

Influence of the Catalytic System on the Methanolysis of Polyethylene Terephthalate at 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

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

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

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

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

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

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

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

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

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

2. Materials and Methods

2.1. Materials

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

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

2.2 Methanolysis

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

previously tested on PET bottle flakes (Pham and Cho, 2021), both in the case of fabrics mixed in cotton and PET and in the case of bottle flakes, the molar ratios of solvent, cosolvent, and catalyst with respect to the PET repeating unit were set to 50, 50, and 1. The flake surface area was kept constant to 1 cm^2 in order to be reproducible, since the surface area for the PET bottle flakes can have an impact on the depolymerisation reaction rate. The use of different cosolvents, namely dichloromethane (DCM), tetrahydrofuran (THF), chloroform (CHCl_3), and catalysts was investigated. As an example, in the case of DCM as cosolvent and K_2CO_3 as a catalyst, 2 g of fabrics (1 g of PET – 5.2 mmol) were added to the round bottom flask together with 8.33 g of methanol (260 mmol), 22.11 g of dichloromethane (260 mmol) and 0.959 g of K_2CO_3 (5.2 mmol), and these ratios between PET, catalyst and cosolvent were kept constant for all the experiments. The reaction was carried out under continuous stirring at 300 rpm for 20 hours. The reaction mixture was then filtered with a Buchner funnel using qualitative filtering paper with $20 \mu\text{m}$ pore size, as depicted in **Figure 1b**.

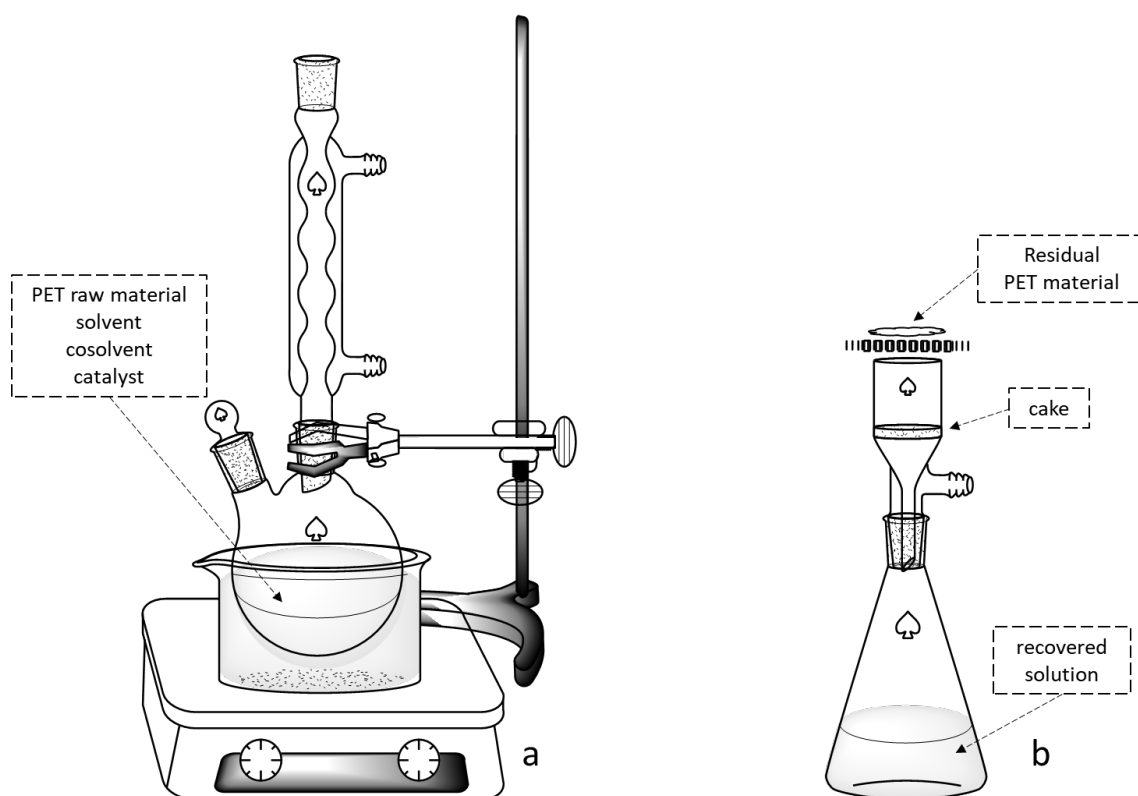


Figure 1 – Schematic representation of the configuration adopted for the PET depolymerization reaction (a) and the product separation (b)

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

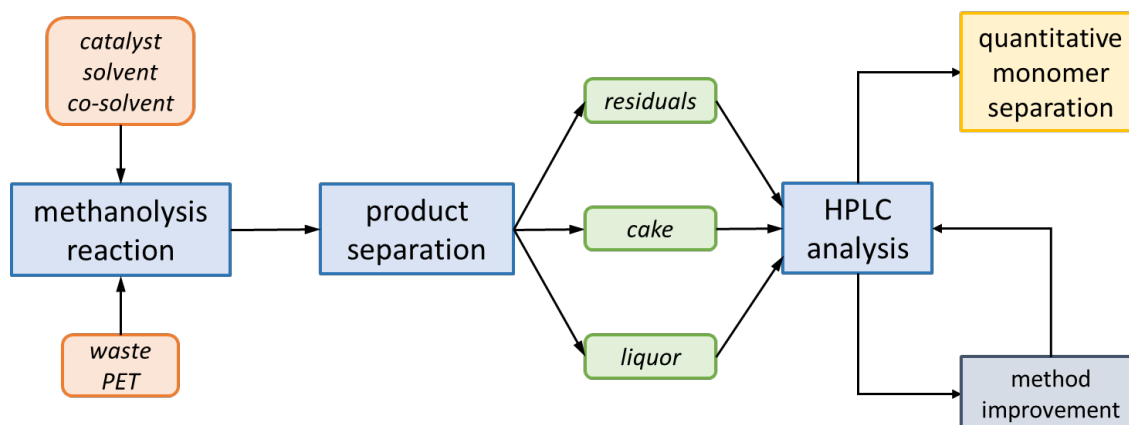


Figure 2 – Representation of the complete procedure followed in this work

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

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

2.3 Synthesis of Ethyl Terminated Monomers

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

2.4 Characterization

The product distribution of the depolymerization mixture were assessed on an Agilent 1100 HPLC with an UV detector set at 290 nm. Similarly to the method used in previous works (Rosenboom et al., 2018), the samples were dissolved in 25% (v/v) HFIP/CHCl₃ and separated in a Restek C18 column (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 mL min⁻¹. TFA 0.1% (v/v) was added as a stabilizer to both the organic and aqueous phases, using acetonitrile as the organic phase and Millipore water as the aqueous phase. The injection volume was kept constant at 10 μL.

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

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

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

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

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

Where m_{PET} is the residual mass of PET which did not depolymerize, m_{PET}^0 is the initial mass of PET, 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 on the fibres, were recovered in the cake, and remained dissolved in the filtered solution, respectively. n_{PET}^0 are the moles of PET repeating units initially present calculated as the ratio m_{PET}^0/MM_{PET} , where MM_{PET} is the molecular mass of the PET repeating unit.

Hereinafter, we will refer to the overall PET conversion and yield to the different monomers as calculated through Eq. 1 and Eq. 2. The contributions of each fraction (*i.e.* fibers, cake and solution) are reported in the Supporting Information section as specified when discussing the different sets of experiments.

3. Results and Discussion

3.1 HPLC Characterisation of the Methanolysis Products

During the PET methanolysis, even if DMT is thermodynamically the most favoured monomer, other products are typically produced, and they can be found in the residual fibres, in the filtered cake and in the recovered solution. These monomers are based on the same terephthalate backbone (shown in **Figure S2**) and are terminated by end-groups such as water, methanol, ethylene glycol, or ethanol. This monomer population is schematized in **Table 1**.

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

Monomers		
<i>structure</i>	<i>full name</i>	<i>name</i>
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

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

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

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

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

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

Table 2 – List of the monomers with their residence time according to the 100-0 method (d) (Sample 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}</i> [min]
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

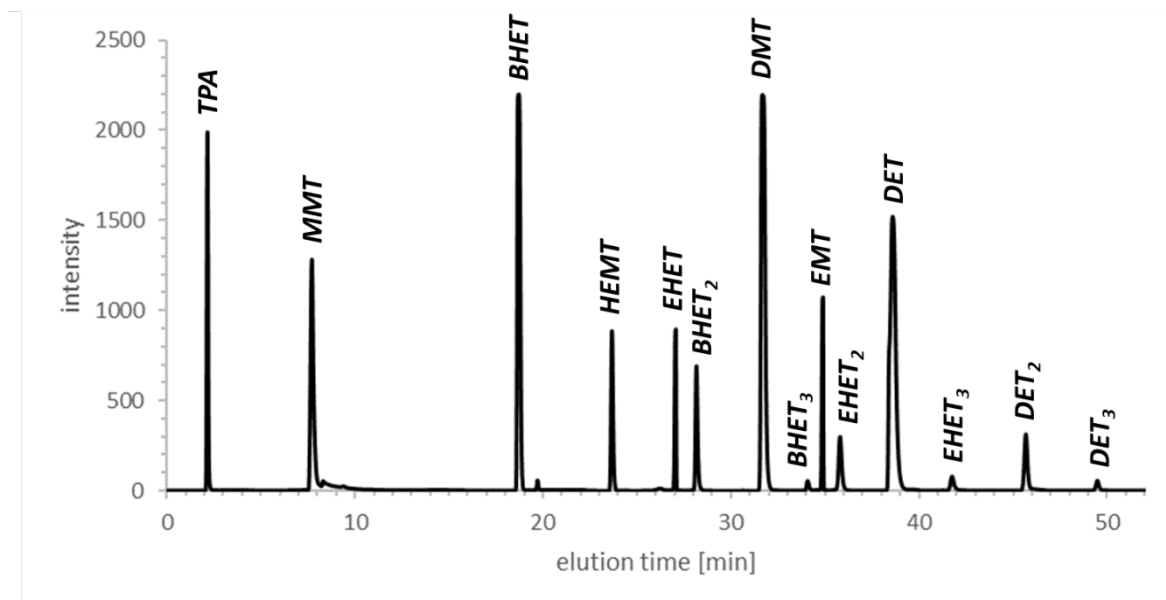


Figure 3 – Complete elugram according to the optimized HPLC method. The sample is prepared with 50% (v/v) HFIP/NaOH water solution at pH 13, and the ACN/H₂O gradient is run from 0/100 % to 100/0 in 45 min.

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

3.2 PET Depolymerisation through Methanolysis

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

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

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

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

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

Na₂CO₃ is still far from being appealing. For this reason, the study of the different monomer (TPA, MMT, MHET, DMT) yields was not performed at this stage.

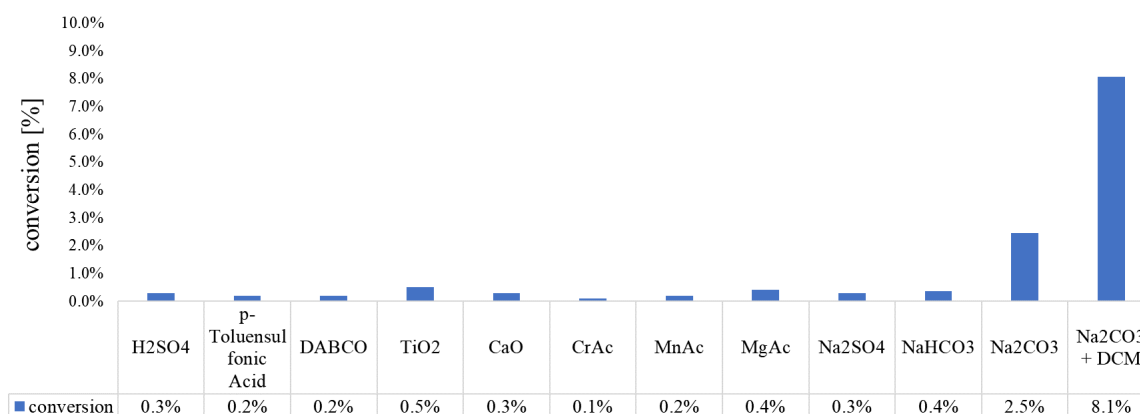


Figure 4 – PET conversion using common transesterification catalyst, MeOH as solvent and without cosolvent unless specified

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

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

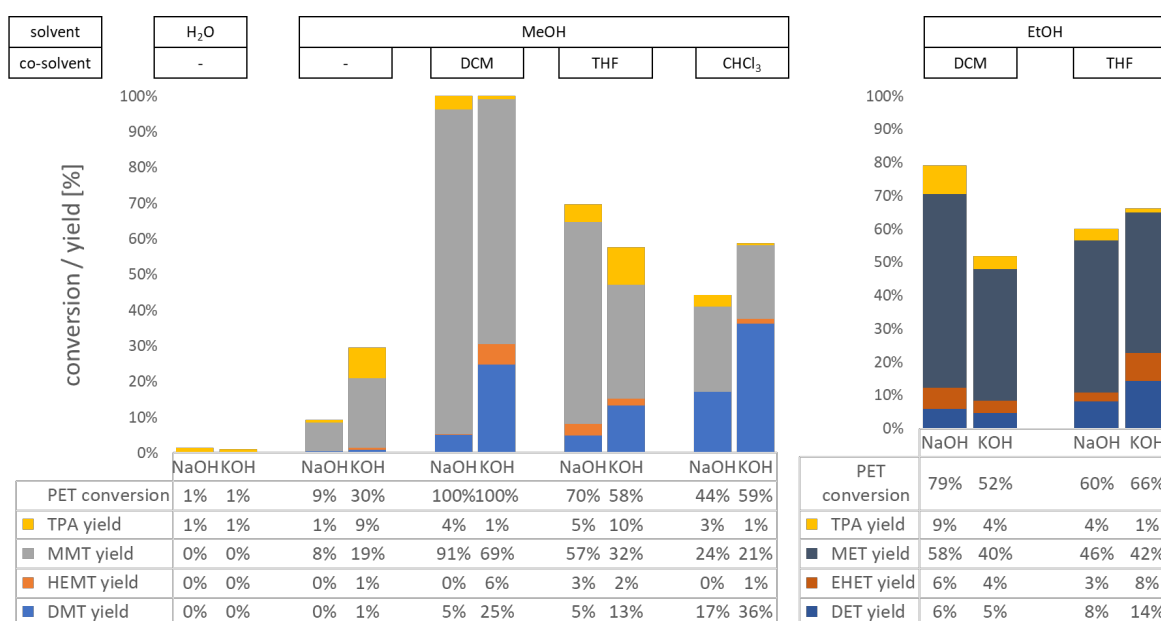


Figure 5 – PET conversion and monomer yields using hydroxy catalyst, H₂O, MeOH or EtOH as solvent and DCM, THF or CHCl₃ as cosolvent. More detailed results related to the liquid and solid compositions are available in Table S3.

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

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

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

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

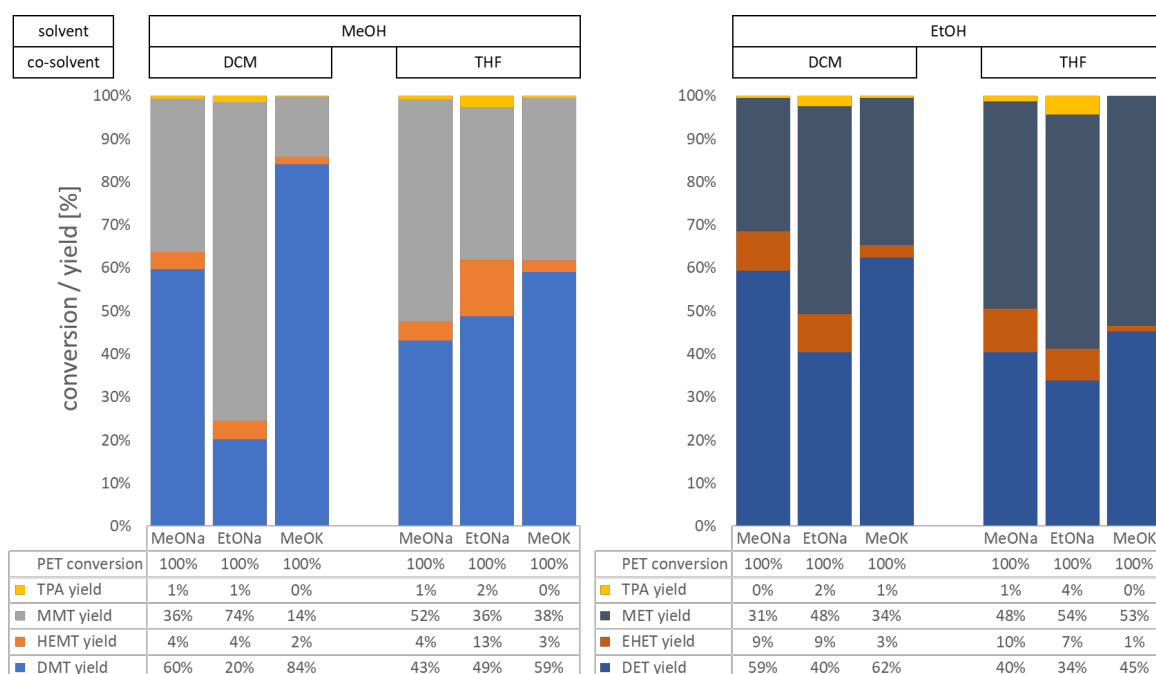


Figure 6 – PET conversion and monomer yields using alkoxy catalyst, MeOH or EtOH as solvent and DCM or THF as cosolvent. More detailed results related to the liquid and solid compositions are available in Table S4.

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

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

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

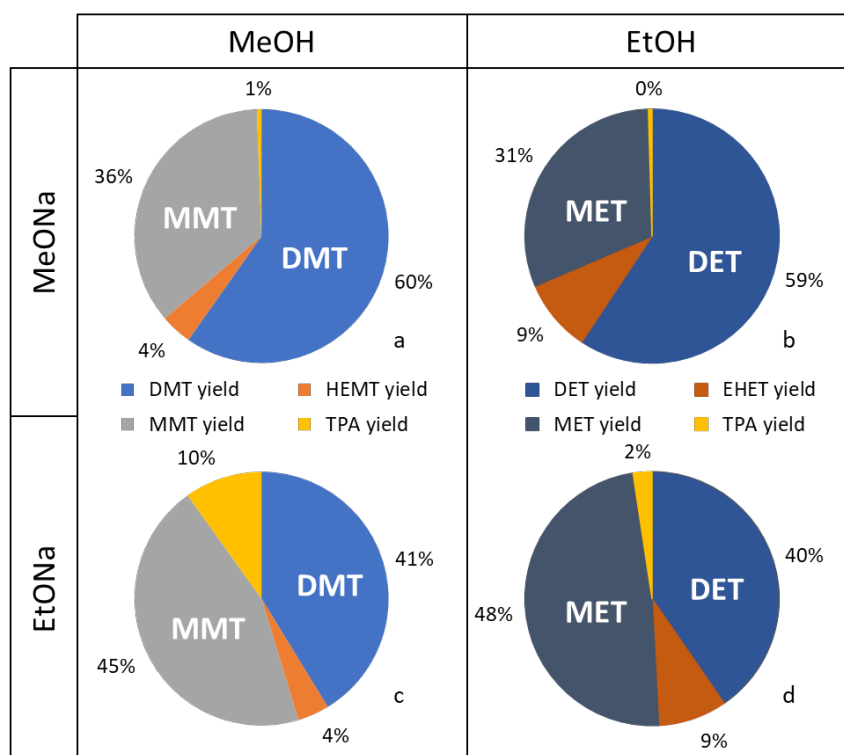


Figure 7 – PET conversion and monomer yields: comparison between the cases of methoxy and ethoxy catalyst in combination with MeOH or EtOH as solvent and using DCM as cosolvent. More detailed results related to the liquid and solid compositions are available in Table S5.

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

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

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

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

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

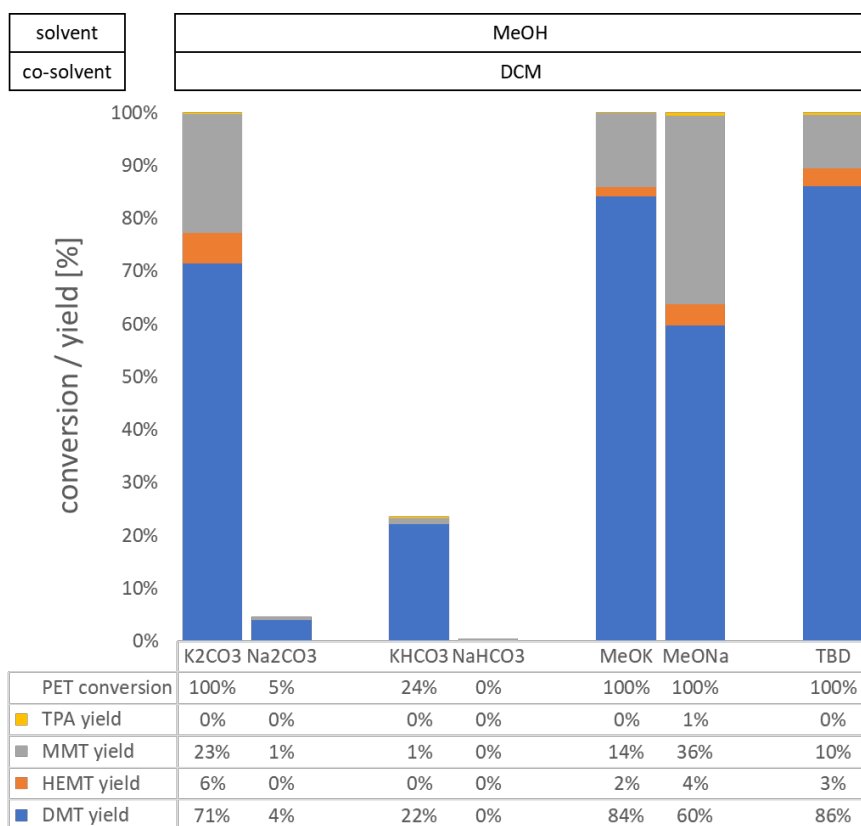


Figure 8 – PET conversion and monomer yields using potassium- and sodium-based catalysts, MeOH as solvent and DCM as cosolvent. More detailed results related to the liquid and solid compositions are available in Table S6.

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

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

3.3 Polyester Fibre Recycling

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

and the DMT yield are lower when treating commercial fabrics, and this gap is higher for the alkoxy catalysts than for potassium carbonate. In particular, the complete set of data showing the relative amount of the monomers collected in the cake and recovered in the solution are shown in **Table S7**.

In general, acidic monomers such as MMT and TPA are formed due to the competition between the methanolysis and the hydrolysis reaction. Indeed, even the presence of a slight fraction of water (moisture) turns out to be detrimental for the DMT selectivity in such a depolymerization system. Indeed, fabrics do hold more moisture than bottle flakes, and, as a consequence, they are more subjected to hydrolysis reactions. Moreover, since the cotton fraction of the fabrics is rich in hydroxyl groups (Essaddam and Essaddam, 2019), the depolymerization process further slows down, and the selectivity towards DMT lowers.

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

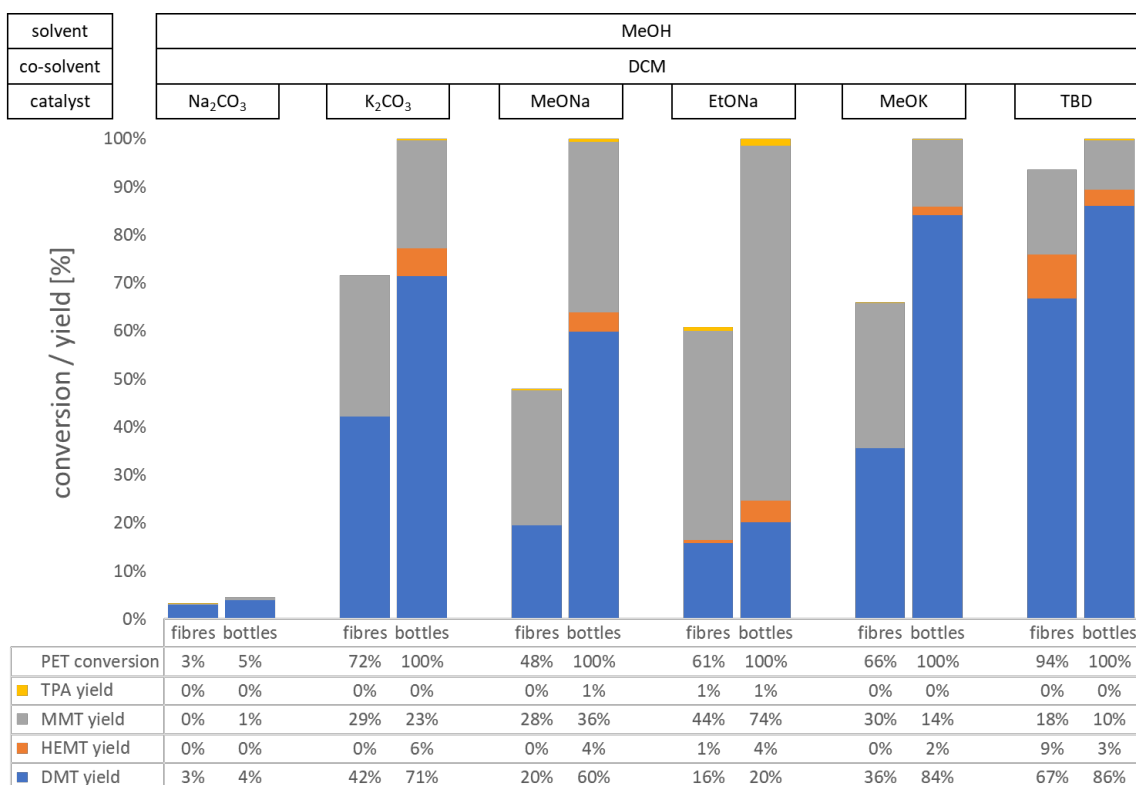


Figure 9 – PET conversion and monomer yields: comparison between fibres and bottles using the best performing catalysts, MeOH as solvent and DCM as cosolvent. More detailed results related to the liquid and solid compositions are available in Table S7.

4. Conclusion

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

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

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

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

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

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

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

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

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

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