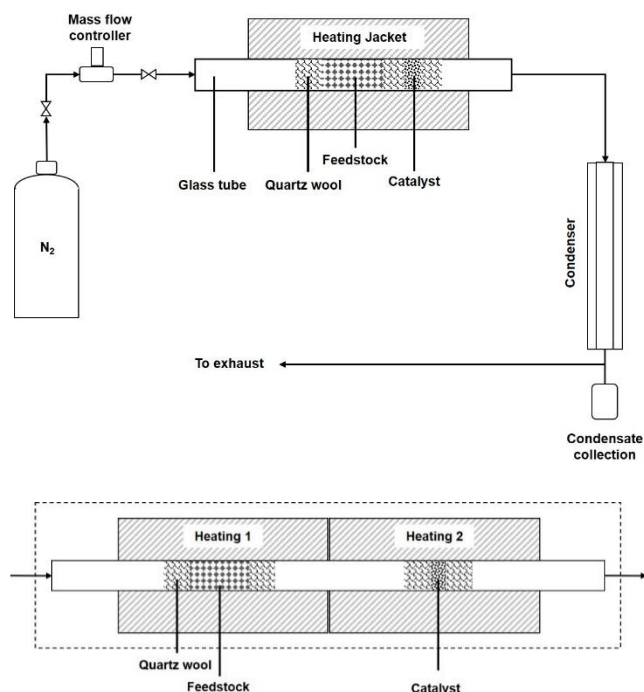
120 In order to obtain a comparable pellet size with VPS and WPS-1, WPS-2 was cut into small
121 pieces. The volume of expanded polystyrene *i.e.* WPS-3 was reduced by simple heat
122 treatment. For this purpose, 10 mm x 10 mm pieces of the original sample were treated at
123 120 °C for 30 minutes. Thermogravimetric analysis (TGA) of all feedstock samples was
124 performed on a LECO TGA 701 (LECO Co., USA) thermogravimetric analyzer. For the
125 experiments, 0.5 g of each sample was heated to 800 °C at a heating rate of 10 °C min⁻¹ in
126 nitrogen atmosphere.

127 For the thermo-catalytic pyrolysis, powder samples of acid (zeolite) and base (MgO)
128 catalysts were employed. The zeolite sample (HZSM-5 type) was produced by the company
129 Süd-Chemie AG, Germany. The data on the structural, textural and acidic properties of the
130 zeolite sample can be found elsewhere (Inayat et al., 2022). As base catalysts, two types of
131 magnesium oxide samples *i.e.* of low and high BET surface area were employed. The low
132 BET surface area sample (MgO-1) was obtained by the thermal decomposition of MgCO₃.
133 The details of the preparation methods can be found elsewhere (Inayat et al., 2021). The
134 MgO sample with high surface area (MgO-2) was prepared by the calcination of hydroxide
135 precursor Mg(OH)₂. The hydroxide precursor was synthesized by the coprecipitation
136 method using aqueous solutions of sodium carbonate decahydrate (2.60 g sample dissolved
137 in 25 g distilled water) and magnesium nitrate hexahydrate (16.05 g sample dissolved in 25

138 g distilled water). The aqueous solution of magnesium nitrate was added drop wise to
139 sodium carbonate solution under constant stirring at 60 °C while maintaining the pH of the
140 mixture at 10.5 by adding 3M NaOH solution. The resulting precipitates were further stirred
141 at 60 °C for 45 min then filtered, washed with distilled water and dried overnight at 70 °C.
142 Finally, the sample was calcined at 400 °C (heating rate 2 °C) for 5 hours.

143 2.2 Experimental setup and procedure

144 The experiments on thermal and thermo-catalytic pyrolysis of VPS and WPS samples were
145 carried out in a lab-scale test rig at 400 and 500 °C. For all experiments, a heating rate of 10
146 °C/min m was used to reach the target temperature and nitrogen with a flowrate of 50
147 mL/min was used as carrier gas. The schematic diagram of the experimental setup is given
148 in Fig. 2. The operating conditions such as temperature, heating rate, nitrogen flow rate etc.
149 were adopted from our previous work (Inayat et al., 2021).



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Fig. 2. Experimental setup: in-situ gas phase (top); ex-situ gas phase (bottom)

153 The main experimental campaign for the catalytic pyrolysis was carried out by applying the
154 *in-situ* gas phase pyrolysis in which the feedstock and catalyst samples (separated by a thin
155 layer of quartz wool) were heated using a single heating source. For the *in-situ* process, a
156 glass tube of 300 mm in length and 20 mm in diameter was used as pyrolysis reactor.

157 In order to investigate the influence of preheating the catalyst to a desired temperature,
158 selected experiments were repeated using the *ex-situ* gas pyrolysis. For this purpose, the
159 feedstock and catalyst samples were packed separately in the reactor tube and were heated
160 using independent heating sources. In this case, a longer reactor tube (500 mm in length)
161 was used and the catalyst sample was preheated to the target temperature before heating of
162 the feedstock was started.

163 **2.3 Product analysis**

164 The amounts of condensate oil, wax and residue were determined gravimetrically. The
165 amount of gas was obtained by subtracting the total mass of oil, wax and residue from the
166 mass of the feedstock used. The yields of all products were determined using the following
167 Eqs. (1) – (3):

$$168 \text{ Oil (wt. \%)} = \frac{\text{Mass of oil}}{\text{Mass of feedstock}} \times 100 \quad (1)$$

$$169 \text{ Wax + Residue (wt. \%)} = \frac{\text{Mass of (wax + Residue)}}{\text{Mass of feedstock}} \times 100 \quad (2)$$

$$170 \text{ Gas (wt. \%)} = \frac{\text{Mass of feedstock} - \text{Mass of (oil + wax + Residue)}}{\text{Mass of feedstock}} \times 100 \quad (3)$$

171 In order to identify the individual oil components, gas chromatography–mass spectrometry
(GC-MS) analysis was performed. For this purpose, an Agilent 8890 GC-MS system
equipped with a single quad detector 5977B and a HP-5 column was used. The yields of
individual components *i.e.* styrene, BTE and alpha-methylstyrene as well as of oligomers

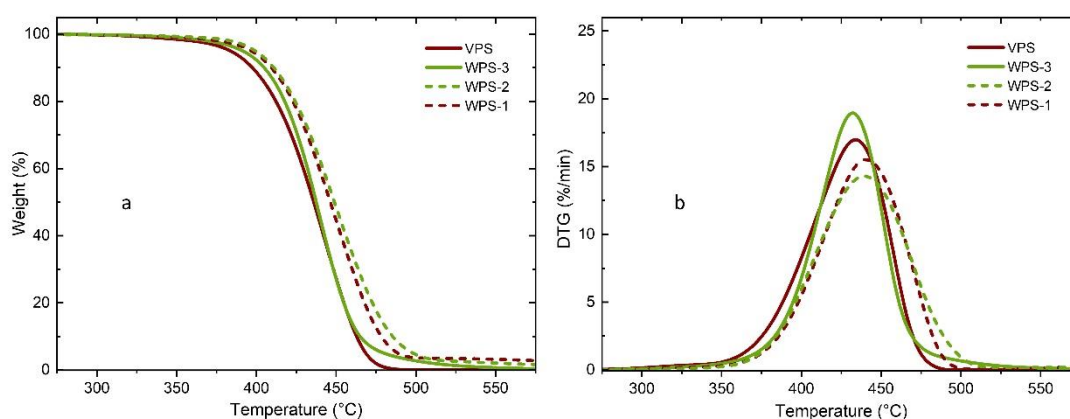
172 were determined by gas chromatography. For this purpose, a YL 6100 GC, equipped with
173 a HP-5 column and a flame ionization detector was used.

174 3. Results and Discussion

175 3.1 Characterization of feedstocks and catalysts

176 The TGA and DTG curves of all feedstocks used in the present study are shown in Fig. 3a
177 and b respectively. For all samples, the main thermal degradation occurred in the
178 temperature range of 400 to 500 °C. The sample WPS-3 (expanded polystyrene) showed
179 very similar thermal behavior as compared to VPS which indicates high PS content in its
180 composition.

181 The different thermal behavior of WPS-1 and 2 as compared to VPS can be attributed to the
182 additives (*e.g.* butadiene rubber (Wang et al., 2010)) added to obtain high impact
183 polystyrene-based materials. Further characterization data *i.e.* FTIR spectra, elemental
184 analysis and density (determined by He pycnometry) of the feedstocks used can be found in
185 the supplementary material.



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Fig. 3. TGA (a) and DTG (b) curves of the feedstocks used.

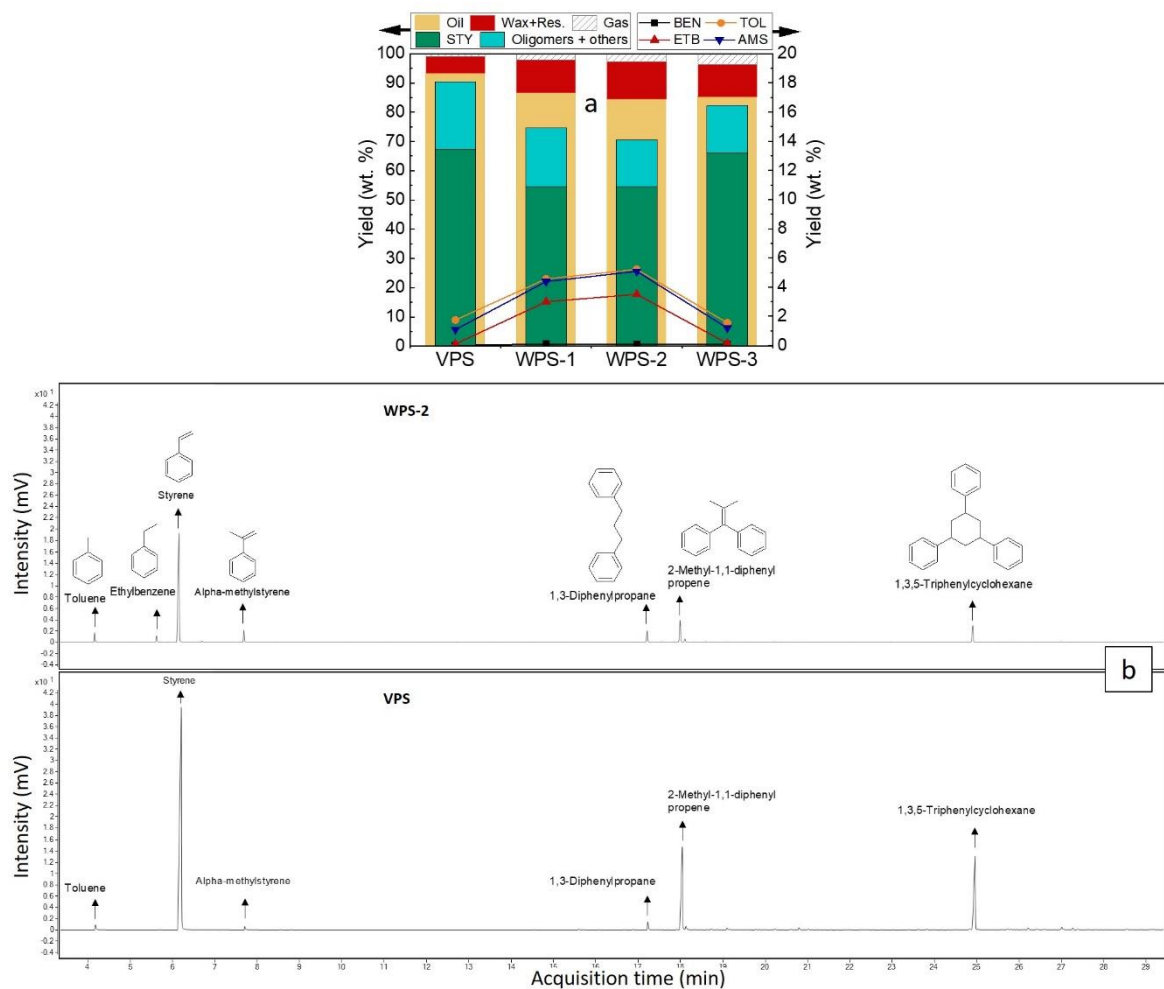
188 For all catalyst samples employed in this work, the textural properties were determined by
189 physisorption of nitrogen. The values of S_{BET} for zeolite, MgO-1 and MgO-2 were found to
190 be 411, 58 and 211 m^2g^{-1} respectively. The characterization data of the acidity of zeolite
191 and basicity of MgO can be found in the supplementary material.

192 **3.2 Thermal and thermo-catalytic pyrolysis**

193 3.2.1 Thermal pyrolysis

194 The results of thermal pyrolysis performed on all feedstock samples are shown in Fig. 4.
195 From these results it can be observed that samples WPS-1 (HIPS) and WPS-2 (hard packing
196 material) produced very similar results. This is evident not only from the amounts of oil,
197 gas and wax/residue but also from the composition of oil. A similar product distribution as
198 well as a thermal behavior in TGA suggests that WPS-1 and 2 share comparable material
199 composition. Likewise, VPS and expanded polystyrene (WPS-3) samples produced similar
200 results in terms of yields of styrene monomer and other mono-aromatic compounds. The
201 main difference was the higher amount wax for WPS-3 and consequently lower amount of
202 oil.

203 This may be attributed to slightly different melting of pellets (in the very beginning of the
204 pyrolysis) for both feedstocks and somewhat shorter residence time of the pyrolysis vapors
205 in the case of expanded PS, possibly due to some retained gas pockets in the pellets.
206 Although, the volume of the expanded polystyrene was reduced (section 2) before the
207 experiments, it still had lower density as compared to VPS (see Supplementary material).
208 In Fig. 4b, a comparison of the chromatograms obtained for VPS and WPS2 is shown. Here,
209 formation of comparatively higher amounts of styrene monomer and oligomers in the case
210 of VPS may be ascribed to its higher styrene content as compared to WPS-2.



211

212 Fig. 4. Thermal pyrolysis at 400 °C: (a) composition of pyrolysis oil; (b) GC-MS chromatograms of the

213

pyrolysis oils obtained from PS and WPS-2.

214 Mo et al (Mo et al., 2014) studied thermal pyrolysis of container PS and expanded PS

215 (weight ratio of 1:1) and reported a styrene content of 64.54% in the pyrolysis oil. This is

216 slightly higher than the average value (ca. 60%) calculated from the ones obtained for

217 expanded PS (ca. 66%) and HIPS (ca. 54.5%) at 400 °C (with heating 10 °C/min and carrier

218 gas flow rate 10 mL/min) in the present work. The dissimilarities with the results as reported

219 by of Mo et al. may be ascribed to the different operating conditions used by them. *e.g.*

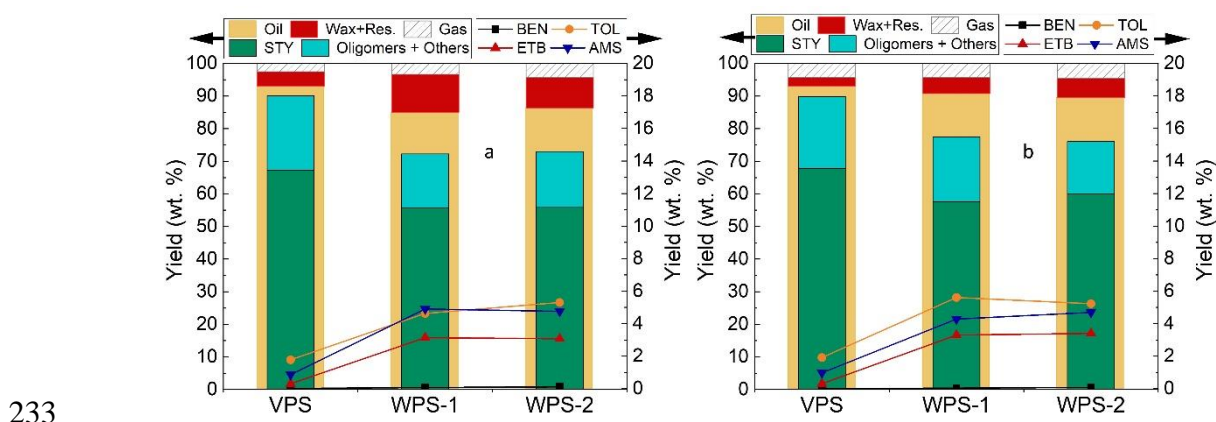
220 higher temperature range (470-505 °C). Also, very recently Zayoud et al. (Zayoud et al.,

221 2022) in their comprehensive study on the pyrolysis of end-of-life PS showed that by just

222 varying process temperature and/or pressure, it was possible to substantially alter the yield
223 of styrene monomer and other mono-aromatic compounds.

224 3.2.2 Thermo-catalytic pyrolysis over base catalysts

225 In Fig. 5a and b the product distributions of thermo-catalytic pyrolysis over MgO-1 at 400
226 and 500°C are shown, respectively. In case of VPS, the increase in temperature did not
227 affect the product distribution appreciably, as the amount and composition of oil fractions
228 are essentially the same at both temperatures. The wax yield however, was decreased and
229 the gas yield increased though, which can be ascribed to the higher temperature. A similar
230 trend was observed for WPS-1 and 2, where the amount of wax was reduced at higher
231 temperature. In this case however, the oil yield was increased, as more wax was converted
232 at 500°C.

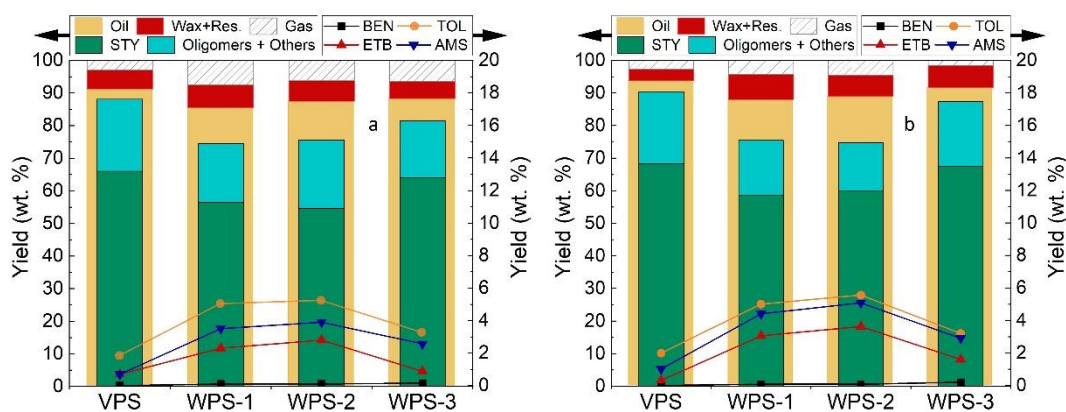


234 **Fig. 5.** Thermo-catalytic pyrolysis (*in-situ*) of different feedstocks over MgO-1 at 400 °C (a) and 500 °C (b)
235 for a catalyst-to-feed ratio of 1:10

236 When the results of thermo-catalytic pyrolysis over MgO-1 catalyst were compared with
237 those obtained from thermolysis, no significant difference was observed. Only a slight
238 increase in the yields of oil and styrene for WPS-1 and 2 was recorded. This shows that the
239 base catalysts did not influence the pyrolysis process significantly. Antonakou et al.

240 (Antonakou et al., 2014) studied catalytic pyrolysis of HIPS and reported slightly higher
 241 monomer yield over MgO, which may be due to the higher temperature (600 °C) they
 242 employed. Furthermore, they used relatively higher amount of catalyst that gave a catalyst-
 243 to-feed ratio of 1:2.

244 Among the MgO catalyst samples used in the present, MgO-1 (Fig. 5) featured lower
 245 specific surface area (S_{BET} : 58 m²g⁻¹). In order to study the effect of S_{BET} , experiments on
 246 MgO-2 (S_{BET} : 211 m²g⁻¹) sample were also carried out. In Fig. 6, a comparison of the
 247 product distributions obtained at 500 °C for MgO-1 and 2 is given.



248
 249 **Fig. 6.** Thermo-catalytic pyrolysis (*in-situ*) of different feedstocks at 500 °C over MgO-1 (a) and MgO-2 (b)
 250 for a catalyst-to-feed ratio of 1:20

251 The results as presented in Fig. 5 and 6 suggest that, at 500 °C, the specific surface area as
 252 well as the catalyst amount (catalyst to feed ratio of 1:10 and 1:20) do not affect the
 253 composition of the pyrolysis products significantly. Moreover, feedstocks of the group 1
 254 (i.e. VPS and WPS-3) and of group two (WPS-1 and 2) continued showing similar behaviors
 255 as they showed in thermal and thermo-catalytic pyrolysis at 400 °C. These results show that
 256 the amount of styrene and that of the BTEX compounds produced during the pyrolysis of
 257 PS-based feedstocks depend mainly on the type (composition of the feedstock) and
 258 operating conditions (e.g. temperature). Thus, it appears that neither the basicity nor the

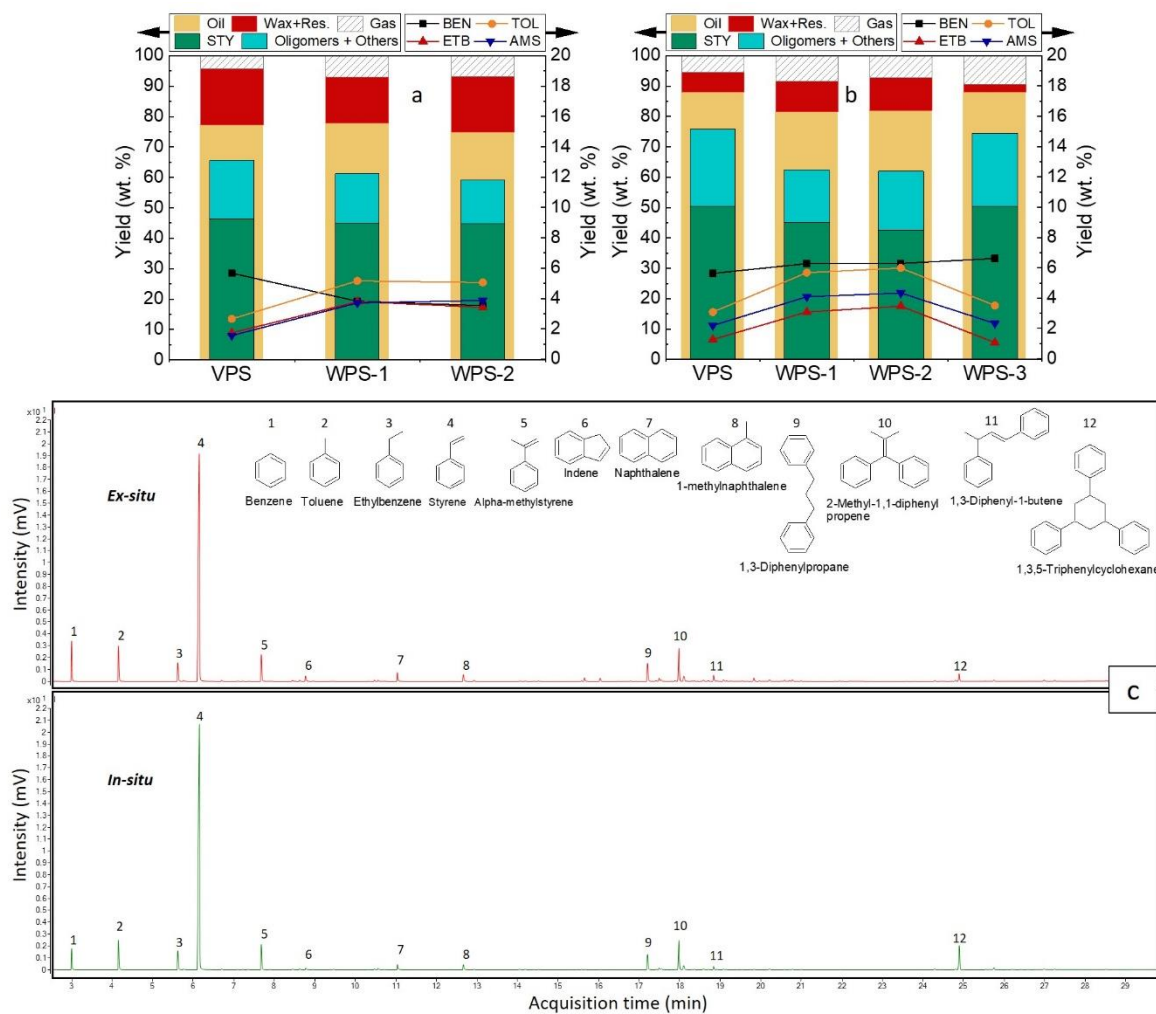
259 S_{BET} of the base catalyst plays a major role in the thermo-catalytic pyrolysis of PS as
260 compared to thermolysis.

261 Furthermore, in order to study the effect of preheating the MgO catalyst, an experiment on
262 VPS was carried out by using the MgO-2 sample in *ex-situ* catalysis and the results obtained
263 (in comparison with the *in-situ* catalysis) are shown in Fig. S4. From the comparison, it can
264 be observed that the *ex-situ* catalytic pyrolysis produced essentially similar results as
265 compared to those obtained from the *in-situ* pyrolysis, both in terms of oil yield and
266 composition. This suggests that preheating the base catalyst during thermo-catalytic
267 pyrolysis of PS does not affect the product distribution appreciably.

268 3.2.3 Thermo-catalytic pyrolysis over acid catalyst

269 The results of the *in-situ* and *ex-situ* catalytic pyrolysis over acid (zeolite) catalyst are shown
270 in Fig. 7a and b respectively. For all experiments performed on the *in-situ* catalytic pyrolysis
271 in this work, interestingly, more residue (inside the reactor) and more wax (inside the
272 condenser) were observed over zeolite (acid) catalyst as compared MgO or non-catalytic
273 pyrolysis. The formation of higher amounts of wax and residue thus led to lower oil yields
274 and consequently lower yields of styrene monomer.

275 A plausible explanation for the formation of high wax and low oil yields over zeolites can
276 be the occurrence of cross-linking reactions that produce crosslinked polymers which need
277 harsh cracking conditions. According to Serrano *et al.* (Serrano et al., 2000), at lower
278 temperatures, the cross-linking reactions over acid catalysts might be favored as compared
279 to cracking reactions. This can lead to the formation of cross-linked polymers which need
280 harsh conditions for cracking and hence remain as waxes.



281

282 **Fig. 7.** Product distribution in thermo-catalytic pyrolysis performed at 500 °C over zeolite catalyst for a feed
 283 to catalyst ratio 1:20: (a) *in-situ* pyrolysis (b) *ex-situ* pyrolysis (c) chromatogram for the samples WPS 2

284 In contrast to the *in-situ* catalysis, the amount of wax was reduced in *ex-situ* catalysis over
 285 zeolites (Fig 7b). This is clearly due to enhanced cracking caused by the preheating of the
 286 catalyst bed during ex-situ process.

287 Note that, for the *in-situ* catalysis, the feedstock and catalyst were heated simultaneously.

288 During heating up, the occurrence of cross-linking reaction might be favored over cracking

289 when the temperature of the reaction zone was still in the low-temperature regime and had

290 not reached the final temperature yet. On the other hand, during *ex-situ* catalysis, the catalyst

291 bed was preheated to the target temperature before pyrolysis vapors (produced by thermal

292 treatment) came in contact with the catalyst particles. Therefore, in this case, the cracking
293 reactions dominated and consequently less wax was produced as compared to the *in-situ*
294 catalysis. This is also shown in Fig. 7c, where the concentration of the heavier molecules
295 (e.g. peak no. 12) was reduced during the *ex-situ* catalysis. Moreover, the use of zeolite
296 catalyst (employed in *in-situ* or *ex-situ*) increased the yield of benzene, toluene and
297 ethylbenzene as compared to thermal and thermo-catalytic pyrolysis over MgO. This can be
298 ascribed to the Bronsted acidity of the catalyst. Zeolite catalysts with Bronsted acid site are
299 effective in depolymerizing styrene dimers to give styrene, toluene, ethylbenzene etc.
300 (Wang et al., 2020).

301 **4. Conclusion**

302 Thermo-catalytic pyrolysis of PS-based plastic wastes was carried out. The influence of
303 different feedstock materials, catalysts, and operation modes on the product distribution was
304 studied. The main findings and concluding remarks are given as follows:

305 Regardless of the feedstock material (Virgin PS, expanded PS, hard PS-based packing
306 material and HIPS), catalyst type (acid and base) and operation mode (*in-situ* and *ex-situ*),
307 oil was obtained as the main pyrolysis product with styrene monomer as the major oil
308 component.

309 Based on the similarity of their behavior in TGA as well as in thermal and thermo-catalytic
310 pyrolysis, the feedstock materials can be divided into two groups. The first group contains
311 virgin and expanded polystyrene, while the second includes hard PS-based packing material
312 and HIPS.

313 A plausible explanation for the lower styrene production during pyrolysis of the feedstocks
314 of second group can be the lower overall styrene content which is due to the presence of

315 additives (e.g. butadiene rubber). Also, in this case, comparatively enhanced formation of
316 mono-aromatics can be attributed to the degradation of styrene butadiene rubber that
317 produces more BTEX compounds.

318 Solid base catalyst influenced the composition of the pyrolysis products only slightly when
319 compared with the one obtained from the non-catalytic pyrolysis. Also, the textural
320 properties of the base catalyst showed no significant impact on the yield and composition
321 of the pyrolysis oil as compared to thermal pyrolysis. Based on these results, it can be
322 concluded that the product distribution (e.g. styrene and BTEX yields) depends more on the
323 type (e.g. polystyrene content) of PS wastes than on the solid base catalyst and that the use
324 of catalytic pyrolysis in this case may not be worthwhile.

325 Solid acid (zeolite) catalyst influenced the composition of the pyrolysis oils significantly as
326 compared to the base catalyst and non-catalytic pyrolysis. The *in-situ* catalysis resulted in
327 higher amount of wax which can be ascribed to the cross-linking reactions (occurred at
328 lower temperature) during heating of the feedstock and catalyst mixture. Ex-situ catalysis
329 reduced the amount of wax due to enhanced cracking over preheated acid zeolite catalyst.
330 Moreover, zeolite catalysts (particularly in *ex-situ*) promote the formation mono-aromatics
331 (*i.e.* BTEX) compounds, which can be attributed to their Bronsted acidity. These findings
332 suggest that acid catalysts have the potential of transforming PS-based materials into more
333 valuable compounds. However, in order to further explore the potential of acid catalysts, a
334 detailed study using harsher conditions (e.g. higher temperature), improved textural
335 properties of the catalyst (e.g. S_{BET} , mesoporosity etc.) and/or using two stage pyrolysis,
336 would be of interest for future studies.

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344 **Appendix A. Supplementary material**

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