Supplementary Information (SI) for Green Chemistry.

# Supplementary Information

# Membranes from bio-based poly (ethylene furanoate) and natural solvents

Malinalli Ramírez-Martínez,[a] Usman T. Syed,[a] Glenda Terán-Cuadrado,[bc] Anissa Nurdiawati,[ac] Maria Di Vincenzo,[a] Iuliana M. Andrei,[a] Dimitrios N. Bikiaris,[d] Sami G. Al-Ghamdi[ac] and Suzana P. Nunes*[abe]

[a.] *Environmental Science and Engineering Program, Biological and Environmental Science and Engineering Division (BESE), King Abdullah University of Science and Technology (KAUST), 23955-6900 Thuwal, Saudi Arabia.*

[b.] *Chemical Engineering Program, Physical Sciences and Engineering, King Abdullah University of Science and Technology (KAUST), Thuwal, 23955-6900, Saudi Arabia.*

[c.] *KAUST Climate and Livability Initiative, King Abdullah University of Science and Technology (KAUST), Thuwal, 23955-6900, Saudi Arabia.*

[d.] *Laboratory of Polymer Chemistry and Technology, Department of Chemistry, Aristotle University of Thessaloniki, GR-54124 Thessaloniki, Greece.*

[e.] *Chemistry Program and Chemical Engineering Program, Physical Science and Engineering Division (PSE), King Abdullah University of Science and Technology*

*Corresponding author: Suzana P. Nunes (suzana.nunes@kaust.edu.sa)

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# 1. Supplementary Texts

## PEF synthesis

Poly (ethylene 2,5-furandiacarboxylate) (PEF) was synthesized via a two-stage polycondensation method. In the first step (esterification), 2,5-furan dicarboxylic acid (FDCA) and ethylene glycol were utilized in a 1:2.1 molar ratio and were added to the reaction flask (250 ml). The reaction mixture was heated at 170°C for 30 min, 190°C for 1 h, 200°C for 30 min, and 210°C for 30 min under nitrogen and a stirring speed of 200 rpm. After the completion of the first step, (400 ppm) catalyst was added to the reaction flask and vacuum (5.0 Pa) was applied slowly for 15 min to initiate the polycondensation process. Furthermore, the temperature was progressively increased to 250°C. The reaction mixture was heated at 250°C and at 260°C for 2h each time. At the same time, the stirring speed decreased (100-70-50 rpm) to avoid high shear stress while the viscosity increased. Finally, the samples were retrieved from the reaction mixture, milled and washed with methanol to remove any unreacted substances. The reaction yield was 95%.

## Nuclear magnetic resonance (NMR) details.

$^1$H NMR and $^{13}$C NMR spectra were recorded on Bruker 600 MHz spectrometer. For samples solubilized in TFA-d, the internal reference peaks were set at 11.50 ppm ($^1$H) and 116 ppm and 164 ppm ($^{13}$C). Chemical shifts ($\delta$) are given in ppm to the nearest 0.01 ppm ($^1$H) and 0.1 ppm ($^{13}$C). The coupling constants (*J*) are given in Hertz (Hz). The signals are reported as follows: chemical shift, multiplicity (s – singlet, d – doublet, m – multiplet), coupling constants (*J*) and integration.

**PEF: $^1$H NMR (TFA-*d*, 600 MHz at 25°C)** $\delta$ (ppm) = 7.4 (s, 2H, C-H furan), 4.82 (s, 4H, $CH_2$). **$^{13}$C NMR (TFA-*d*, 600 MHz at 25°C)** $\delta$ (ppm) = 162.5 (s, 2C, C=O), 148.5 (s, 2C, C-O furan), 122.4 (s, 2C, C=C furan), 66.12 (s, 2C, $CH_2$).

**Thymol: $^1$H NMR (TFA-*d*, 600 MHz at 25°C)** $\delta$ (ppm) = 7.3 (s, 1H, C-H aromatic), 6.99 (d, 1H, *J* = 6.9 Hz, C-H aromatic), 6.88 (s, 1H, C-H aromatic), 3.28 (m, 1H, *J* = 3.2 Hz, C-H aliphatic), 2.4 (s, 3H, $CH_3$-C=H), 1.38 (d, 6H, *J* = 1.38 Hz, $CH_3$-C-H). **$^{13}$C NMR (TFA-*d*, 600 MHz at 25°C)** $\delta$ (ppm) = 151.9 (d, 1C, =C-OH), 139.4 (d, 1C, C=C aromatic), 134.5 (s, 1C, C=C aromatic), 128.3 (d, 1C, C=C aromatic), 125.6 (m, 1C, C=C aromatic), 118.6 (m, 1C, C=C aromatic), 28.22 (s, 1C, C-H aliphatic), 23.71 (s, 2C, $CH_3$-C-H), 21.6 (d, 1C, $CH_3$-C=H).

**Vanillin: $^1$H NMR (TFA-*d*, 600 MHz at 25°C)** $\delta$ (ppm) = 9.67 (s, 1H, CH=O), 7.61 (d, 2H, *J* = 7.6 Hz, =C-H aromatic), 7.14 (d, 1H, *J* = 7.13 Hz, =C-H aromatic), 4.01 (s, 3H, O-$CH_3$ aliphatic). **$^{13}$C NMR (TFA-*d*, 600 MHz at 25°C)** $\delta$ (ppm) = 198.4 (S, 1C, CH=O), 155.2 (s, 1C, =C-C aromatic), 150.07 (s, 1C, C=C aromatic), 132.3 (s, 1C, C=C aromatic), 131.09 (s, 1C, C=C aromatic ), 117.1 (s, 1C, C=C aromatic), 112.5 (s, 1C, C=C aromatic), 57.6 (s, 1C, O-$CH_3$ aliphatic).

## Life Cycle Assessment (LCA) methodology.

In compliance with ISO 14040 and 14044 standards,[1, 2] the present LCA analysis encompassed four phases: (i) goal and scope definition, including selection of the functional unit (FU) and system boundaries; (ii) life cycle inventory (LCI) analysis, documenting all material and energy inputs and outputs; (iii) life cycle impact assessment (LCIA), which evaluates the significance of each process and impact category; and (iv) interpretation of LCIA results, facilitating the selection of the optimal product or processes within the study's objectives and boundaries.

*Goal and Scope.* As depicted in Fig. 4, a cradle-to-gate analysis was conducted, including the industrial production of material and energy inputs, the membrane production at the laboratory scale, and waste generation from membrane fabrication. The fabrication parameters were selected based on experimental data for PEF and on the reported values for a PET membrane with a molecular weight cut-off in the ultrafiltration range (Supplementary Tables 9 and 11). 1 $m^2$ of free-standing polymer membrane was selected as FU, considering a weight/area ratio of 33.9 g $m^{-2}$ based on experimental measurements. The LCA was performed using LCA for Experts software version 10.9.1.17 with its 2025.1 version database and ecoinvent 3.9.1 cut-off database.

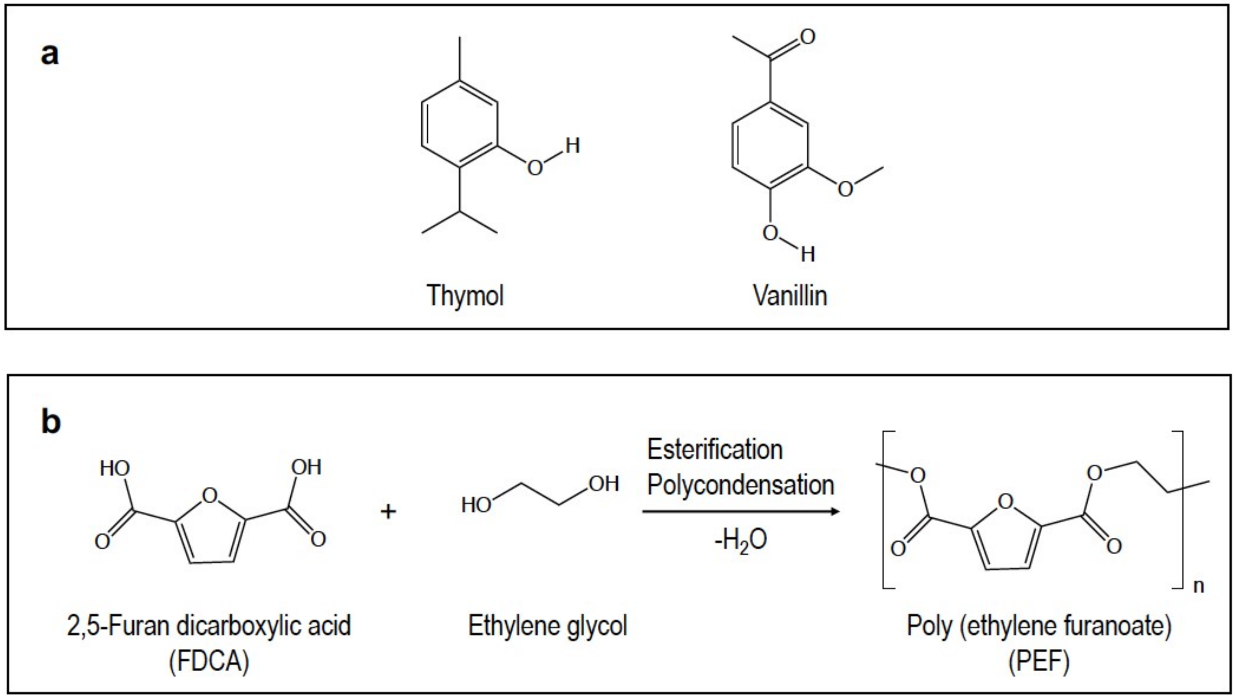
*Life Cycle Inventory.* We relied on "Rest of the Word" or "Global" market datasets from the selected databases to account for transportation of materials from their production sites to the membrane fabrication facility. Some elements excluded from the study are the production of capital goods for equipment manufacturing (machines and facilities) and internal transport. An upscaling approach was applied for PEF synthesis, solvent distillation, and thymol crystallization based on Piccino et al.[3] The detailed inventory, datasets, assumptions and allocation used in each individual process can be found in the Supplementary Tables 9 to 26.

*Life Cycle Impact Assessment*. Nineteen environmental indicators from the ReCiPe 2016 v1.1 (H) midpoint method were employed in this analysis. The potential impact categories assessed were Global Warming Potential (GWP) excluding biogenic carbon over 100 year time horizon [kg $CO_2$ eq.]; GWP including biogenic carbon [kg $CO_2$ eq.]; fine particulate matter formation [kg PM2.5 eq.]; fossil depletion [kg oil eq.]; freshwater consumption [$m^3$]; freshwater ecotoxicity [kg 1,4 DB eq.]; freshwater eutrophication [kg P eq.]; human toxicity, cancer [kg 1,4-DB eq.]; human toxicity, non-cancer [kg 1,4-DB eq.]; ionizing radiation [kBq Co-60 eq. to air]; land use [Annual crop eq.·y]; marine ecotoxicity [kg 1,4-DB eq.];

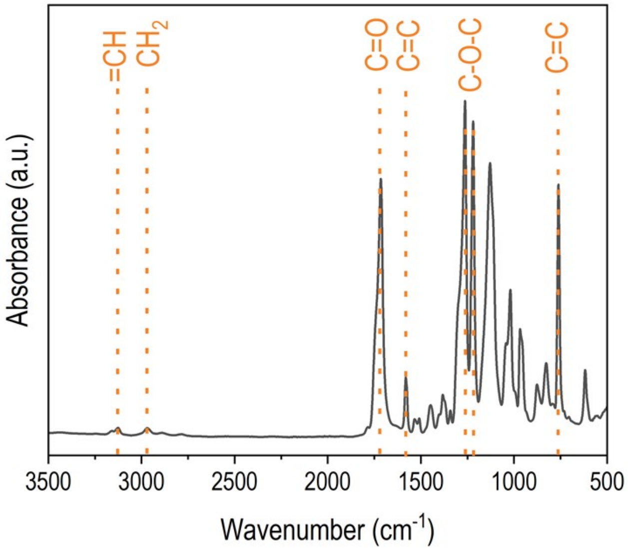
marine eutrophication [kg N eq.]; metal depletion [kg Cu eq.]; photochemical ozone formation, ecosystems [kg NOx eq.]; photochemical ozone formation, human health [kg NOx eq.]; stratospheric ozone depletion [kg CFC-11 eq.]; terrestrial acidification [kg $SO_2$ eq.]; and terrestrial ecotoxicity [kg 1,4-DB eq.].

*Scenarios investigated*. Four different types of parameter changes were explored in this study (Supplementary Tables 6 and 7): (1) extraction technology within thymol production; (2) source of nonsolvent (ethanol) for the coagulation bath, (3) treatment of the waste solvents and polymer residue resulting from the membrane fabrication process, and (4) electricity grid mix during membrane production. Supercritical fluid extraction and hydrodistillation were evaluated as thymol extraction technologies. Fossil-based or bio-based ethanol from fermentation was modeled as the coagulation bath during membrane production. Incineration with and without energy recovery and internal recycling were considered to treat the waste solvents and polymer produced during membrane fabrication. Four different electricity and thermal energy geographical scopes were explored, namely global average, North America, Europe, and the Middle East. The baseline scenario was a combination of the following parameters: supercritical fluid extraction during thymol production, fossil-based ethanol in the coagulation bath, incineration of the solvents and polymer residue with energy recovery, all under a global average electricity mix and thermal energy production from natural gas. The same parameters were applied to PET-based membranes for comparison purposes. By varying each parameter, we identified the scenario with the lowest environmental footprint.

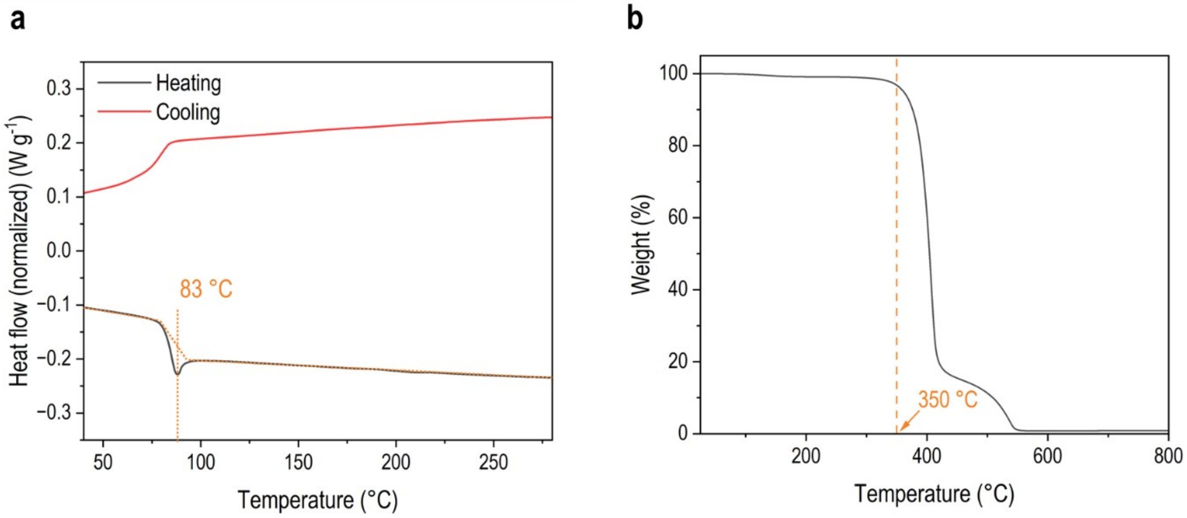
## 2. Supplementary Figures



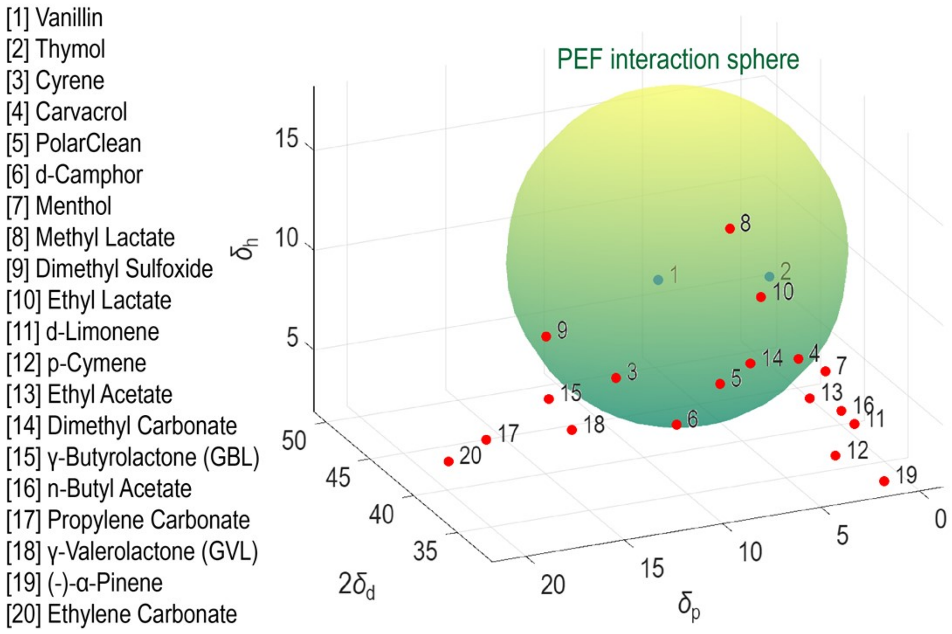
**Supplementary Figure 1. Chemical structures and reactions for PEF membrane production. a**, Solvents: thymol, and vanillin. **b**, PEF synthesis reaction.



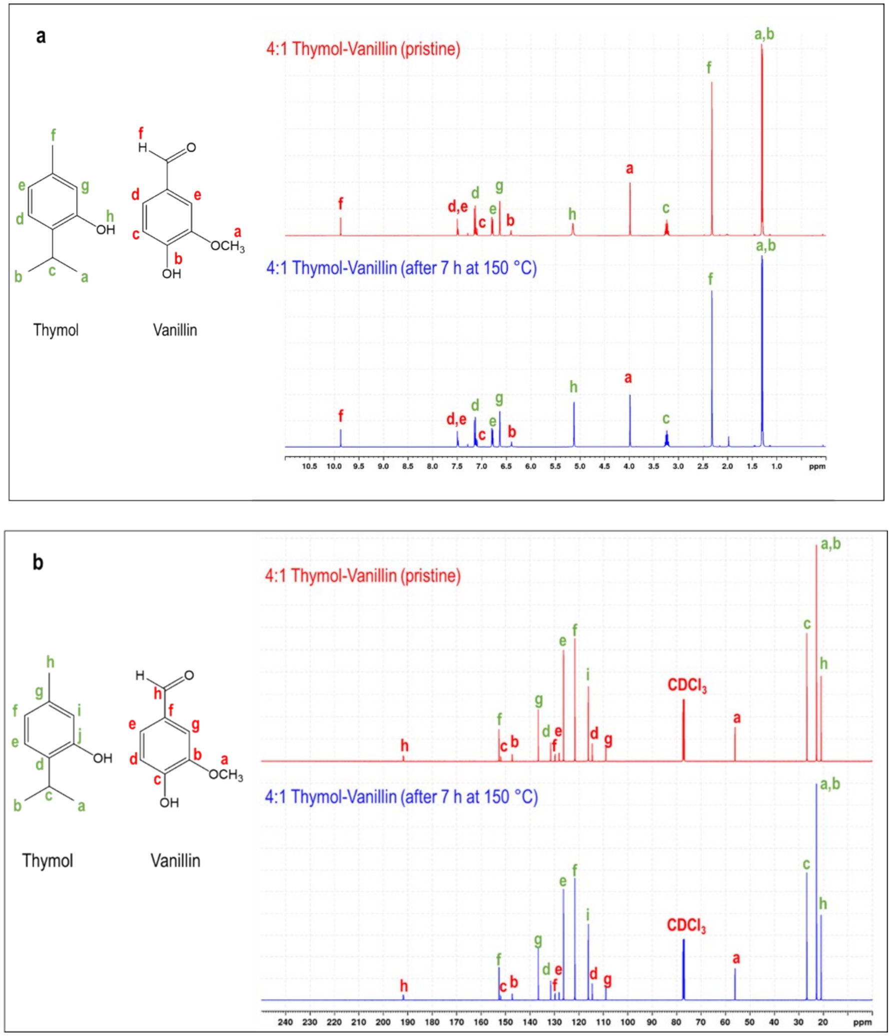
**Supplementary Figure 2. FTIR analysis of the synthesized PEF.** The sample exhibited the characteristic peaks of C=C bending at 761 cm$^{-1}$, C-O-C stretching at 1220 and 1263 cm$^{-1}$, C=C stretching at 1581 cm$^{-1}$, C=O stretching at 1715 cm$^{-1}$, CH$_2$ at 2975 cm$^{-1}$, and =CH (furan ring) at 3128 cm$^{-1}$.



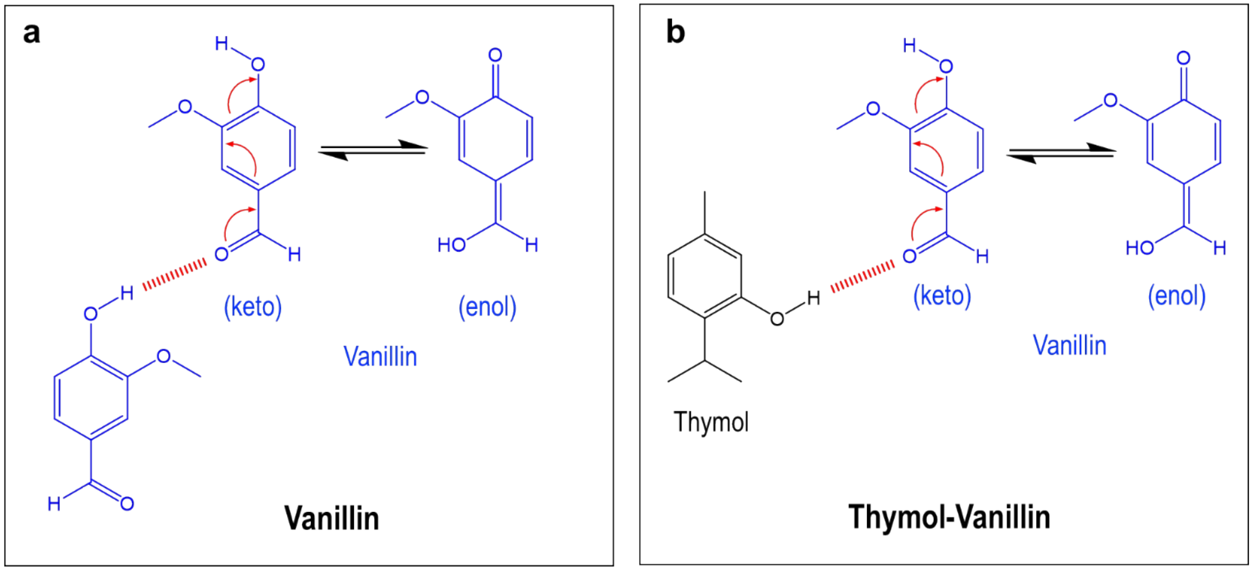
**Supplementary Figure 3. Thermal analysis of the synthesized PEF. a,** Differential Scanning Calorimetry (DSC) analysis of PEF heating/cooling at a rate of 10 °C min$^{-1}$ and glass transition temperature identification (83 °C). **b,** Thermogravimetric analysis (TGA) of PEF under nitrogen with a heating rate of 10 °C min$^{-1}$.



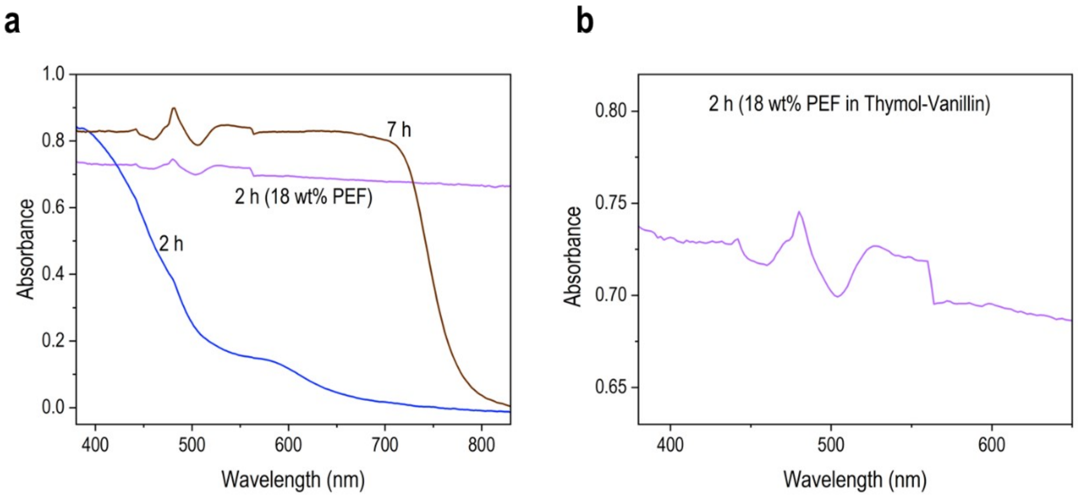
**Supplementary Figure 4. PEF Hansen interaction sphere and green solvent screening.** Solvents and PEF interaction sphere in the Hansen Solubility Parameters space. Blue dots are in the center of the sphere; red ones are in the periphery of the sphere.



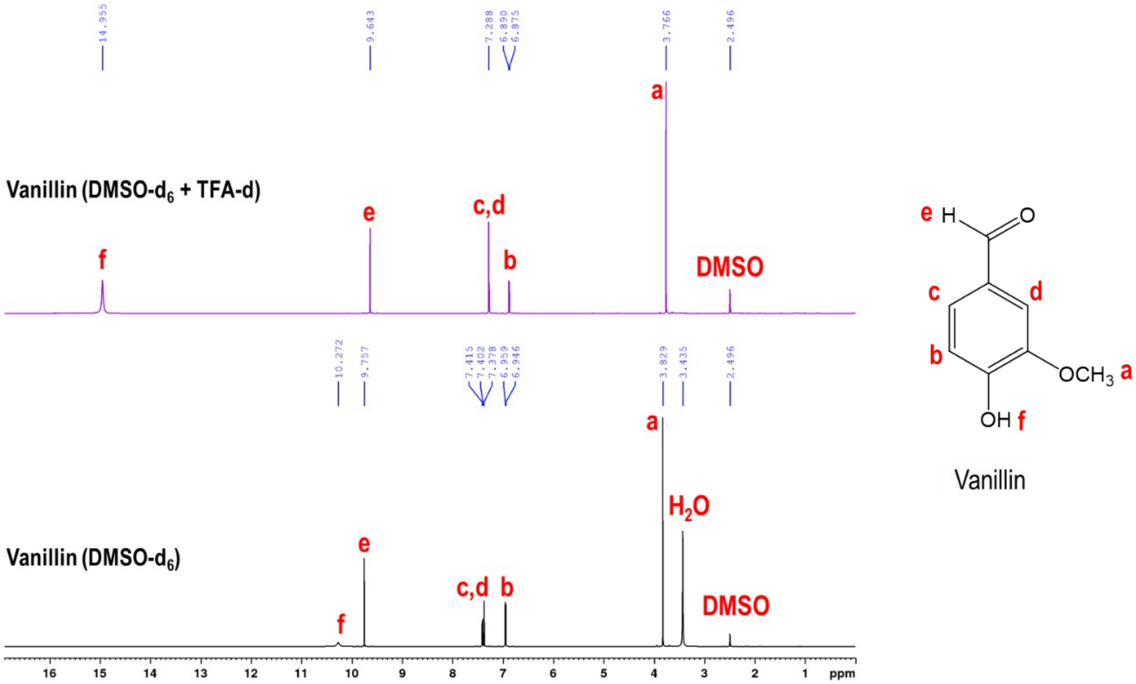
**Supplementary Figure 5. NMR spectra of pristine and heated 4:1 thymol-vanillin solutions. a**, $^1$H NMR. **b**, $^{13}$C NMR. Solutions preparation started with mixing 4:1 molar ratio thymol-vanillin at 90 °C for two hours and cooling it down to room temperature (20 °C). The spectrum referred to as 'pristine' corresponds to a sample retrieved at that moment. The second spectrum corresponds to the previous thymol-vanillin solution heated at 150 °C for seven hours.



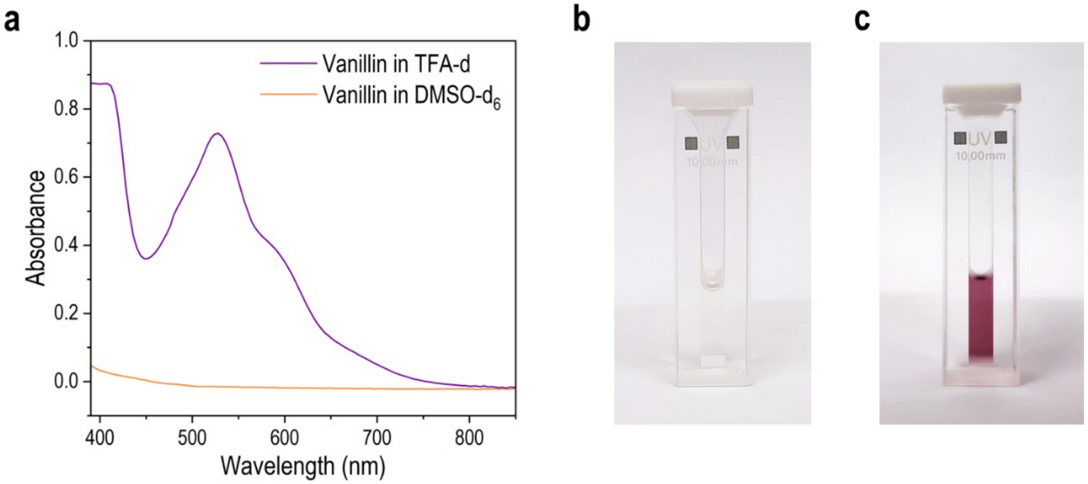
**Supplementary Figure 6. Vanillin hydrogen bond and tautomerism in solution.** Vanillin keto and enol tautomers in different solutions: **a**, Vanillin. **b**, Thymol-vanillin solution.



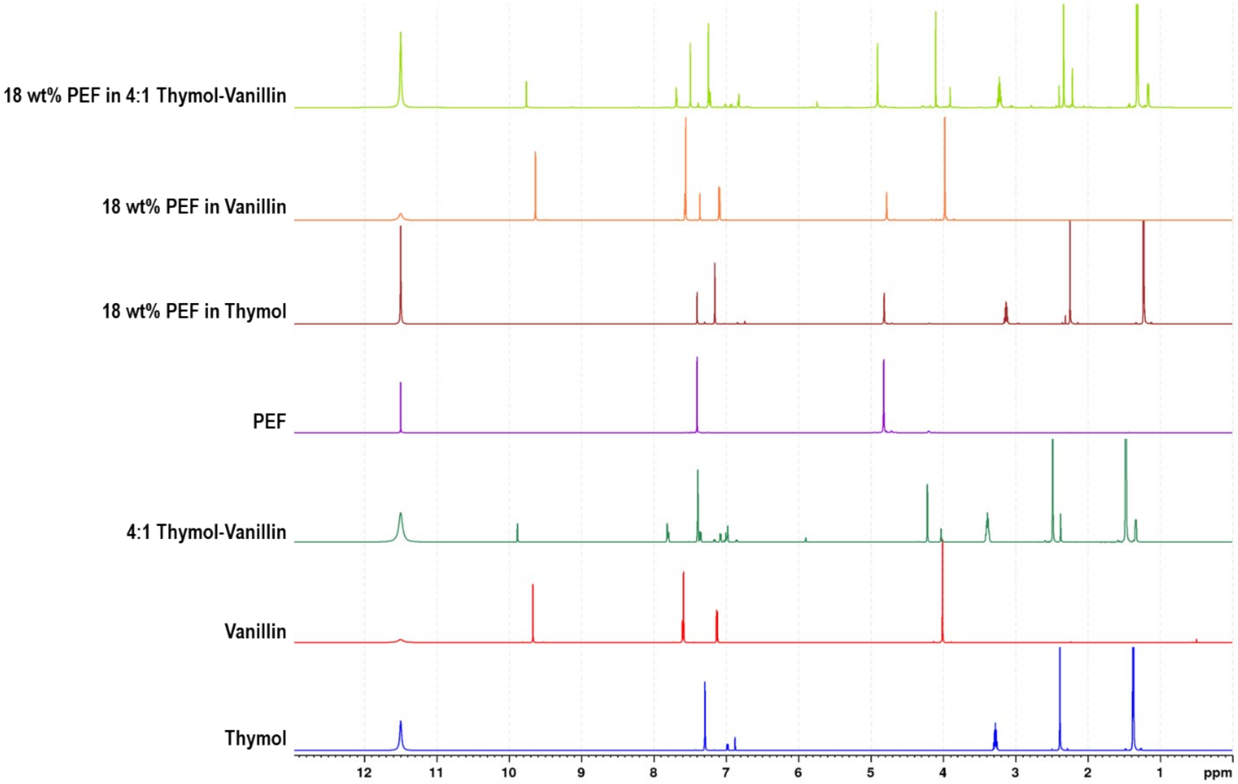
**Supplementary Figure 7. UV-Vis spectra of 4:1 thymol-vanillin solutions. a,** Comparison between thymol-vanillin solutions heated at 150°C for two and seven hours and an 18 wt% PEF solution in 4:1 thymol-vanillin heated at 150°C for two hours. **b,** Amplified UV-Vis spectra of an 18 wt% PEF solution in 4:1 thymol-vanillin heated at 150°C for two hours. All solutions preparation started with mixing 4:1 molar ratio thymol-vanillin at 90 °C for two hours and cooling it down to room temperature (20 °C). 18 wt% PEF was added to the thymol-vanillin solution at room temperature. The mixture was then heated to 150 °C for two hours for full solubilization of the polymer. The solution was cooled down to 20 °C inside a quartz cuvette to record the spectra. The samples of pure thymol-vanillin solutions were heated to 150 °C for different timespans (2, 6, and 7 hours) to mimic the heating required for PEF solubilization and then cooled down to 20 °C to record the spectra in a quartz cuvette.



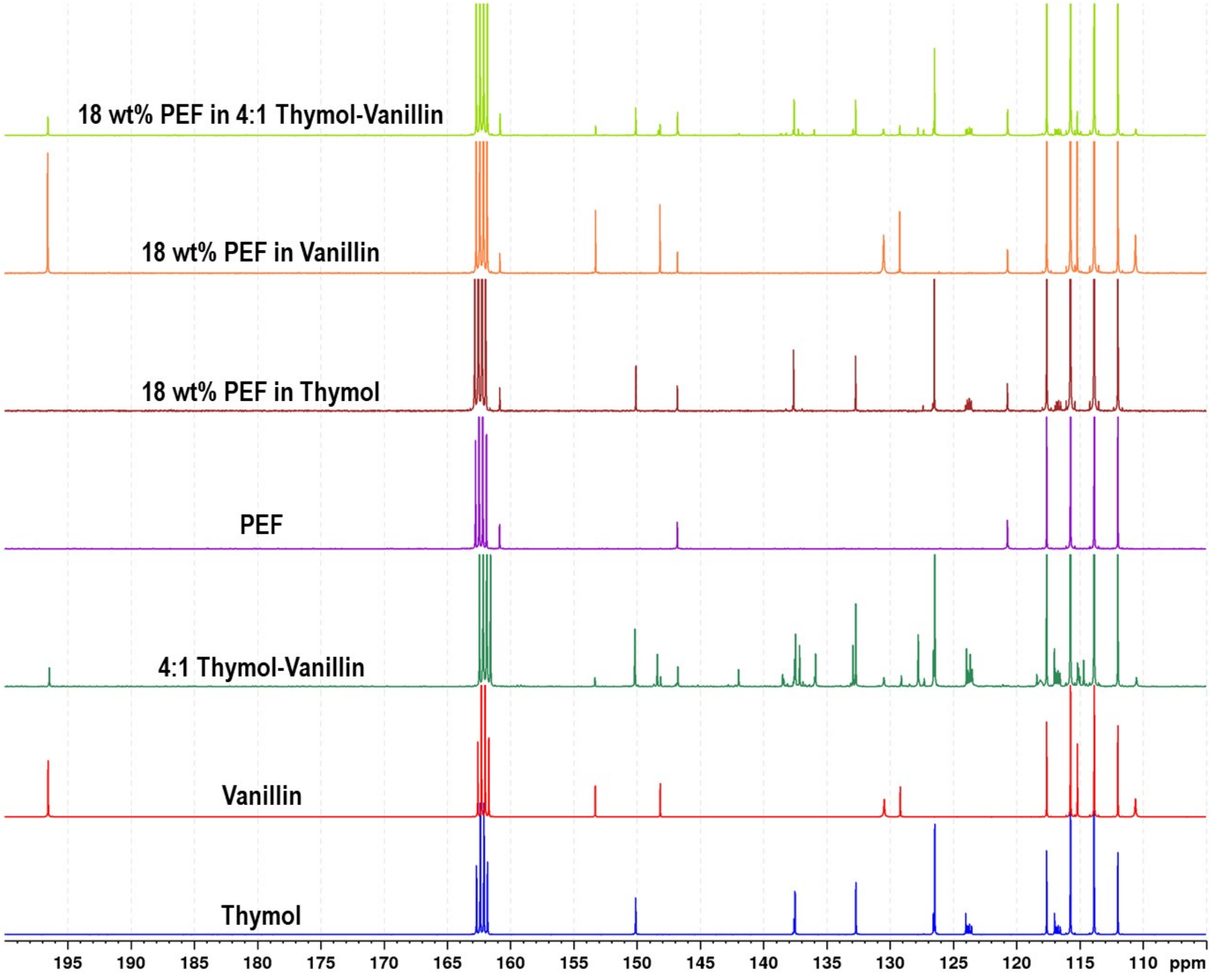
**Supplementary Figure 8. $^1$H NMR spectra of pure vanillin solutions.** Vanillin was dissolved in deuterated dimethyl sulfoxide (DMSO-$d_6$) or DMSO-$d_6$ with few drops of deuterated trifluoroacetic acid (TFA-d). The spectra shows a chemical shift for the hydroxyl group signal, denoting a strong hydrogen bonding. We further studied the color change of vanillin by the addition of trifluoroacetic acid (TFA), which has been utilized to prove the utility of vanillin-based derivatives as fluorine ion chemosensors. The $^1$H NMR spectra of pure vanillin in DMSO-$d_6$ with a small amount of TFA-d shows a shift of the -OH signal from vanillin downfield from 10.27 to 14.96 ppm, caused by proton deshielding due to interaction with the highly electronegative fluorine atom[4].



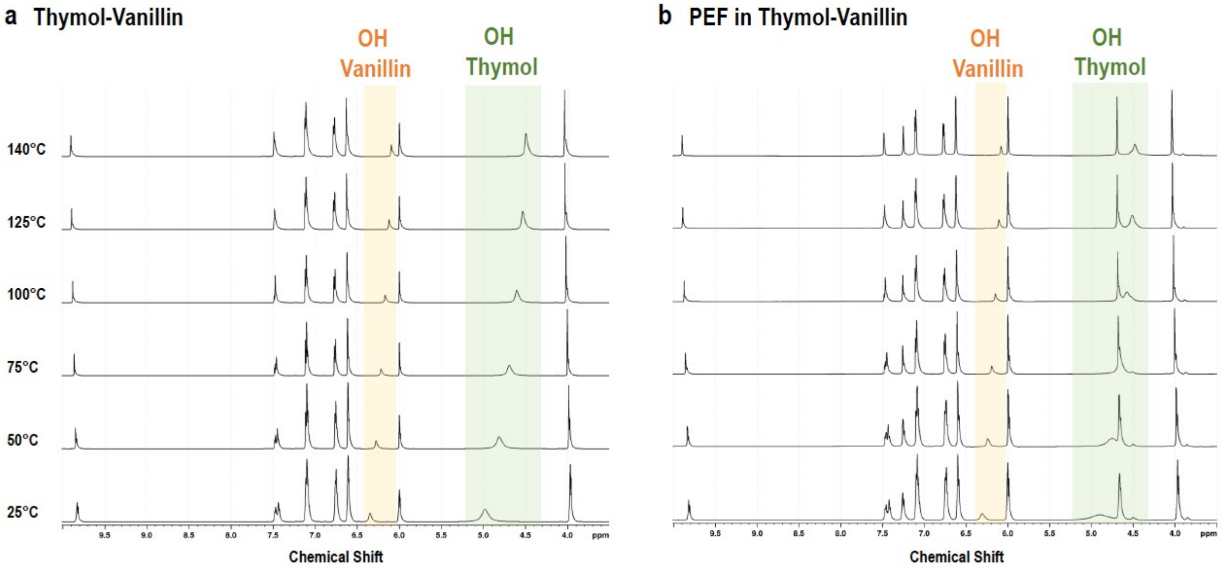
**Supplementary Figure 9. Color change in pure vanillin solutions. a,** UV-Vis spectra of vanillin in deuterated trifluoroacetic acid (TFA-d) or deuterated DMSO (DMSO-$d_6$). **b,** Photograph of the vanillin solution in DMSO-$d_6$. **c,** Photograph of the vanillin solution in TFA-d.



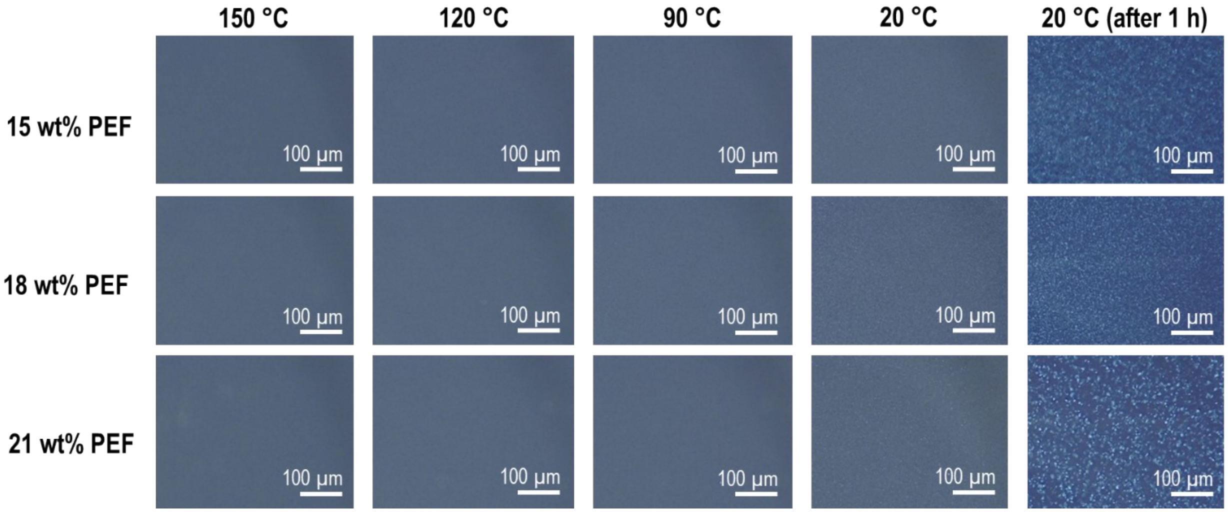
**Supplementary Figure 10. $^1$H NMR of PEF solutions and single components.** 18 wt% PEF solutions in thymol-vanillin, vanillin and thymol were diluted in deuterated trifluoroacetic acid. The solvent signal at 11.5 was used for axis calibration. The PEF and PEF solutions spectra show the characteristic peaks of CH at 7.4 ppm and $CH_2$ at 4.8 ppm. Thymol exhibits peaks for $CH_3$ at 1.4 and 2.4 ppm, CH at 3.3 and 7.3 ppm. Vanillin exhibits peaks for $CH_3$ at 4.0 ppm, CH (aromatic ring) at 7.1 and 7.6 ppm, and CH=O at 9.7 ppm. The OH signal for thymol and vanillin is absent due to the strong hydrogen bonding with TFA-d.



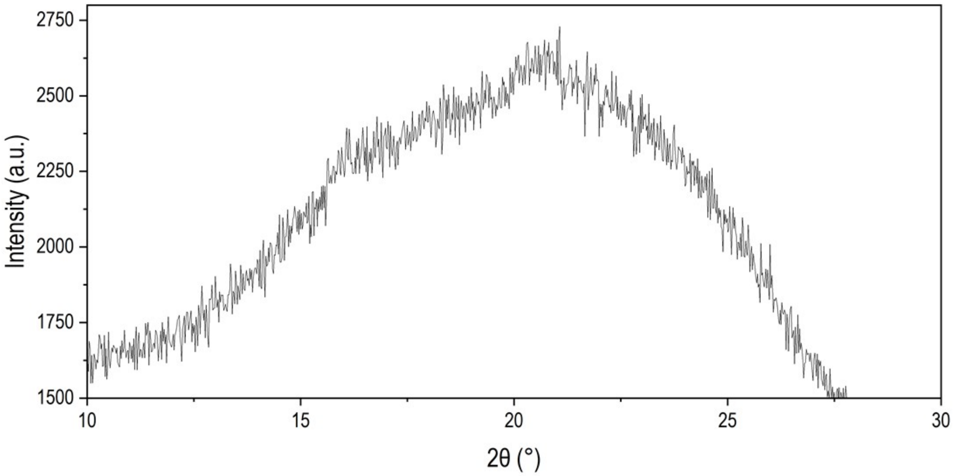
**Supplementary Figure 11. $^{13}$C NMR of PEF solutions and single components.** 18 wt% PEF solutions in thymol-vanillin, vanillin and thymol were diluted in deuterated trifluoroacetic acid. The PEF and PEF solutions spectra show the characteristic peaks of CH at 146.57 ppm, C=O at 160.62 ppm. Pure thymol exhibits peaks for $CH_3$ at 20.9 and 23.5 ppm, CH at 28.0 ppm, CH from the aromatic ring at 118.6, 125.6, and 128.1 ppm, C from the C-$CH_3$ group at 139.1 ppm, and C from the C-OH group at 151.7 ppm. Vanillin exhibits peaks for $CH_3$ at 57.4, CH (aromatic ring) at 112.3, 116.9, and 130.9 ppm, C in the aromatic ring at 132.2, 149.9, and 155.0 ppm, and CH=O 198.2 ppm.



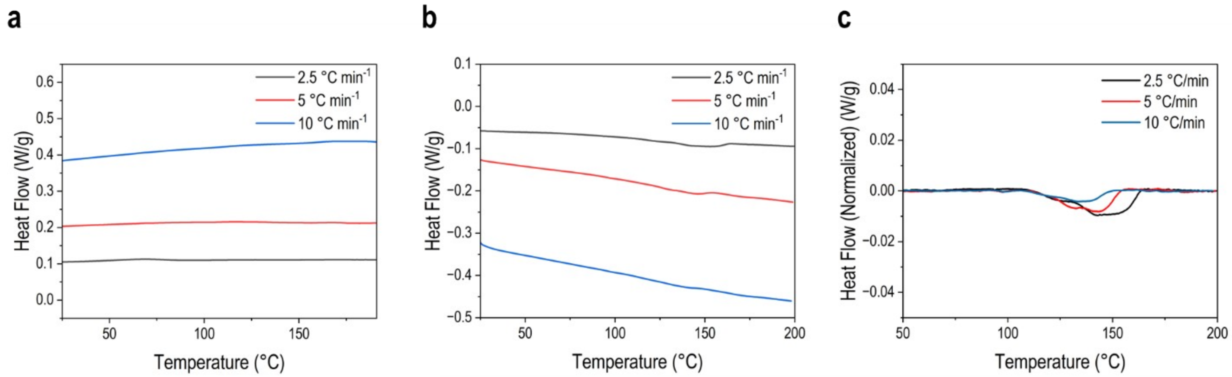
**Supplementary Figure 12. $^1$H NMR investigation of hydrogen bond as a function of temperature. a,** thymol-vanillin and b, PEF in thymol-vanillin. OH signal for vanillin at 6.0 to 6.5 ppm and for thymol at 4.3 to 5.2 ppm. Experiments conducted on a Bruker Avance III operating at 600 MHz with 1,1,2,2-tetrachloeoethane-d2 as deuterated solvent.



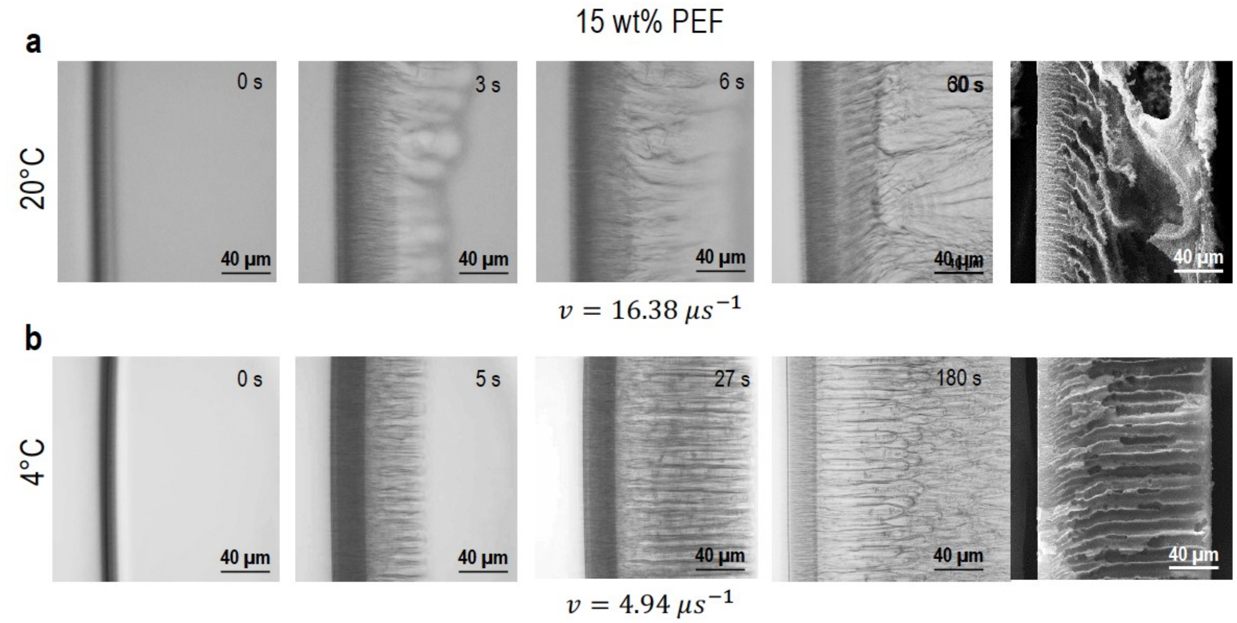
**Supplementary Figure 13. Optical micrographs of PEF solutions with polarizer.** Solutions of 18 wt% PEF in 4:1 molar ratio thymol-vanillin were heated 150 °C until PEF was fully solubilized. After that, one drop of approximately 2 µl was placed on a 1 mm thick microscope glass slide and covered with a 0.1 mm thick glass at room temperature. The sample was then placed inside a heating stage and heated to 150 °C at a rate of 50 °C min$^{-1}$. Then, it was cooled down to 20 °C at a rate of 50 °C min$^{-1}$ to mimic the rapid cooling taking place during membrane fabrication, and a video was recorded. A light polarizer filter was used to observe the presence of crystalline nuclei in the case that thermally induced phase separation took place.



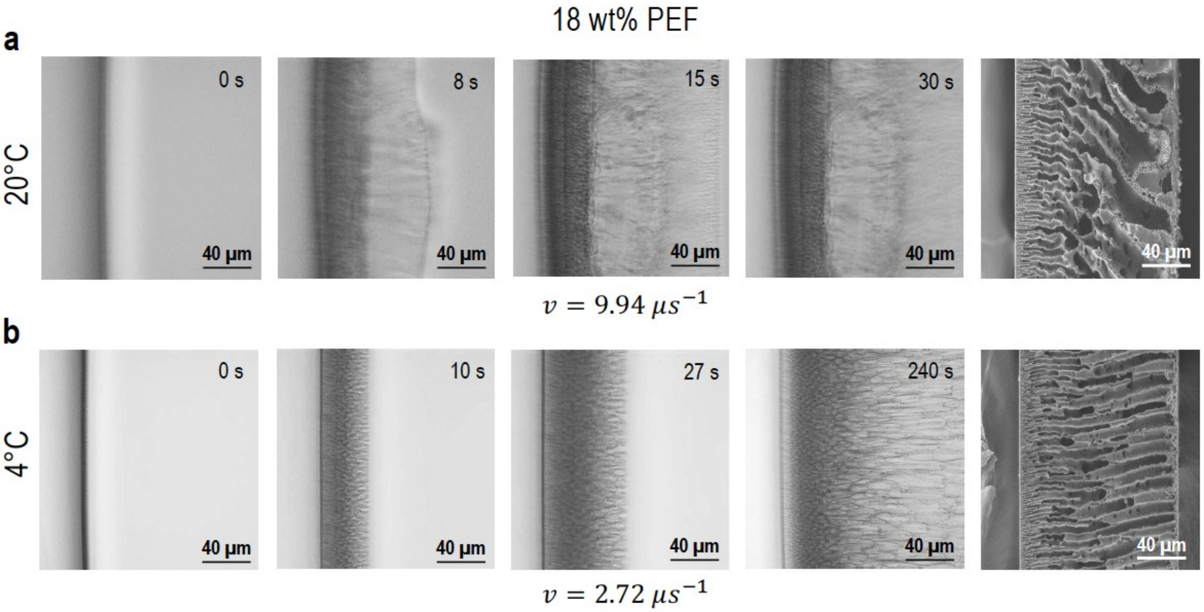
**Supplementary Figure 14. XRD diffractogram of a PEF membrane sample.** The resulting curve denotes an amorphous polymer structure.



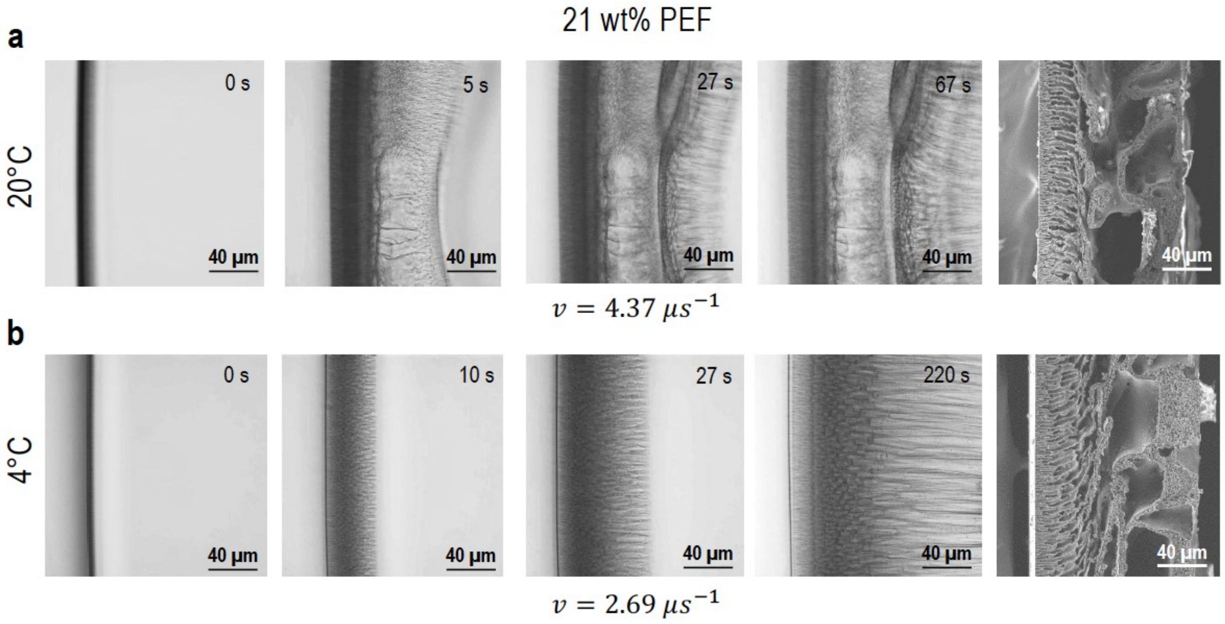
**Supplementary Figure 15. DSC analysis of 18 wt% PEF solutions in 4:1 thymol-vanillin. a**, Heat flow for solution cooling from 200 °C to 20 °C at different cooling rates. **b**, Heat flow for solution heating from 20 °C to 200 °C at different heating rates (second heating). **c**, Normalized heat flow for solution heating from 20 °C to 200 °C at different heating rates (second heating). Solutions of 18 wt% PEF in 4:1 M thymol-vanillin were prepared at 150 °C. After that, samples of approximately 10 mg were placed inside an aluminum hermetic pan at 20 °C and sealed. The DSC experiments were carried out with nitrogen gas. The results show indication of polymer melting at around 150 °C in the normalized heating curves, result of the crystallization happening during the 5 min isothermal step at room temperature prior to heating.



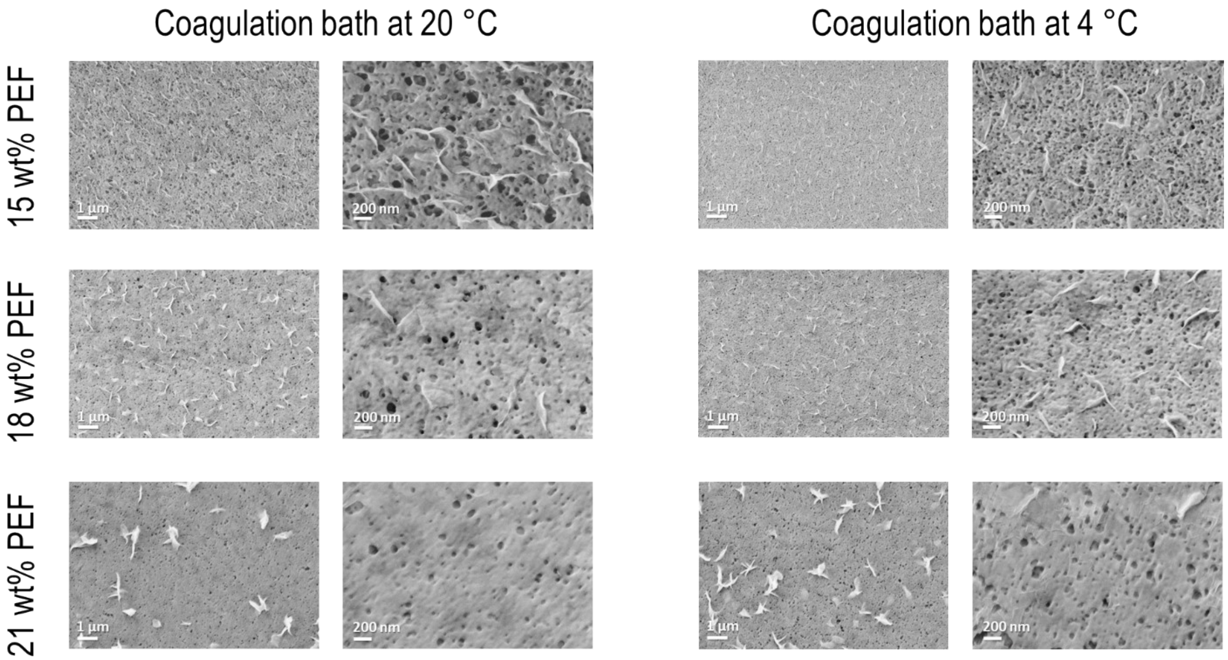
**Supplementary Figure 16. Phase separation of 15 wt% PEF in 4:1 thymol-vanillin induced by solvent-ethanol exchange. a**, Ethanol at 20 °C. **b**, Ethanol at 4 °C. The polymer solution demixing rate ($v$) was calculated by measuring how fast the demixing front moves (distance between the initial position to the front position per time).



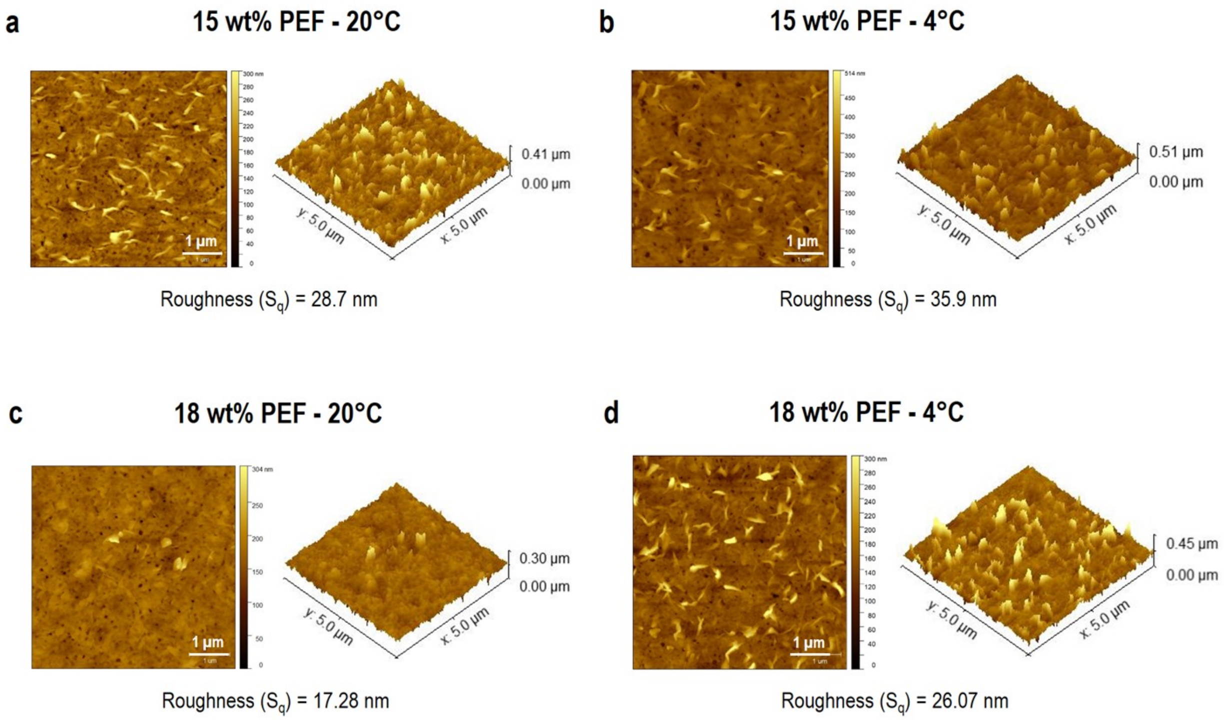
**Supplementary Figure 17. Phase separation of 18 wt% PEF in 4:1 thymol-vanillin induced by solvent-ethanol exchange. a**, Ethanol at 20 °C. **b**, Ethanol at 4 °C. The polymer solution demixing rate ($v$) was calculated by measuring how fast the demixing front moves (distance between the initial position to the front position per time).



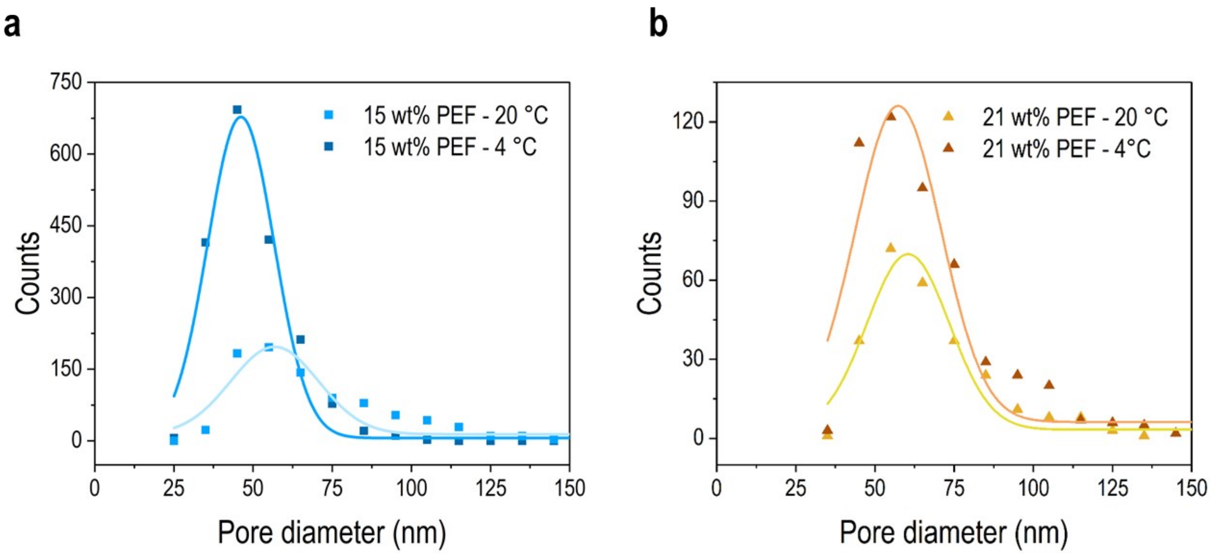
**Supplementary Figure 18. Phase separation of 21 wt% PEF in 4:1 thymol-vanillin induced by solvent-ethanol exchange. a**, Ethanol at 20 °C. **b**, Ethanol at 4 °C. The polymer solution demixing rate ($v$) was calculated by measuring how fast the demixing front moves (distance between the initial position to the front position per time).



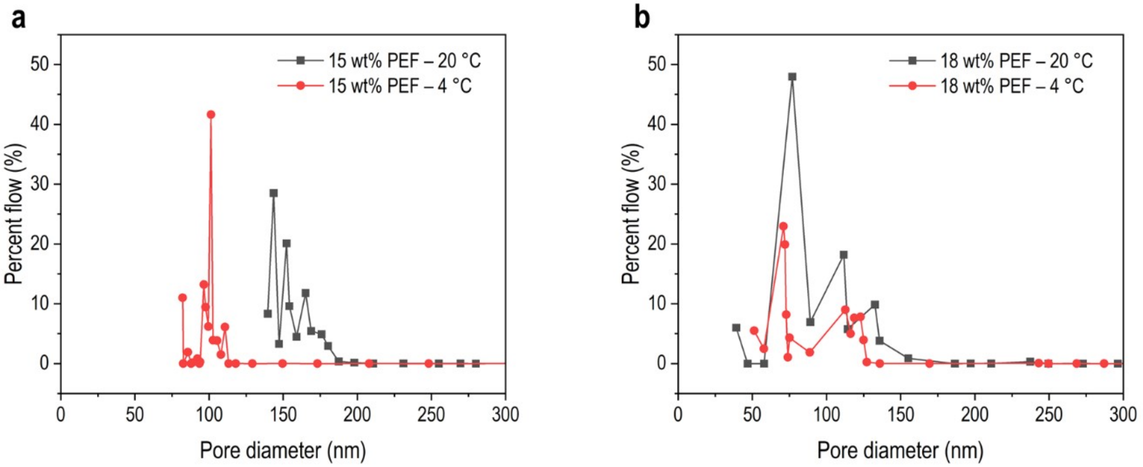
**Supplementary Figure 19. Surface SEM micrographs of PEF membranes.** Membranes prepared by casting 15, 18, or 21 wt% PEF solutions in 4:1 thymol-vanillin followed by immersion in ethanol at 20 °C or 4 °C.



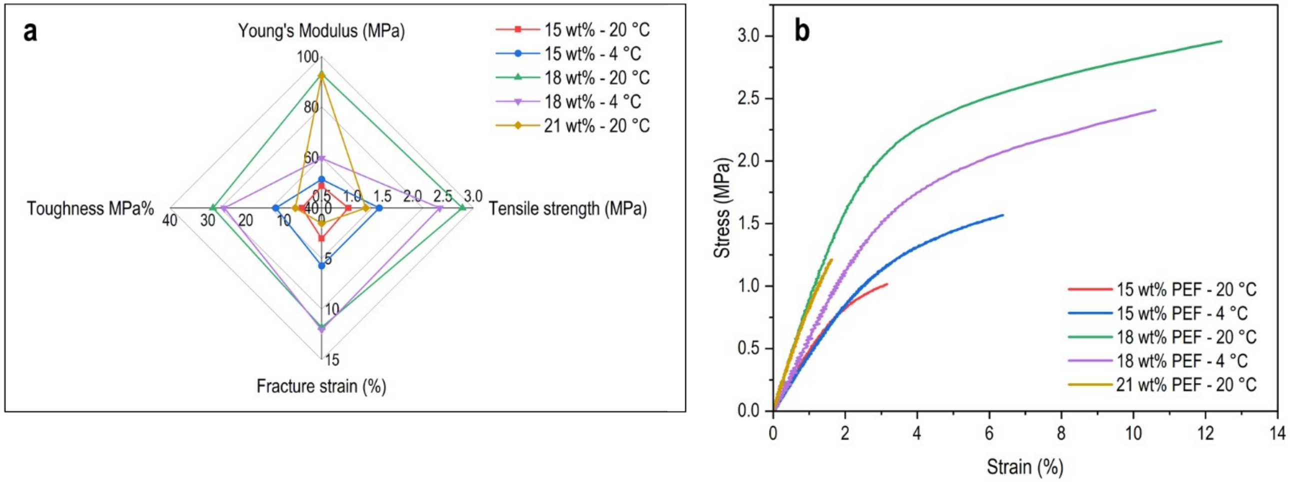
**Supplementary Figure 20. AFM analysis of PEF membranes.** Membranes prepared by casting **a**, **b**, 15 wt% PEF and **c**, **d**, 18 wt% PEF solutions in 4:1 thymol-vanillin followed by immersion in ethanol at **a**, **c**, 20 °C or **b**, **d**, 4 °C.



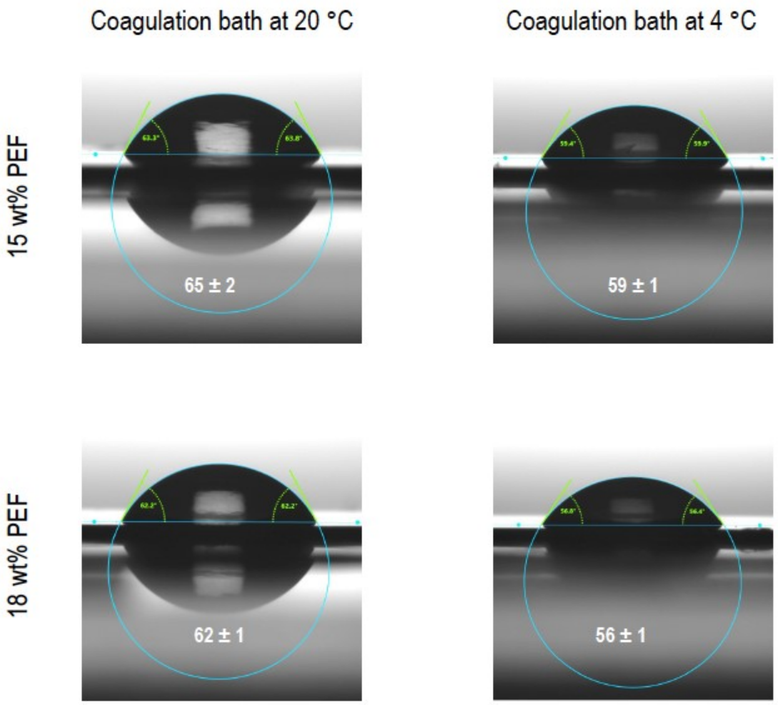
**Supplementary Figure 21. Surface pore size distribution of PEF membranes.** Membranes prepared from **a,** 15 wt% or **b,** 21 wt% PEF in 4:1 thymol-vanillin. Analysis performed via an AI-based image analysis model.



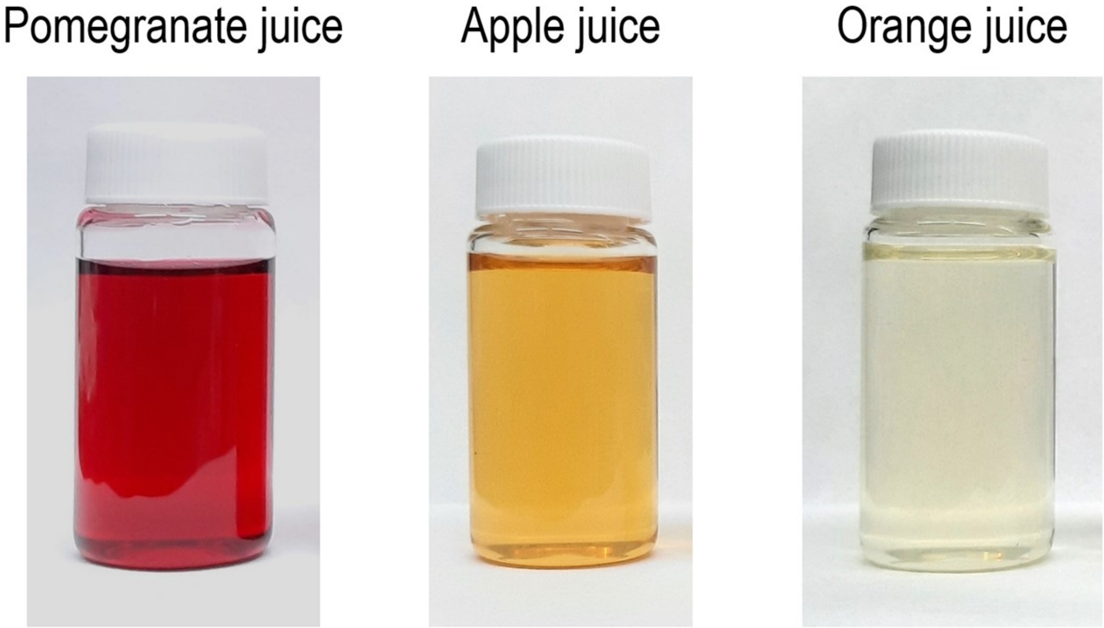
**Supplementary Figure 22. Pore size distribution measured by gas-liquid displacement capillary flow porometry.** Membranes prepared by casting **a**, 15 or **b**, 18 wt% PEF solutions in 4:1 thymol-vanillin followed by immersion in ethanol at 20 °C or 4 °C as the nonsolvent.



**Supplementary Figure 23. Mechanical properties of PEF membranes.** Membranes prepared by casting 15, 18 and 21 wt% PEF solutions in 4:1 thymol-vanillin, followed by immersion in ethanol at 20°C or 4 °C.



**Supplementary Figure 24. Contact angle of PEF membranes.** Membranes prepared by casting 15 and18 wt% PEF solutions in 4:1 thymol-vanillin followed by immersion in ethanol at 20 °C or 4 °C.

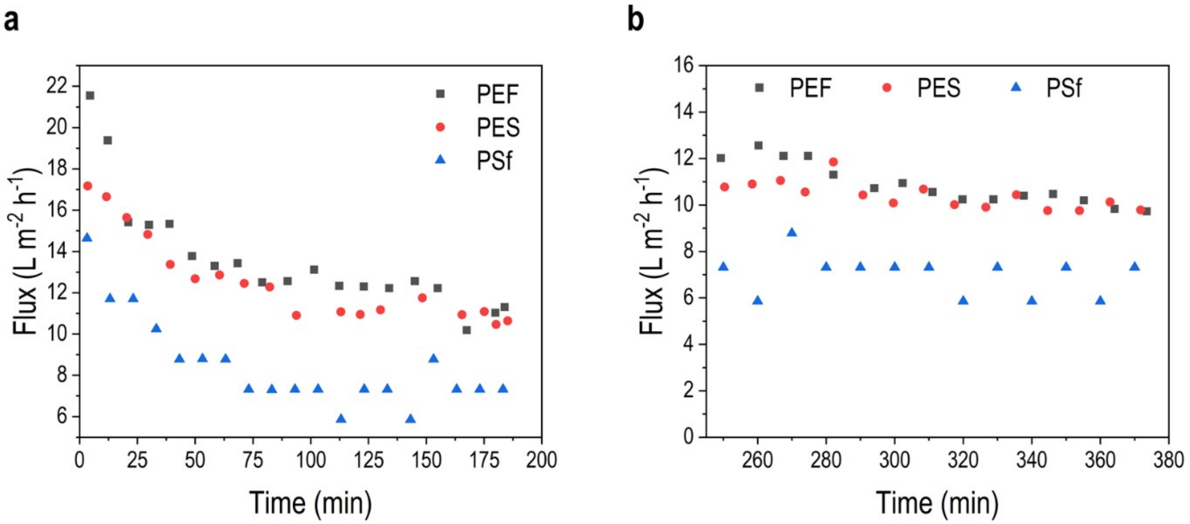


Pomegranate juice

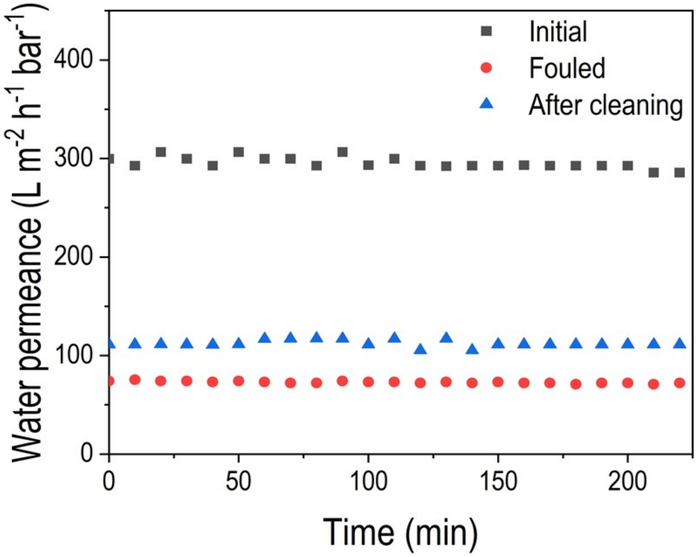
Apple juice

Orange juice

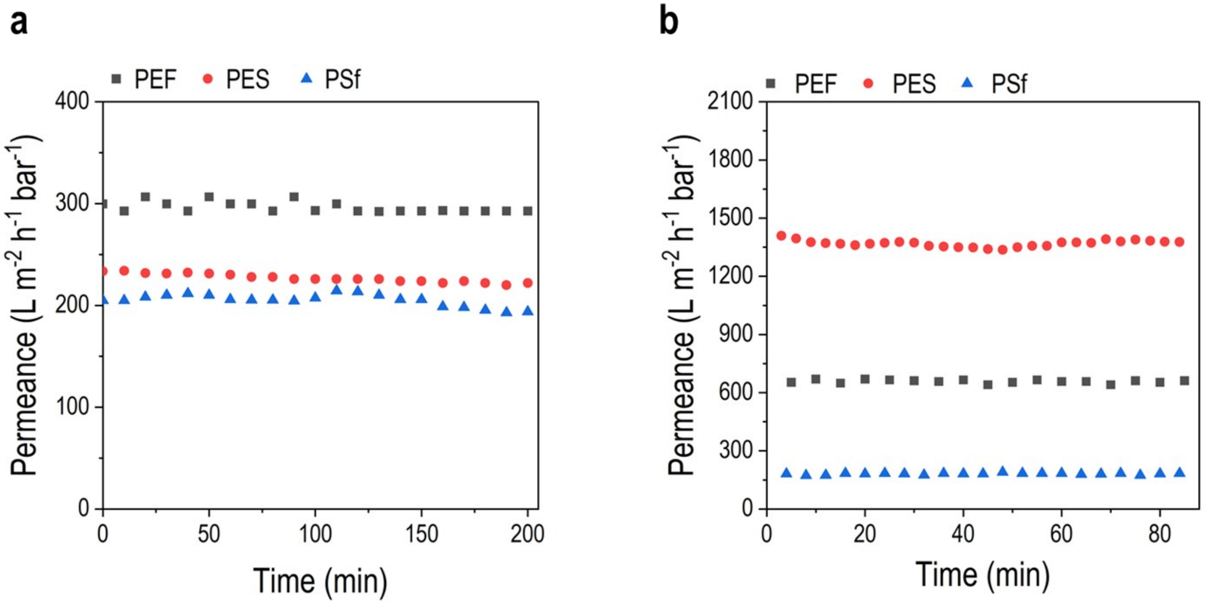
**Supplementary Figure 25. Photographs of juice feed.**



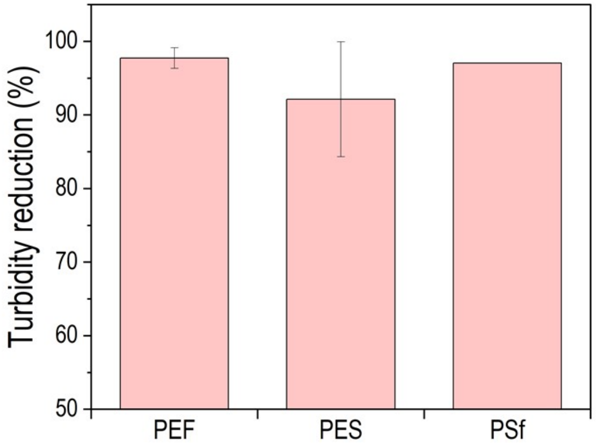
**Supplementary Figure 26. Pomegranate juice flux for PEF, PES, and PSf membranes.** Filtrations carried out in dead-end configuration with a pressure of 0.2 bar.



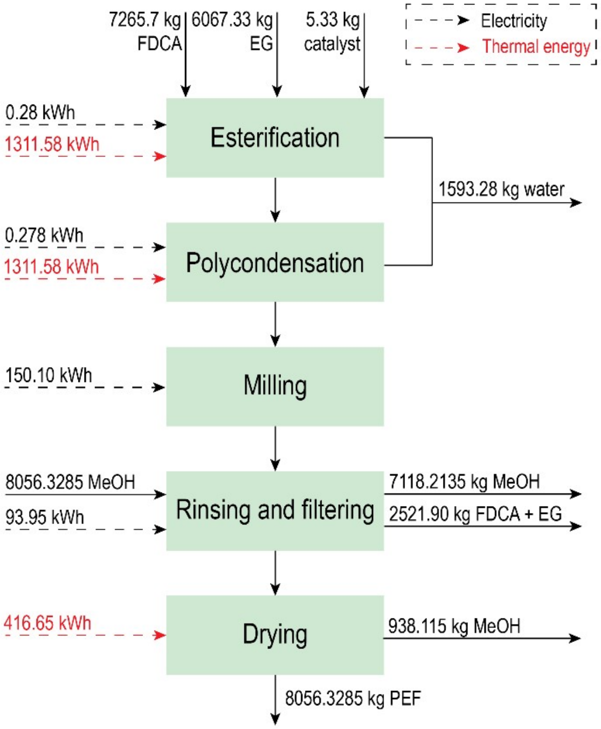
**Supplementary Figure 27. Effect of membrane fouling and backwashing on PEF water permeance.** The PEF membrane was used for pomegranate juice filtration until achieving a weight reduction factor of four. The membrane backwashing was carried out by flipping the membrane within the filtration cell and permeating MiliQ water for 30 minutes with a pressure of 0.4 bar.



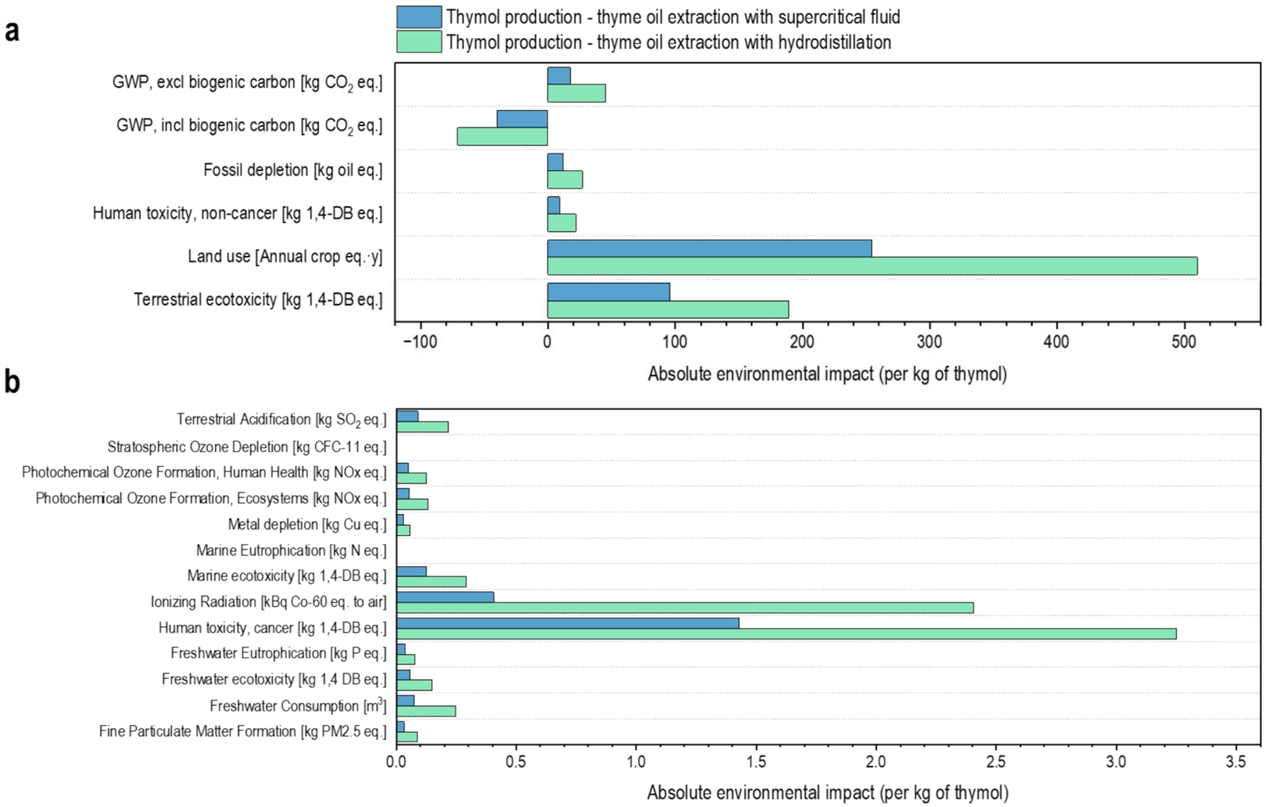
**Supplementary Figure 28. Water permeance comparison of polymeric membranes.** Water flux of the optimized PEF membrane (18 wt% PEF in thymol-vanillin precipitated in 4°C ethanol), and commercial polyethersulfone (Synder MK-30 kDa) and polysulfone (Solecta M-PS20-GPP) in **a,** dead-end, and **b,** cross-flow configuration.



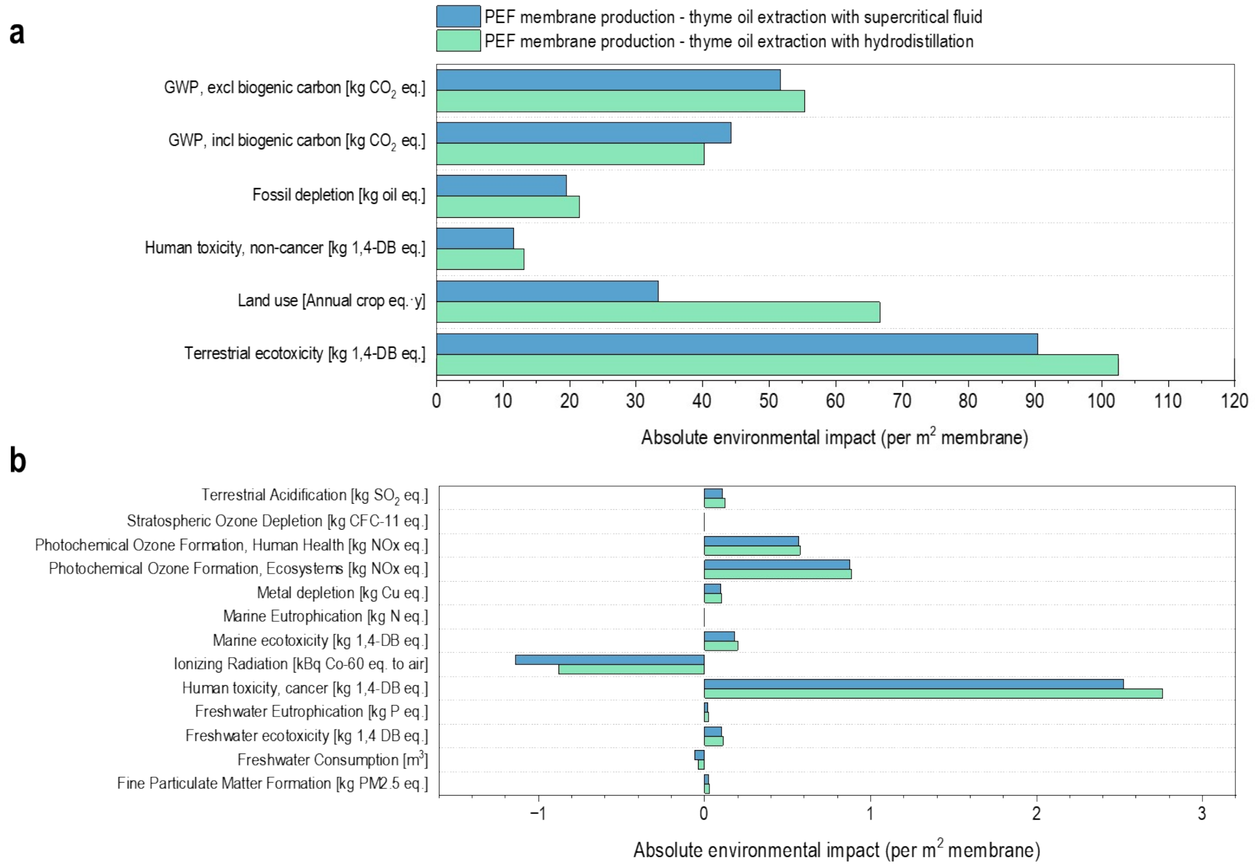
**Supplementary Figure 29. Juice turbidity reduction in pomegranate juice after clarification with the optimized PEF membrane or commercial PES and PSf membranes.** Filtrations carried out in dead-end configuration with a pressure of 0.2 bar until reaching a weight reduction factor of four.



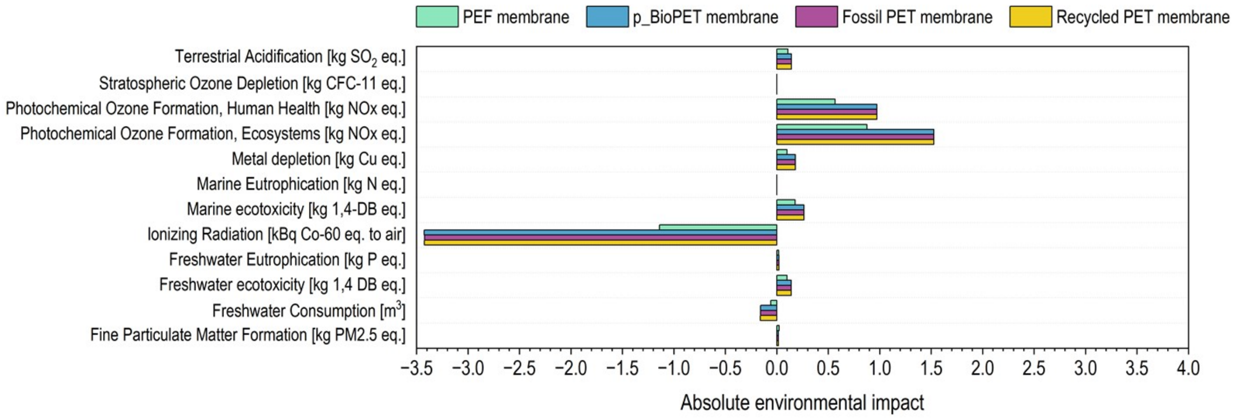
**Supplementary Figure 30. Up-scaled process diagram for PEF production.** Calculations are described in detail in Supplementary Table 15.



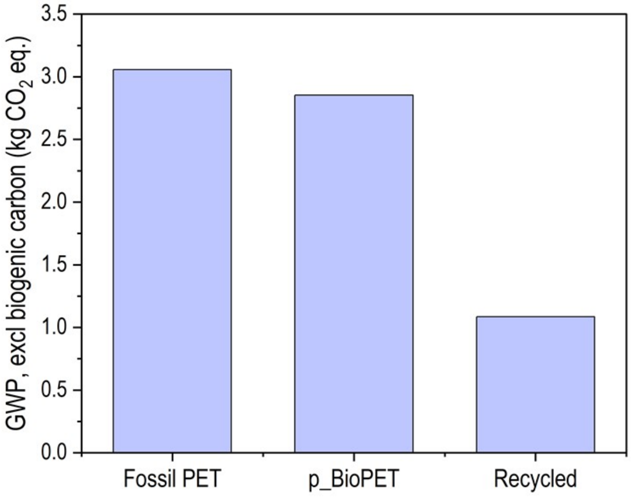
**Supplementary Figure 31. Comparison of the environmental impacts of hydrodistillation and supercritical fluid extraction for thymol production.** Functional unit is 1 kg of thymol produced. **a,** GWP, fossil depletion, human toxicity (non-cancer), land use, and terrestrial ecotoxicity. **b,** terrestrial acidification, stratospheric ozone depletion, photochemical ozone formation, metal depletion, marine eutrophication, marine ecotoxicity, ionizing radiation, human toxicity (cancer), freshwater eutrophication, freshwater ecotoxicity, freshwater consumption, and fine particulate matter formation.



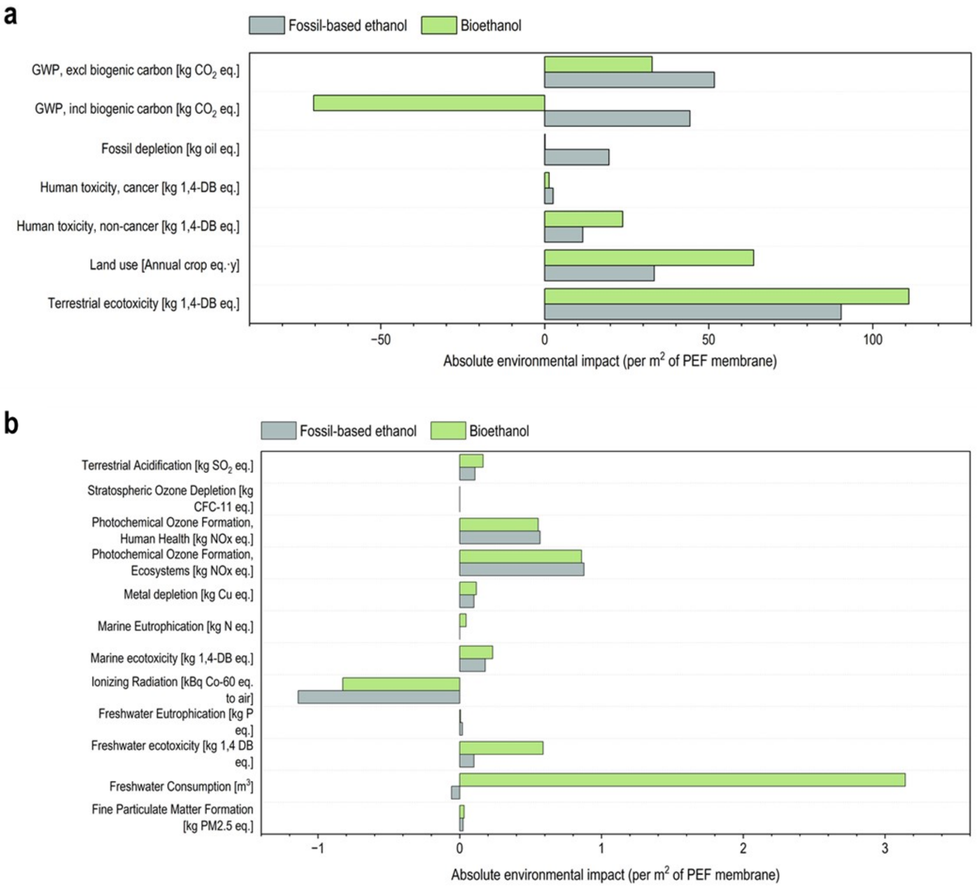
**Supplementary Figure 32. Comparison of the environmental impact of PEF membrane production with hydrodistillation or supercritical fluid extraction within thymol production.** Functional unit is 1 m$^2$ of PEF membrane produced. **a,** GWP, fossil depletion, human toxicity (non-cancer), land use, and terrestrial ecotoxicity. **b,** terrestrial acidification, stratospheric ozone depletion, photochemical ozone formation, metal depletion, marine eutrophication, marine ecotoxicity, ionizing radiation, human toxicity (cancer), freshwater eutrophication, freshwater ecotoxicity, freshwater consumption, and fine particulate matter formation.



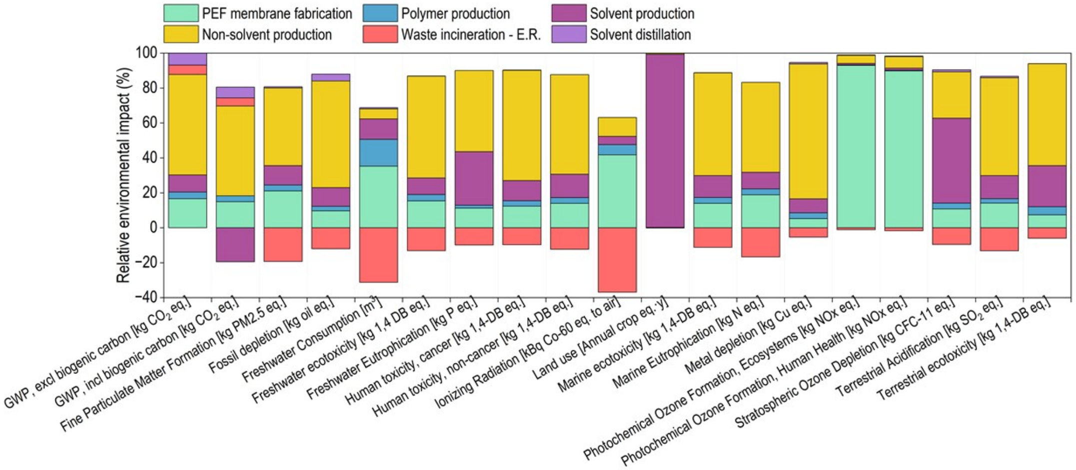
**Supplementary Figure 33. Comparison of the environmental impacts of PEF and different types of PET membrane production.** Functional unit is 1 m$^2$ of PEF membrane produced.



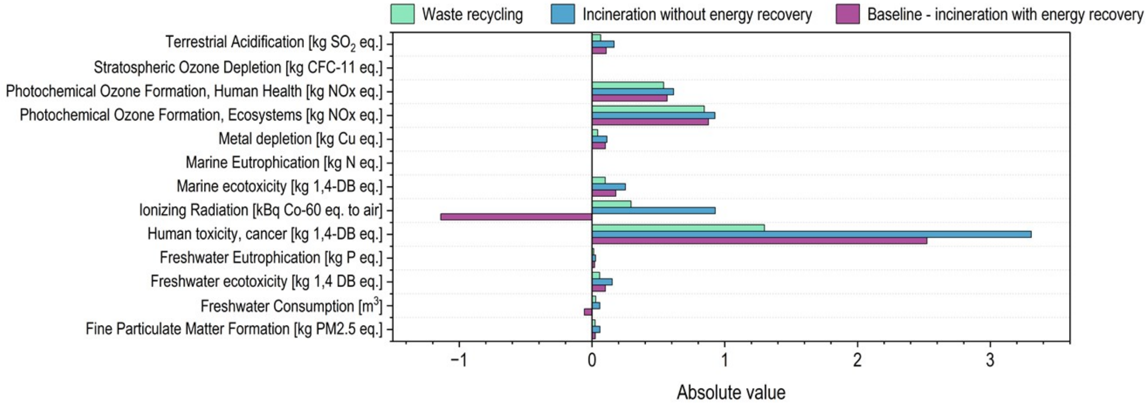
**Supplementary Figure 34. GWP of the different types of PET studied in this work.** Functional unit is 1 kg of polymer produced.



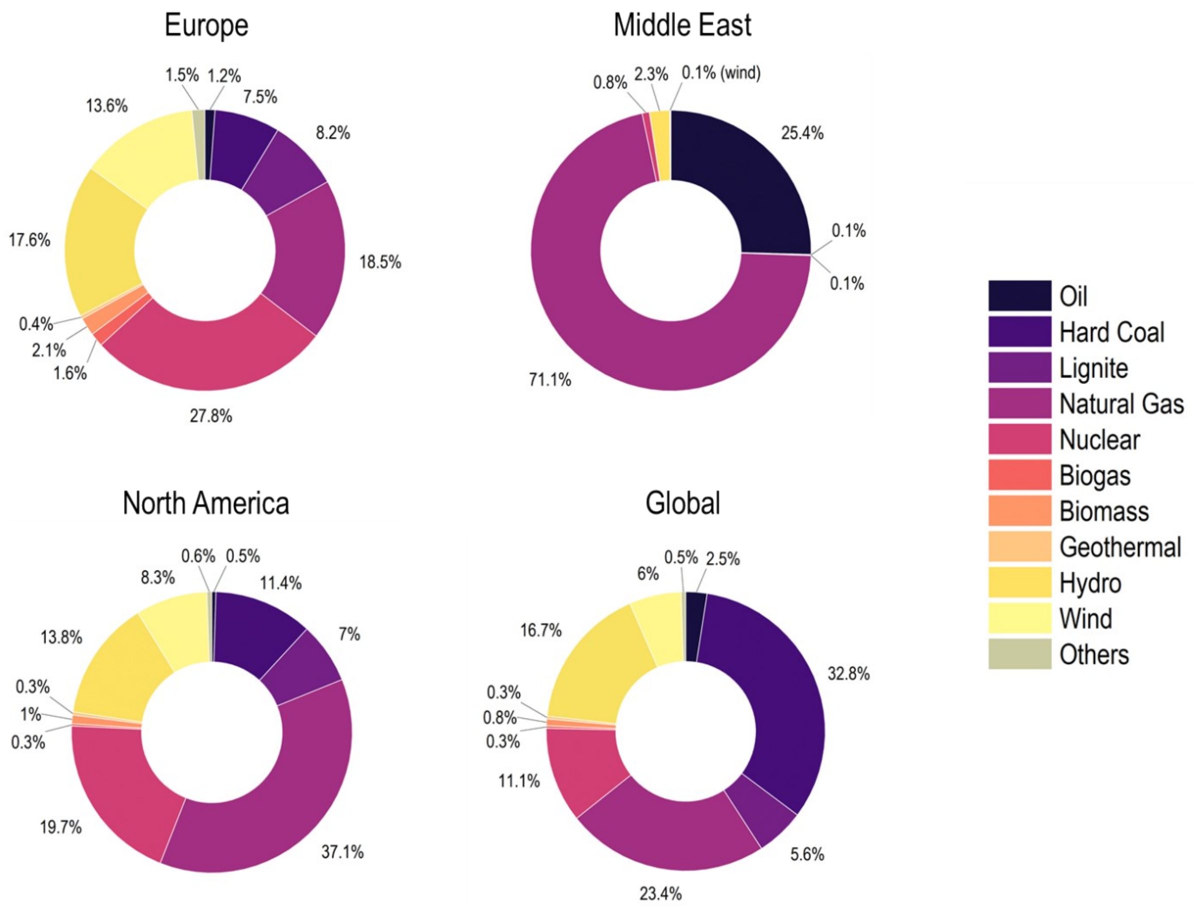
**Supplementary Figure 35. Effect of ethanol type on the environmental impacts of PEF membrane fabrication**. All other parameters were kept as the baseline scenario. Functional unit is 1 m$^2$ of PEF membrane produced. **a,** GWP, fossil depletion, human toxicity, land use, and terrestrial ecotoxicity. **b,** terrestrial acidification, stratospheric ozone depletion, photochemical ozone formation, metal depletion, marine eutrophication, marine ecotoxicity, ionizing radiation, freshwater eutrophication, freshwater ecotoxicity, freshwater consumption, and fine particulate matter formation.



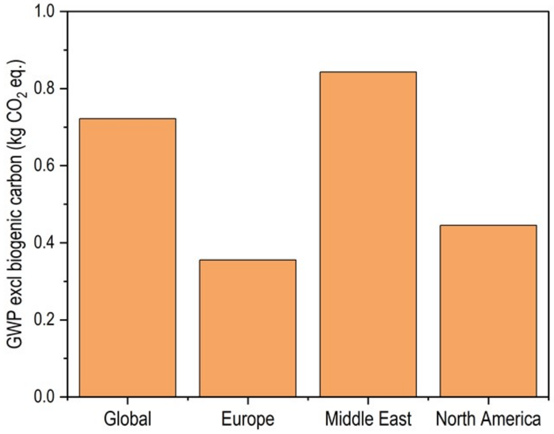
**Supplementary Figure 36. Process contribution of 1 m$^2$ PEF membrane production with waste recycling scenario.** All other parameters were kept as the baseline scenario.



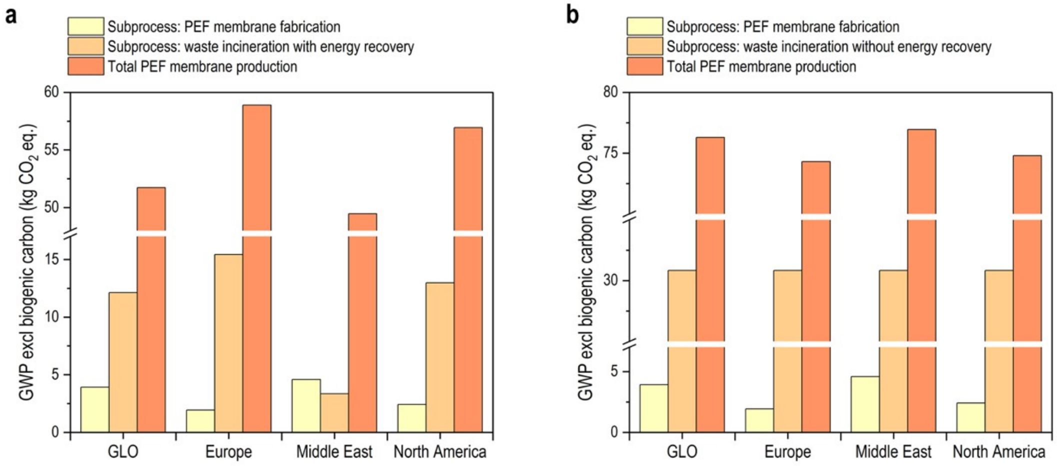
**Supplementary Figure 37. Environmental impact of the production of 1 m$^2$ of PEF membrane with different waste treatment scenarios.** All other parameters were kept as the baseline scenario.



**Supplementary Figure 38. Electricity mix in the regions analyzed in this work.** Data obtained from Ecoinvent 3.9.1.



**Supplementary Figure 39. Global Warming Potential (GWP) of electricity generation in different regions.** Functional unit is 1 kWh of electricity produced.



**Supplementary Figure 40. Effect of different electricity scenarios for PEF membrane production a, with and b, without energy recovery.** The rest of parameters were kept as: supercritical fluid extraction and Bio-EtOH. Functional unit is 1 $m^2$ of PEF membrane produced.

## 3. Supplementary Tables

Supplementary Table 1. Hansen Solubility Parameters of PEF and selected green solvents, *Ra* distance, and *RED* value calculated as $R_a/R_0$ with $R_0$ = 8.0 $MPa^{0.5}$.

| Chemical | $\delta_D$ | $\delta_P$ | $\delta_H$ | $R_a$ | *RED* |
|---|---|---|---|---|---|
| PEF* | 21.7 | 6.8 | 10.2 | - | |
| Vanillin | 19.4 | 9.8 | 11.2 | 5.6 | 0.70 |
| Thymol | 19 | 4.5 | 10.8 | 5.9 | 0.74 |
| Cyrene | 18.9 | 12.4 | 7.1 | 8.5 | 1.06 |
| Carvacrol | 17.9 | 4 | 7.4 | 8.6 | 1.07 |
| PolarClean | 17.1 | 8.7 | 7.5 | 9.8 | 1.22 |
| d-Camphor | 17.8 | 10.3 | 5.2 | 9.9 | 1.24 |
| Menthol | 16.7 | 3.7 | 7.6 | 10.8 | 1.35 |
| Methyl Lactate | 16.9 | 8.4 | 15.4 | 11.0 | 1.38 |
| Dimethyl Sulfoxide | 18.4 | 16.4 | 10.2 | 11.6 | 1.46 |
| Ethyl Lactate | 16 | 7.6 | 12.5 | 11.7 | 1.46 |
| d-Limonene | 17.2 | 1.8 | 4.3 | 11.9 | 1.48 |
| p-Cymene | 17.5 | 2.5 | 2.6 | 12.1 | 1.51 |

|  |  |  |  |  |  |
|---|---|---|---|---|---|
| Ethyl Acetate | 15.8 | 5.3 | 7.2 | 12.3 | 1.53 |
| Dimethyl Carbonate | 15.5 | 8.6 | 9.7 | 12.5 | 1.57 |
| γ-Butyrolactone (GBL) | 18 | 16.6 | 7.4 | 12.6 | 1.57 |
| n-Butyl Acetate | 15.8 | 3.7 | 6.3 | 12.8 | 1.60 |
| Propylene Carbonate | 20 | 18 | 4.1 | 13.2 | 1.65 |
| γ-Valerolactone (GVL) | 16.8 | 16.5 | 6.7 | 14.2 | 1.78 |
| (-)-α-Pinene | 16.4 | 1 | 1.9 | 14.7 | 1.83 |
| Ethylene Carbonate | 18 | 21.7 | 5.1 | 17.4 | 2.18 |

*Calculated using the HSPiP software available at https://www.hansen-solubility.com with SMILES: XO=C(OCC)C1=CC=C(C([O])=O)O1X

Supplementary Table 2. Juice properties before (feed) and after (permeate) clarification with PEF membranes in dead-end configuration.

| **Parameter** | **Unit** | **Apple juice** | | **Orange juice** | | **Pomegranate juice** | |
|---|---|---|---|---|---|---|---|
| | | **Feed** | **Permeate** | **Feed** | **Permeate** | **Feed** | **Permeate** |
| Color | $A_{420}$ | 0.714 | 0.39 | 0.221 | 0.1 | 0.25 | 0.237 |
| Clarity | $\%T_{625}$ | 95 | 100 | 98 | 100 | 99.5 | 100 |
| Turbidity | NTU | 33.8 | 0.07 | 48.2 | 0.12 | 45.8 | 1.5 |
| Soluble solids | °Brix | 8.2 | 8.1 | 3.0 | 2.8 | 11.2 | 11.1 |
| pH | - | 3.9 | 3.9 | 3.3 | 3.3 | 2.98 | 2.87 |

Supplementary Table 3. Pomegranate juice properties before (feed) and after (permeate) clarification with PEF, PES or PSf membranes in dead-end configuration.

| **Parameter** | **Unit** | **PEF** | | **PES** | | **PSf** | |
|---|---|---|---|---|---|---|---|
| | | **Feed** | **Permeate** | **Feed** | **Permeate** | **Feed** | **Permeate** |
| Color | $A_{420}$ | 0.25 | 0.237 | 0.274 | 0.256 | 0.25 | 0.226 |
| Clarity | $\%T_{625}$ | 99.5 | 100 | 96.6 | 98.6 | 99.5 | 100 |
| Turbidity | NTU | 45.8 | 1.5 | 21.7 | 2.91 | 45.8 | 1.33 |
| Soluble solids | °Brix | 11.2 | 11.1 | 11.4 | 11.2 | 11.2 | 11.1 |
| pH | - | 2.98 | 2.87 | 3.33 | 3.21 | 2.98 | 2.96 |

Supplementary Table 4. Pomegranate juice properties during clarification with a PEF membrane in cross-flow configuration.

| **Time (min)** | **Recovery (wt %)** | **Feed/Retentate** | | | **Permeate** | | |
|---|---|---|---|---|---|---|---|
| | | **Turbidity (NTU)** | **pH** | **°Brix** | **Turbidity (NTU)** | **pH** | **°Brix** |
| 0 | 0 | 29.8 | 3.07 | 10.8 | - | - | - |
| 40 | 6.33 | - | - | - | 2.45 | 3.11 | 10.5 |
| 178 | 21.67 | - | - | - | 2.15 | 3.1 | 10.6 |
| 256 | 28.33 | 25.9 | 3.14 | 10.8 | 3.35 | 3.12 | 10.6 |
| 380 | 37.33 | - | - | - | 8.43 | 3.12 | 10.6 |
| 475 | 43.33 | - | - | - | 7.79 | 3.08 | 10.6 |
| 605 | 50.00 | 88.6 | 3.08 | 10.4 | 7.27 | 3.09 | 10.7 |

Supplementary Table 5. Pomegranate juice properties during clarification with a commercial PES membrane in cross-flow configuration.

| **Time (min)** | **Recovery (wt %)** | **Feed/Retentate** | | | **Permeate** | | |
|---|---|---|---|---|---|---|---|
| | | **Turbidity (NTU)** | **pH** | **°Brix** | **Turbidity (NTU)** | **pH** | **°Brix** |
| 0 | 0 | 39 | 2.04 | 10.8 | - | - | - |
| 54 | 6.33 | - | - | - | 2.1 | 2.5 | 10.1 |
| 258 | 21.67 | - | - | - | 0.09 | 2.47 | 10.4 |
| 386 | 28.33 | 26.1 | 2.22 | 10.7 | 10.3 | 2.48 | 10.8 |
| 558 | 36.67 | - | - | - | 7.27 | 2.52 | 10.8 |
| 720 | 43.33 | - | 2.47 | 10.8 | 0.31 | 2.62 | 10.2 |
| 874 | 53.33 | 46.4 | 2.87 | 9.7 | 19.8 | 2.52 | 10.8 |

Supplementary Table 6. Description of the scenarios explored in the LCA study.

| Type of scenario | Nomenclature | Description |
|---|---|---|
| Thymol extraction technology | HD | Extraction of thyme essential oil by hydrodistillation within the thymol production process. |
| | SFE | Extraction of thyme essential oil with supercritical $CO_2$ within the thymol production process. |
| Non-solvent type | F-EtOH | Fossil-based ethanol as non-solvent in the membrane coagulation bath during membrane production. |
| | Bio-EtOH | Bioethanol as non-solvent in the membrane coagulation bath during membrane production. |
| Treatment of waste solvent and polymer from membrane fabrication | INC-ER | A combined efficiency of 40% was assumed for cogeneration of heat and power, with equal shares allocated to each output. Energy production was avoided by credit scheme. |
| | INC-NER | Incineration without energy recovery. |
| | WT-REC | Recycling approach. Reuse of the polymer residue and reintroduction of 80% of the ethanol in the coagulation bath (recovered by distillation), and incineration of the remaining solvent waste with energy recovery. |
| Energy geographical scope for membrane fabrication | GLO | Electricity and thermal energy from global average conditions in all processes and subprocesses. |
| | RNA | Electricity and thermal energy from North America dataset in the membrane production stage. All upstream processes kept as GLO. |
| | RER | Electricity and thermal energy from Europe dataset. All upstream processes kept as GLO. |
| | MER | Electricity from Middle East Region and thermal energy from Asia-Pacific Region. All upstream processes were kept as GLO. |

Supplementary Table 7. Description of the two types of general scenarios mentioned in this LCA study.

| Name of scenario | Description |
|---|---|
| Baseline | Scenario comprising SFE, F-EtOH, INC-ER, and GLO. |
| Optimal | Least carbon-intensive scenario, comprising SFE, Bio-EtOH, WT-REC, and GLO. |

Supplementary Table 8. Description of the subprocesses explored in the LCA study.

| Subprocess | Description |
|---|---|
| Membrane production | Energy associated with the production of the polymer membrane, excluding the materials production. For PEF membranes, it includes the preparation of the solvent mixture, the dope solution, and the membrane fabrication. |
| Polymer production | Production of the polymer utilized for membrane fabrication including all upstream processes. In the case of PEF, all steps during the PEF synthesis. |
| Solvent production | Production of the solvent used for polymer solubilization: addition of the production of vanillin and thymol for PEF membranes, and production of TFA for PET membranes. |
| Non-solvent production | Production of the non-solvent used in the coagulation bath: ethanol or bioethanol depending on the scenario. |
| Waste treatment | Treatment of waste solvent and polymer from membrane fabrication. In the recycling scenario, it was divided in two subprocesses: waste incineration with energy recovery and solvent distillation. |

Supplementary Table 9. Life Cycle Inventory of the production of 1 m$^2$ PEF membrane.
Primary data at the laboratory scale.

| Flow type | Name | Unit | Amount | Dataset/Source |
|---|---|---|---|---|
| Inputs | PEF | kg | 0.03568 | Built-in LCI (Supplementary Table 19) |
| | Thymol-vanillin DES | kg | 0.16272 | Built-in LCI (Supplementary Table 14) |
| | Ethanol | kg | 19.84042 | RoW: market for ethanol, without water (Ecoinvent 3.9.1.) |
| | Electricity (stirring, heating, fumehood) | kWh | 5.31195 | GLO: market group for electricity, medium voltage (Ecoinvent 3.9.1.) |
| Outputs | PEF membrane | m$^2$ | 1 (0.0339 kg) | Defined within the model |
| | PEF waste | kg | 0.00178 | Plastic (ground, unspecific) (Sphera) |
| | Solvent waste (ethanol, thymol, and vanillin) | kg | 16.00314 | Solvent [Hazardous waste for recovery] (Sphera) |
| | Ethanol vapor | kg | 4 | Ethanol [Group NMVOC to air] (Sphera) |

*Assumptions: 5 wt% membrane material stays in the casting knife denoted as PEF waste. 100 wt% of the thymol-vanillin solutions dissolve in ethanol with no reaction happening. 20% of ethanol vaporizes during the complete process. Materials quantities were based on experimental laboratory data. Electricity data was recorded with an energy meter connected to the heating plate and stirring plates. The fume hood energy consumption was calculated based on the manufacturer specifications (electrical power of 1.15 kW).

Supplementary Table 10. Life Cycle Inventory of the production of 1 kg of thymol-vanillin mixture. Primary data at the laboratory scale.

| Flow type | Name | Unit | Amount | Dataset/Source |
|---|---|---|---|---|
| Inputs | Thymol | kg | 0.79825 | Built-in LCI (Table S27) |
| | Vanillin | kg | 0.20175 | Built-in LCI (Table S25) |
| | Electricity (heating and stirring) | kWh | 0.02697 | GLO: market group for electricity, medium voltage (Ecoinvent 3.9.1.) |
| Outputs | Thymol-vanillin mixture | kg | 1.00000 | Defined within the model |

Supplementary Table 11. Life Cycle Inventory of the production of 1 m$^2$ PET membrane.
Adapted from Pulido et al.[5] with conditions for membrane M8 (10 wt% PET, 4 wt% PEG, coagulated in ethanol).

| Flow type | Name | Unit | Amount | Dataset/Source |
|---|---|---|---|---|
| Inputs | PET | kg | 0.03568 | GLO: market for polyethylene terephthalate, granulate, bottle grade (Ecoinvent 3.9.1)<br>US: Polyethylene terephthalate bottle grade granulate (PET) via PTA (partially biobased from sugar cane) (Sphera)<br>RoW: market for polyethylene terephthalate, granulate, bottle grade, recycled (Ecoinvent 3.9.1) |
| | Trifluoroacetic acid (TFA) | kg | 0.30688 | RoW: market for trifluoroacetic acid (Ecoinvent 3.9.1.) |
| | Polyethylene glycol (PEG) (1 kg mol-1) | kg | 0.01427 | RoW: market for triethylene glycol (Ecoinvent 3.9.1.) (used as proxy) |
| | Ethanol | L | 35.68421 | RoW: market for ethanol, without water (Ecoinvent 3.9.1.)<br>RoW: market for ethanol, without |

| | | | | |
|---|---|---|---|---|
| | | | | water, from fermentation, vehicle grade (Ecoinvent 3.9.1.) |
| | Electricity (fumehood, stirring) | kWh | 4.623 | GLO: market group for electricity, medium voltage (Ecoinvent 3.9.1.) |
| Outputs | PET membrane | $m^2$ | 1 (0.0339 kg) | Defined within the model |
| | PET waste | kg | 0.00178 | Plastic (ground, unspecific) (Sphera) |
| | Waste solvent (ethanol, TFA, and PEG) | kg | 36.00394 | Solvent [Hazardous waste for recovery] (Sphera) |
| | Ethanol vapor | kg | 7.137 | Ethanol [Group NMVOC to air] (Sphera) |

*Assumptions: same as for PEF membrane.

Supplementary Table 12. Life Cycle Inventory of the distillation of ethanol from the solvent waste generated during PEF membrane fabrication. Data obtained by calculations following the upscaling framework proposed by Piccinno et al.[3]

| Flow type | Name | Unit | Amount | Dataset/Source |
|---|---|---|---|---|
| Inputs | Solvent waste (ethanol, thymol, and vanillin) | kg | 1.25000 | Solvent [Hazardous waste for recovery] (Sphera) |
| | Cooling water | kg | 0.03375 | GLO: market group for tap water (Ecoinvent 3.9.1.) |
| | Thermal energy (distillation) | kWh | 0.46930 | ROW: Thermal energy from natural gas (Sphera) |
| | Electricity (pumping) | KJ | 0.12330 | GLO: market group for electricity, medium voltage (Ecoinvent 3.9.1.) |
| Outputs | Ethanol | kg | 1.00000 | RoW: market for ethanol, without water (Ecoinvent 3.9.1.) |
| | Solvent waste | kg | 0.25000 | Solvent [Hazardous waste for recovery] (Sphera) |
| | Water | kg | 0.03375 | Water (cooling water) [Operating materials] |

*Assumptions: No reflux was considered for the energy calculations given the large difference between the mixture components' vapor pressure.

The thermal energy required for distillation was calculated according to eq. S1:

$$Q_{dist} = \frac{Q_{heat} + Q_{vap}}{\eta_{heat} - 0.1} = \frac{C_p(m_{mix})(T_d - T_0) + \Delta H_{vap}(m_{dist})}{\eta_{heat} - 0.1} \qquad \text{Eq. S1}$$

where $C_p$ is the specific heat of the mixture (2.51KJ/kg K); $m_{mix}$ is the mass of the mixture, $T_r$ is the distillation temperature (78.4°C); $T_0$ is the initial temperature (20 °C), $\Delta H_{vap}$ is the volatile solvent heat of vaporization (837.023 KJ/kg); $m_{dist}$ is the mass of the distillate (80% of ethanol in the mixture), and $\eta_{heat}$ is the efficiency of the heating element (0.7 assumed).

Supplementary Table 13. Life Cycle Inventory of incineration of the remaining solvent after distillation.

| Flow type | Name | Unit | Amount | Dataset/Source |
|---|---|---|---|---|
| Inputs | Solvent for incineration | kg | 1.0000 | Defined within the model |
| Outputs | Electricity | MJ | 5.4 | GLO: market group for electricity, medium voltage (Ecoinvent 3.9.1.) (Credit) |
| | Steam | MJ | 5.4 | ROW: process steam from natural gas (Ecoinvent 3.9.1.) (credit) |
| | Carbon dioxide | kg | 1.925 | Carbon dioxide [Inorganic emissions to air (group VOC)] (Sphera) |
| | Methane | kg | 3.01E-005 | Methane [Organic emissions to air] (Sphera) |
| | Nitrous oxide | kg | 3.35E-006 | Nitrous oxide (laughing gas) [Inorganic emissions to air] (Sphera) |

*Assumptions: LHV of 27 MJ kg$^{-1}$ (ethanol). 40% conversion efficiency during energy recovery. 50% of generated energy as electricity and 50% as thermal energy. Impact mitigation by credit scheme.

Supplementary Table 14. Life Cycle Inventory of incineration of PEF residue.

| **Flow type** | **Name** | **Unit** | **Amount** | **Dataset/Source** |
|---|---|---|---|---|
| Inputs | PEF waste | kg | 1.0000 | Defined within the model |
| Outputs | Electricity | MJ | 2.516 | GLO: market group for electricity, medium voltage (Ecoinvent 3.9.1.) (Credit) |
| | Steam | MJ | 4.505 | ROW: process steam from natural gas (Ecoinvent 3.9.1.) (credit) |
| | Carbon dioxide | kg | 1.582 | Carbon dioxide [Inorganic emissions to air (group VOC)] (Sphera) |
| | Methane | kg | 0.0002 | Methane [Organic emissions to air] (Sphera) |
| | Nitrous oxide | kg | 0.0001 | Nitrous oxide (laughing gas) [Inorganic emissions to air] (Sphera) |

*Assumptions: LHV of 17 MJ $kg^{-1}$ (PEF)[6]. 40% conversion efficiency during energy recovery. 36% of generated energy as electricity and 64% as thermal energy. Impact mitigation by credit scheme.

Supplementary Table 15. Life Cycle Inventory of the synthesis of 1 kg of PEF. Primary lab-scale data adapted to the production of 8056.3285 kg of PEF following the upscaling framework proposed by Piccinno et al.[3]

| **Flow type** | **Name** | **Unit** | **Amount** | **Dataset/Source** |
|---|---|---|---|---|
| Inputs | 2,5-Furandicarboxylic acid (FDCA) | kg | 0.90186 | Built-in LCI (Table S21) |
| | Ethylene glycol (EG) | kg | 0.75311 | RER: ethylene glycol (from ethane and oxygen via EO, Sphera) |
| | Antimony trioxide ($Sb_2O_3$) | kg | 0.00066 | GLO: market group for antimony (Ecoinvent 3.9.1.) |
| | Methanol | kg | 1.00000 | GLO: market for methanol (Ecoinvent 3.9.1.) |
| | Electricity | kWh | 0.03039 | GLO: market group for electricity, medium voltage (Ecoinvent 3.9.1.) |
| | Thermal energy | kWh | 0.25935 | ROW: Thermal energy from natural gas (Sphera) |
| Outputs | PEF | kg | 1.00000 | Defined within the model |
| | Water vapor | kg | 0.19777 | Water (evapotranspiration) [Inorganic emissions to air] (Sphera) |
| | Solvent waste (methanol and unreacted substances) | kg | 1.45787 | Solvent [Hazardous waste for recovery] (Sphera) |

*Assumptions: The reaction yield was 95%. The process consisted of five steps: esterification, polycondensation, polymer milling, rinsing and filtering, and drying. The catalyst integrated with the polymer. The upscaling framework considered the production of 8056.3285 kg of PEF in a reactor with a volume of 11 m$^3$. The resulting process flows from the upscaling calculations are shown in Fig. S27.

Calculations for each unit process were as follows:

1. **Esterification**. Heating energy (temperature increase and compensation of heat losses) and stirring energy.

$$Q_{react} = \frac{Q_{heat} + Q_{loss}}{\eta_{heat}} = \frac{[(C_{p(FDCA)}) * m_{FDCA} + (C_{p(EG)}) * m_{EG}](T_r - T_0) + A\left(\frac{k_a}{s}\right)(T_{r2} - T_{out})t}{\eta_{heat}}$$

Due to lack of data on FDCA, the specific heat of terephthalic acid was used in the energy calculations. ($C_{pTA}$ = 1201.46 J/kg· K) (specific heat of terephthalic acid); $C_{pEG}$ = 1778.7 J/kg·K (specific heat of ethylene glycol); $T_r$ = 533.15 K (reaction temperature); $T_0$ = 293.15 K (initial temperature); $m_{mix}$ = 1.42 kg (mass of mixture); $A$ = 0.0476 m$^2$ (surface area of the reactor); $k_a$ = 0.042 W/m·K (thermal conductivity of insulation material); s = 1 cm (thickness of insulator); $T_{out}$ = 293.15 K (temperature outside reactor); $(T_{r2} - T_{out})*t$ was calculated for the different reaction steps described in the Materials and Methods section; $\eta_{heat}$ = 0.7 (efficiency of heating element).

$$E_{stirring}[J] = \frac{N_P \cdot \rho_{mix} \cdot N^3 d^5 \cdot t}{\eta_{stir}}$$

$N_P$ = 0.79 (dimensionless number related to power number of an impeller stirrer); $\rho_{mix}$ = 1.3325 g/cm$^3$ (density of the reaction mixture); $N$ = 0.658 s$^{-1}$ (rotational speed of agitator); $d$ = 0.803 m (impeller diameter); $t$ = 2.5 h (reaction time); and $\eta_{stir}$ = 90% (efficiency of agitator).

2. **Polycondensation**. Heating energy (temperature increase and compensation of heat losses) and stirring energy. Calculated similarly to esterification.
3. Milling. Used energy for grinding as an approximation.
   $E_{milling} = 16\ kWh\ (ton\ of\ material)$
4. **Rinsing with methanol**. Pumping energy calculated assuming 1 kg of methanol per kg of polymer.

   $E_{pumping} = 55\ J\ (kg\ of\ material)$

5. **Filtration**.
   $E_{filtration} = 10\ kWh\ (ton\ of\ material)$

6. **Drying.** Assumed 10 wt% of the weight of the wet polymer is methanol.

$$Q_{dry} = \frac{(C_{p(liq)}) * m_{liq} * (T_{boil} - T_0) + \Delta H_{vap}(m_{vap})}{\eta_{dry}}$$

where $C_p$ (specific heat of the solvent in liquid state); $m_{liq}$ = 938.15 kg (mass of methanol in the wet polymer), $T_{boil}$ = 64.7 °C (boiling point of methanol); $T_0$ = 20 °C (room temperature), $\Delta H_{vap}$ = 1165 KJ/kg (heat of vaporization of methanol); $m_{vap}$ = 938.115 kg (mass of methanol), and $\eta_{dry}$ = 0.8 (drier efficiency).

Supplementary Table 16. Life Cycle Inventory of the distillation of ethanol from the solvent waste generated during PEF synthesis. Data obtained by calculations following the upscaling framework proposed by Piccinno et al.[3]

| **Flow type** | **Name** | **Unit** | **Amount** | **Dataset/Source** |
|---|---|---|---|---|
| Inputs | Methanol waste (MeOH, EG, FDCA) | kg | 1.82234 | Solvent [Hazardous waste for recovery] (Sphera) |
| | Cooling water | kg | 0.04920 | GLO: market group for tap water (Ecoinvent 3.9.1) |
| | Thermal energy (distillation) | MJ | 0.33941 | ROW: Thermal energy from natural gas (Sphera) |
| | Electricity (pumping) | KJ | 0.15523 | GLO: market group for electricity, medium voltage (Ecoinvent 3.9.1.) |
| Outputs | Methanol (99%) | kg | 1.00000 | Defined within the model |
| | Solvent waste | kg | 0.36447 | Solvent [Hazardous waste for recovery] (Sphera) |
| | Water | kg | 0.04920 | Water (tap water) [Operating materials] (Sphera) |

*Assumptions: No reflux was considered for the energy calculations given the large difference between the mixture components' vapor pressure. The thermal energy required for distillation was calculated similarly to ethanol considering the solvent volume obtained from the upscaled PEF synthesis. The following values were used: $C_p$ = 79.5 J/mol K, $m_{mix}$ = 11745.08, $T_d$ = 65°C), $T_0$ = 20 °C, $\Delta H_{vap}$ = 37.34 KJ/mol, $m_{dist}$ = 6445.0628 kg (80% of methanol in the mixture), and $\eta_{heat}$ = 0.7.

Supplementary Table 17. Life Cycle Inventory of the synthesis of 1 kg of 2,5-furan dicarboxylic acid (FDCA) from hydroxymethyl furfural. Adapted from Bello et al.[7]

| Flow type | Name | Unit | Amount | Dataset/Source |
|---|---|---|---|---|
| Inputs | Hydroxymethyl furfural | kg | 0.8200 | Built-in LCI (Table S22) |
| | Acetic acid | kg | 3.6700 | RoW: market for acetic acid (Ecoinvent 3.9.1.) |
| | Water | kg | 5.5000 | RoW: market for tap water (Ecoinvent 3.9.1.) |
| | $PtZrO_2$ catalyst | kg | 0 | Reuse of the catalyst was considered |
| | Electricity | kWh | 15.8470 | GLO: market group for electricity, medium voltage (Ecoinvent 3.9.1.) |
| | Thermal energy | kWh | 14.0800 | ROW: Thermal energy from natural gas (Sphera) |
| | Cooling energy | kWh | 17.0600 | GLO: market for cooling energy (Ecoinvent 3.9.1.) |
| Outputs | FDCA | kg | 1.0000 | Defined within the model |
| | Water vapour | kg | 0.3200 | Water (evapotranspiration) [Inorganic emissions to air] (Sphera) |
| | Acetic acid to air | kg | 0.2300 | Acetic acid (Group NMVOC to air] (Sphera) |
| | Nitrogen | kg | 16.6200 | Nitrogen, total [Inorganic emissions to air] (Sphera) |
| | Oxygen | kg | 4.6400 | Oxygen [Inorganic emissions to air] (Sphera) |
| | Wastewater | $m^3$ | 0.0088 | Wastewater [Production residues in life cycle] (Sphera) |

Supplementary Table 18. Life Cycle Inventory of the synthesis of 1 kg of hydroxymethyl furfural from wood biomass. Adapted from Bello et al.[7]. Economic allocation was applied to this production system.

| Flow type | Name | Unit | Amount | Dataset/Source |
|---|---|---|---|---|
| Inputs | Biomass feedstock | kg | 0.04647 | RoW: hardwood forestry, birch, sustainable forest management (Ecoinvent 3.9.1.) |
| | Water | $m^3$ | 29.77920 | GLO: market group for tap water (Ecoinvent 3.9.1) |
| | Sulfuric acid | kg | 0.00319 | RoW: market for sulfuric acid (Ecoinvent 3.9.1.) |
| | Dimethyl sulfoxide | kg | 0.00881 | GLO: market for dimethyl sulfoxide (Ecoinvent 3.9.1) |
| | Dichloromethane | kg | 0.10311 | RoW: market for dichloromethane (Ecoinvent 3.9.1.) |
| | Natural gas | kg | 0.00957 | RoW: market for natural gas, high pressure (Ecoinvent 3.9.1.) |
| | Electricity | kWh | 0.03538 | GLO: market group for electricity, medium voltage (Ecoinvent 3.9.1.) |
| | Thermal energy | kWh | 0.05942 | ROW: Thermal energy from natural gas (Sphera) |
| Outputs | Hydroxymethyl furfural | kg | 1.00000 | Defined within the model |
| | Wastewater | $m^3$ | 0.33599 | Wastewater [Production residues in life cycle] (Sphera) |
| | $CO_2$ fossil | kg | 0.00805 | Carbon dioxide [Inorganic emissions to air] (Sphera) |
| | $CO_2$ biogenic | kg | 0.02627 | Carbon dioxide (biotic) [Inorganic emissions to air] (Sphera) |

**Supplementary Table 19. Life Cycle Inventory of the production of 1 kg of vanillin from kraft lignin.** Adapted from Sánchez et al.[8] (scenario with $CO_2$). Mass allocation was applied to this production system considering vanillin, phenolic compounds, and acetic acid as valuable products produced.

| **Flow type** | **Name** | **Unit** | **Amount** | **Dataset/Source** |
|---|---|---|---|---|
| Inputs | Lignin feed for vanillin production | kg | 22.70000 | Built-in LCI (Table S25) |
| | PODIC 0.2 M | kg | 3813.79000 | Built-in LCI (Table S24) |
| | Ethanol | kg | 0.02613 | RoW: market for ethanol, without water (Ecoinvent 3.9.1.) |
| | Acetic acid | kg | 0.69322 | GLO: market for acetic acid, without water, in 98% solution state (Ecoinvent 3.9.1.) |
| | Carbon dioxide | kg | 3.58000 | RoW market for carbon dioxide, liquid (Ecoinvent 3.9.1.) |
| | Electricity | kWh | 1.96734 | GLO: market group for electricity, medium voltage (Ecoinvent 3.9.1.) |
| | Thermal energy | kWh | 198.07000 | ROW: Thermal energy from natural gas (Sphera) |
| | Cooling energy | kWh | 51.73000 | GLO: market for cooling energy (Ecoinvent 3.9.1.) |
| Outputs | Vanillin | kg | 1.00000 | Defined within the model |
| | Phenolic compunds | kg | 330.40000 | Defined within the model |
| | Acetic acid | kg | 0.96000 | Acetic acid [Organic intermediate product] (Sphera) |
| | Water vapour | kg | 1.70034 | Water (evapotranspiration) [Inorganic emissions to air] (Sphera) |
| | Hydrogen | kg | 0.73536 | Hydrogen [Inorganic emissions to air] (Sphera) |
| | Carbon dioxide | kg | 5.69152 | Carbon dioxide [Inorganic emissions to air] (Sphera) |
| | Oxygen | kg | 6.19746 | Oxygen [Inorganic emissions to air] (Sphera) |
| | Alcohols | kg | 0.00169 | Alcohols (unspec.) [Group NMVOC to |

| | | | | |
|---|---|---|---|---|
| | | | | air] (Sphera) |
| | Wastewater | $m^3$ | 174.70573 | Wastewater [Production residues in life cycle] (Sphera) |

Supplementary Table 20. Life Cycle Inventory of the production of 1 kg of PODIC 0.2 M for vanillin production. Adapted from Sánchez et al.[8] (scenario with $CO_2$).

| **Flow type** | **Name** | **Unit** | **Amount** | **Dataset/Source** |
|---|---|---|---|---|
| Inputs | Soda ash | kg | 0.01575 | GLO: market for soda ash, dense (Ecoinvent 3.9.1.) |
| | Tap water | kg | 0.11388 | GLO: market group for tap water (Ecoinvent 3.9.1) |
| | Electricity (reactor and pumping) | kWh | 0.07744 | GLO: market group for electricity, medium voltage (Ecoinvent 3.9.1.) |
| | Cooling energy | kWh | 0.09872 | GLO: market for cooling energy (Ecoinvent 3.9.1.) |
| Outputs | PODIC 0.2 M | kg | 1.00000 | Defined within the model |

Supplementary Table 21. Life Cycle Inventory of the production of 1 kg of lignin feed for vanillin production. Adapted from Sánchez et al.[8] (scenario with $CO_2$).

| Flow type | Name | Unit | Amount | Dataset/Source |
|---|---|---|---|---|
| Inputs | Kraft Lignin | kg | 1.00000 | Built-in LCI (Table S26) |
| | Carbon dioxide liquid | kg | 0.30000 | RoW: market for carbon dioxide, liquid (Ecoinvent 3.9.1.) |
| | Sulfuric acid | kg | 0.23000 | RoW: market for sulfuric acid (Ecoinvent 3.9.1.) |
| | Sodium hydroxide (50% NaOH) | kg | 0.10700 | GLO: market for sodium hydroxide, without water, in 50% solution state (Ecoinvent 3.9.1.) |
| | Limestone, crushed | kg | 0.23000 | RoW: market for limestone, crushed, for mill (Ecoinvent 3.9.1.) |
| | Tap water | kg | 4.85000 | GLO: market group for tap water (Ecoinvent 3.9.1) |
| | Thermal energy | MJ | 31.50000 | ROW: Thermal energy from natural gas (Sphera) |
| | Electricity | kWh | 0.01000 | GLO: market group for electricity, medium voltage (Ecoinvent 3.9.1.) |
| Outputs | **Lignin feed for vanillin production** | **kg** | **1.00000** | Defined within the model |
| | Sulfur to air | kg | 0.00105 | Sulfur to air |
| | Nitrogen oxides to air | kg | 0.00200 | Nitrous oxide (laughing gas) [Inorganic emissions to air] (Sphera) |
| | Sodium sulfate to air | kg | 0.00080 | Sodium sulfate |
| | Sodium carbonate to air | kg | 0.00080 | Sodium carbonate |

Supplementary Table 22. Life Cycle Inventory of the production of 1 kg of kraft lignin. Adapted from Moretti et al.[9] (conditions for Avantium).

| Flow type | Name | Unit | Amount | Dataset/Source |
|---|---|---|---|---|
| Inputs | Wood chips | kg | 3.00000 | RoW: hardwood forestry, birch, sustainable forest management (Ecoinvent 3.9.1.) |
| | Hydrochloric acid | kg | 0.30000 | RoW: market for hydrochloric acid, without waster, in 30% solution state (Ecoinvent 3.9.1.) |
| | Process water | kg | 24.60000 | GLO: market group for tap water (Ecoinvent 3.9.1) |
| | Sodium hydroxide | kg | 0.10000 | RER: Sodium hydroxide (caustic soda) mix 100% (Sphera) |
| | Active carbon | kg | 0.00050 | GLO: market for activated carbon, granular (Ecoinvent 3.9.1) |
| | Electricity | kWh | 0.90000 | GLO: market group for electricity, medium voltage (Ecoinvent 3.9.1.) |
| | Natural gas for heat/steam | MJ | 52.26700 | ROW: Thermal energy from natural gas (Sphera) |
| | Cooling energy | MJ | 0.02160 | GLO: market group for cooling energy (Ecoinvent 3.9.1.) |
| Outputs | Kraft lignin | kg | 1.00000 | Defined within the model |
| | Wastewater | m3 | 0.01500 | Wastewater [Production residues in life cycle] (Sphera) |

Supplementary Table 23. Life Cycle Inventory of the production of 1 kg of thymol by crystallization from thyme essential oil. Adapted from US Patent 2020/0385326A1.[10]

| Flow type | Name | Unit | Amount | Dataset/Source |
|---|---|---|---|---|
| Inputs | Thyme essential oil | kg | 2.38182 | Built-in LCI (Table S28 and 29) |
| | Hexane | kg | 1.71688 | GLO: market for hexane (Ecoinvent 3.9.1.) |
| | Cooling energy | KJ | 185.99740 | GLO: market for cooling energy (Ecoinvent 3.9.1.) |
| Outputs | Thymol | kg | 1.00000 | Defined within the model |
| | Liquid waste | kg | 3.09870 | Liquid hazardous waste [Hazardous waste] (Sphera) |

Supplementary Table 24. Life Cycle Inventory of the extraction of thyme essential oil by hydrodistillation. Adapted from Limam et al.[11] (eucalyptus essential oil extraction as proxy).

| Flow type | Name | Unit | Amount | Dataset/Source |
|---|---|---|---|---|
| Inputs | Thyme leaves (fresh) | kg | 134.70437 | Built-in LCI (Table S30) |
| | Water | kg | 12.11440 | GLO: market group for tap water (Ecoinvent 3.9.1) |
| | Thermal energy | MJ | 2.37156 | ROW: Thermal energy from natural gas (Sphera) |
| | Electricity | MJ | 37.72494 | GLO: market group for electricity, medium voltage (Ecoinvent 3.9.1.) |
| Outputs | Thyme essential oil | kg | 1.00000 | Defined within the model |
| | Water vapor | kg | 74.06812 | Water (evapotranspiration) [Inorganic emissions to air] |
| | Biomass waste | kg | 30.32940 | Biowaste [Waste for recovery] |
| | Hydrosol | kg | 41.42124 | Defined within the model |

*Assumptions: Yield of 1.65 wt% from dry leaves based on Gavrila, et al.[12] Mass allocation was applied considering thymol and hydrosol as the valuable products from the whole thymol production process (hydrodistillation + crystallization).

Supplementary Table 25. Life Cycle Inventory of the extraction of thyme essential oil by supercritical fluid extraction. Adapted from Limam et al.[11] (eucalyptus essential oil extraction as proxy).

| Flow type | Name | Unit | Amount | Dataset/Source |
|---|---|---|---|---|
| Inputs | Thyme leaves (fresh) | kg | 67.15691 | Built-in LCI (Table S30) |
| | $CO_2$ | kg | 0.29533 | RoW: market for carbon dioxide, liquid (Ecoinvent 3.9.1.) |
| | Thermal energy | MJ | 3.24858 | ROW: Thermal energy from natural gas (Sphera) |
| | Electricity | MJ | 4.23496 | GLO: market group for electricity, medium voltage (Ecoinvent 3.9.1.) |
| Outputs | Thyme essential oil | kg | 1.00000 | Defined within the model |
| | $CO_2$ emissions | kg | 0.29533 | Carbon dioxide [Inorganic emissions to air] |
| | Water vapor | kg | 43.53091 | Water (evapotranspiration) [Inorganic emissions to air] |
| | Biomass waste | kg | 22.62600 | Biowaste [Waste for recovery] |

*Assumptions: Yield of 3.31 wt% from dry leaves based on Bermejo, et al.[13].

Supplementary Table 26. Life Cycle Inventory of the cultivation of thyme. Adapted from De Falco et al.[14]

| Flow type | Name | Unit | Amount | Dataset/Source |
|---|---|---|---|---|
| Inputs | Diesel oil | kg | 0.03188 | RER: Diesel mix at filling station (100% fossil) (Sphera) |
| | Lubricants | kg | 0.00065 | RoW: lubricating oil production (Ecoinvent 3.9.1.) |
| | Phosphorous pentoxide | kg | 0.00976 | US: Phosphorous fertilizer, production mix, at plan (Sphera) |
| | Nitrogen | kg | 0.00781 | US: Nitrogen fertilizer, production mix, at plant (Sphera) |
| | Irrigation water | $m^3$ | 0.05921 | GLO: market group for tap water (Ecoinvent 3.9.1) |
| | Land use | $m^2$ yr | 1.58730 | Agriculture [Occupation] |
| | Seedlings | pcs | 16 | GLO: market for eucalyptus seedling, for planting (Ecoinvent 3.9.1) (proxy) |
| Outputs | Fresh thyme | kg | 1.00000 | Defined within the model |

*Assumptions: yield of 6.3 ton of fresh thyme $ha^{-1}$ $yr^{-1}$. 10 seedlings planted per $m^2$.

Supplementary Table 27. Environmental impacts of thymol extraction with hydrodistillation or supercritical fluid extraction technologies. The functional unit is 1 kg of thymol produced.

| **Environmental impact category** | **Thymol production** | |
|---|---|---|
| | **Hydrodistillation** | **Supercritical fluid extraction** |
| GWP, excl biogenic carbon [kg $CO_2$ eq.] | 45.27 | 17.36 |
| GWP, incl biogenic carbon [kg $CO_2$ eq.] | -70.99 | -39.91 |
| Fine Particulate Matter Formation [kg PM2.5 eq.] | 0.09 | 0.03 |
| Fossil depletion [kg oil eq.] | 26.90 | 11.99 |
| Freshwater consumption [$m^3$] | 0.25 | 0.07 |
| Freshwater ecotoxicity [kg 1,4 DB eq.] | 0.15 | 0.06 |
| Freshwater eutrophication [kg P eq.] | 0.08 | 0.04 |
| Human toxicity, cancer [kg 1,4-DB eq.] | 3.25 | 1.43 |
| Human toxicity, non-cancer [kg 1,4-DB eq.] | 21.81 | 9.12 |
| Ionizing Radiation [kBq Co-60 eq. to air] | 2.41 | 0.41 |
| Land use [Annual crop eq.·y] | 510.06 | 254.22 |
| Marine ecotoxicity [kg 1,4-DB eq.] | 0.29 | 0.12 |
| Marine eutrophication [kg N eq.] | 0.00 | 0.00 |
| Metal depletion [kg Cu eq.] | 0.06 | 0.03 |
| Photochemical Ozone Formation, Ecosystems [kg NOx eq.] | 0.13 | 0.05 |
| Photochemical Ozone Formation, Human Health [kg NOx eq.] | 0.13 | 0.05 |
| Stratospheric Ozone Depletion [kg CFC-11 eq.] | 0.00 | 0.00 |
| Terrestrial Acidification [kg $SO_2$ eq.] | 0.22 | 0.09 |
| Terrestrial ecotoxicity [kg 1,4-DB eq.] | 189.16 | 95.87 |

Supplementary Table 28. Environmental impacts of the production of 1 m$^2$ of PEF membrane with hydrodistillation or supercritical fluid extraction as technologies for thymol extraction. The remaining parameters were kept as the baseline.

| **Environmental impact category** | **PEF membrane fabrication** | |
|---|---|---|
| | **Hydrodistillation for thymol extraction** | **Supercritical fluid extraction for thymol extraction** |
| GWP, excl biogenic carbon [kg $CO_2$ eq.] | 55.35 | 51.73 |
| GWP, incl biogenic carbon [kg $CO_2$ eq.] | 40.26 | 44.30 |
| Fine Particulate Matter Formation [kg PM2.5 eq.] | 0.03 | 0.02 |
| Fossil depletion [kg oil eq.] | 21.53 | 19.60 |
| Freshwater Consumption [m$^3$] | -0.04 | -0.06 |
| Freshwater ecotoxicity [kg 1,4 DB eq.] | 0.11 | 0.10 |
| Freshwater Eutrophication [kg P eq.] | 0.02 | 0.02 |
| Human toxicity, cancer [kg 1,4-DB eq.] | 2.76 | 2.52 |
| Human toxicity, non-cancer [kg 1,4-DB eq.] | 13.21 | 11.56 |
| Ionizing Radiation [kBq Co-60 eq. to air] | -0.88 | -1.14 |
| Land use [Annual crop eq.·y] | 66.61 | 33.38 |
| Marine ecotoxicity [kg 1,4-DB eq.] | 0.20 | 0.18 |
| Marine eutrophication [kg N eq.] | 0.00 | 0.00 |
| Metal depletion [kg Cu eq.] | 0.10 | 0.10 |
| Photochemical Ozone Formation, Ecosystems [kg NOx eq.] | 0.89 | 0.88 |
| Photochemical Ozone Formation, Human Health [kg NOx eq.] | 0.58 | 0.57 |
| Stratospheric Ozone Depletion [kg CFC-11 eq.] | 0.00 | 0.00 |
| Terrestrial Acidification [kg $SO_2$ eq.] | 0.12 | 0.11 |
| Terrestrial ecotoxicity [kg 1,4-DB eq.] | 102.46 | 90.34 |

Supplementary Table 29. Environmental impacts of the production of 1 m$^2$ of PEF membrane under the baseline scenario (hydrodistillation, fossil-based ethanol, incineration with energy recovery, and global raw materials production and energy mix).

| **Environmental impact category** | **PEF membrane fabrication** | **Polymer production** | **Solvent production** | **Non- solvent production** | **Waste incineration with energy recovery** | **Total** |
|---|---|---|---|---|---|---|
| GWP, excl biogenic carbon [kg $CO_2$ eq.] | 3.92 | 0.95 | 2.31 | 38.27 | 6.27 | 51.73 |
| GWP, incl biogenic carbon [kg $CO_2$ eq.] | 3.94 | 0.95 | -5.16 | 38.35 | 6.22 | 44.30 |
| Fine Particulate Matter Formation [kg PM2.5 eq.] | 0.01 | 0.00 | 0.00 | 0.05 | -0.04 | 0.02 |
| Fossil depletion [kg oil eq.] | 1.40 | 0.40 | 1.56 | 24.96 | -8.72 | 19.60 |
| Freshwater Consumption [m$^3$] | 0.03 | 0.01 | 0.01 | 0.01 | -0.12 | -0.06 |
| Freshwater ecotoxicity [kg 1,4 DB eq.] | 0.01 | 0.00 | 0.01 | 0.13 | -0.05 | 0.10 |
| Freshwater Eutrophication [kg P eq.] | 0.00 | 0.00 | 0.00 | 0.02 | -0.01 | 0.02 |
| Human toxicity, cancer [kg 1,4-DB eq.] | 0.20 | 0.05 | 0.19 | 2.87 | -0.79 | 2.52 |
| Human toxicity, non-cancer [kg 1,4-DB eq.] | 1.24 | 0.31 | 1.19 | 14.30 | -5.48 | 11.56 |
| Ionizing Radiation [kBq Co-60 eq. to air] | 0.47 | 0.07 | 0.05 | 0.34 | -2.07 | -1.14 |
| Land use [Annual crop eq.·y] | 0.05 | 0.01 | 33.03 | 0.52 | -0.23 | 33.38 |
| Marine ecotoxicity [kg 1,4-DB eq.] | 0.02 | 0.00 | 0.02 | 0.21 | -0.07 | 0.18 |
| Marine eutrophication [kg N eq.] | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Metal depletion [kg Cu eq.] | 0.00 | 0.00 | 0.00 | 0.11 | -0.01 | 0.10 |
| Photochemical Ozone Formation, Ecosystems [kg NOx eq.] | 0.80 | 0.00 | 0.01 | 0.11 | -0.05 | 0.88 |
| Photochemical Ozone Formation, Human Health [kg NOx eq.] | 0.50 | 0.00 | 0.01 | 0.10 | -0.05 | 0.57 |
| Stratospheric Ozone Depletion [kg CFC-11 eq.] | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Terrestrial Acidification [kg $SO_2$ eq.] | 0.01 | 0.00 | 0.01 | 0.14 | -0.06 | 0.11 |
| Terrestrial ecotoxicity [kg 1,4-DB eq.] | 3.91 | 2.58 | 12.48 | 87.33 | -15.98 | 90.34 |

Supplementary Table 30. Environmental impacts of the production of 1 m$^2$ of fossil PET membrane. Parameters were fossil-based ethanol, incineration with energy recovery, and global raw materials production and energy mix.

| **Environmental impact category** | **Fossil PET membrane fabrication** | **Polymer production** | **Solvent production** | **Non- solvent production** | **Waste incineration with energy recovery** | **Total** |
|---|---|---|---|---|---|---|
| GWP, excl biogenic carbon [kg $CO_2$ eq.] | 3.37 | 0.11 | 2.74 | 68.84 | 14.11 | 89.18 |
| GWP, incl biogenic carbon [kg $CO_2$ eq.] | 3.38 | 0.11 | 2.75 | 68.98 | 13.99 | 89.21 |
| Fine Particulate Matter Formation [kg PM2.5 eq.] | 0.01 | 0.00 | 0.01 | 0.08 | -0.08 | 0.02 |
| Fossil depletion [kg oil eq.] | 1.21 | 0.06 | 1.00 | 44.89 | -19.62 | 27.54 |
| Freshwater Consumption [m$^3$] | 0.02 | 0.00 | 0.06 | 0.02 | -0.26 | -0.16 |
| Freshwater ecotoxicity [kg 1,4 DB eq.] | 0.01 | 0.00 | 0.01 | 0.23 | -0.12 | 0.14 |
| Freshwater Eutrophication [kg P eq.] | 0.00 | 0.00 | 0.00 | 0.04 | -0.02 | 0.02 |
| Human toxicity, cancer [kg 1,4-DB eq.] | 0.19 | 0.01 | 0.34 | 5.16 | -1.77 | 3.95 |
| Human toxicity, non-cancer [kg 1,4-DB eq.] | 1.06 | 0.05 | 2.15 | 25.72 | -12.34 | 16.65 |
| Ionizing Radiation [kBq Co-60 eq. to air] | 0.40 | 0.00 | 0.22 | 0.61 | -4.65 | -3.42 |
| Land use [Annual crop eq.·y] | 0.05 | 0.00 | 0.06 | 0.94 | -0.53 | 0.52 |
| Marine ecotoxicity [kg 1,4-DB eq.] | 0.02 | 0.00 | 0.03 | 0.38 | -0.16 | 0.27 |
| Marine eutrophication [kg N eq.] | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Metal depletion [kg Cu eq.] | 0.00 | 0.00 | 0.02 | 0.19 | -0.03 | 0.18 |
| Photochemical Ozone Formation, Ecosystems [kg NOx eq.] | 1.43 | 0.00 | 0.01 | 0.20 | -0.11 | 1.53 |
| Photochemical Ozone Formation, Human Health [kg NOx eq.] | 0.89 | 0.00 | 0.01 | 0.19 | -0.11 | 0.97 |
| Stratospheric Ozone Depletion [kg CFC-11 eq.] | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Terrestrial Acidification [kg $SO_2$ eq.] | 0.01 | 0.00 | 0.01 | 0.25 | -0.13 | 0.14 |
| Terrestrial ecotoxicity [kg 1,4-DB eq.] | 3.71 | 0.53 | 23.04 | 157.08 | -35.95 | 148.41 |

Supplementary Table 31. Environmental impacts of the production of 1 $m^2$ of PET membrane from different PET types. Parameters were fossil-based ethanol, incineration with energy recovery, and global raw materials production and energy mix.

| **Environmental impact category** | **Fossil PEF membrane** | **Recycled PET** | **Partially biobased PET** |
|---|---|---|---|
| GWP, excl biogenic carbon [kg $CO_2$ eq.] | 89.1783 | 89.1079 | 89.17 |
| GWP, incl biogenic carbon [kg $CO_2$ eq.] | 89.2095 | 89.14213 | 89.19 |
| Fine Particulate Matter Formation [kg PM2.5 eq.] | 0.016047 | 0.015977 | 0.02 |
| Fossil depletion [kg oil eq.] | 27.53959 | 27.48943 | 27.53 |
| Freshwater Consumption [$m^3$] | -0.15793 | -0.15905 | -0.16 |
| Freshwater ecotoxicity [kg 1,4 DB eq.] | 0.140411 | 0.140139 | 0.14 |
| Freshwater Eutrophication [kg P eq.] | 0.021858 | 0.021848 | 0.02 |
| Human toxicity, cancer [kg 1,4-DB eq.] | 3.946625 | 3.941063 | 3.94 |
| Human toxicity, non-cancer [kg 1,4-DB eq.] | 16.65411 | 16.61871 | 16.62 |
| Ionizing Radiation [kBq Co-60 eq. to air] | -3.42266 | -3.42485 | -3.43 |
| Land use [Annual crop eq.·y] | 0.519642 | 0.519662 | 0.57 |
| Marine ecotoxicity [kg 1,4-DB eq.] | 0.265714 | 0.265231 | 0.26 |
| Marine eutrophication [kg N eq.] | 0.000739 | 0.000743 | 0.00 |
| Metal depletion [kg Cu eq.] | 0.181918 | 0.18164 | 0.18 |
| Photochemical Ozone Formation, Ecosystems [kg NOx eq.] | 1.525673 | 1.525515 | 1.53 |
| Photochemical Ozone Formation, Human Health [kg NOx eq.] | 0.973421 | 0.973273 | 0.97 |
| Stratospheric Ozone Depletion [kg CFC-11 eq.] | 6.97E-06 | 6.28E-06 | 0.00 |
| Terrestrial Acidification [kg $SO_2$ eq.] | 0.143705 | 0.143531 | 0.14 |
| Terrestrial ecotoxicity [kg 1,4-DB eq.] | 148.406 | 148.1717 | 147.89 |

Supplementary Table 32. Environmental impacts of the production of 1 m$^2$ of PEF membrane under different energy geographical scopes. Other parameters were kept as: supercritical fluid extraction, Bio-EtOH, and incineration without energy recovery. S-MF refers to the membrane fabrication subprocess, and S-WI refers to the waste incineration subprocess (without energy recovery).

| **Environmental impact category** | **GLO** | | | **EUROPE** | | | **MIDDLE EAST** | | | **NORTH AMERICA** | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **S-MF** | **S-WI** | **Total** | **S-MF** | **S-WI** | **Total** | **S-MF** | **S-WI** | **Total** | **S-MF** | **S-WI** | **Total** |
| GWP, excl biogenic carbon [kg $CO_2$ eq.] | 3.92 | 30.84 | 76.29 | 1.93 | 30.84 | 74.30 | 4.58 | 30.84 | 76.95 | 2.42 | 30.84 | 74.79 |
| GWP, incl biogenic carbon [kg $CO_2$ eq.] | 3.94 | 30.84 | 68.92 | 1.99 | 30.84 | 66.97 | 4.58 | 30.84 | 69.56 | 2.43 | 30.84 | 67.41 |
| Fine Particulate Matter Formation [kg PM2.5 eq.] | 0.01 | 0.00 | 0.06 | 0.00 | 0.00 | 0.05 | 0.00 | 0.00 | 0.06 | 0.00 | 0.00 | 0.06 |
| Fossil depletion [kg oil eq.] | 1.40 | 0.00 | 28.31 | 1.09 | 0.00 | 28.01 | 1.57 | 0.00 | 28.49 | 1.13 | 0.00 | 28.05 |
| Freshwater Consumption [m$^3$] | 0.03 | 0.00 | 0.06 | 0.03 | 0.00 | 0.07 | 0.01 | 0.00 | 0.04 | 0.03 | 0.00 | 0.06 |
| Freshwater ecotoxicity [kg 1,4 DB eq.] | 0.01 | 0.00 | 0.15 | 0.01 | 0.00 | 0.15 | 0.00 | 0.00 | 0.14 | 0.01 | 0.00 | 0.15 |
| Freshwater Eutrophication [kg P eq.] | 0.00 | 0.00 | 0.03 | 0.00 | 0.00 | 0.03 | 0.00 | 0.00 | 0.03 | 0.00 | 0.00 | 0.03 |
| Human toxicity, cancer [kg 1,4-DB eq.] | 0.20 | 0.00 | 3.31 | 0.17 | 0.00 | 3.28 | 0.09 | 0.00 | 3.20 | 0.15 | 0.00 | 3.26 |
| Human toxicity, non-cancer [kg 1,4-DB eq.] | 1.24 | 0.00 | 17.04 | 1.01 | 0.00 | 16.82 | 0.27 | 0.00 | 16.07 | 0.83 | 0.00 | 16.64 |
| Ionizing Radiation [kBq Co-60 eq. to air] | 0.47 | 0.00 | 0.93 | 1.15 | 0.00 | 1.61 | 0.04 | 0.00 | 0.50 | 0.83 | 0.00 | 1.29 |
| Land use [Annual crop eq.·y] | 0.05 | 0.00 | 33.62 | 0.06 | 0.00 | 33.62 | 0.01 | 0.00 | 33.57 | 0.05 | 0.00 | 33.61 |
| Marine ecotoxicity [kg 1,4-DB eq.] | 0.02 | 0.00 | 0.25 | 0.02 | 0.00 | 0.25 | 0.01 | 0.00 | 0.24 | 0.01 | 0.00 | 0.25 |
| Marine eutrophication [kg N eq.] | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Metal depletion [kg Cu eq.] | 0.00 | 0.00 | 0.11 | 0.00 | 0.00 | 0.11 | 0.00 | 0.00 | 0.11 | 0.00 | 0.00 | 0.11 |
| Photochemical Ozone Formation, Ecosystems [kg NOx eq.] | 0.80 | 0.00 | 0.93 | 0.80 | 0.00 | 0.92 | 0.80 | 0.00 | 0.93 | 0.80 | 0.00 | 0.92 |
| Photochemical Ozone Formation, Human Health [kg NOx eq.] | 0.50 | 0.00 | 0.61 | 0.50 | 0.00 | 0.61 | 0.50 | 0.00 | 0.61 | 0.50 | 0.00 | 0.61 |
| Stratospheric Ozone Depletion [kg CFC-11 eq.] | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Terrestrial Acidification [kg $SO_2$ eq.] | 0.01 | 0.00 | 0.17 | 0.01 | 0.00 | 0.16 | 0.01 | 0.00 | 0.17 | 0.00 | 0.00 | 0.16 |
| Terrestrial ecotoxicity [kg 1,4-DB eq.] | 3.91 | 0.00 | 106.31 | 3.23 | 0.00 | 105.63 | 9.77 | 0.00 | 112.17 | 2.53 | 0.00 | 104.93 |

Supplementary Table 33. Environmental impacts and coefficients of variation to produce 1 m$^2$ of PEF membrane fabrication under different energy geographical scopes. The rest of parameters were kept as the baseline.

| **Environmental impact category** | **GLO** | **EU** | **MER** | **RNA** | **Coefficient of variation (%)** |
|---|---|---|---|---|---|
| GWP, excl biogenic carbon [kg $CO_2$ eq.] | 51.73 | 58.89 | 49.46 | 56.94 | 7.03 |
| GWP, incl biogenic carbon [kg $CO_2$ eq.] | 44.30 | 51.30 | 42.07 | 49.52 | 8.02 |
| Fine Particulate Matter Formation [kg PM2.5 eq.] | 0.02 | 0.04 | 0.04 | 0.04 | 19.42 |
| Fossil depletion [kg oil eq.] | 19.60 | 20.61 | 18.87 | 20.65 | 3.74 |
| Freshwater Consumption [m$^3$] | -0.06 | -0.08 | 0.01 | -0.06 | -68.54 |
| Freshwater ecotoxicity [kg 1,4 DB eq.] | 0.10 | 0.10 | 0.13 | 0.11 | 10.63 |
| Freshwater Eutrophication [kg P eq.] | 0.02 | 0.02 | 0.02 | 0.02 | 11.19 |
| Human toxicity, cancer [kg 1,4-DB eq.] | 2.52 | 2.64 | 2.89 | 2.68 | 4.88 |
| Human toxicity, non-cancer [kg 1,4-DB eq.] | 11.56 | 12.34 | 14.87 | 12.95 | 9.47 |
| Ionizing Radiation [kBq Co-60 eq. to air] | -1.14 | -3.46 | 0.32 | -2.36 | -84.81 |
| Land use [Annual crop eq.·y] | 33.38 | 33.37 | 33.54 | 33.39 | 0.20 |
| Marine ecotoxicity [kg 1,4-DB eq.] | 0.18 | 0.19 | 0.20 | 0.19 | 4.85 |
| Marine eutrophication [kg N eq.] | 0.00 | 0.00 | 0.00 | 0.00 | 10.37 |
| Metal depletion [kg Cu eq.] | 0.10 | 0.10 | 0.10 | 0.10 | 1.58 |
| Photochemical Ozone Formation, Ecosystems [kg NOx eq.] | 0.88 | 0.90 | 0.87 | 0.90 | 1.52 |
| Photochemical Ozone Formation, Human Health [kg NOx eq.] | 0.57 | 0.59 | 0.56 | 0.59 | 2.26 |
| Stratospheric Ozone Depletion [kg CFC-11 eq.] | 0.00 | 0.00 | 0.00 | 0.00 | 11.20 |
| Terrestrial Acidification [kg $SO_2$ eq.] | 0.11 | 0.13 | 0.11 | 0.14 | 10.99 |
| Terrestrial ecotoxicity [kg 1,4-DB eq.] | 90.34 | 92.69 | 70.33 | 95.07 | 11.28 |

Supplementary Table 34. Environmental impacts of the production of 1 $m^2$ of PEF membrane under the optimal scenario (supercritical fluid extraction, bio-based ethanol, waste recycling plus incineration with energy recovery, global raw materials production and energy mix).

| **Environmental impact category** | **Membrane production** | **Non-solvent production** | **Polymer production** | **Solvent distillation** | **Solvent production** | **Waste incineration with energy recovery** | **Total** |
|---|---|---|---|---|---|---|---|
| GWP, excl biogenic carbon [kg $CO_2$ eq.] | 3.92 | 6.83 | 0.90 | 1.63 | 2.31 | 1.25 | 16.85 |
| GWP, incl biogenic carbon [kg $CO_2$ eq.] | 3.94 | -27.11 | 0.90 | 1.63 | -5.16 | 1.24 | -24.56 |
| Fine Particulate Matter Formation [kg PM2.5 eq.] | 0.01 | 0.02 | 0.00 | 0.00 | 0.00 | -0.01 | 0.03 |
| Fossil depletion [kg oil eq.] | 1.40 | 1.93 | 0.38 | 0.57 | 1.56 | -1.74 | 4.10 |
| Freshwater Consumption [$m^3$] | 0.03 | 1.14 | 0.01 | 0.00 | 0.01 | -0.02 | 1.16 |
| Freshwater ecotoxicity [kg 1,4 DB eq.] | 0.01 | 0.22 | 0.00 | 0.00 | 0.01 | -0.01 | 0.23 |
| Freshwater Eutrophication [kg P eq.] | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 |
| Human toxicity, cancer [kg 1,4-DB eq.] | 0.20 | 0.60 | 0.05 | 0.00 | 0.19 | -0.16 | 0.88 |
| Human toxicity, non-cancer [kg 1,4-DB eq.] | 1.24 | 9.40 | 0.30 | 0.00 | 1.19 | -1.10 | 11.04 |
| Ionizing Radiation [kBq Co-60 eq. to air] | 0.47 | 0.23 | 0.07 | 0.00 | 0.05 | -0.41 | 0.41 |
| Land use [Annual crop eq.·y] | 0.05 | 10.95 | 0.01 | 0.00 | 33.03 | -0.05 | 44.00 |
| Marine ecotoxicity [kg 1,4-DB eq.] | 0.02 | 0.09 | 0.00 | 0.00 | 0.02 | -0.01 | 0.12 |
| Marine eutrophication [kg N eq.] | 0.00 | 0.02 | 0.00 | 0.00 | 0.00 | 0.00 | 0.02 |
| Metal depletion [kg Cu eq.] | 0.00 | 0.04 | 0.00 | 0.00 | 0.00 | 0.00 | 0.05 |
| Photochemical Ozone Formation, Ecosystems [kg NOx eq.] | 0.80 | 0.03 | 0.00 | 0.00 | 0.01 | -0.01 | 0.84 |
| Photochemical Ozone Formation, Human Health [kg NOx eq.] | 0.50 | 0.03 | 0.00 | 0.00 | 0.01 | -0.01 | 0.54 |
| Stratospheric Ozone Depletion [kg CFC-11 eq.] | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Terrestrial Acidification [kg $SO_2$ eq.] | 0.01 | 0.07 | 0.00 | 0.00 | 0.01 | -0.01 | 0.09 |
| Terrestrial ecotoxicity [kg 1,4-DB eq.] | 3.91 | 38.33 | 2.46 | 0.01 | 12.48 | -3.20 | 54.00 |

**Supplementary Table 35. Comparison with other literature reports on LCA on bio-based materials for membrane fabrication.**

| System | Bio-based membrane | | Fossil-based membrane | | Non-solvent | Membrane type | GWP 100 (kg $CO_2$ eq per $m^2$) | | GWP change (%) | Reference |
|---|---|---|---|---|---|---|---|---|---|---|
| | Polymer | Solvent | Polymer | Solvent | | | Bio-based membrane | Fossil-based membrane | | |
| Biobased polymer and solvent | Polyethylene furanoate | 1:4 M tymol/vanillin | Polyethylene terephthalate | Trifluoroacetic acid | Ethanol | Flat sheet | 51.73 | 89.18 | -42.0 | This work (baseline) |
| | Polyethylene furanoate | 1:4 M tymol/vanillin | Polyethylene terephthalate | Trifluoroacetic acid | Bio-ethanol | Flat sheet | 16.85 | 25.98 | -35.1 | This work (optimal vs. PET with bioethanol + waste recycling) |
| | Cellulose diacetate | Methyl lactate | Cellulose triacetate | N-methyl-2-pyrrolidone | 15 v% glycerol in water | Hollow fiber | 9.4 | 11 | -14.5 | Prézélus, et al.[15] |
| Biobased polymers | Polyethylene terephthalate (partially biobased) | Trifluoroacetic acid | Polyethylene terephthalate | Trifluoroacetic acid | Ethanol | Flat sheet | 89.17 | 89.18 | -1.1E-4 | This work (fossil ethanol and incineration with energy recovery) |
| | Polyethylene terephthalate (partially biobased) | Trifluoroacetic acid | Polyethylene terephthalate | Trifluoroacetic acid | Bio-ethanol | Flat sheet | 25.97 | 25.98 | -3.8E-4 | This work (bioethanol and waste recycling) |
| | Cellulose acetate | N-methyl-2-pyrrolidone | Polyvinylidene fluoride | N-methyl-2-pyrrolidone | Water | Hollow fiber | 5.375 | 6.377 | -15.7 | Prézélus, et al.[15] |
| Green solvents | Polyvinylidene fluoride | Ethylene carbonate | Polyvinylidene fluoride | N-methyl-2-pyrrolidone | Water | Hollow fiber | 4.532 | 6.377 | -28.9 | Yadav, et al.[16] (GLO) |
| | 6FDA-durene polyimide | Dimethyl sulfoxide | 6FDA-durene polyimide | N-methyl-2-pyrrolidone | N/A | Flat sheet | 162.93 | 182.84 | -10.9 | Yadav, et al.[16] (GLO) |
| | 6FDA-durene polyimide | Ethyl acetate | 6FDA-durene polyimide | N-methyl-2-pyrrolidone | N/A | Flat sheet | 166.47 | 182.84 | -9.0 | Hong, et al.[17] |
| | 6FDA-durene polyimide | γ-butyrolactone | 6FDA-durene polyimide | N-methyl-2-pyrrolidone | N/A | Flat sheet | 175.38 | 182.84 | -4.1 | Hong, et al.[17] |

# References

1. I. ISO, *Environmental management—Life cycle assessment—principles and framework*, 2006, **578**, 235-248.
2. I. ISO, *Environmental management—Life cycle assessment—Requirements and guidelines*, 2006, 1-46.
3. F. Piccinno, R. Hischier, S. Seeger and C. Som, *Journal of Cleaner Production*, 2016, **135**, 1085-1097.
4. P. D. Beer and P. A. Gale, *Angewandte Chemie International Edition*, 2001, **40**, 486-516.
5. B. A. Pulido, O. S. Habboub, S. L. Aristizabal, G. Szekely and S. P. Nunes, *ACS Applied Polymer Materials*, 2019, **1**, 2379-2387.
6. A. Muralidhara, E. De Jong, H. A. Visser, G.-J. M. Gruter, C. Len, J.-P. Bertrand and G. Marlair, *ACS omega*, 2022, **7**, 9181-9195.
7. S. Bello, I. Salim, P. Méndez-Trelles, E. Rodil, G. Feijoo and M. T. Moreira, *Holzforschung*, 2018, **73**, 105-115.
8. Á. C. Sánchez, O. T. Berglihn, E. Ottaviano, T. Rücker, T. Pettersen, B. Wittgens, A. Aliko, L. Gálvez and M. López, *Open Research Europe*, 2024, **4**, 5.
9. C. Moretti, R. Hoefnagels, M. van Veen, B. Corona, S. Obydenkova, S. Russell, A. Jongerius, I. Vural-Gürsel and M. Junginger, *Journal of Cleaner Production*, 2022, **343**, 131063.
10. 2021.
11. Z. Limam, C. Azzaro-Pantel, N. Hajjaji, M. Romdhane and J. Bouajila, *Computers & Chemical Engineering*, 2025, **200**, 109140.
12. A. I. Gavrila, C. G. Chisega-Negrila, L. Maholea, M. L. Gavrila, O. C. Parvulescu and I. Popa, *Agronomy*, 2023, **13**, 2331.
13. D. Villanueva Bermejo, I. Angelov, G. Vicente, R. P. Stateva, M. Rodriguez García-Risco, G. Reglero, E. Ibañez and T. Fornari, *Journal of the Science of Food and Agriculture*, 2015, **95**, 2901-2907.
14. E. De Falco, M. Pergola, A. Vece, C. Angiuoni and G. Celano, *Italian Journal of Agronomy*, 2020, **15**, 1505.
15. F. Prézélus, J.-C. Remigy, C. Guigui and L. Tiruta-Barna, *Journal of Cleaner Production*, 2022, **337**, 130476.
16. P. Yadav, N. Ismail, M. Essalhi, M. Tysklind, D. Athanassiadis and N. Tavajohi, *Journal of Membrane Science*, 2021, **622**, 118987-118987.
17. S. U. Hong, Y. Wang, L. S. Soh and W. F. Yong, *Green Chemistry*, 2023, **25**, 4501-4512.