



Cite this: *RSC Sustainability*, 2026, 4, 2355

## Heterogeneous-catalyzed methanolysis for efficient chemical recycling of bio-based PEF

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The promising bio-based polymer poly(ethylene 2,5-furandicarboxylate) (PEF) is expected to be produced on a large scale worldwide to meet demands across various market segments due to its superior properties and performance, although its end-of-life management still remains challenging due to its non-(bio) degradable nature. In this work, two different heterogeneous catalysts, Amberlyst 70 and Zeolite H–Y, were studied for the first time in the methanolysis of PEF. The depolymerization conditions, such as time, temperature, and catalyst loading, were optimized to maximize the depolymerization of PEF, resulting in high selectivity to dimethyl 2,5-furandicarboxylate (DMFDC), as confirmed by <sup>1</sup>H NMR and GC-MS. A complete PEF conversion and 100% DMFDC yield were achieved during a 1 hour reaction at 175 °C with 5 wt% zeolite. The potential to reuse the most effective catalyst (Zeolite H–Y) across two depolymerization cycles while maintaining its catalytic activity comparable to that of virgin zeolite was also demonstrated, enhancing process greenness as assessed by its E-factor. Additionally, a closed-loop PEF value chain is confirmed by reusing the recovered monomers to produce PEF polyester with physical and thermal properties, such as *T<sub>g</sub>* and thermal stability, identical to those of the original, as verified by <sup>1</sup>H and <sup>13</sup>C NMR, GPC, DSC, and TGA.

Received 24th December 2025  
Accepted 19th March 2026

DOI: 10.1039/d5su00905g

rsc.li/rscsus

### Sustainability spotlight

Bio-based poly(ethylene 2,5-furandicarboxylate) (PEF), due to its non-biodegradable nature and limited number of mechanical recycling cycles, is expected to face similar environmental persistence challenges as fossil-based polyesters like PET at their end-of-life (EoL), contributing to its unsustainable accumulation in the environment. To address the urgent need to find greener chemical recycling strategies that are efficient and easily scalable, this study explores the use of a commercially available zeolite acidic heterogeneous catalyst. The possibility for catalyst recovery and reusability was demonstrated, and the closed-loop PEF value chain was confirmed by reusing recycled monomers to produce new PEF with identical physical and thermal properties. This work aligns with the following UN Sustainable Development Goals: Responsible Consumption and Production (SDG 12) and Climate Action (SDG 13).

## Introduction

Polymers have become an indispensable and valuable commodity in our society due to their unique properties, with global production surpassing 413 Mt in 2023.<sup>1</sup> Most of these polymers are currently derived from fossil-based resources, with negative impacts associated with massive environmental pollution and greenhouse gas emissions (GHG)<sup>2,3</sup> Hence, the use of biomass feedstocks and agro-industrial residues in the sustainable production of chemicals and polymers under the biorefinery concept has been widely advocated as an alternative strategy for producing more sustainable polymers. Among the numerous bio-based polymers that have been investigated, furan-based polyesters, mainly poly(ethylene 2,5-

furandicarboxylate) (PEF), derived from C6 sugars like D-fructose or D-glucose feedstocks, have received attention due to their superior properties and performances compared to their fossil-based analogue, poly(ethylene terephthalate) (PET).<sup>4</sup> For this reason, PEF is expected to play a key role in several markets over the next few years.<sup>5</sup> One of the main expected applications of PEF is in the packaging sector due to its comparable thermal and mechanical properties to those of PET (with a glass transition temperature (*T<sub>g</sub>*) of around 75–80 °C, a melting temperature (*T<sub>m</sub>*) of 210–215 °C, thermal stability up to 300 °C, a Young's modulus of 2070–2450 MPa)<sup>6–8</sup> and superior gas barrier properties.<sup>9</sup> More recently, PEF has also been considered for textile applications.<sup>10</sup>

Although PEF is known to be more prone to (bio)degradation than PET under accelerated composting conditions,<sup>11</sup> this does not necessarily mean that it will be readily assimilated in relevant environmental conditions.<sup>12</sup> It is expected that PEF faces similar environmental persistence challenges as fossil-based polyesters like PET at their end-of-life (EoL). This is especially

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concerning since in 2022, around 24% of polymer waste ended up in landfills, around 50% was incinerated, and only 27% was recycled.<sup>13</sup>

Recycling of polymers, at the end of their usage, has proven to be an important alternative for EoL, especially for polymers used in packaging materials, with PEF, for example, expected to play a key role in this sector.<sup>13</sup> Currently, the standard approach is mechanical recycling; however, it shows some drawbacks, especially when polymer mixtures, and/or additives (*e.g.*, colour agents) or other additives are present, often leading to the deterioration of mechanical and thermal properties of the recycled material.<sup>14</sup> In this context, chemical recycling has recently attracted growing attention as a complementary process to the established mechanical recycling, as it allows the recovery of pristine monomers that can then be repolymerized into virgin-quality polymers.<sup>15,16</sup> Nevertheless, studies describing the chemical recycling of PEF through hydrolysis<sup>17–21</sup> and alcoholysis (namely glycolysis,<sup>22–24</sup> and methanolysis<sup>25–27</sup>) have been reported. The methanolysis approach<sup>4,7</sup> is particularly relevant since the ensuing depolymerization product, dimethyl 2,5-furandicarboxylate (DMFDC), is typically used as the starting monomer for PEF synthesis. However, the limited literature on this topic mainly reports the use of homogeneous catalysts, which can hamper their easy recovery and reuse. For example, Sipos *et al.*<sup>26</sup> used an organic base, 1,5,7-triazabicyclo [4.4.0]dec-5-ene (10.7 mol%), to facilitate the mild methanolysis of PEF. The reaction was carried out at 90 °C for 30 minutes, yielding DMFDC, although with a 63% yield. Qu *et al.*<sup>25</sup> described PEF methanolysis catalysed by a series of tetrabutylphosphonium-based ionic liquids (ILs) at 130 °C for 30 minutes, achieving a complete PEF conversion and a 78% yield of DMFDC. In this study, it was demonstrated that ILs could be recovered six times (through vacuum distillation) without loss of their catalytic activity. PEF methanolysis catalysed by zinc acetate under microwave heating at 120 °C for 30 minutes was also reported,<sup>27</sup> resulting in an 86% yield of DMFDC. However, in the above-mentioned studies, catalyst recovery and reuse were not addressed, and purifying the target monomers from the crude reaction mixtures typically required a laborious process.

The use of heterogeneous catalysts has gained considerable attention mainly because of the ease of separating and recovering the catalyst from the reaction medium, as well as the potential to restore its original activity for reuse.<sup>28</sup> Examples of heterogeneous catalysts include ion exchange resins and zeolites. One such ion exchange resin is Amberlyst, a commercial acidic resin that can, in some cases, be used at temperatures up to 190 °C (Amberlyst 70).<sup>29</sup> This catalyst is used industrially in processes, such as olefin hydration, aromatic alkylation, and esterification;<sup>29,30</sup> however, it has never been employed in polyester depolymerization. Amberlyst functions as a Brønsted acid catalyst due to sulfonic groups (SO<sub>3</sub>H) immobilized on the resin.<sup>31</sup>

Other interesting heterogeneous catalysts not yet explored for PEF recycling are zeolites. They are microporous aluminosilicate minerals with high crystallinity, characterized by their high surface area.<sup>32</sup> Due to their impressive catalytic properties,

unique selectivity, high-temperature stability, and relatively low cost, zeolites have been produced commercially and are widely used in various applications.<sup>33</sup> A ZSM-5-based zeolite has been examined as an acidic catalyst in the microwave-assisted hydrolytic depolymerization of PET.<sup>34</sup> It was shown that PET depolymerization with 50 wt% of ZSM-5 zeolite at 230 °C led to almost a 100% yield of terephthalic acid (TPA), maintaining its catalytic activity over six depolymerization cycles, highlighting its potential in the recycling of similar PET polymers, such as PEF, which is yet to be explored. For this type of Zeolite H-Y, the aluminium within the silicate framework contains Si-(OH)-Al bridging sites, contributing to the reaction as strong Brønsted acidic sites that enable acidic polymer depolymerization. Furthermore, researchers observed that PET hydrolysis mainly occurred on the external acid sites of the zeolite because PET molecules were too bulky to penetrate its pores.<sup>34</sup> To the best of our knowledge, the Zeolite H-Y catalyst remains unexplored in methanolysis pathways to mediate polyester recycling.

Therefore, in this study, the aim was to investigate the use of two heterogeneous acid catalysts for PEF depolymerization *via* methanolysis: Amberlyst 70 and Zeolite H-Y (5.1), which, to the best of our knowledge, have not been used as catalysts in methanolysis pathways, nor in the particular case of PEF recycling. The reaction conditions, such as time, temperature, and catalyst ratio, were optimized to maximize PEF depolymerization and achieve high selectivity and yield towards DMFDC. The depolymerized products were characterized by proton nuclear magnetic resonance (<sup>1</sup>H-NMR) and gas chromatography-mass spectrometry (GC-MS). The potential to reuse the most promising catalyst over two depolymerization cycles while maintaining its catalytic activity was studied to highlight the advantages of heterogeneous catalysis. Furthermore, to verify the efficiency of the process, the recovered monomers were used to produce PEF, whose physical and thermal properties, such as *T<sub>g</sub>* and thermal stability, were identical to those of the original, as analysed by <sup>1</sup>H and <sup>13</sup>C NMR, GPC, DSC, and TGA.

## Materials and methods

### Materials

Dimethyl 2,5-furandicarboxylate (DMFDC, 99.9%) was purchased from Sarchem Laboratories. Narrow standard PolycAL poly(methyl methacrylate) (PMMA, 50 kD) was purchased from Viscotek, Malvern Panalytical, UK. Amberlyst 70 was purchased from Lenntech. 1,4-Dinitrobenzene, 1,1,1,6,6,6-hexafluoro-2-propanol (HFIP, for GPC analysis), titanium(IV) isopropoxide (((Ti(O-*i*Pr)<sub>4</sub>), 97%), titanium(IV) *tert*-butoxide ((Ti(O-Bu)<sub>4</sub>), 97%), ethylene glycol (EG, 99.8%), chloroform (CHCl<sub>3</sub>, analytical grade), methanol (≥99.8%), deuterated chloroform (CDCl<sub>3</sub>-d, 99.8 atom% D), and deuterated trifluoroacetic acid (TFA-d, 99.5 atom% D) were purchased from Sigma Aldrich. Amberlyst 70 was dried overnight at 40 °C under vacuum (Thermo Scientific VACUtherm vacuum oven, maximum final vacuum of 0.001 mbar). Zeolite H-Y (silica to alumina ratio – SAR: 5.1) was calcinated at 600 °C for 12 h and subsequently dried at 200 °C for two more hours before each



depolymerization experiment. All other reagents were used as received.

## Methods

**Poly(ethylene 2,5-furandicarboxylate) synthesis.** PEF (with a number-average molecular weight ( $M_n$ ) of 21 700) was synthesized according to a reported literature procedure.<sup>35</sup> For the recycled PEF (rPEF), a small-scale repolymerization experiment<sup>23,36</sup> was conducted using the monomers recovered from the depolymerization reaction, without any further purification. The monomer DMFDC (1.0 g, recovered, ethylene glycol (DMFDC/EG = 1/2.2 (mol mol<sup>-1</sup>))), and the catalyst TBT (400 ppm) were charged into a two-neck round-bottom flask. The reaction was carried out under a nitrogen atmosphere at ambient pressure for 5 hours at 190 °C (step one), followed by a vacuum step for 3 hours at 230 °C (using a Value V-i240SV 2-stage vacuum pump at 0.02 mbar). The resulting polymer was further purified by dissolving the reaction mixture in a chloroform-TFA mixture (6 : 1) and pouring it into an excess of cold methanol. The white precipitate was then filtered, washed, and dried in a vacuum oven at 40 °C for 12 hours.

**Methanolysis of PEF.** All the methanolysis reactions were performed using a 75 mL stainless steel autoclave reactor (Parr Series 5000 Multiple Reactor System, maximum pressure of 20 bar). In a typical experiment, PEF (0.5 g, powder as after purification), methanol (35 mL), and a variable amount (5, 10, 30, and 50 wt%) of the catalyst, either Zeolite H-Y or Amberlyst 70, were charged into the reactor, purged with 5 bar of nitrogen gas (3 cycles) and magnetically stirred (750 rpm) at the temperature and for the time specified in Tables S1 and S2. After completion, the reactor was cooled to room temperature, and the excess pressure was carefully vented. The catalyst and any unreacted polymer were filtered off, rinsed thoroughly with methanol, and weighed. The filtrate was evaporated under reduced pressure in the rotary evaporator, resulting in a white crystalline solid that was subsequently dried overnight under vacuum at 40 °C.

Since the catalyst mass is known and remains unchanged, the recovered unreacted polymer ( $m_{\text{recovered,PEF}}$ ) can be quantified to calculate the percentage of PEF conversion, as depicted in eqn (1).

$$\text{Conversion}_{\text{PEF}}(\text{wt}\%) = \frac{m_{\text{initial PEF}} - m_{\text{recovered PEF}}}{m_{\text{initial PEF}}} \times 100\% \quad (1)$$

**Recovery and reuse of the Zeolite H-Y (5.1).** Under optimized conditions, Zeolite H-Y was recovered by filtration using a G-3 glass filter, washed with methanol, dried at 40 °C overnight, and then dried for two additional hours at 200 °C. The reuse of the recovered zeolite was tested over multiple depolymerization methanolysis cycles.

**Green chemistry metrics.** The *E*-factor, Atom Economy (AE), Process Mass Intensity (PMI), and Solvent Mass Intensity (SMI)<sup>37,38</sup> were calculated to assess the greenness of the proposed reaction using eqn (2)–(5):

$$E\text{-factor} = \frac{\text{Total mass of waste}}{\text{Total mass of DMFDC}} \quad (2)$$

$$\text{AE}(\%) = \frac{M_{w, \text{desired product}}}{M_{w, \text{reactants}}} \times 100 \quad (3)$$

$$\text{PMI} = \frac{\text{Total mass of raw materials}}{\text{Total mass of DMFDC}} \quad (4)$$

$$\text{SMI} = \frac{\text{Total mass of solvent}}{\text{Total mass of DMFDC}} \quad (5)$$

**Characterization.** <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded using Varian 400-MR and Bruker Avance III spectrometers operating at 400.17 MHz and 100.62 MHz, respectively. A known amount of the polymer sample and an internal standard (1,4-dinitrobenzene) were dissolved in a CDCl<sub>3</sub> : TFA-d mixture (6 : 1) for NMR analyses for the quantification of PEF polymer conversion and DMFDC yield from the depolymerization reactions. These parameters are calculated using the eqn (6)–(9) below:

$$n_{\text{DMFDC}} = n_{\text{IS}} \times \frac{I_{\text{F}}}{2} \times \frac{4}{I_{\text{IS}}} \quad (6)$$

where  $n_{\text{DMFDC}}$  and  $n_{\text{IS}}$  represent the number of moles of DMFDC and the internal standard, respectively.  $I_{\text{F}}$  stands for the area above the resonances of H3 and H4 protons ascribed to the furan ring at 7.2 ppm with 2 protons;  $I_{\text{IS}}$  represents the area of the resonances of H2, H3, H5, and H6 protons of the 1,4-dinitrobenzene internal standard at 8.4 ppm corresponding to 4 protons.

The DMFDC yield was calculated using eqn (7)–(9).

$$\text{Yield}(\%) = \frac{\text{Isolated mass}_{\text{DMFDC}}(\text{g})}{\text{Calculated mass}_{\text{DMFDC}}(\text{g})} \times 100\% \quad (7)$$

$$\text{Isolated mass}(\text{g}) = n_{\text{DMFDC}} \times M_{\text{DMFDC}} \times \frac{m_{\text{product, recovered}}}{m_{\text{product, NMR}}} \quad (8)$$

$$\text{Calculated mass}(\text{g}) = \frac{m_{\text{initial PEF}} - m_{\text{recovered PEF}}}{M_{\text{PEF, r.u.}}} \times M_{\text{DMFDC}} \quad (9)$$

$M_{\text{DMFDC}}$  corresponds to the DMFDC molar mass (184.15 g mol<sup>-1</sup>),  $m_{\text{product, recovered}}$  corresponds to the mass of the recovered depolymerization product,  $m_{\text{product, NMR}}$  corresponds to the mass of the product used for NMR analysis, and  $M_{\text{PEF, r.u.}}$  corresponds to the PEF repeating unit molar mass (182.10 g mol<sup>-1</sup>).

The GC-MS analysis was performed on an Interscience Trace GC Ultra GC instrument equipped with a AS3000 II autosampler (He carrier gas, flow 1 mL min<sup>-1</sup>, split flow 20 mL min<sup>-1</sup>; Restek GC column Rxi-5 ms 30 m × 0.25 mm × 0.25 μm; GC program: hold 2 min at 70 °C, ramp 10 °C min<sup>-1</sup>, final temperature 300 °C) connected to an Interscience Trace DSQ II XL quadrupole mass selective detector (EI, mass range 35–500 Dalton, 150 ms sample speed). Electrospray ionisation (ESI) mass spectrometric measurements were carried out using a Waters LCT Premier XE Micromass system.

Differential scanning calorimetry (DSC) was carried out on a Netzsch Caliris 300 equipment, and the thermograms were



recorded following a heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$  under a nitrogen flow of  $40\text{ mL min}^{-1}$  in a temperature range between  $25\text{ }^{\circ}\text{C}$  and  $250\text{ }^{\circ}\text{C}$ .

Gel permeation chromatography (GPC) was carried out on a Viscotek HP-SEC system, VE-2001 GPC max (pump and auto-sampler) equipped with TDA305 Triple Detector Array (Right Angle Light Scattering (RALS) + Low Angle Light Scattering (LALS), Refractive Index (RI) Detector and Viscometer), a 2X GPC column (PSS, PFG, analytical linear M), and a guard column, molecular range of  $250\text{--}2.5 \times 10^6\text{ D}$  (PMMA in HFIP). Data were calculated with OmniSEC™, Version 4.6 software. HFIP containing  $0.02\text{ M}$  potassium trifluoroacetate was used as the eluent with a flow rate of  $0.7\text{ mL min}^{-1}$ . Control measurements were performed with Easy vial PMMA standards from Agilent Technologies.

## Results and discussion

### PEF methanolysis

Amberlyst 70 and Zeolite H-Y, two heterogeneous acid catalysts with the advantage of being commercially available, were initially evaluated to assess their effectiveness in PEF methanolysis (Scheme 1).

To identify the most effective catalyst, PEF depolymerization was conducted under standard depolymerization conditions:  $175\text{ }^{\circ}\text{C}$ , 2 h, and 50 wt% catalyst loading with respect to PEF, following a prior PET depolymerization study.<sup>39</sup> The results are summarized in Table 1.

The results in Table 1 show that depolymerization using Amberlyst 70 or Zeolite H-Y yields a similar PEF conversion, with values reaching around 89%. However, in both cases, the composition of the depolymerized product(s), as analysed by  $^1\text{H}$  NMR (Fig. 1), indicated the presence of both the DMFDC monomer and oligomeric PEF-derived species (low-degree oligomers), consistent with the predicted depolymerization reaction pathway. In Fig. 1, the  $^1\text{H}$  NMR spectrum of the initial PEF displays the characteristic furanic protons at  $7.33\text{ ppm}$  (a) and the methylene protons at  $4.73\text{ ppm}$  (f), with only trace

Table 1 Screening of catalysts in the methanolysis of PEF: yields corresponding to PEF conversion and DMFDC monomer recovery

Catalyst	Catalyst amount (wt%)	Time/h	Temperature/ $^{\circ}\text{C}$	PEF Conversion <sup>a</sup> (wt%)	DMFDC yield <sup>b</sup> (wt%)
Amberlyst 70	50	2	175	89	36
Zeolite H-Y	50			86	55

<sup>a</sup> Calculated using eqn 1. <sup>b</sup> Calculated using eqn (6)–(8).

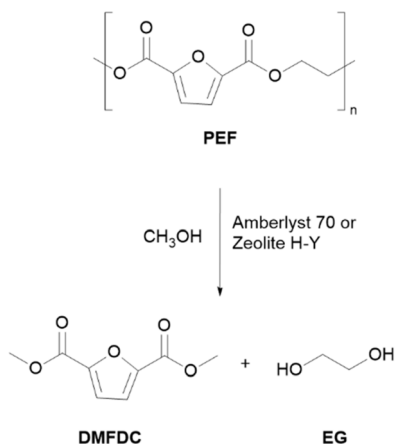
signals at  $4.59$  and  $4.40\text{ ppm}$  assigned to terminal protons (g and h). By contrast, in the depolymerization mixture, the  $^1\text{H}$  NMR spectrum retains the typical PEF proton resonances, but the signals attributed to DMFDC dominate, notably the  $\text{OCH}_3$  terminal group at  $3.87\text{ ppm}$  (d). The relatively intensified resonances at  $4.59\text{ ppm}$  (g) and  $4.40\text{ ppm}$  (h), corresponding to terminal  $\text{CH}_2\text{CH}_2\text{OH}$  groups, corroborate the formation of oligomeric depolymerization products. Additionally, signals from the monosubstituted FDCA derivative protons around  $7.23\text{ ppm}$  (b and c) are visible (Fig. S1), indicating concurrent hydrolysis driven by residual moisture during the reaction, which helps explain the lower observed yields.

Nonetheless, utilising Zeolite H-Y resulted in a substantially higher DMFDC yield of 55%, compared to Amberlyst at 36%. This result can be attributed to several factors: (a) the presence of both Brønsted and Lewis acidic sites,<sup>40</sup> in contrast to Amberlyst, which possesses only Brønsted acid sites; (b) the zeolite's porous structure, which enables a pore confinement effect that can enhance reactivity,<sup>41</sup> whereas the Amberlyst-mediated reaction occurs at the resin surface. Hence, Zeolite H-Y was chosen as the catalyst for further tuning the reaction conditions, providing additional benefits, including the possibility of recovery, regeneration of active sites, and reuse in subsequent depolymerization cycles.

### Optimization of PEF methanolysis catalysed by Zeolite H-Y

After selecting Zeolite H-Y as the most appropriate catalyst, the reaction parameters (time, temperature, and catalyst weight percentage) were investigated to achieve the complete PEF conversion and maximal DMFDC yield. First, the Zeolite H-Y loading was investigated by lowering it from 50 to 5 wt% at  $175$  and  $200\text{ }^{\circ}\text{C}$  (Fig. 2), while maintaining the depolymerization reaction time constant at a relatively short duration of 2 hours. Interestingly, Fig. 2(a) clearly shows that the lowest catalyst loadings (5 or 10 wt%) gave the most promising results, with PEF conversions reaching 99%, at both  $175$  and  $200\text{ }^{\circ}\text{C}$ .

In terms of the DMFDC yield, Fig. 2 (b) shows that the lowest loading of zeolite (5 and 10 wt%) also gave interesting results, achieving maximum DMFDC yield, regardless of the temperature employed. This result could be explained by the fact that zeolite performance depends not only on the total catalyst amount but also on acid-site accessibility since the reaction



Scheme 1 Reaction scheme depicting PEF methanolysis, producing the key monomers DMFDC and ethylene glycol.



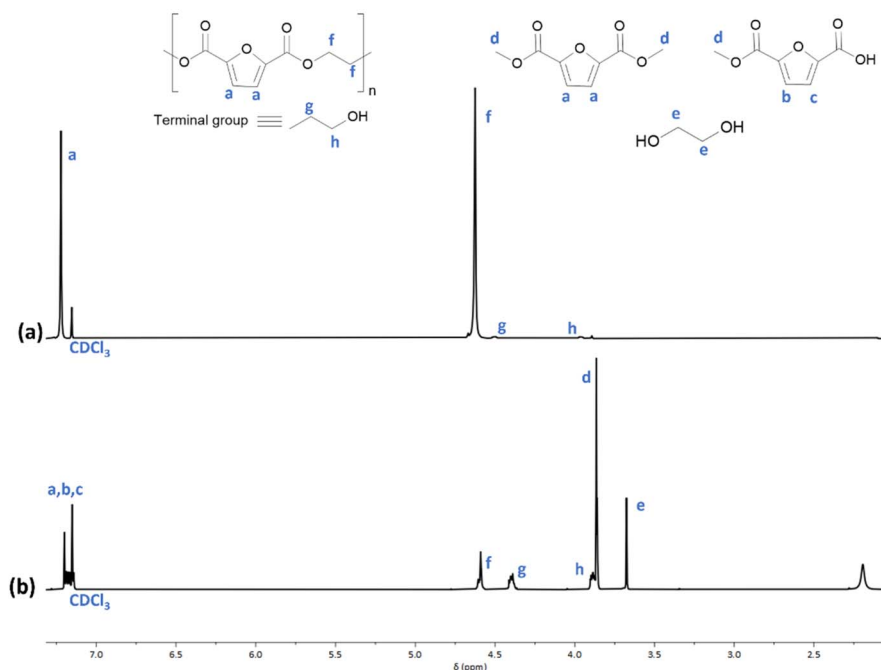


Fig. 1 <sup>1</sup>H NMR spectra of the initial PEF (a) and crude depolymerization reaction mixture (b) using Amberlyst 70 (175 °C, 2 h, and 50% wt).

mainly takes place at the external acid sites of the zeolite.<sup>40,42,43</sup> It may also be due to diffusion limitations at higher catalyst loadings during mass transfer reactions.<sup>44</sup> Further increasing

the Zeolite H-Y loading can raise diffusion resistance, resulting in lower PEF conversion and DMFDC yield.

These are important criteria from a green chemistry perspective since the depolymerization reactions screened at 175 °C and the lowest 5 wt% Zeolite H-Y gave the most promising results with respect to PEF conversion and DMFDC yield. Therefore, the effect of lowering the temperature even further, in combination with the lowest catalyst loadings for short depolymerization reaction time was investigated, and the results are shown in Fig. 3.

Fig. 3 (a) demonstrates that a reaction time of 1 hour is sufficient to achieve complete PEF conversion, yielding 100% DMFDC; despite reducing the temperature from 200 to 175 °C, PEF conversion and DMFDC yield remain at their maximum. However, lowering the methanolysis reaction temperature further from 175 to 150 °C resulted in a considerably lower PEF conversion and DMFDC yield (less than 60%), indicating that 175 °C is the optimal temperature for the PEF methanolysis reaction. In summary, the best results are achieved by minimizing energy and catalyst resources. Using a 1.0 h reaction time in combination with 5 wt% zeolite loading at 175 °C gave full conversion of PEF, resulting in the maximum DMFDC yield. On the other hand, compared with the literature reports on PEF methanolysis, a 100% DMFDC yield was not achieved in previous studies, with maximum reported values reaching around 86%.<sup>26,27</sup>

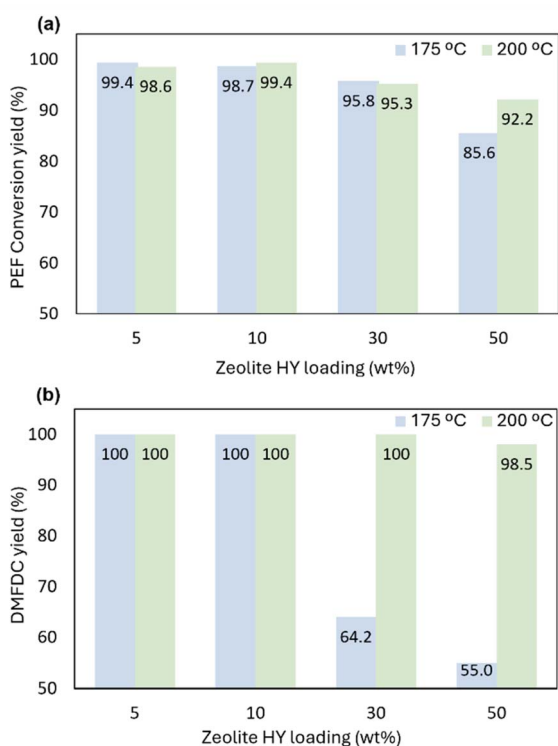


Fig. 2 (a) PEF conversion yield and (b) DMFDC yield, with respect to zeolite loadings and reaction temperatures for 2 hours of reaction time.

### Characterization of the product from the methanolysis reaction under optimized conditions

The product mixture obtained from the methanolysis reaction under optimal conditions was thoroughly characterised by <sup>1</sup>H



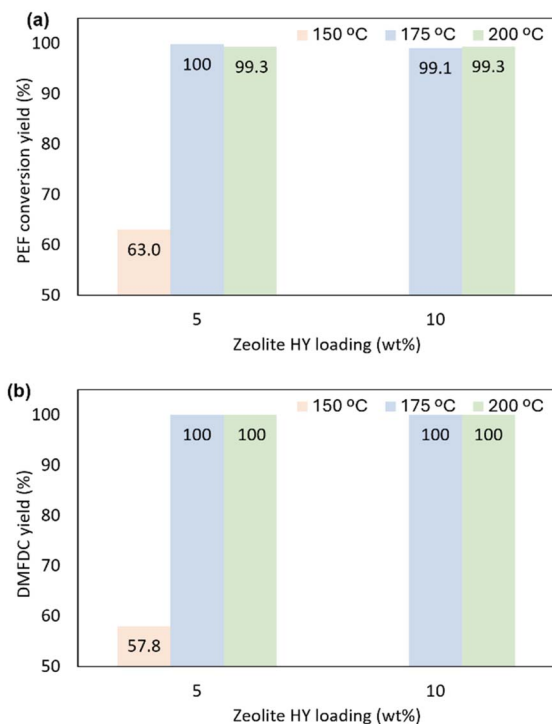


Fig. 3 (a) PEF conversion yield and (b) DMFDC yield, with respect to zeolite loadings and reaction temperatures for a 1 h reaction time.

NMR (Fig. 4) and GC-MS (Fig. 5 and S2). The representative  $^1\text{H}$  NMR spectrum of the reaction mixture yielding 100% of DMFDC (Fig. 4) shows the proton resonances attributed to DMFDC, furanic protons (a),  $\text{OCH}_3$  group (d), and ethylene glycol protons (e).

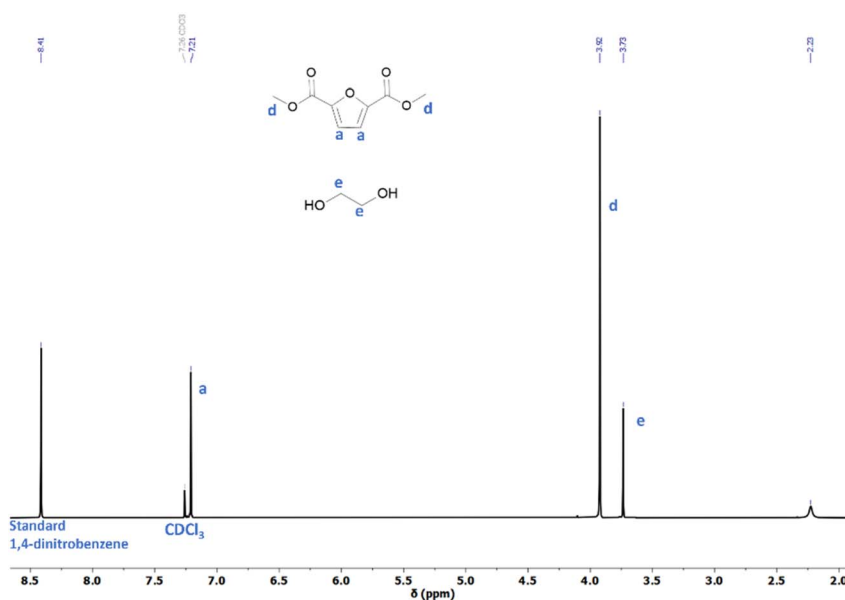


Fig. 4 Representative  $^1\text{H}$  NMR spectrum of crude reaction mixtures from the optimal methanolysis reaction conditions: 5 wt% of zeolite, 1 hour, 175 °C, and a PEF conversion of 100% and a DMFDC yield of 100%.

The recovered DMFDC was further analysed by GC-MS analysis. The chromatogram in Fig. 5 shows a single peak with a retention time of 9.4 min, demonstrating the high purity of DMFDC (>95%). The corresponding mass spectrum (Fig. S2) shows a molecular ion peak at  $m/z$  184 and a fragmentation at  $m/z$  153, indicating that the  $\text{OCH}_3$  group loss is consistent with DMFDC.

### Zeolite H-Y recovery and recycling

As a proof of concept, the recovery and subsequent reuse of the Zeolite H-Y catalyst for two consecutive PEF methanolysis cycles were studied, enabling resource utilization and minimising any waste in the recycling process. The catalyst was recovered by a filtration process using a G-3 glass filter after cooling the reaction mixture, followed by vacuum drying at 40 °C to remove any residual volatiles present. Notably, the recovered Zeolite H-Y did not require an additional calcination process prior to reuse, representing a substantial advantage in terms of energy efficiency. Methanol could also be efficiently collected by distillation and reused in the subsequent methanolysis process. The results of methanolysis assays with recycled zeolites (Table 2) show a PEF conversion of  $\geq 99\%$  with a 100% DMFDC yield when using a zeolite recycled twice.

In Fig. S3, TGA analysis of the virgin and second-cycle recovered zeolites was performed, with all samples pre-dried at 100 °C overnight, ensuring no traces of methanol or moisture were present. Analysing Fig. S3, for the virgin zeolite, the majority of the weight loss (around 9%) occurs before 200 °C, after which the weight remains relatively constant until 600 °C, for a total loss of 12%. On the other hand, after two depolymerization cycles, the recovered zeolite exhibits an initial weight loss similar to the virgin one, around 12%, but experiences a more pronounced weight loss from 200 to 600 °C,



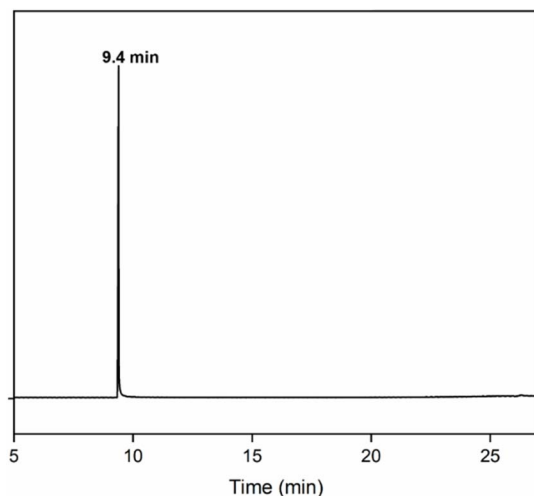


Fig. 5 Representative GC chromatogram of crude DMFDC obtained from the methanolysis reaction (5 wt% of zeolite, 1 hour, 175 °C, and PEF conversion = 99.8% and DMFDC yield = 100%).

totalling 24%. This indicates that some traces of the depolymerization product may have been trapped in the zeolite pores, despite not affecting the zeolite's performance. Overall, the results further validate that the catalyst continues to function with high activity without the need for calcination for two consecutive depolymerization cycles and an energy-intensive step performed at higher temperatures (600 °C), which is typically required to regenerate the active sites of pores. This offers an additional advantage in terms of the environmental friendliness of the process, as it saves energy and time.

### Green chemistry metrics

To effectively evaluate the greenness of the process, the *E*-factor, AE, and PMI were calculated. Since the zeolite shows that it is active even after two cycles of reuse and could catalyse future depolymerization processes, as well as the fact that the excess methanol can be efficiently recovered by a simple distillation approach, these factors contributed to the obtained *E*-factor value of 12. The use of methanol was the single most contributing factor to the obtained *E*-factor value. Still, the methanol is collected at the end of the purification process, and for these calculations, around 80% of methanol was considered to be

recovered. The zeolite recovery mass loss between depolymerization reactions was estimated to be around 12% of the initial mass, which also contributes to the metric value. However, one can anticipate that the mass loss during catalyst recovery could be substantially minimized if reactions were performed at larger volumes, where losses due to handling are much less impactful than in this work case, where low gram-scale screening experiments were performed. These considerations mean that if methanol and the zeolite were not recovered, the *E*-factor would be around 71 rather than 12. Nevertheless, the *E*-factor is still within the low limit range of the fine chemical industry, according to literature, within 5 to 50.<sup>37</sup>

Regarding AE, which indicates the atom efficiency of the reaction, the value obtained is 86%, meaning most reactants are converted into the desired DMFDC. Finally, regarding PMI, which measures the total mass of materials used (as opposed to the *E*-factor, which is based on waste produced), the value is approximately 50. This is mainly due to the methanol used in the methanolysis reaction and in DMFDC purification, which is proven by SMI being approximately 48.

### Feasibility study of using recycled DMFDC in PEF synthesis

In this study, as a proof-of-concept, the DMFDC obtained from the methanolysis of PEF was utilized as a key starting monomer in the re-polymerisation reaction of recycled PEF (rPEF). rPEF was obtained in 60% yield, with the <sup>1</sup>H and <sup>13</sup>C NMR analyses validating the polyester structure (Fig. S4 and S5, respectively). The typical PEF spectrum is shown in Fig. S4, where the protons H3 and H4 of the furan ring have a resonance at around 7.33 ppm (a) and the protons from the methylene groups originate a resonance close to 4.74 ppm (b). Additionally, residual resonances corresponding to the polymer end groups are observed at 4.62 (c) and 4.08 ppm (d). According to GPC analysis, the number-average molecular weight of the rPEF was 22 900, with a dispersity of 1.93. The thermal properties were characterized using DSC (Fig. S6) and TGA (Fig. S7) analyses. The *T<sub>g</sub>* of rPEF was 77 °C, which is in accordance with the reported values (75 to 80 °C).<sup>7</sup> The melting temperature (*T<sub>m</sub>*) is 184 °C, which is slightly lower than the typical values of 210 to 215 °C, as reported in the literature.<sup>7</sup> This can be justified by the higher diethylene glycol content (due to side reactions) in rPEF when compared to the initial PEF, 4.10 and 1.97 mol%, respectively (calculated by <sup>1</sup>H NMR)<sup>39,45</sup>. According to TGA

Table 2 PEF conversion and DMFDC yield using virgin and recovered zeolite after one and two cycles. All reactions were performed for 1 hour at 200 °C

Zeolite H-Y			
Number of recovering cycles	Amount (wt%)	PEF conversion <sup>a</sup> (%)	DMFDC yield <sup>b</sup> (%)
Virgin	10	99.3	100
	5	99.3	
1	10	99.0	100
	5	99.5	

<sup>a</sup> Calculated using eqn (1). <sup>b</sup> calculated using eqn (7)–(9).



analyses, the maximum decomposition temperature is 387 °C, and at 5% weight loss, the decomposition temperature is 329 °C, which is within the literature values of thermal stability up to 300 °C.<sup>7</sup> These data demonstrate that the recovered monomers have substantial potential for reuse in new polymer synthesis, enabling the production of rPEF with some thermal properties, such as  $T_g$  and thermal stability, comparable to virgin polymers.

## Conclusions

This study demonstrates the potential of using commercially available heterogeneous catalysts as an alternative strategy to address the end-of-life management of PEF polymer. Among the catalysts tested, Zeolite H-Y emerged as the most promising, and its activity for PEF methanolysis was evaluated for the first time. Optimal performance was achieved with the shortest reaction time of 1.0 h at 175 °C and a low catalyst loading of 5 wt%, yielding complete conversion of PEF to the target DMFDC with high purity. This result was further confirmed by GC-MS.

Zeolite H-Y exhibits favorable greenness and circularity characteristics: it can be reused over several depolymerization cycles while retaining catalytic activity, with PEF conversion and DMFDC yield comparable to those obtained with the virgin zeolite. A further advantage is that the methanolysis-recycled DMFDC is suitable, as-is, for PEF re-polymerization without additional purification, thereby closing the loop on PEF end-of-life. Regarding future work, it would be valuable to conduct scale-up reactions (e.g., 10 g of PEF) and to expand this methanolysis approach based on commercially available Zeolite H-Y to other polyesters, such as the widely produced PET.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

The data supporting this study have been included as part of the supplementary information (SI). Supplementary information: PEF methanolysis optimization data, MS spectra of the recovered monomer, TGA traces of virgin and recovered zeolites, green metrics calculation considerations, and NMR (<sup>1</sup>H and <sup>13</sup>C), DSC and TGA of rPEF. See DOI: <https://doi.org/10.1039/d5su00905g>.

## Acknowledgements

This work was developed within the scope of the project CICECO Aveiro Institute of Materials, UID/50011/2025 (DOI 10.54499/UID/50011/2025) and LA/P/0006/2020 (DOI 10.54499/LA/P/0006/2020), financed by national funds through the FCT/MCTES (PIDDAC). The FCT is also acknowledged for the research contract with AFS (CEECINSTLA/00002/2022) and a doctorate grant to BA 2020.04495.BD (DOI 10.54499/2020.04495.BD). Part of the research work was funded by the Knowledge Base programme “Towards a circular and climate

neutral society” of Wageningen University & Research (WUR) in the project “Bio-(chemical) recycling of products” (KB-34-011-002). The WUR Knowledge Base programme is financed by the Dutch Ministry of Agriculture, Nature and Food Quality.

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