

1 Influence of the Catalytic System on the
2 Methanolysis of Polyethylene Terephthalate at
3 Mild Conditions: A Systematic Investigation

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ABSTRACT

Plastic disposal is becoming a threat to our environment because of the severe lack of technologies producing high-quality polymers from scraps at a competitive cost compared to the virgin versions. Regarding polyethylene terephthalate (PET), different recycling technologies have been proposed, but they have several disadvantages in terms of cost, process flexibility, and safety. This work systematically investigates the efficiency of different catalytic systems in the methanolysis of PET, operated at mild temperature. High-performance liquid chromatography was adopted to assess the depolymerization efficacy and the product distribution, allowing a quantitative comparison between the different catalytic systems. Potassium carbonate and dichloromethane proved to be the best performing catalyst/cosolvent pair, leading to almost complete depolymerization of PET from bottle flakes and high yield to dimethyl terephthalate. On the other side, when treating PET/cotton fabrics, the hydrolysis catalyzed by hydroxyl groups in the cotton hampered the complete PET depolymerization, leaving room for further research.

KEYWORDS: polyethylene terephthalate, mixed fabrics depolymerization, low-temperature methanolysis, HPLC characterization, product distribution.

1. Introduction

According to a recent analysis, 368 million tons of plastic were produced in 2019 (*Global-Plastic-Production_1950-2019*, 2019), and if the growth persists at similar rates, this number is expected to grow to 1600 million tons by 2050 (Chateaux and Bibas, 2020). These numbers significantly impact the waste generation, especially when most plastic products are designed for single use and often have a short shelf-life (PlasticsEurope, 2018). Indeed, in 2016 more than 260 million tons of plastic wastes

61 were generated, and this number is expected to rise to 460 million tons by 2030 (Hundertmark et al.,
62 2018). According to a recent estimation, to worsen this scenario, only 30% of all the plastic ever
63 produced is currently in use¹³. In particular, 9% was recycled, but only 0.9% was recycled more than
64 once (Geyer et al., 2017), and more than 8 million tons of plastic are being thrown into the oceans every
65 year (Jambeck et al., 2015). At the same time, the unique properties of polymers in terms of elasticity,
66 mechanical resistance, thermal and electrical insulation, versatility in terms of morphology and
67 geometry make plastic hardly replaceable. Therefore, the available options are the replacement of the
68 current plastics with bio-based and biodegradable ones, which is hampered by the obtainment of
69 thermomechanical properties comparable with their oil-derived counterparts, or a more responsible and
70 sustainable management of the current polymers. Indeed, recycling is one of the three leading players
71 in pursuing a solution for plastic accumulation.

72 This holds particularly true for polyethylene terephthalate (PET), the 6th most-produced plastic
73 worldwide (Beckman, 2018; Plastics Europe and Conversio Market & Strategy GmbH, 2019) with the
74 current production of 70 million tons per year (Grant and Lahme, n.d.), having the highest ratio between
75 generated waste and produced plastic. This fact can be explained considering that most PET products
76 are used in the packaging and textile industries. Therefore, they have a very short shelf-life. Indeed,
77 PET is almost ubiquitous in the packaging sector because of its excellent chemical and physical
78 properties combined with its highly inert behaviour. As an example, PET has low gas diffusivity and
79 low moisture permeability. It is highly clear and transparent, it is lightweight, it has high strength and
80 stiffness, it is resistant to a broad range of temperatures and a broad range of chemicals commonly used
81 daily (alcohols, acids, oils, hydrocarbons) (Das et al., 2021).

82 PET recycling can be carried out using thermal, mechanical, or chemical methods (Damayanti and Wu,
83 2021), but only the latter has the potential to achieve the “circular economy” goal. Indeed, the already
84 well-established thermal and mechanical recycling methods can only perform a down-cycle path (Del
85 Mar Castro López et al., 2014; Frounchi, 1999; Triantafyllou et al., 2002), thus reducing the product
86 quality (open-loop recycling). On the contrary, chemical recycling can perform an up-cycle path, thus
87 increasing the product quality (Damayanti and Wu, 2021; George and Kurian, 2014). In other words,
88 chemical recycling allows the closure of the loop (Kosloski-Oh et al., 2021). The three leading

89 technologies currently employed to perform PET chemical recycling are glycolysis (Karayannidis and
90 Achilias, 2007; Sheel and Pant, 2019; Z.I.Takai, 2018), methanolysis (Arzamendi et al., 2008; Han,
91 2019), and hydrolysis (Han, 2019; Pellis et al., 2016). All these methods employ a solvent that allows
92 the depolymerization of PET towards the monomers bis(2-hydroxyethyl) terephthalate (BHET),
93 dimethyl terephthalate (DMT), and terephthalic acid (TPA), respectively. Other methods such as
94 aminolysis and ammonolysis (Gupta and Bhandari, 2018) have been recently introduced, and some
95 more complex depolymerization processes employing microwaves or ionic liquids were proposed (Al-
96 Sabagh et al., 2016; Damayanti and Wu, 2021). However, these latter methods are far from reaching
97 the industrial scale.

98 Despite the promise held by the conventional methods such as glycolysis, methanolysis, and hydrolysis
99 in the chemical recycling of PET, they also have serious drawbacks (Karayannidis and Achilias, 2007),
100 mainly related to the complex monomer purification procedures and high plant energy demand. In
101 particular, methanolysis leads to the production of the monomer DMT, which is easier to purify if
102 compared to the monomers coming from other technologies (BHET, TPA, etc.), but has the
103 considerable drawback of requiring high energy costs since the reaction needs supercritical conditions
104 (Han, 2019; Sheel and Pant, 2019).

105 Recently, industries and researchers are developing other methods to carry out methanolysis. For
106 instance, the Loop industries claimed the invention of a methanolysis process working at milder
107 conditions (Essaddam, 2020), while other studies on low-temperature methanolysis were published
108 lately (Pham and Cho, 2021). However, all these studies were performed on PET coming from waste
109 bottles, a relatively clean feedstock, while the great advantage of the methanolysis process is that it
110 could treat also impure feedstocks, like fabrics mixed in cotton and PET. Indeed, when dealing with
111 clean and controlled wastes like bottle flakes, the glycolysis process may be preferred since it is cheaper
112 and since the problem of monomer purification is not crucial (Karayannidis and Achilias, 2007; Sheel
113 and Pant, 2019). As a matter of fact, most PET chemical recycling plants currently in use exploit
114 glycolysis on clean feedstocks (Jared Paben, 2021). On the other hand, methanolysis may be preferred
115 to treat feedstocks containing, in addition to PET, other components, such as natural fibers, additives
116 and dyes that may contaminate the obtained monomer preventing its repolymerization. In fact, it leaves

117 the possibility of purifying the monomer (DMT) to a larger extent by crystallization, melt-crystallization
118 or distillation. As a matter of fact, the products are DMT and EG, which have boiling point of 288 °C
119 and 198 °C, respectively. Hence, a standard distillation can be applied to separate the products from the
120 unconverted PET and other compounds, which have a boiling point higher than 400 °C . Therefore, the
121 interest in improving the methanolysis for treating low-quality feedstocks is gaining much attention
122 (Pudack et al., 2020).

123 Methanolysis is typically operated in supercritical conditions to achieve high PET conversion and high
124 yield to DMT. In fact, the conventional catalysts used for these transesterification reactions (i.e. metal
125 acetates and metal oxides) are active at high temperatures, far above the methanol boiling point (Du et
126 al., 2020; Kurokawa et al., 2003; Liu et al., 2013). Therefore, the identification of catalysts enabling the
127 methanolysis to occur at milder conditions is urgently needed to make the process less energy-intensive
128 and then promote the chemical recycling to a wider extent.

129 Different studies available in the literature provide examples of catalytic systems active at mild
130 conditions (Pham and Cho, 2021). However, a systematic investigation of the role played by different
131 catalysts, counterions and cosolvents on the distribution of monomers obtained from the methanolysis
132 of PET allowing a conscious choice based on the different feedstocks that may happen to treat is
133 missing. In order to provide a clear understanding of the role of these species, in this work we
134 investigated the performance of different combinations of catalysts and cosolvents in the methanolysis
135 and ethanolysis of PET coming from both a high-quality feedstock as the bottle flakes, and from a more
136 impure product represented by fabrics mixed in cotton and polyester. The reactions were conducted at
137 mild conditions, *i.e.* ambient pressure and methanol normal boiling point, and key performance
138 parameters such as PET conversion and distribution of the monomers recovered were used to draw a
139 comparison between the different catalysts/cosolvent combinations. These parameters were determined
140 through an improved high-performance liquid chromatography (HPLC) methodology developed to
141 analyze the composition of the reaction mixture and allowing a good separation of the different
142 monomers and oligomers. Guidelines are then provided on the selection of the most suitable reactive
143 system based on considerations related to the feedstock to be handled, yield in DMT, safety and
144 economicity of the catalytic system.

145

146 2. Materials and Methods

147 2.1. Materials

148 Bis(2-Hydroxyethyl) terephthalate (BHET, Aldrich, >94.5%), dimethyl terephthalate (DMT,
149 Aldrich, >99.0%), terephthalic acid (TPA, Aldrich, 98%), mono-Methyl terephthalate (MMT, Aldrich,
150 97%), 1-(2-hydroxyethyl) 4-methyl terephthalate (HEMT, Aldrich, 97%), acetonitrile (ACN, Sigma
151 Aldrich, \geq 99.7%), hexafluoro-isopropanol (HFIP, Fluorochem, 99.9%), anhydrous ethylene glycol
152 (EG, Sigma Aldrich, 99.8%), dichloromethane (DCM, Sigma Aldrich, >99.9%), chloroform (Sigma
153 Aldrich, >99.98%), methanol (MeOH, Sigma Aldrich, >99.9%), ethanol (EtOH, Sigma Aldrich,
154 >99.9%), trifluoroacetic acid (TFA, Sigma Aldrich, 99%), sulfuric acid (H₂SO₄, Sigma Aldrich, 98%),
155 p-Toluenesulfonic acid (Sigma Aldrich, \geq 98.5%), 1,4-Diazabicyclo[2.2.2]octane (DABCO, Sigma
156 Aldrich, \geq 99%), titanium oxide (TiO₂, Sigma Aldrich, >99%), calcium oxide (CaO, Sigma Aldrich,
157 >99.9%), chromium acetate (CrAc, Sigma Aldrich, >98.0%), manganese acetate (MnAc, Sigma
158 Aldrich, >99%), magnesium acetate (MgAc, Sigma Aldrich, >98%), sodium sulphate (Na₂SO₄, Sigma
159 Aldrich, 99%), sodium carbonate (Na₂CO₃, Sigma Aldrich, >99%), sodium bicarbonate (NaHCO₃,
160 Sigma Aldrich, >99.7%), potassium carbonate (K₂CO₃, Sigma Aldrich, >99%), potassium bicarbonate
161 (KHCO₃, Sigma Aldrich, >99.7%), sodium hydroxide (NaOH, Sigma Aldrich, >98%), potassium
162 hydroxide (KOH, Sigma Aldrich, >85%), sodium methoxide (MeONa, Sigma Aldrich, 95%), sodium
163 ethoxide (EtONa, Sigma Aldrich, 95%), potassium methoxide (MeOK, Sigma Aldrich, 95%), 1,5,7-
164 Triazabicyclo[4.4.0]dec-5-ene (TBD, Sigma Aldrich, 98%).

165 Waste fabrics made of 50% PET and 50% cotton in shredded flakes and postconsumer PET bottles were
166 obtained from an industrial supplier (Corepla, Italy) in the form of prewashed flakes. The waste
167 materials were dried in an oven at 50 °C for 6 hours and then stored in a dryer.

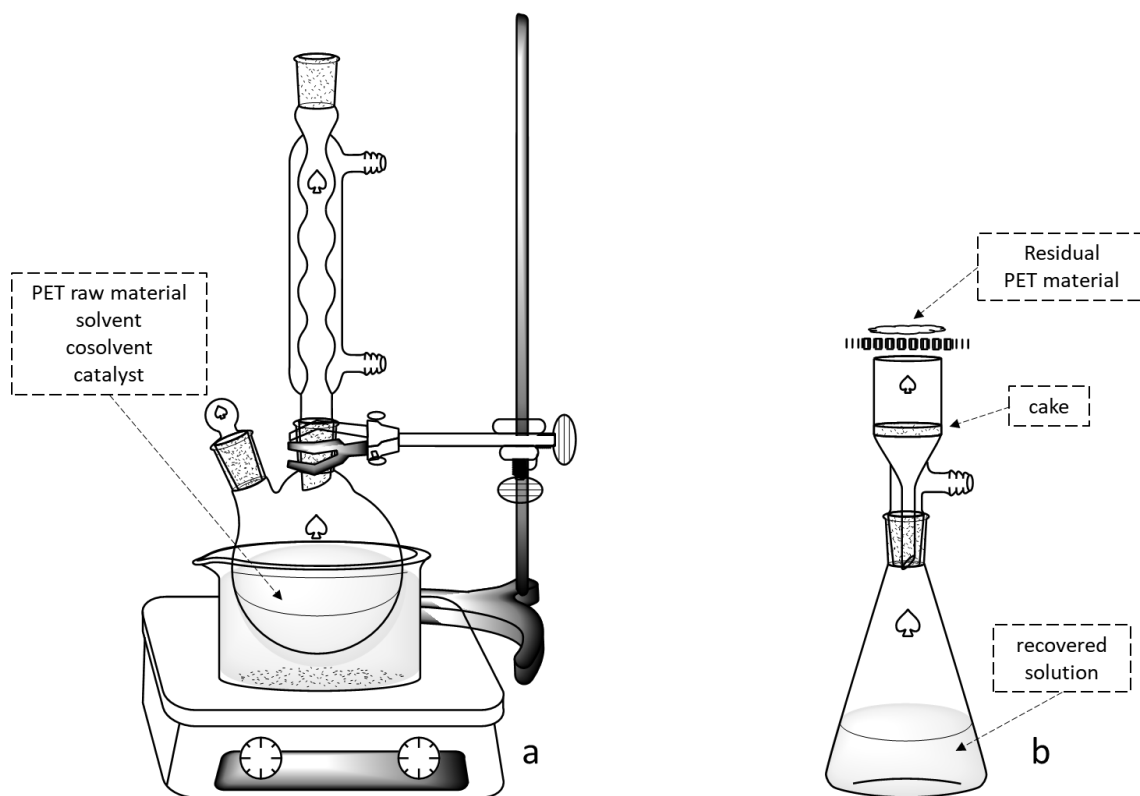
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169 2.2 Methanolysis

170 The methanolysis reaction was carried out in a 50 mL round bottom flask equipped with a magnetic
171 stirrer and a reflux condenser. The flask was immersed in a stirred oil bath, and the temperature was set
172 at the boiling point of the reaction mixture, *i.e.* 70 °C, as depicted in **Figure 1a**. Similarly to a procedure

173 previously tested on PET bottle flakes (Pham and Cho, 2021), both in the case of fabrics mixed in cotton
174 and PET and in the case of bottle flakes, the molar ratios of solvent, cosolvent, and catalyst with respect
175 to the PET repeating unit were set to 50, 50, and 1. The flake surface area was kept constant to 1 cm²
176 in order to be reproducible, since the surface area for the PET bottle flakes can have an impact on the
177 depolymerisation reaction rate. The use of different cosolvents, namely dichloromethane (DCM),
178 tetrahydrofuran (THF), chloroform (CHCl₃), and catalysts was investigated. As an example, in the case
179 of DCM as cosolvent and K₂CO₃ as a catalyst, 2 g of fabrics (1 g of PET – 5.2 mmol) were added to
180 the round bottom flask together with 8.33 g of methanol (260 mmol), 22.11 g of dichloromethane (260
181 mmol) and 0.959 g of K₂CO₃ (5.2 mmol), and these ratios between PET, catalyst and cosolvent were
182 kept constant for all the experiments. The reaction was carried out under continuous stirring at 300 rpm
183 for 20 hours. The reaction mixture was then filtered with a Buchner funnel using qualitative filtering
184 paper with 20 μm pore size, as depicted in **Figure 1b**.

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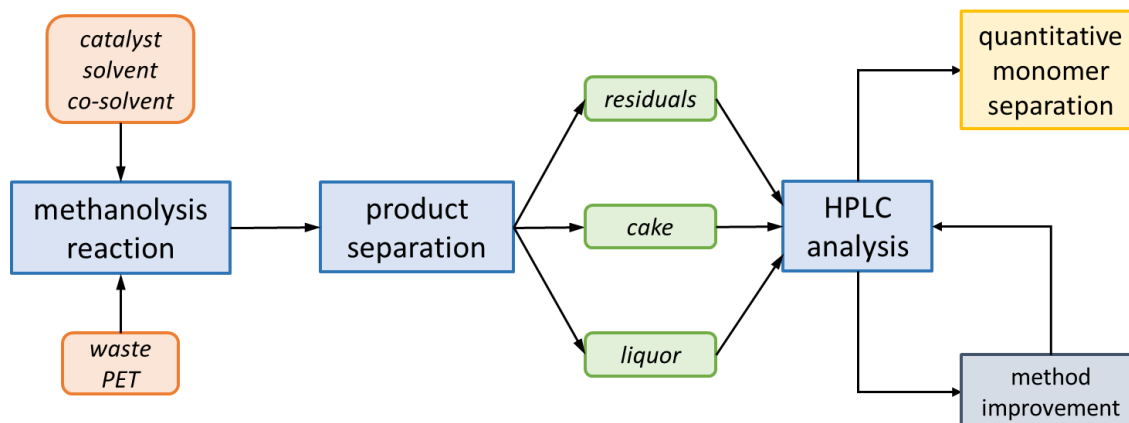


187

188 **Figure 1** – Schematic representation of the configuration adopted for the PET depolymerization
189 reaction (a) and the product separation (b)

189

190 Finally, the residual fibres, the cake, and the recovered solution were analyzed *via* HPLC to
191 determine the PET depolymerization efficiency and the monomer distribution, as schematized in the
192 block diagram shown in **Figure 2**.



193

194 **Figure 2** – Representation of the complete procedure followed in this work

195

196 This reaction configuration was applied to bottle flakes to validate and integrate the results
197 previously obtained by Pham and Cho (Pham and Cho, 2021). For these reactions, the molar ratios of
198 solvent, cosolvent, and catalyst with respect to the PET repeating unit were set to 50, 50, and 1. As an
199 example, 1 g of PET (5.2 mmol) was added in the round bottom flask together with 8.31 g of methanol
200 (260 mmol), 22.10 g of dichloromethane (260 mmol) and 521.4 mg of K_2CO_3 (5.2 mmol). As for the
201 fabrics, the reaction was carried out at 70 °C for 20 h under stirring at 300 rpm. After cooling to 10 °C,
202 the product was filtered.

203 The filtration and separation procedure were slightly tailored whether the products came from bottle
204 flakes or fabrics. In the easier case of bottle flakes, the product mixture was filtered through a fine net
205 to recover the unreacted PET fraction, washed with fresh methanol, and filtered through a Buchner
206 funnel. On the contrary, a squeezing step and a second washing step were added after the filtration
207 through the fine net when fabrics were employed. Then, a fibre flake was weighted and immersed in an
208 excess amount of the HPLC eluent to dissolve all the remaining products stuck on the fibre. Finally,
209 this solvent and all the obtained liquids and cakes were analyzed via HPLC.

210

211 **2.3 Synthesis of Ethyl Terminated Monomers**

212 The ethyl terminated PET monomers, *i.e.*, 1-(2-Hydroxyethyl) 4-ethyl terephthalate (EHET),
213 1-ethyl 4-methyl terephthalate (EMT), and diethyl terephthalate (DET), have been synthesized through
214 transesterification reactions. For example, in one of these reactions, 6 g of DMT (0.031 mol) together
215 with 14.08 g of ethanol (0.306 mol) and 0.57 g of zinc acetate (3.13 mmol) were added in a 50 mL
216 round bottom flask equipped with a magnetic stirrer and a reflux condenser. The flask was immersed
217 in an oil bath, and the reaction was carried out at 70 °C under stirring at 500 rpm. Every hour, samples
218 were taken to spot the growing and vanishing peaks to characterize the ethyl-terminated PET
219 monomers.

220

221 **2.4 Characterization**

222 The product distribution of the depolymerization mixture were assessed on an Agilent 1100 HPLC
223 with an UV detector set at 290 nm. Similarly to the method used in previous works (Rosenboom et al.,
224 2018), the samples were dissolved in 25% (v/v) HFIP/CHCl₃ and separated in a Restek C18 column
225 (250 x 4.6 mm, 5 µm pore size) with an acetonitrile/H₂O gradient from 20/80 to 80/20 over 40 min at 1
226 mL min⁻¹. TFA 0.1% (v/v) was added as a stabilizer to both the organic and aqueous phases, using
227 acetonitrile as the organic phase and Millipore water as the aqueous phase. The injection volume was
228 kept constant at 10 µL.

229 Different methods are proposed and further discussed in this work to improve the quality and the
230 resolution of the separation, which are differentiated by the solvent used to prepare the samples, the
231 eluent composition, its pH, and its gradient.

232 The monomer species were unambiguously identified via this HPLC-UV setup, and monomer
233 purity was computed by integrating the resulting peaks after external calibration (see **Figure S1** and
234 **Table S1**). Indeed, the UV absorptivity of different monomer species was assessed before these
235 measurements (as illustrated in **Figure S1**) to ensure unbiased evaluation and was found almost equal
236 for all species (as shown in **Table S1**).

237 Since all the HPLC analyses were quantitative, the evaluations of the depolymerization efficiency (PET
238 conversion, X_{PET}) and the monomer yields were computed straightforwardly, as illustrated in Eq. 1 and
239 Eq. 2.

240

$$x_{PET} = \frac{m_{PET}}{m_{PET}^0} \quad \text{Eq. 1}$$

$$yield_i = \frac{n_i^{res} + n_i^{cake} + n_i^{sol}}{n_{PET}^0} \quad \text{Eq. 2}$$

241

242 Where m_{PET} is the residual mass of PET which did not depolymerize, m_{PET}^0 is the initial mass of PET,243 while n_i^{res} , n_i^{cake} , and n_i^{sol} are the number of moles of the generic i-th monomer that remained stuck

244 on the fibres, were recovered in the cake, and remained dissolved in the filtered solution, respectively.

245 n_{PET}^0 are the moles of PET repeating units initially present calculated as the ratio m_{PET}^0/MM_{PET} , where246 MM_{PET} is the molecular mass of the PET repeating unit.

247 Hereinafter, we will refer to the overall PET conversion and yield to the different monomers as

248 calculated through Eq. 1 and Eq. 2. The contributions of each fraction (*i.e.* fibers, cake and solution)

249 are reported in the Supporting Information section as specified when discussing the different sets of

250 experiments.

251

252 **3. Results and Discussion**253 **3.1 HPLC Characterisation of the Methanolysis Products**

254 During the PET methanolysis, even if DMT is thermodynamically the most favoured monomer, other

255 products are typically produced, and they can be found in the residual fibres, in the filtered cake and in

256 the recovered solution. These monomers are based on the same terephthalate backbone (shown in

257 **Figure S2**) and are terminated by end-groups such as water, methanol, ethylene glycol, or ethanol. This258 monomer population is schematized in **Table 1**.

259

260 **Table 1** – List of the monomers formed during the PET methanolysis and ethanolysis. *L1* in the
261 structure indicates the terephthalate backbone, to which different substituents are bounded.

Monomers		
structure	full name	name
H-L1-H	Terephthalic acid	TPA
EG-L1-EG	Bis(2-hydroxyethyl) terephthalate	BHET
H-L1-Me	monomethylterephthalate	MMT

EG-L1-Me	2-Hydroxyethyl methyl terephthalate	HEMT
EG-L1-Et	2-Hydroxyethyl ethyl terephthalate	EHET
Me-L1-Me	dimethyl terephthalate	DMT
Me-L1-Et	methyl-ethyl terephthalate	EMT
Et-L1-Et	diethyl terephthalate	DET

262

263 Thus, HPLC was adopted to separate and characterize all these monomers. Since not all of them are
 264 directly present on the market, only the available samples of TPA, MMT, HEMT, DMT, and BHET
 265 were used for the HPLC external calibration. BHET was the only one that contained small oligomers
 266 (dimers and trimers) among these samples, as shown in **Table S2**. Therefore, they were also
 267 characterized by HPLC analysis. The external calibration done on these 5 samples showed that, at the
 268 low concentrations used for the analyses (around 1 mg mL⁻¹), all the PET monomers and oligomers
 269 have a similar molar absorptivity (see **Figure S1**). Therefore, the species that were not available on the
 270 market were reasonably considered to have the same absorbance coefficient as the measured ones. This
 271 assumption is supported by the fact that at 290 nm, the absorbance is maximized for the aromatic ring,
 272 and the different substituent groups do not perturb it. Thus, all the monomer peak intensities from the
 273 HPLC analyses were easily related to their concentrations in the sample. In particular, the samples
 274 which were not available on the market are all the ethyl terminated ones (EHET, EMT, and DET). At
 275 the same time, it is important to consider also these latter species since ethanol is frequently used
 276 instead of methanol in PET transesterification reactions (De Castro et al., 2006; Kucek et al., 2007;
 277 Reyero et al., 2015). Therefore, they were synthesized on purpose, according to the procedure reported
 278 in Section 2.3. Then, their peaks on the HPLC spectrum were attributed by exclusion.

279 The methanolysis reaction products were analyzed using HPLC initially operated using a mixture
 280 of water and acetonitrile and a mixture (1:3) of hexafluoro-isopropanol and chloroform as the solvent
 281 for the sample preparation, as it is often operated in literature (Espinosa et al., 2000; Fleckenstein and
 282 Fleckenstein, 1988; Rosenboom et al., 2018). However, when applying these operating conditions, not
 283 all the monomers get solubilized, thus leading to inaccurate analysis. Indeed, TPA is entirely insoluble
 284 in such solvents, and it is also insoluble in the large majority of the commonly used solvents (Harper
 285 and Janik, 1970). As a result, its peak in the elugram reported in **Figure S3a** is much smaller than the
 286 actual TPA concentration.

287 On the contrary, terephthalic acid is particularly soluble in alkaline water environments (Harper and
 288 Janik, 1970). Therefore, the mixture previously used to prepare the samples was substituted by a mixture
 289 of HFIP and alkaline water at pH=13 (50:50 vol.), which allowed the TPA peak to be properly
 290 characterized, as shown in **Figure S3b**. However, the establishment of an equilibrium between the
 291 acidic and the neutralized form of the TPA monomer led to a very broad peak. The acidic water was
 292 then substituted with neutral water and the two peaks corresponding to the acidic monomers (TPA and
 293 MMT) do clearly get narrower, even if their elution time lowers a lot, as shown in **Figure S3c**. Finally,
 294 to better separate these two monomers, the eluent ratio (H₂O/acetonitrile) at the beginning of the
 295 separation was changed from 80/20 to 100/0 and the gradient was run until 0/100 in 45 min, as depicted
 296 in **Figure S3d**.

297 This analytical protocol allows a complete characterization of the methanolysis reaction products
 298 and can be applied to the monomers produced from every kind of waste material: from transparent
 299 bottle flakes to dirty fibres and fabrics mixed in cotton and PET. Indeed, the experimental procedure to
 300 separate the produced monomers from the unreacted PET fraction has to be slightly tailored depending
 301 on the starting waste material as described above, while the method for the HPLC analysis stays the
 302 same.

303 Finally, according to the optimized analytical method, the whole monomer population with their
 304 residence times is reported in **Table 2**, while in **Figure 3** the peaks of all the characterized species are
 305 shown. Moreover, the complete list of the characterized monomers and oligomers with their residence
 306 times is shown in **Table S2**.

307

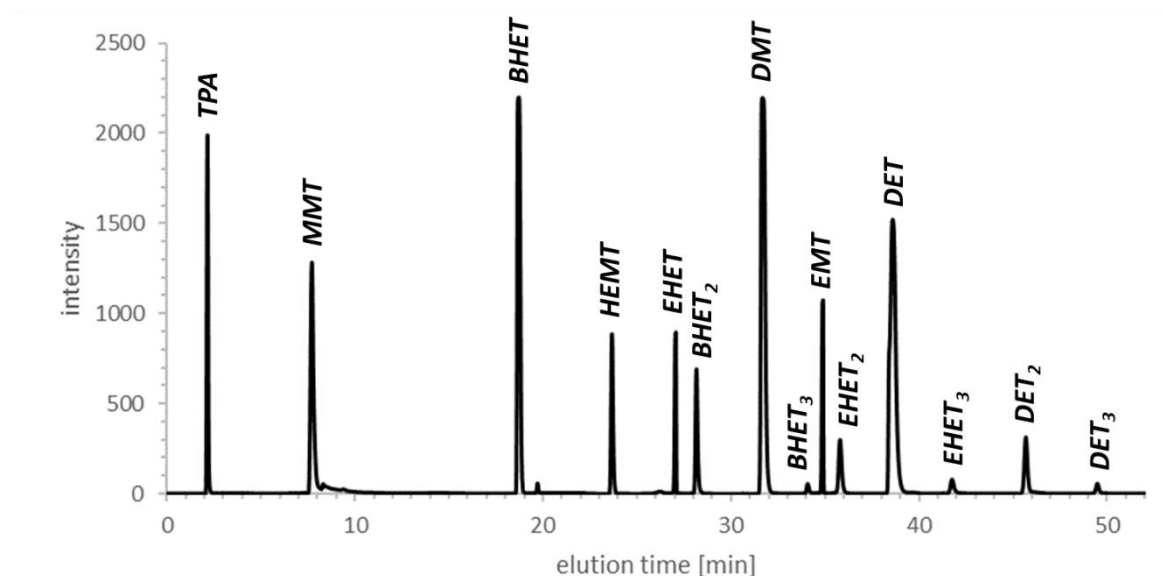
308 **Table 2** – List of the monomers with their residence time according to the 100-0 method (d) (Sample
 309 prepared with 50% (v/v) HFIP/NaOH water solution at pH 13, from 0-100 % to 100-0 % ACN-Water)

monomers		
<i>structure</i>	<i>name</i>	<i>t_{res} [min]</i>
H-L1-H	TPA	2.15
H-L1-Me	MMT	7.70
EG-L1-EG	BHET	18.70
EG-L1-Me	HEMT	23.66
EG-L1-Et	EHET	27.08

Me-L1-Me	DMT	31.66
Me-L1-Et	EMT	34.87
Et-L1-Et	DET	38.63

310

311



312

313 **Figure 3** – Complete elugram according to the optimized HPLC method. The sample is prepared with
 314 50% (v/v) HFIP/NaOH water solution at pH 13, and the ACN/H₂O gradient is run from 0/100 % to
 315 100/0 in 45 min.

316

317 In conclusion, this method allowed for the detection and separation of all the PET monomers, with
 318 sufficiently good resolution for quantitative analysis. Therefore, this method was applied in the
 319 following to characterize the monomer distribution and yields from the PET depolymerization
 320 reactions.

321

322 3.2 PET Depolymerisation through Methanolysis

323 The PET methanolysis is a transesterification with methanol, which cleaves the ester bonds in
 324 the PET, ideally producing the monomer DMT and ethylene glycol. This reaction is attracting growing
 325 industrial attention since it leads to a monomer relatively easy to purify through unit operations
 326 commonly adopted in the chemical engineering practice, like crystallization and distillation (Das et al.,
 327 2021; Han, 2019). However, the currently installed pilot plants for PET methanolysis are operated in

328 supercritical conditions since the catalyst activities are not compatible with the methanol boiling
329 temperature at atmospheric pressure. Therefore, this methanolysis configuration turns out to be
330 economically feasible only on very large-scale plants since it requires high amounts of energy to be
331 operated (Han, 2019). In principle, this problem may be overcome by adding a cosolvent. However,
332 reaching a temperature at which common transesterification catalysts are active is not feasible unless
333 one employs excessive amounts of very high boiling solvents. Indeed, even if it is still not wholly clear
334 (Guclu et al., 1998; Sharma et al., 2013), the role of cosolvents in the methanolysis reaction is not
335 related to the mixture boiling temperature rising. On the contrary, the cosolvent is supposed to swell
336 the polymer, lower the reaction energy barrier, and thus speed up the reaction kinetics (Pham and Cho,
337 2021).

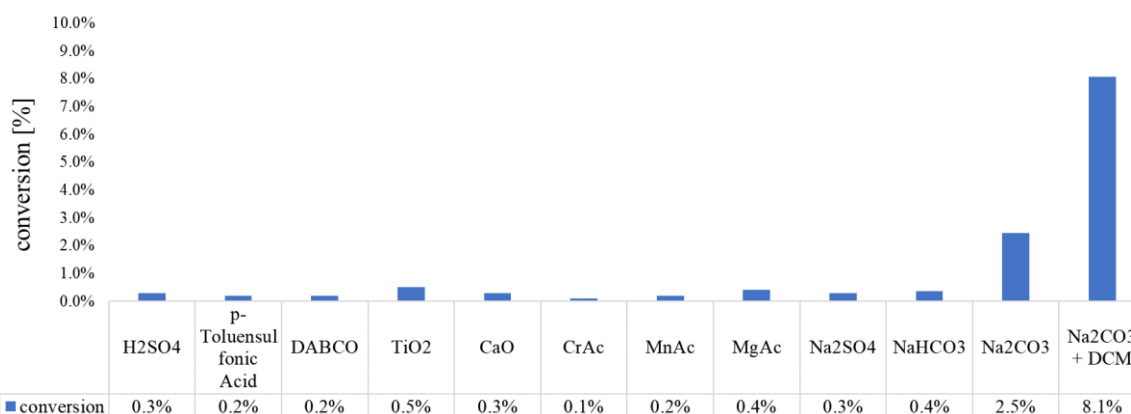
338 To assess the bottle flakes and fiber mesh size to be used, a preliminary study was conducted
339 under the same conditions using PET scraps in the range 1 mm² to 5 cm². No significant variations were
340 observed in this range for the fiber scraps since they are porous, and their monodimensional-like
341 geometry already has a high surface area that cannot be increased significantly by reducing the mesh
342 size. However, for PET bottle scrap, it was observed a slight difference and for this reason it was
343 decided to work with flakes mesh size around 1 cm² because it is widely industrially available.

344 As a first screening, PET bottle flakes were depolymerized in the presence of methanol and
345 without any cosolvent, using common transesterification catalysts such as inorganic and organic acids,
346 metal oxides, metal acetates, and carbonates. These reactions were carried out at the mixture boiling
347 point, *i.e.*, methanol. The results in terms of PET depolymerization efficiency are shown in **Figure 4**,
348 from which it is clear that none of these catalysts is active at such low temperatures when no cosolvent
349 is employed.

350 Among all these conventional transesterification catalysts, the only one that showed appreciable results
351 was Na₂CO₃. Therefore, this one was further tested by adding a cosolvent to the reacting mixture. In
352 particular, DCM was chosen as a cosolvent since it had been already proved effective for this kind of
353 reactions (Pham and Cho, 2021). As shown in **Figure 4**, the addition of DCM significantly improved
354 the depolymerization efficiency (from 2% to 8%), but the final result in the presence of the catalyst

355 Na_2CO_3 is still far from being appealing. For this reason, the study of the different monomer (TPA,
 356 MMT, MHET, DMT) yields was not performed at this stage.

357



358

359 **Figure 4** – PET conversion using common transesterification catalyst, MeOH as solvent and without
 360 cosolvent unless specified

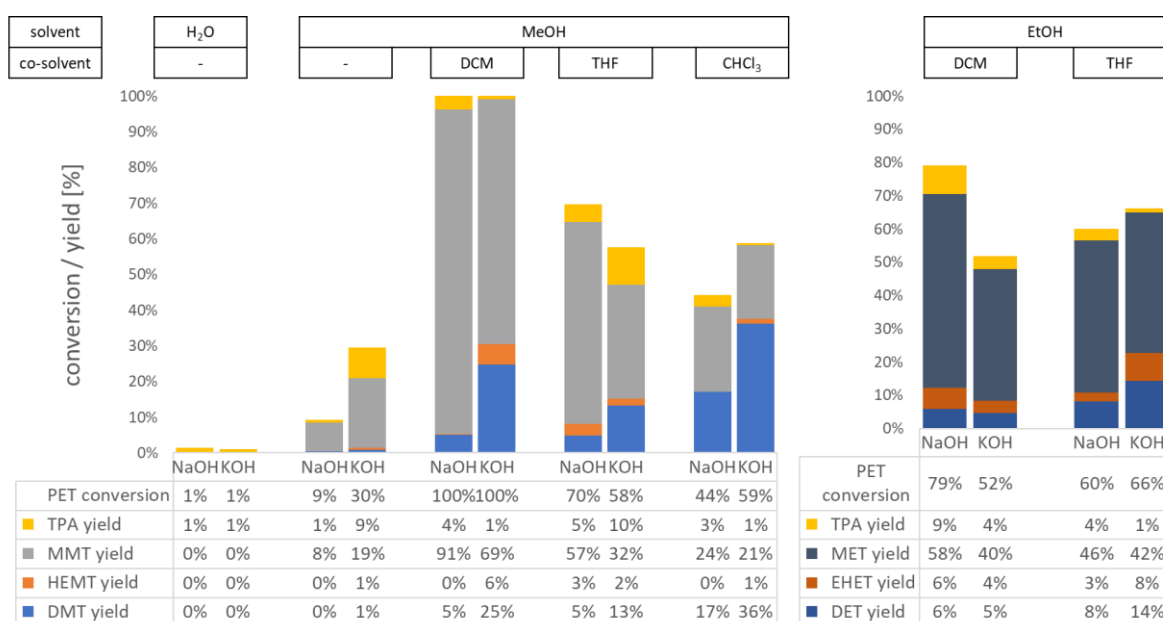
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362 On the contrary, replacing these metal oxides and acetates catalysts with alkaline metal hydroxides
 363 led to more exciting results. Indeed, sodium and potassium hydroxides are reported to be active catalysts
 364 used in the transesterification reactions for biodiesel treatments at low temperatures in the presence of
 365 either methanol or ethanol (Kucek et al., 2007; Reyero et al., 2015; Vicente et al., 2004; Wu et al.,
 366 2016). **Figure 5** shows the results in terms of depolymerization efficiency and monomer yields of the
 367 methanolysis reaction of PET bottle flakes in the presence of sodium and potassium hydroxides as
 368 catalysts, while the complete set of data showing the relative amount of the monomers collected in the
 369 cake and recovered in the solution are shown in **Table S3**. It can be appreciated the substantial
 370 improvement in terms of depolymerization efficiency compared to the previous case. In addition, no
 371 significant difference was observed between the activity and the selectivity of the two employed
 372 catalysts as they led to similar depolymerization efficiencies when used in experiments under the same
 373 conditions. Moreover, in both cases the primary product is MMT, which could be either in the acidic or
 374 in the corresponding salt form, with the latter more favourable as a result of the large excess of base
 375 used. Then, it is possible to observe that the transesterification reaction requires both the solvent
 376 (methanol or ethanol) and the catalyst (sodium or potassium hydroxide) to run. Indeed, when using
 377 water instead of methanol, depolymerization does not occur at all. Moreover, a suitable polar cosolvent

378 like DCM or THF considerably impacts depolymerization efficiency. Efficiencies up to 100% were
 379 achieved for depolymerization in the presence of DCM, and up to 70% with THF, even if the yields to
 380 DMT always remained very low. As a matter of fact, the hydroxyl catalysts are not highly selective
 381 towards methanolysis and could have promoted hydrolysis from the residual moisture present in the
 382 reacting mixture (Arzamendi et al., 2008; Ng et al., 2009).

383

384



385

386 **Figure 5** – PET conversion and monomer yields using hydroxy catalyst, H₂O, MeOH or EtOH as
 387 solvent and DCM, THF or CHCl₃ as cosolvent. More detailed results related to the liquid and solid
 388 compositions are available in Table S3.

389

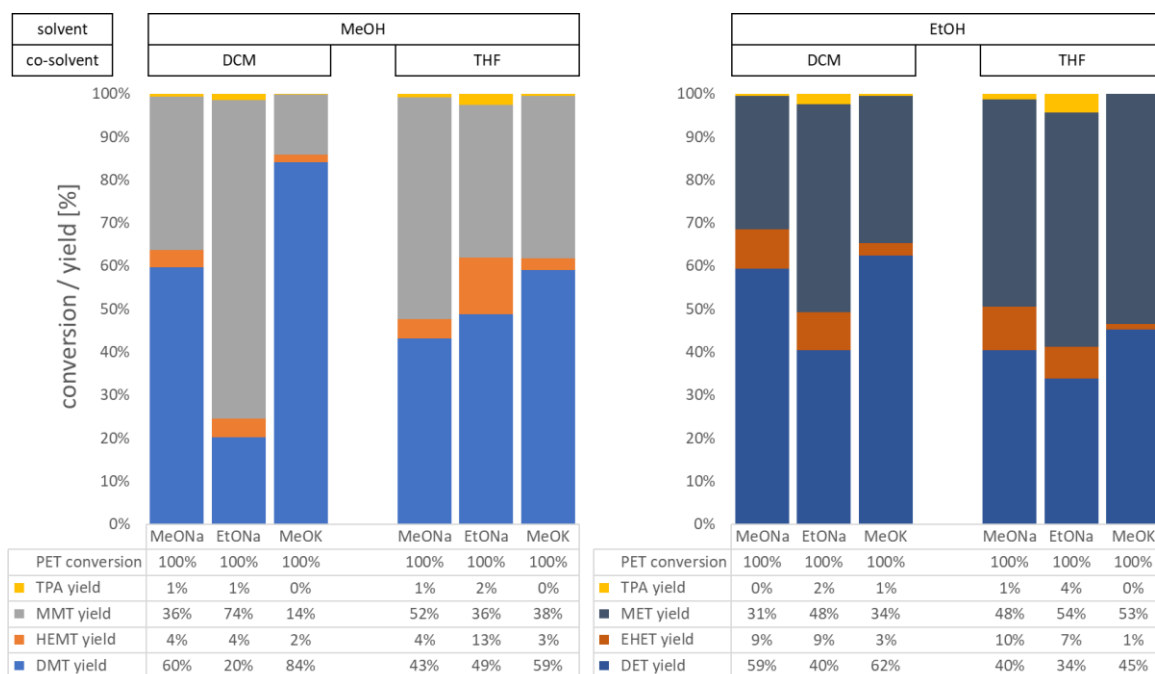
390 These considerations are confirmed from the depolymerization results in the presence of both
 391 sodium and potassium hydroxides.

392 Moreover, as shown in **Figure 5**, concerning the solvent, choosing ethanol instead of methanol does
 393 not considerably affect the monomer distribution. Methanol is slightly more selective towards DMT
 394 than ethanol towards DET, but this difference is far from being outstanding. A relevant difference
 395 between the two solvents is in the depolymerization efficiency, which is considerably reduced, in
 396 particular when DCM is used as cosolvent, for the case of ethanol. This drawback should be balanced
 397 with the advantages that ethanol brings about in terms of lower toxicological profile and safety when

398 selecting the most suitable solvent for the PET depolymerization, as also these points are crucial in the
 399 conduction of a chemical plant.

400 A drawback related to the use of hydroxides as methanolysis catalysts is the poor yield to DMT,
 401 which is typically appreciated in the industry for its simple recovery. Therefore, to increase the DMT
 402 yield without sacrificing the depolymerization efficiency, sodium and potassium hydroxides were
 403 substituted with the corresponding alkoxides, *i.e.*, sodium and potassium methoxides. Sodium ethoxide
 404 was tested as well in combination with both methanol and ethanol. According to Mohsin et al. (Mohsin
 405 et al., 2018) and Essaddam et al. (Essaddam and Essaddam, 2019), these catalysts introduce a different
 406 depolymerization mechanism and should be more selective towards DMT (or DET when ethanol is
 407 used instead of methanol). Indeed, the DMT yield sharply rises in all these trials, and the
 408 depolymerization does always go to completion, as shown in **Figure 6**. The complete set of data
 409 showing the relative amount of the monomers collected in the cake and recovered in the solution are
 410 shown in **Table S4**.

411
 412



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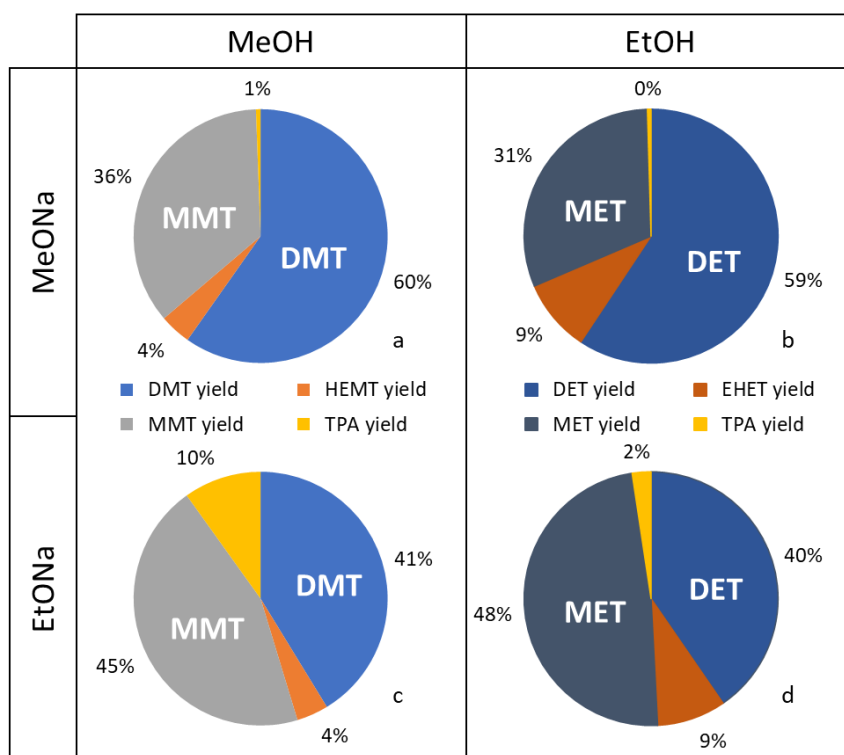
414 **Figure 6** – PET conversion and monomer yields using alkoxy catalyst, MeOH or EtOH as solvent and
 415 DCM or THF as cosolvent. More detailed results related to the liquid and solid compositions are
 416 available in Table S4.

417

418 The solvent and cosolvent that showed the best results in terms of DMT selectivity were methanol
419 and dichloromethane, respectively. Concerning the catalysts, potassium methoxide was more selective
420 than sodium methoxide and sodium ethoxide. The combination of these 3 optimal choices led to the
421 exciting value of 84% for the yield to DMT. However, the formation of by-products such as the acidic
422 monomers (MMT and TPA) is still relevant and cannot be avoided in any case.

423 Further analysis on the performances of the alkoxy catalysts can be performed comparing the results
424 obtained from the combinations of the two sodium alkoxy catalysts (MeONa and EtONa) and the two
425 solvents (MeOH and EtOH). Indeed, this allows us to validate the reaction mechanism proposed for
426 this catalytic reaction. The mechanism proposed for the transesterification reaction promoted by an
427 alkoxide in an alcoholic solvent (Patel and Shah, 2015) is shown in **Figure S4**.

428 The alkoxy group reacts with the PET chain, leading to a monomer terminated by the group of the initial
429 alkoxy catalyst. However, this step causes the formation of a new alkoxide, which is terminated by the
430 solvent end-group. Therefore, since an excessive amount of solvent was employed in these reactions,
431 the initial alkoxy catalyst is quickly replaced by the alkoxide terminated with the solvent end-group.
432 Thus, the transesterification reaction completely shifts toward the monomers terminated with the latter
433 group. Of course, this behaviour is not visible when one uses the MeOH-MeONa or EtOH-EtONa
434 combinations since the solvent and the alkoxide end-groups are the same, but it becomes evident when
435 mixing the species, as shown in **Figure 7**.



437

438 **Figure 7** – PET conversion and monomer yields: comparison between the cases of methoxy and
 439 ethoxy catalyst in combination with MeOH or EtOH as solvent and using DCM as cosolvent. More
 440 detailed results related to the liquid and solid compositions are available in Table S5.

441

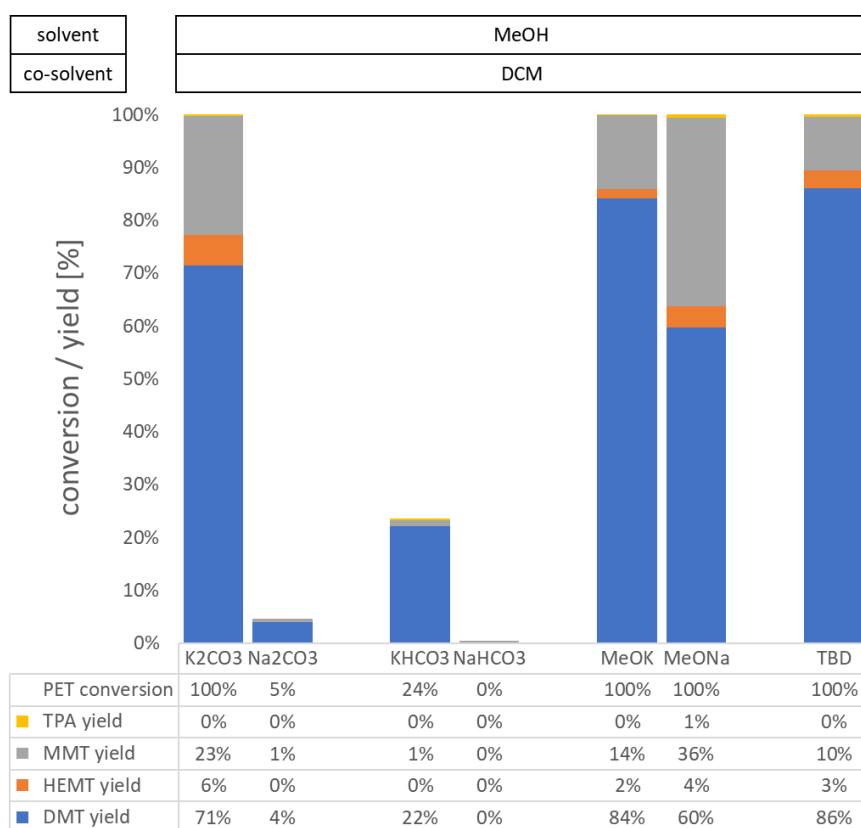
442 For example, when EtOH and MeONa are combined (see **Figure 7b**), the methyl terminated
 443 monomers turn out to be just intermediates, and as the reaction proceeds, they get replaced by their
 444 ethyl-terminated versions. Indeed, in the latter case, the peaks corresponding to DMT and MMT are
 445 practically null, while most of the products are monomers terminated with the ethyl groups, *i.e.* DET
 446 and MET. The same reasoning applies to the case represented in **Figure 7c**, where even if the ethyl
 447 terminated monomers are spotted, they are virtually inexistent. In particular, the complete set of data
 448 showing the relative amount of the monomers collected in the cake and recovered in the solution are
 449 shown in **Table S5**. Furthermore, concerning the general differences between the reaction using
 450 methanol and those using ethanol, the results shown in **Figure 6** do totally confirm all the evaluations
 451 done for the trials in **Figure 5**.

452 Besides the alkoxy catalysts, two other molecules were tested for PET methanolysis at moderate
 453 temperatures, namely potassium carbonate and TBD. Indeed, they led to satisfying results in terms of

454 depolymerization efficiency and DMT yield, as shown in **Figure 8**. The complete set of data showing
455 the relative amount of the monomers collected in the cake and recovered in the solution are shown in
456 **Table S6**. For the sake of completeness, potassium bicarbonate was also tested. While in previous works
457 it came out not to be working at all (Pham and Cho, 2021), it resulted to be slightly effective both
458 concerning PET conversion (31%) and DMT yield (19%), especially when compared to the
459 corresponding sodium bicarbonate.

460 Interestingly, all the potassium forms of the catalysts (carbonates, bicarbonates, methoxides, and
461 hydroxides) proved to be more effective than their sodium counterparts for PET low-temperature
462 methanolysis. Specifically, this can be explained considering that potassium is bigger than sodium, thus
463 it has lower ionization energy, and its valence electron can be more easily removed. Thus, potassium is
464 more reactive than sodium, and this concept is recognized and employed in various applications
465 (Dubina et al., 2013).

466 On the other hand, TBD leads to very high values of DMT yield, comparable to potassium
467 methoxide, but they both have the drawbacks of being relatively expensive and soluble in methanol.
468 Thus, they lead to homogeneous catalysis and require a more complex procedure for the monomer
469 separation.



471

472 **Figure 8** – PET conversion and monomer yields using potassium- and sodium-based catalysts, MeOH
 473 as solvent and DCM as cosolvent. More detailed results related to the liquid and solid compositions
 474 are available in Table S6.

475

476 Overall, potassium carbonate and the ethoxy and methoxy catalysts demonstrated to be valuable choices
 477 for the low-temperature methanolysis of PET from bottle flakes, leading to both high depolymerization
 478 efficiency and high yield to DMT, with the potential of scale-up of this technology.

479 To further corroborate the possibility of conducting the PET methanolysis at mild conditions, the
 480 conclusions drawn so far were extended to the treatment of fabrics.

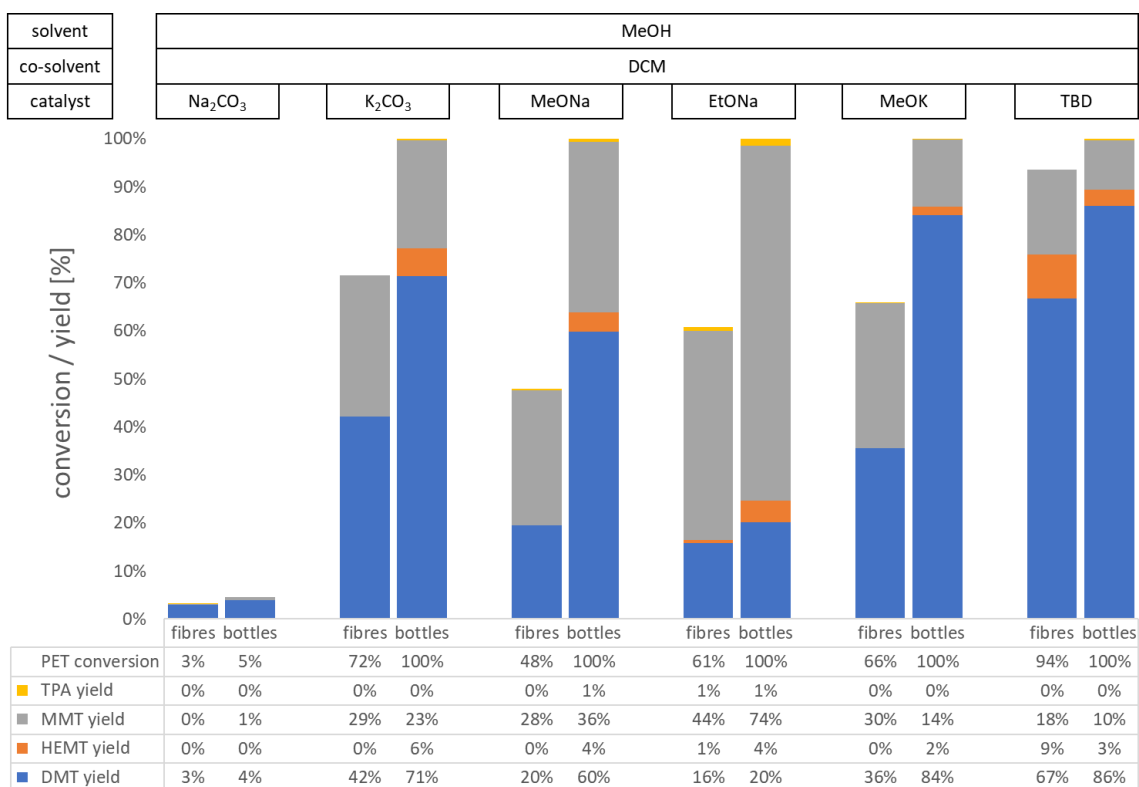
481

482 3.3 Polyester Fibre Recycling

483 Once the best performing cosolvent (DCM) and catalysts (K₂CO₃, MeONa, EtONa, MeOK, and
 484 TBD) were recognized, they were further employed to the methanolysis of mixed fabrics in cotton and
 485 PET, aiming to check if similar performances were achievable. The experiments carried out at the same
 486 conditions on bottles and fabrics are directly compared in **Figure 9**. The depolymerization efficiency

487 and the DMT yield are lower when treating commercial fabrics, and this gap is higher for the alkoxy
488 catalysts than for potassium carbonate. In particular, the complete set of data showing the relative
489 amount of the monomers collected in the cake and recovered in the solution are shown in **Table S7**.
490 In general, acidic monomers such as MMT and TPA are formed due to the competition between the
491 methanolysis and the hydrolysis reaction. Indeed, even the presence of a slight fraction of water
492 (moisture) turns out to be detrimental for the DMT selectivity in such a depolymerization system.
493 Indeed, fabrics do hold more moisture than bottle flakes, and, as a consequence, they are more subjected
494 to hydrolysis reactions. Moreover, since the cotton fraction of the fabrics is rich in hydroxyl groups
495 (Essaddam and Essaddam, 2019), the depolymerization process further slows down, and the selectivity
496 towards DMT lowers.

497 On the other hand, among all the catalysts that have been tested, TBD is the best performing one in
498 treating the fabrics mixed in cotton and PET. It leads to yields to DMT above 72% and depolymerization
499 efficiencies close to 100%. However, TBD has a crucial drawback, as mentioned previously: it leads to
500 a homogeneous product in the liquid phase, then the different monomers are all found in the recovered
501 solution, and their subsequent separation gets more complex. Moreover, considering the catalyst high
502 cost and its environmental and health harmfulness issue, TBD is not the ideal candidate for an industrial
503 scale-up.



505

506 **Figure 9** – PET conversion and monomer yields: comparison between fibres and bottles using the
 507 best performing catalysts, MeOH as solvent and DCM as cosolvent. More detailed results related to
 508 the liquid and solid compositions are available in Table S7.

509

510

511 4. Conclusion

512 In this work, we relied on an optimized HPLC method for the quantitative analysis of all the monomers
 513 produced during the PET depolymerization by methanolysis and ethanolysis conducted at mild
 514 conditions using different catalyst systems.

515 Key performance parameters, including PET conversion and yields to the different monomers found in
 516 the solvent mixture, in the separated cake, and in the residual fibres were considered for providing a
 517 systematic comparison of different catalyst/cosolvent combinations in the depolymerization of bottle
 518 flakes as well as a more impure feedstock represented by fabrics comprising cotton and polyester
 519 (50/50).

520 Among all the tested heterogeneous catalysts, potassium carbonate turned out to be the best performing
 521 one in terms of DMT selectivity, which reached 71% in the case of bottle flakes and 42% in the case of

522 mixed fabrics. Thus, it may be the best candidate for a possible scale-up to an industrial plant,
523 considering that most of the monomer DMT remains dissolved in the liquid phase, and thus the
524 monomer separation is not problematic. On the contrary, catalysts such as potassium methoxide and
525 TBD, even if they led to the best performances in terms of DMT yield, seem less attractive from an
526 industrial point of view since they are soluble in the reacting mixture and, thus, they lead to subsequent
527 issues in terms of monomer purification.

528 However, the main drawback of these depolymerization configurations is the relevant fraction of by-
529 products produced, particularly MMT. Indeed, all these catalysts can also promote the hydrolysis
530 reaction from the residual moisture present in the reaction environment.

531 This problem is enhanced when one tries to replace the bottle flakes with fabrics mixed in cotton
532 and PET since fabrics hold more moisture than bottle flakes, and the cotton fraction also has many
533 hydroxyl groups that can promote the PET hydrolysis reaction rather than methanolysis. Indeed, the
534 depolymerization and DMT yield were worsened when using mixed fabrics.

535 Nonetheless, the proposed methanolysis configuration led to satisfactory results since almost all of
536 the valuable product, *i.e.*, DMT, is found in the recovered solution and thus can be quite easily recovered
537 by crystallization and subsequently devolatilization without proceeding through complex separation
538 trains. Further investigation will be focused from the analytical side on the purity and color
539 characterization for the recovered DMT. From the process side, additional studies are required to
540 optimize the particle size, solvent-to-PET ratio and reaction time that will be necessary to scale-up this
541 processes for the most promising catalyst and cosolvents.

542

543 **Supporting Information:** Electronic supplementary information are available at the publisher's
544 website and report additional characterization data of the materials, complete analysis of the
545 depolymerization reactions, proposed mechanisms of chemolysis in different environments.

546

547 **Author Contributions:** Conceptualization: F.T, L.B.; Data curation: L.B., F.T.; Investigation: F.T,
548 L.B.; Supervision: M.S; Funding acquisition: D.M., P.I.; Writing – Original draft: F.T., L.B.; Writing

549 – Review and editing: M.S. All authors have read and given approval to the final version of the
550 manuscript.

551

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