

ARTICLE

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

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### Supporting Information

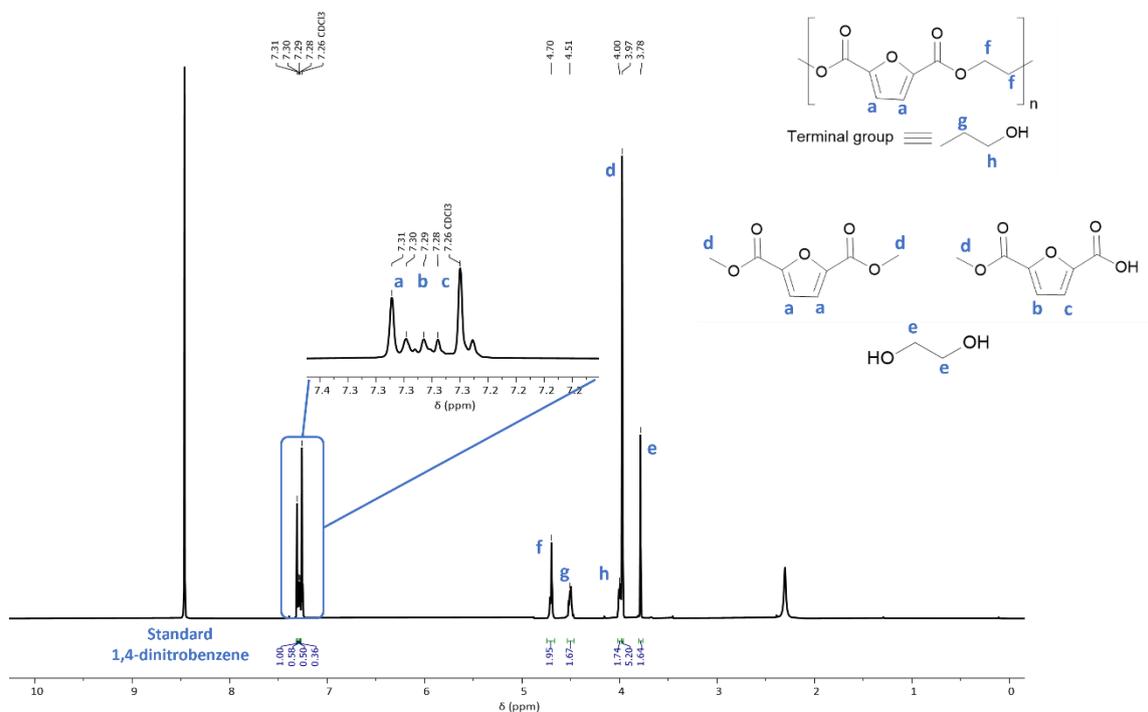


Figure S <sup>1</sup>H NMR spectrum of crude depolymerization reaction mixture using Amberlyst 70 (175 °C, 2h, 50 %wt), with the proton resonances corresponding monosubstituted FDCA derivative highlighted (b,c) .

Table S 1 PEF conversion and DMFDC yield for different loadings of zeolite and reaction temperatures (2-hour reaction).

| Zeolite HY loading (wt%) | Time / h | Temperature / °C | PEF Conversion (wt%) <sup>a</sup> | DMFDC yield (wt%) <sup>b</sup> |
|--------------------------|----------|------------------|-----------------------------------|--------------------------------|
| 50                       |          | 175              | 85.6                              | 55                             |
|                          |          | 200              | 92.2                              | 98                             |
| 30                       |          | 175              | 95.8                              | 64                             |
|                          |          | 200              | 95.3                              | 100                            |
| 10                       | 2        | 175              | 98.7                              | 100                            |
|                          |          | 200              | 99.4                              | 100                            |
| 5                        |          | 175              | 99.4                              | 100                            |
|                          |          | 200              | 98.6                              | 100                            |

a) Calculated using equation 1; b) Calculated using equations 7, 8 and 9.

Table S 2 PEF conversion and DMFDC yield for different loadings of zeolite H-Y and reaction temperatures (1 hour reaction time).

| Zeolite H-Y loading (wt%) | Time / h | Temperature/ °C | PEF Conversion (%) <sup>a</sup> | DMFDC yield (%) <sup>b</sup> |
|---------------------------|----------|-----------------|---------------------------------|------------------------------|
| 10                        |          | 175             | 99.1                            | 100                          |
|                           |          | 200             | 99.4                            | 100                          |
| 5                         | 1        | 150             | 63.0                            | 58                           |
|                           |          | 175             | 99.8                            | 100                          |
|                           |          | 200             | 99.3                            | 100                          |

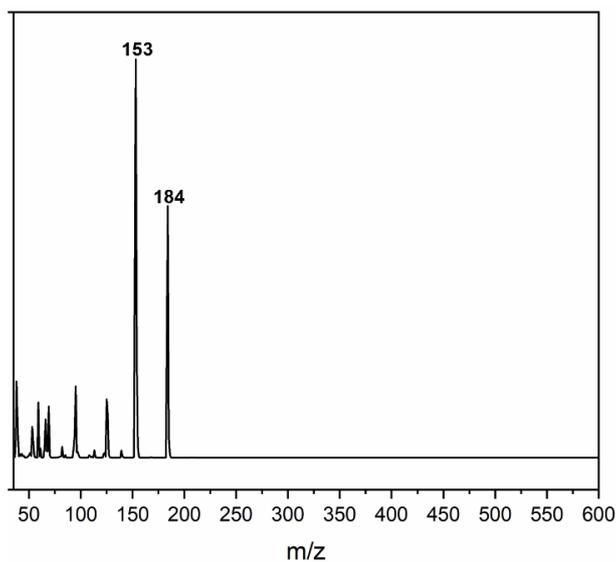


Figure S 2 MS spectra of crude DMFDC obtained from the methanolysis reaction (5 wt% of zeolite, 1 hour, 175 °C, and PEF conversion = 99.8% and DMFDC yield = 100%).

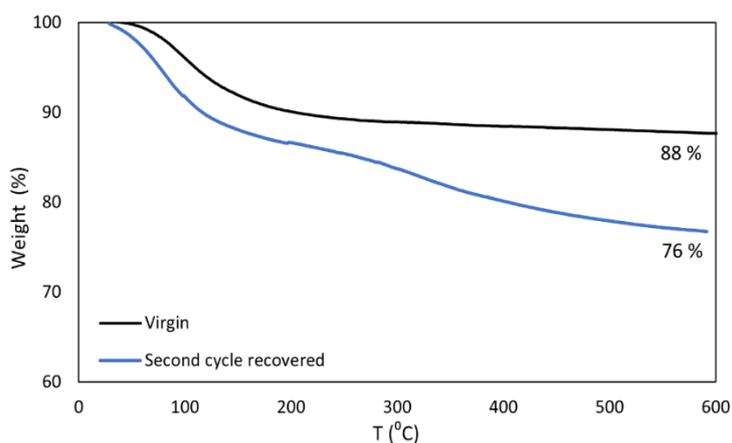
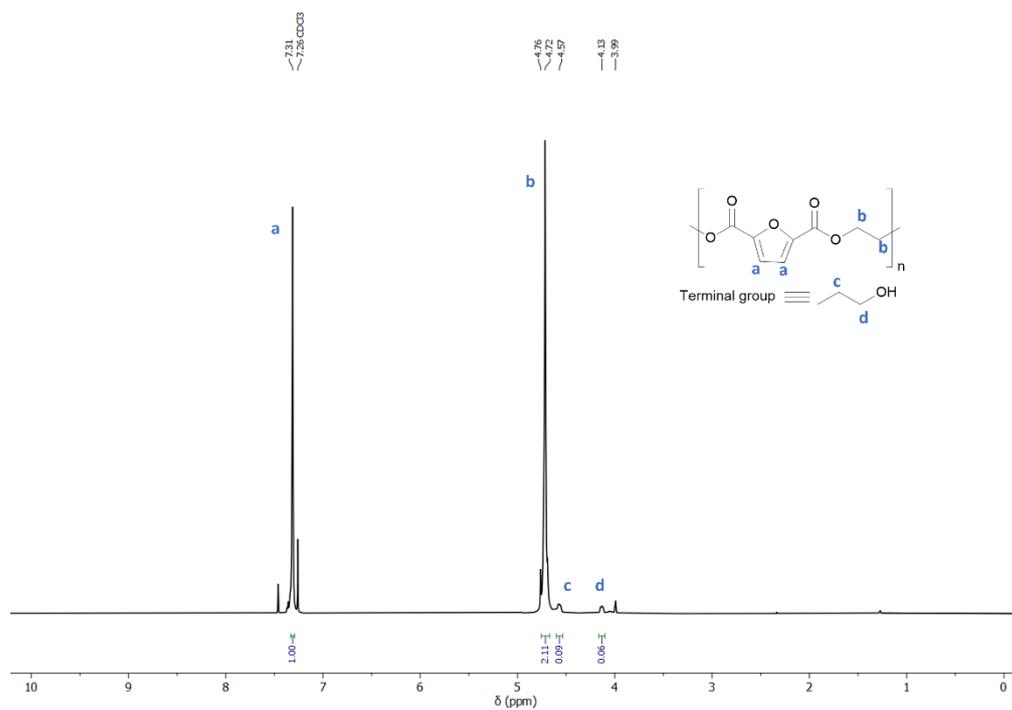
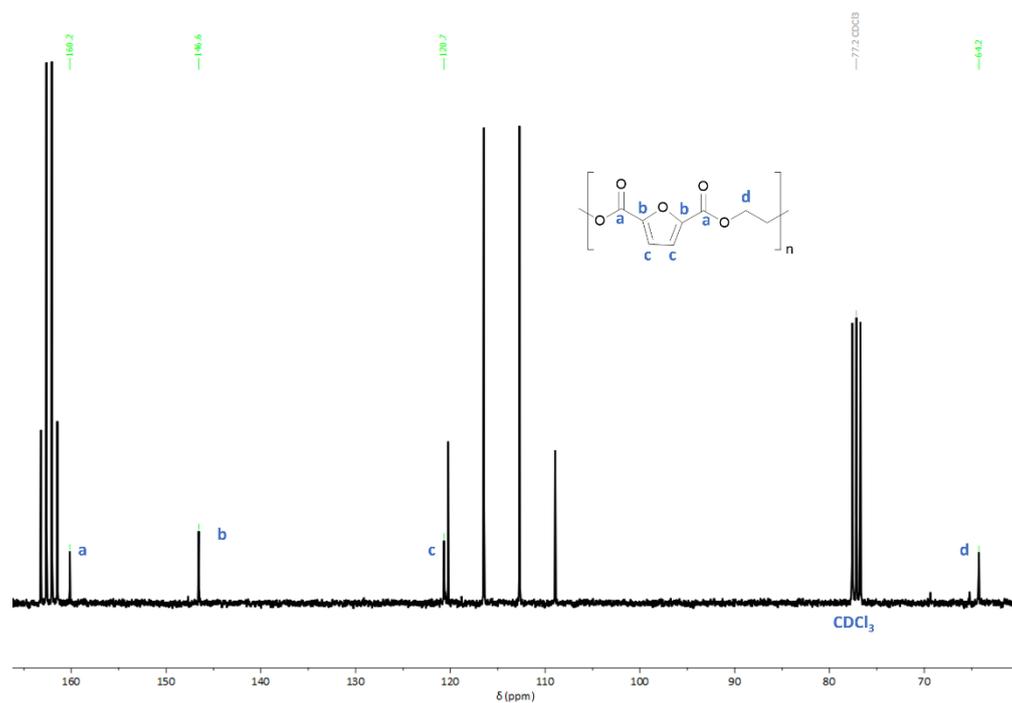


Figure S 3 TGA traces of virgin zeolite and recovered zeolite from the second depolymerization cycle.

Table S 3 Weight (m) and molecular weight (MW) values considered for the process Green Metrics calculations.

|            | PEF   | Zeolite <sup>a</sup> | Methanol <sup>b</sup> | Ethylene glycol | DMFDC |
|------------|-------|----------------------|-----------------------|-----------------|-------|
| m (g)      | 0.50  | 0.025                | 55.4                  | 0.07            | 0.50  |
| MW (g/mol) | 182.1 | -                    | 32.04                 | -               | 184.1 |

a) 5 wt% of zeolite, which can be isolated and recovered with 12% mass loss; b) total methanol used for depolymerization and purification, which can be partially recovered;

Figure S 4  $^1\text{H}$  NMR spectra of rPEF synthesized using the monomer recovered from the methanolysis reaction.Figure S 5  $^{13}\text{C}$  NMR spectra of rPEF synthesized using the monomer recovered from the methanolysis reaction.

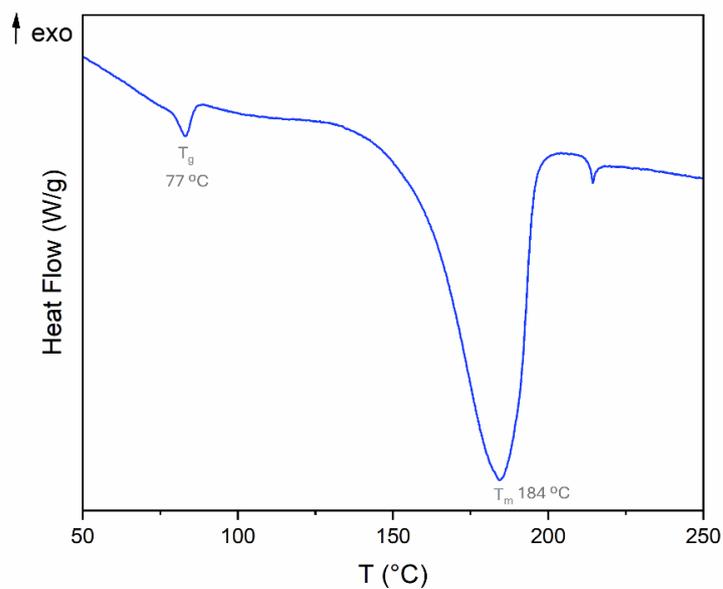


Figure S 6 DSC thermogram of rPEF, first heating scan recorded at 10 °C/min, under N<sub>2</sub> atmosphere.

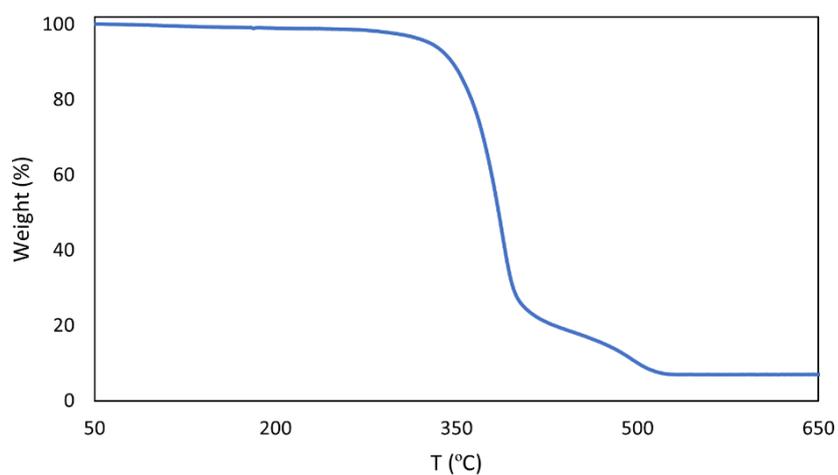


Figure S 7 TGA traces of PEF synthesized using the recycled monomer from PEF methanolysis.