Greening Physical Recycling of HDPE: Dissolution Precipitation with Natural Solvents

Sofia Aparício[1], Pedro M. Castro[2], Bernardo D. Ribeiro[3], and Isabel M. Marrucho[1†]

Supporting Information

[1]Departamento de Engenharia Química e Centro de Química Estrutural, Instituto Superior de Lisboa, Universidade de Lisboa, Av. Rovisco Pais 1, 1049-001 Lisboa, Portugal

[2] CERENA, Departamento de Engenharia Química, Instituto Superior Técnico, Universidade de Lisboa, Lisboa 1049-001, Portugal.

[3]Escola de Química, Universidade Federal Do Rio de Janeiro, 21941-598, Rio de Janeiro, Brazil

[†]Corresponding author. Tel.: +351 218413385. E-mail address: isabel.marrucho@tecnico.ulisboa.pt (I. M. Marrucho).

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1. Materials and Methods

1.1. Materials

Table S1 - Identification, purity, source, and indicative price of solvents used for HDPE dissolution and precipitation.

	Solvent	CAS	Purity (mass fraction)	Source	Price (€/kg)[1]
Solvent	**Limonene**			Sumol-Compal	78.04
	(1S)-(-)-α-Pinene	7785-26-4	98%	Thermo scientific	64.5
	p-cymene	99-87-6	>95%	Fluka	61.5
	Thymol	89-83-8	99%	Sigma-Aldrich	426
	Carvacrol	499-75-2		Thermo scientific	352
Antisolvent	**Ethanol**	64-17-5	96%	LABCHEM	2.82
	2-propanol	67-63-0	>99.9%	Carlo Erba	66.24
	1-butanol	71-36-3	99.5%	Sigma-Aldrich	51.36
	1,2-propanediol	57-55-6	>99%	Fischer scientific	31.57
	1,2-butanediol	584-03-2	>98%	Sigma-Aldrich	65.71
	Glycerol	56-81-5	>99%	Alfa aesar	36.80
	Ethylene glycol	203-473-3	>99.5%	Carlo Erba	57.86
	Diethylene glycol	11-46-6	99%	Sigma-Aldrich	34.78
	Triethylene glycol	112-27-6	99%	Sigma-Aldrich	34.31

1.2. Thermodynamic estimations: COSMO-SAC solvent screening

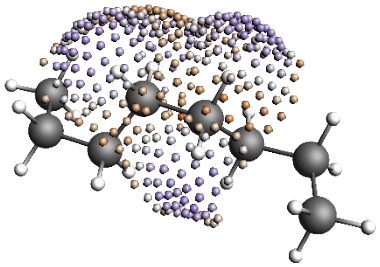

Figure S1 - HDPE molecule (with charge density points) used for the COSMO-SAC calculations (orange points represent positive polarity and blue points negative polarity).

Table S2 - Solvent and antisolvent properties considered in COSMO calculations[2,3].

		ρ (g/cm³)	T_m (°C)	ΔH_f (kcal/mol)
Solvents	**Toluene**	0.862	-94.9	1.59
	p-xylene	0.861	13.3	4.09
	d-limonene	0.841	-95.5	2.72
	α-pinene	0.858	-62.0	2.73
	p-cymene	0.857	-68.9	2.31
	Terpinolene	0.863	-93.3	NA
	γ-terpinene	0.843	-10.0	NA
	3-carene	0.860	NA	NA
	β-caryophyllene	0.908	NA	NA
Antisolvents	**Water**	0.995	0.0	1.44
	Ethanol	0.790	-114.1	1.19
	1-butanol	0.810	-88.6	2.22
	2-propanol	0.786	-90	1.62
	1,2-propanediol	1.036	-60	2.01
	1,2-butanediol	1.002	-50.0	NA
	Glycerol	1.260	16.9	4.37
	Ethylene glycol	1.114	-12.7	2.38
	Diethylene glycol	1.120	-10,2	NA
	Triethylene glycol	1.125	-7.0	NA

1.3. Process simulation in Aspen Plus

Table S3 - Properties and unitary cost of utilities used in Aspen Plus simulation[4].

	Inlet temperature (°C)	**Outlet temperature (°C)**	**Cost**
Air	100	95	0.96 €/GJ
Low pressure steam	125	124	5.08 €/GJ
Cooling water	20	25	0.42 €/GJ
Refrigeration water	5	15	5.34 €/GJ

2. Results and Discussion

2.1. Solvent screening in COSMO-SAC

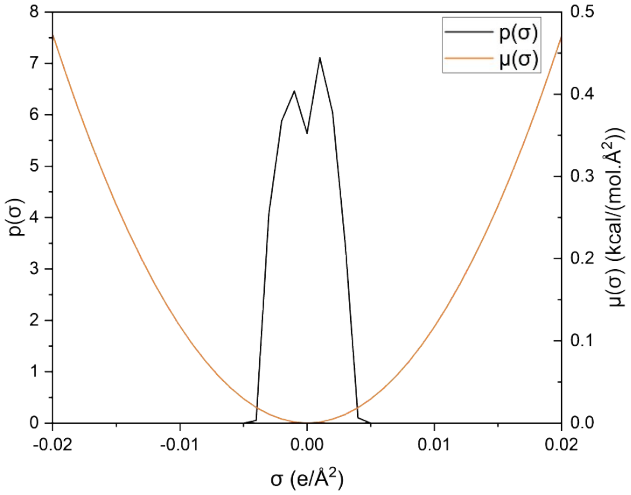

Figure S2 - σ-profile and σ-potential of HDPE, drawn in COSMO-SAC.

Table S4 - Solubility (wt%) of HDPE in different solvents at 110°C, 120°C and 130°C, as calculated in COSMO-SAC.

Solubility (wt%)	110°C	120°C	130°C
Toluene	0.00	11.89	71.98
p-Xylene	0.00	0.93	66.88
d-Limonene	0.00	0.00	54.47
α-Pinene	0.00	1.06	58.01
p-Cymene	0.00	0.00	55.05
Terpinolene	0.00	0.07	57.22
γ-Terpinene	0.00	0.01	55.46
3-Carene	0.00	0.02	56.35
β-Caryophyllene	0.00	0.00	32.11

2.2. Limonene as HDPE solvent

Table S5 – HDPE and limonene recovery at different dissolution temperatures and initial solid contents.

	HDPE recovery (wt%)			Limonene recovery (wt%)		
HDPE content (wt%)	**100ºC**	**110ºC**	**120ºC**	**100ºC**	**110ºC**	**120ºC**
1	56.53 ± 0.40	70.00 ± 2.83	59.57 ± 13.88	47.35 ± 4.46	46.70 ± 10.73	54.11 ± 11.00
2	62.50 ± 11.79	75.13 ± 8.27	73.69 ± 1.10	48.74 ± 6.47	53.60 ± 0.94	48.75 ± 16.74
3	72.87 ± 3.02	80.51 ± 3.55	80.71 ± 0.51	42.76 ± 2.44	47.26 ± 4.96	37.59 ± 7.61
4	81.13 ± 2.67	81.23 ± 5.48	89.14 ± 1.95	23.92 ± 3.28	41.58 ± 2.32	34.25 ± 14.74

5	81.34 ± 5.76	83.08 ± 1.68	90.55 ± 4.32	18.48 ± 0.38	33.44 ± 6.21	13.58 ± 4.32

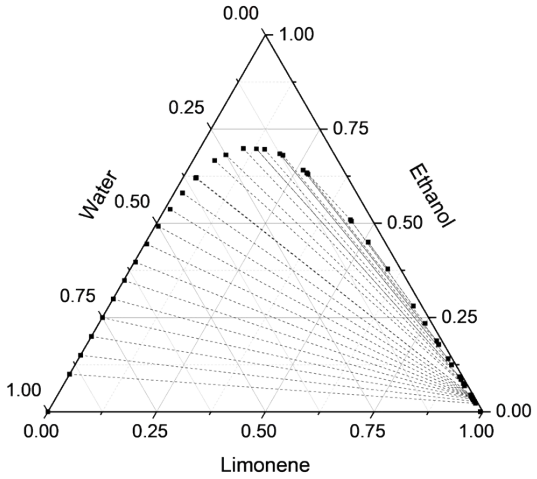

Figure S3 - Ternary liquid-liquid equilibrium of limonene, ethanol and water, drawn in COSMO-SAC.

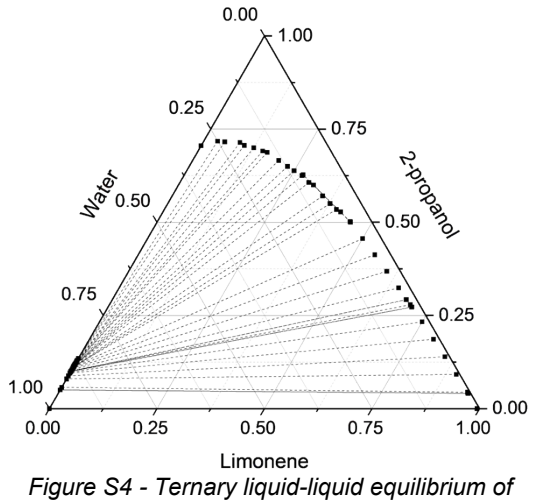

Figure S4 - Ternary liquid-liquid equilibrium of limonene, 2-propanol and water, drawn in COSMO-SAC.

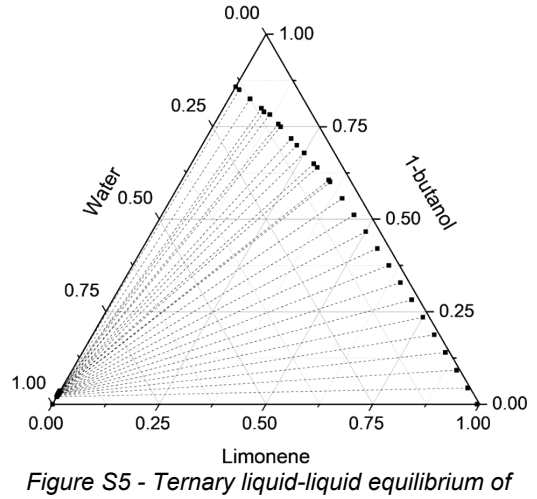

Figure S5 - Ternary liquid-liquid equilibrium of limonene, 1-butanol and water, drawn in COSMO-SAC.

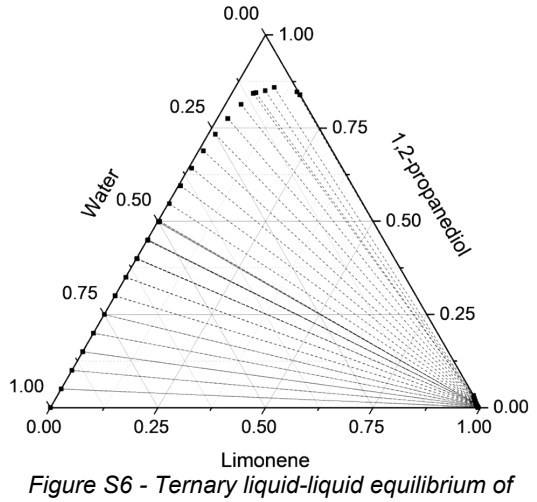

Figure S6 - Ternary liquid-liquid equilibrium of limonene, 1,2-propanediol and water, drawn in COSMO-SAC.

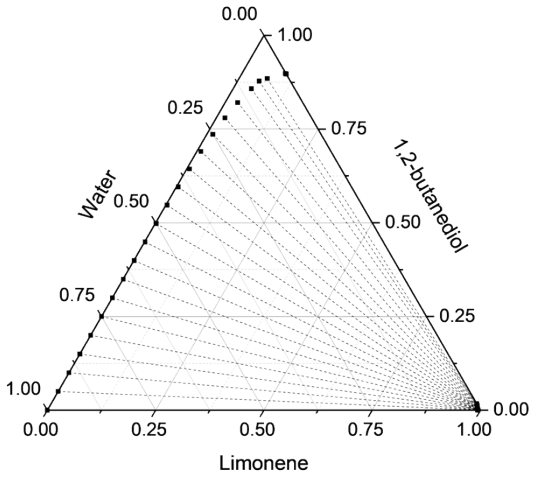

Figure S7 - Ternary liquid-liquid equilibrium of limonene, 1,2-butanediol and water, drawn in COSMO-SAC.

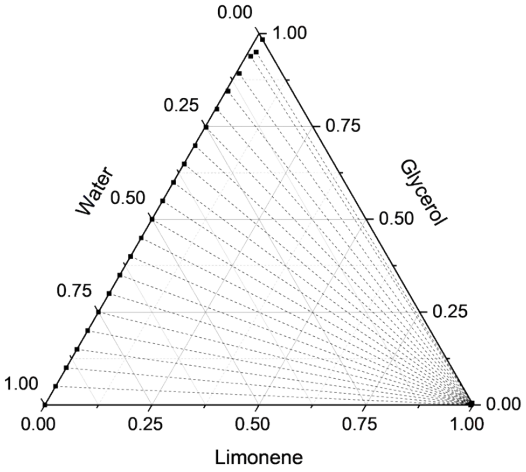

Figure S8 - Ternary liquid-liquid equilibrium of limonene, glycerol and water, drawn in COSMO-SAC.

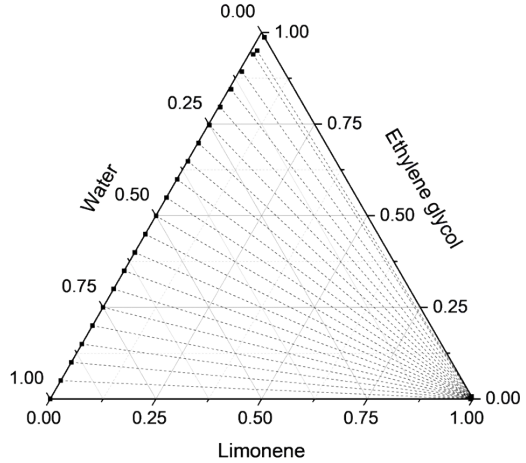

Figure S9 - Ternary liquid-liquid equilibrium of limonene, ethylene glycol and water, drawn in COSMO-SAC.

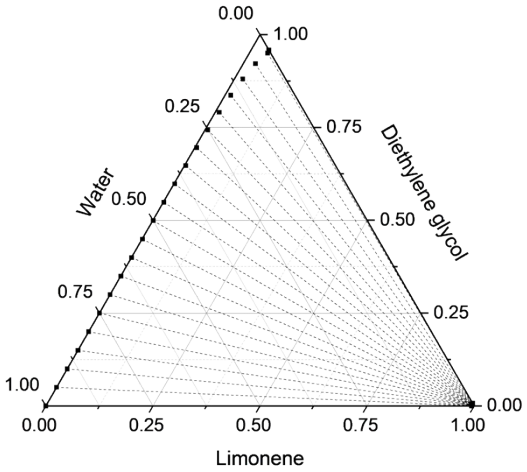

Figure S10 - Ternary liquid-liquid equilibrium of limonene, diethylene glycol and water, drawn in COSMO-SAC.

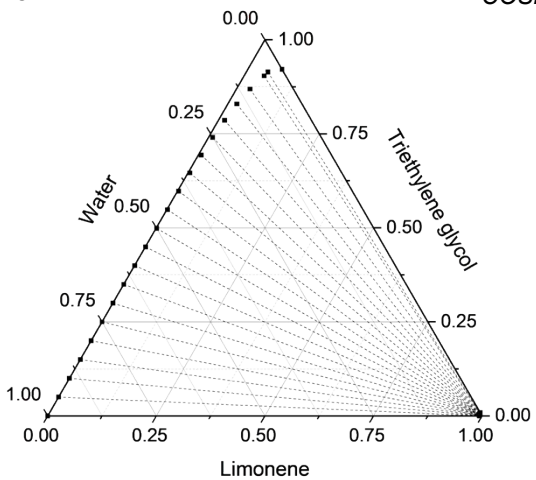

Figure S11 - Ternary liquid-liquid equilibrium of limonene, triethylene glycol and water, drawn in COSMO-SAC.

Table S6 - HDPE and limonene recovery for different antisolvents and antisolvent/solvent ratios, after dissolution at 110°C for 10 min.

	HDPE recovery (wt%)			Limonene recovery (wt%)		
Ratio	**1/1**	**2/1**	**3/1**	**1/1**	**2/1**	**3/1**
Water	92.87 ± 7.15	88.39 ± 13.45	98.72 ± 4.29	9.30 ± 12.51	7.07 ± 6.69	2.64 ± 4.58
Ethanol	76.76 ± 1.58	77.73 ± 3.09	79.11 ± 1.35	43.09 ± 5.21	56.99 ± 5.67	53.56 ± 6.58
2-propanol	74.09 ± 8.42	61.75 ± 6.57	72.96 ± 2.13			
1-butanol	79.44 ± 5.15	72.80 ± 7.89	70.16 ± 2.67			
1,2-butanediol	82.69 ± 2.53	84.47 ± 1.27	86.37 ± 0.85	16.87 ± 5.24	12.93 ± 11.05	13.85 ± 2.06
1,2-propanediol	82.60 ± 7.21	84.45 ± 4.49	85.52 ± 1.49	19.83 ± 5.05	20.58 ± 8.46	20.50 ± 9.11
Glycerol	102.72 ± 8.25	116.25 ± 14.24	102.18 ± 14.44	0.00	14.82 ± 10.02	19.20 ± 4.17
Ethylene glycol	90.47 ± 4.26	86.63 ± 8.00	86.75 ± 3.63	21.89 ± 5.32	31.95 ± 5.82	19.59 ± 6.10
Diethylene glycol	83.92 ± 2.62	86.59 ± 5.79	83.69 ± 3.12	7.00 ± 5.61	9.72 ± 4.81	27.52 ± 3.78
Triethylene glycol	89.80 ± 3.03	84.03 ± 3.21	87.50 ± 4.44	5.45 ± 2.47	20.40 ± 5.26	13.78 ± 6.79

2.3. α-pinene and p-cymene as HDPE solvents

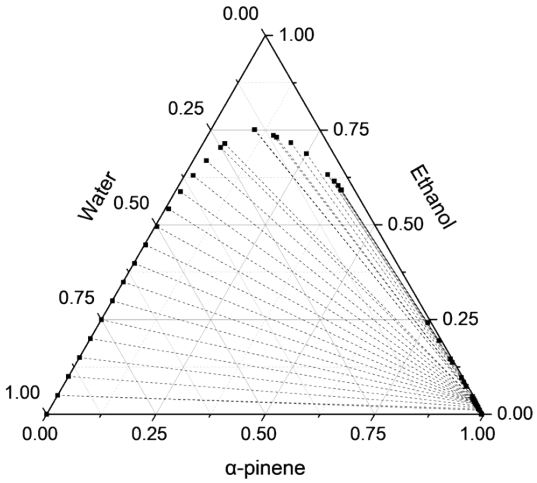

Figure S12 - Ternary liquid-liquid equilibrium of α-pinene, ethanol and water, drawn in COSMO-SAC.

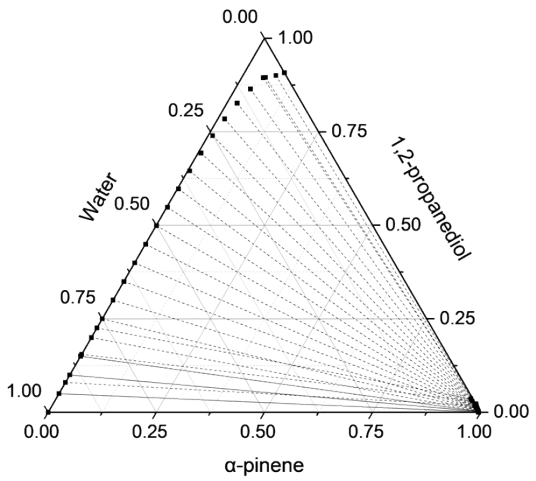

Figure S13 - Ternary liquid-liquid equilibrium of α-pinene, 1,2-propanediol and water, drawn in COSMO-SAC.

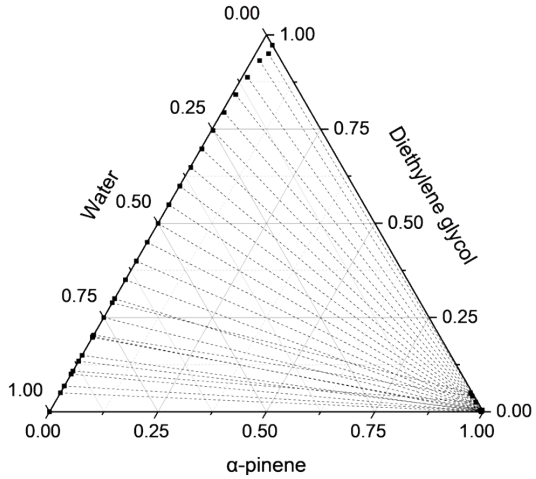

Figure S14 - Ternary liquid-liquid equilibrium of α-pinene, diethylene glycol and water, drawn in COSMO-SAC.

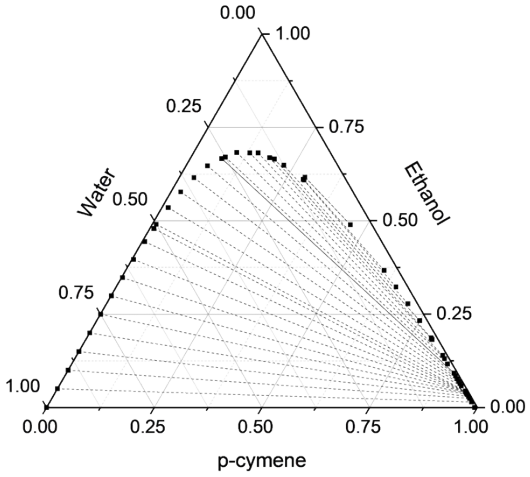

Figure S15 - Ternary liquid-liquid equilibrium of p-cymene, ethanol and water, drawn in COSMO-SAC.

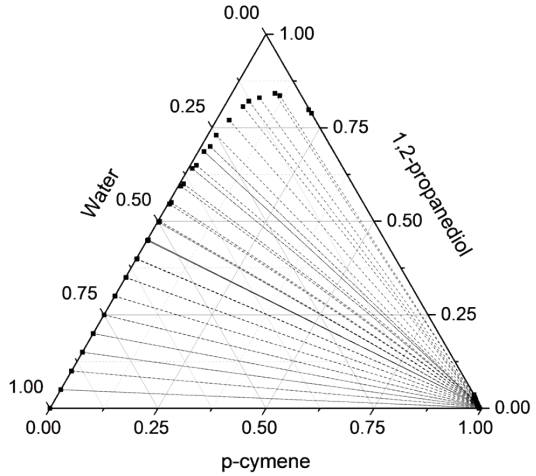

Figure S16 - Ternary liquid-liquid equilibrium of p-cymene, 1,2-propanediol and water, drawn in COSMO-SAC.

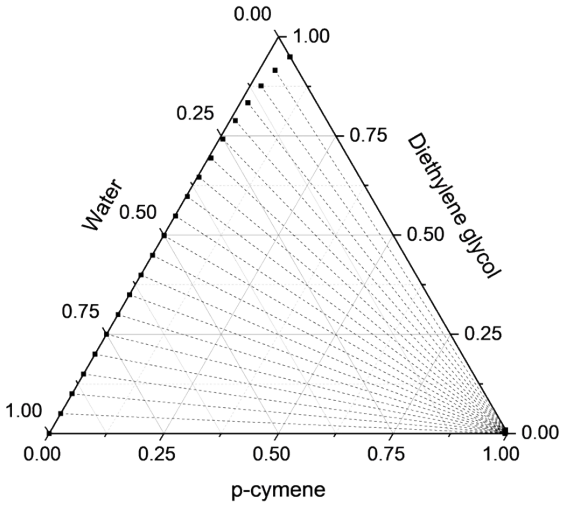

Figure S17 - Ternary liquid-liquid equilibrium of p-cymene, diethylene glycol and water, drawn in COSMO-SAC.

Table S7 - HDPE and α-pinene recovery for different antisolvents, after dissolution at 110°C for 10 min.

Recovery (wt%)	HDPE	α-pinene
Ethanol	86.84 ± 2.47	50.52 ± 3.95
1,2-propanediol	90.09 ± 5.72	16.19 ± 2.04
Diethylene glycol	89.97 ± 6.83	7.59 ± 1.68

Table S8 - HDPE and p-cymene recovery for different antisolvents, after dissolution at 110°C for 10 min.

	HDPE recovery (wt%)	α-pinene recovery (wt%)
Ethanol	72.09 ± 1.94	48.17 ± 1.92
1,2-propanediol	81.75 ± 0.78	8.38 ± 10.47
Diethylene glycol	75.29 ± 0.33	7.64 ± 7.22

2.4. Solvent Selection for HDPE dissolution-precipitation- Tukey Honestly Significant Difference (HSD) test

Tukey HSD tests were performed in the software IBM SPSS Statistics 27, through a univariate analysis. This test is suitable for a wide range of situations, namely for pair-wise comparisons[5]. The solvent was defined as fixed factor and the recovery as dependent variable. The degree of significance was set at 95%.

Table S9 - Tukey HSD test regarding HDPE recovery with different solvents.

solvent	N	Subset	
		1	2
p-cymene	2	72.0900	
Limonene	3	77.7300	
α-pinene	3		86.8433
Significance		0.079	1.000

Table S10 - Tukey HSD test regarding solvent recovery after HDPE dissolution in different solvents and precipitation.

Solvent	N	Subset
		1
p-cymene	3	46.0633
α-pinene	3	50.5267
Limonene	3	56.9900
Significance		0.060

2.5. Recovered HDPE Characterization

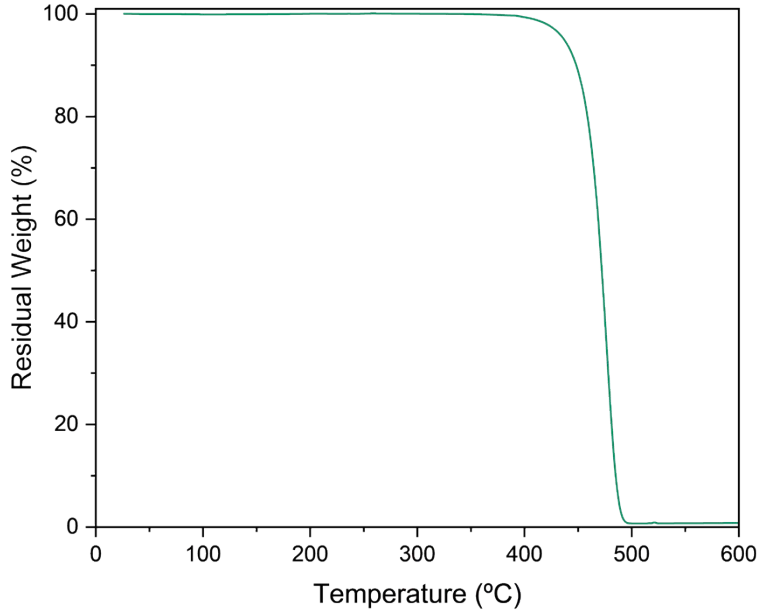

Figure S18 – Thermogram of recovered HDPE from α-pinene/ethanol system, from TGA analysis.

Table S11 - Characteristic FTIR bands of HDPE and corresponding vibrations[6].

HDPE bands (cm^{-1})	**Correspondence**
719	CH_2 bending
730	CH_2 bending
1368	methyl C-H bend
1463	CH_2 bending
1473	CH_2 bending
2848	C-H symmetric stretching
2916	CH_2 asymmetric stretching

2.6. Recovered solvent characterization

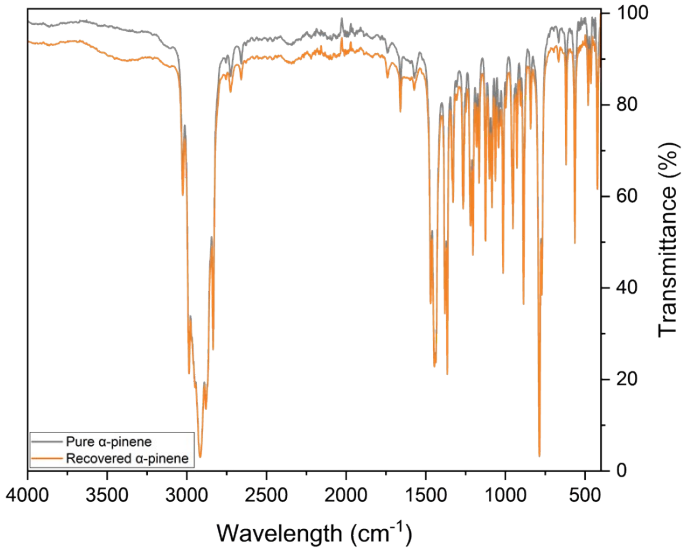

Figure S19 - FTIR spectra of pure and recovered α-pinene.

Table S12 - Characteristic FTIR bands of α-pinene and corresponding vibrations[7]. (NA stands for not available)

α-pinene band (cm-1)	**Correspondence**	**α-pinene band (cm-1)**	**Correspondence**
564	NA	1329	C-H bending
619	NA	1335	C-H bending
772	C-H bending	1365	C-H bending
787	C=C bending	1375	C-H bending
886	C-H bending	1381	C-H bending
928	NA	1437	C-H bending
953	NA	1446	C-H bending
1015	NA	1470	C-H bending
1063	NA	1659	C=C stretching
1084	NA	2725	C-H stretching
1101	NA	2835	C-H stretching
1125	NA	2880	C-H stretching
1166	NA	2916	C-H stretching
1182	NA	2949	C-H stretching
1204	NA	2986	C-H stretching
1220	NA	3026	C-H stretching (alkene)
1265	NA		

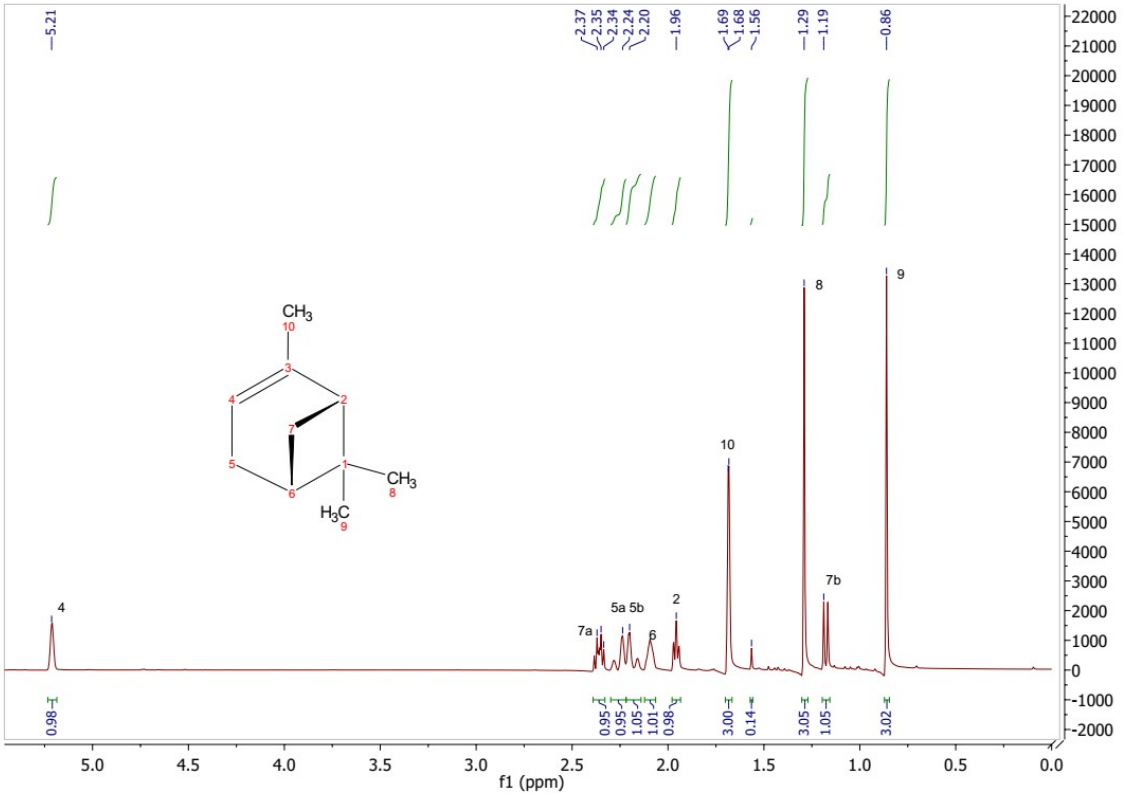

Figure S20 - ^{1}H NMR spectra of recovered α-pinene.

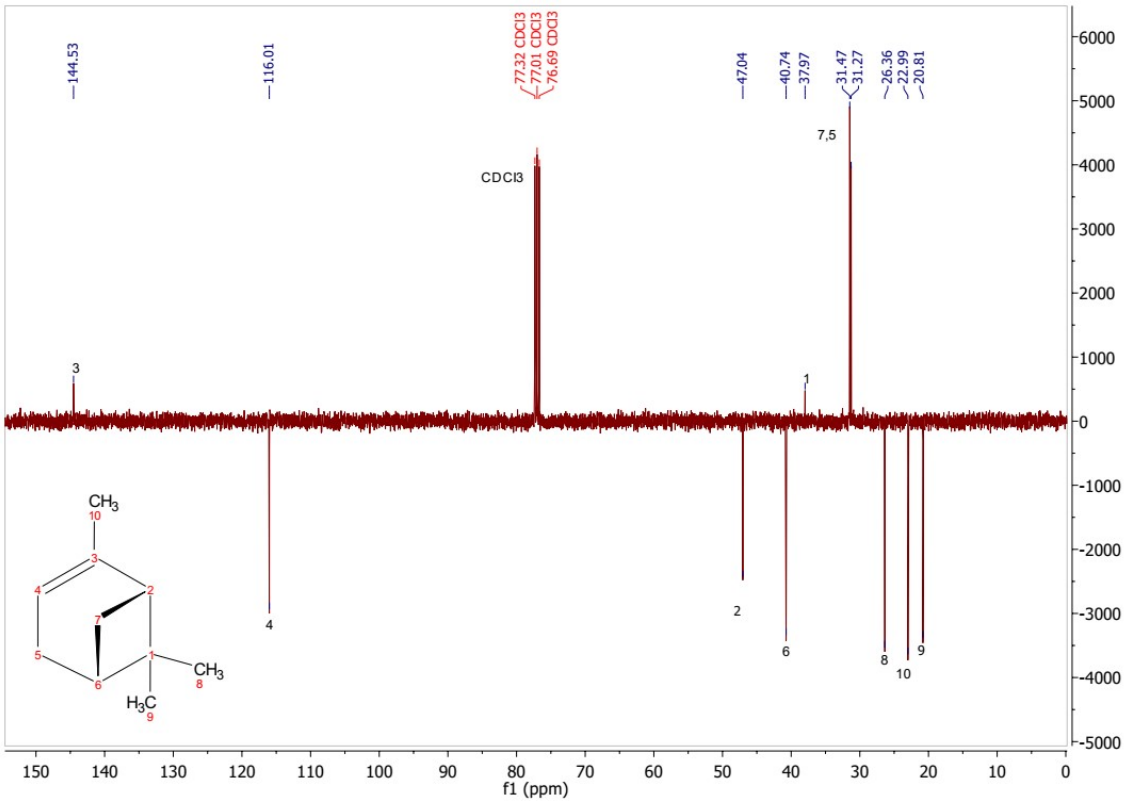

Figure S21 - ^{13}C NMR spectra of recovered α-pinene.

Figure S22 - ^{1}H NMR spectra of pure α-pinene.

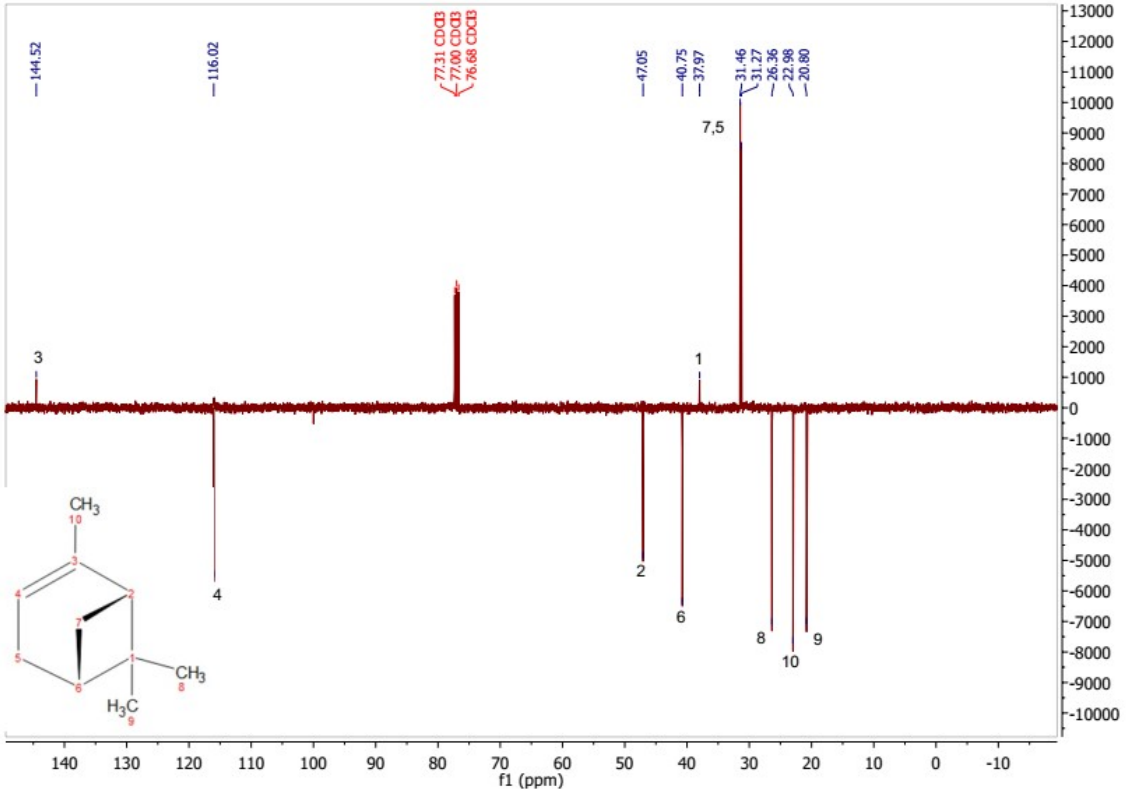

Figure S23 - ^{13}C NMR spectra of pure α-pinene.

2.7. Scale-up

Table S13 - HDPE and α-pinene recovery using ethanol as antisolvent, in the antisolvent/solvent ratio 2/1, at two different scales: 50 mg HDPE and 250 mg HDPE.

Recovery (wt%)	Initial scale (50 mg)	Scale-up (250 mg)
HDPE	83.85 ± 3.00	93.21 ± 0.13
α-pinene from precipitation step	53.96 ± 2.93	56.85 ± 6.91
α-pinene from washing step	17.62 ± 1.75	16.48 ± 2.29
α-pinene total	71.58 ± 1.18	73.32 ± 4.62

2.8. Solvent reuse

Table S14 – HDPE and α-pinene recovery using ethanol as antisolvent, in the antisolvent/solvent ratio 2/1, for 3 consecutive solvent utilizations.

Recovery (wt%)	1st cycle	2nd cycle	3rd cycle
HDPE	93.21 ± 0.13	92.10 ± 0.22	89.74 ± 0.59
α-pinene from precipitation step	56.85 ± 6.91	58.39 ± 5.43	45.68 ± 2.15
α-pinene from washing step	16.48 ± 2.29	11.96 ± 0.38	19.44 ± 1.21
α-pinene total	73.32 ± 4.62	70.36 ± 5.05	65.12 ± 3.36

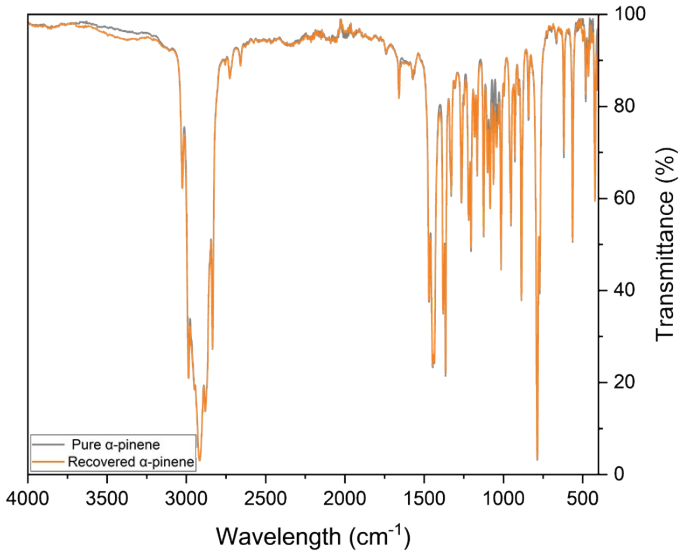

Figure S24 – FTIR spectra of pure and recovered α-pinene after 3 consecutive uses, using ethanol as antisolvent.

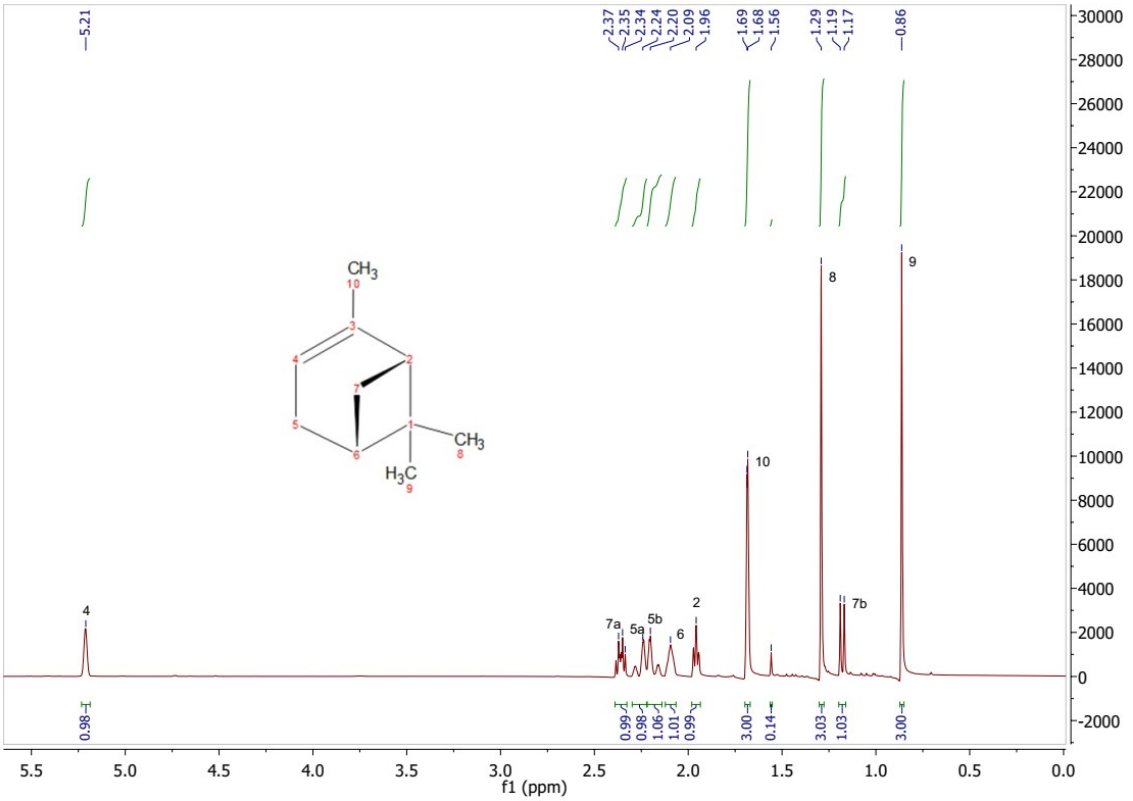

Figure S25 - [1]H NMR spectra of recovered α-pinene after 3 consecutive uses.

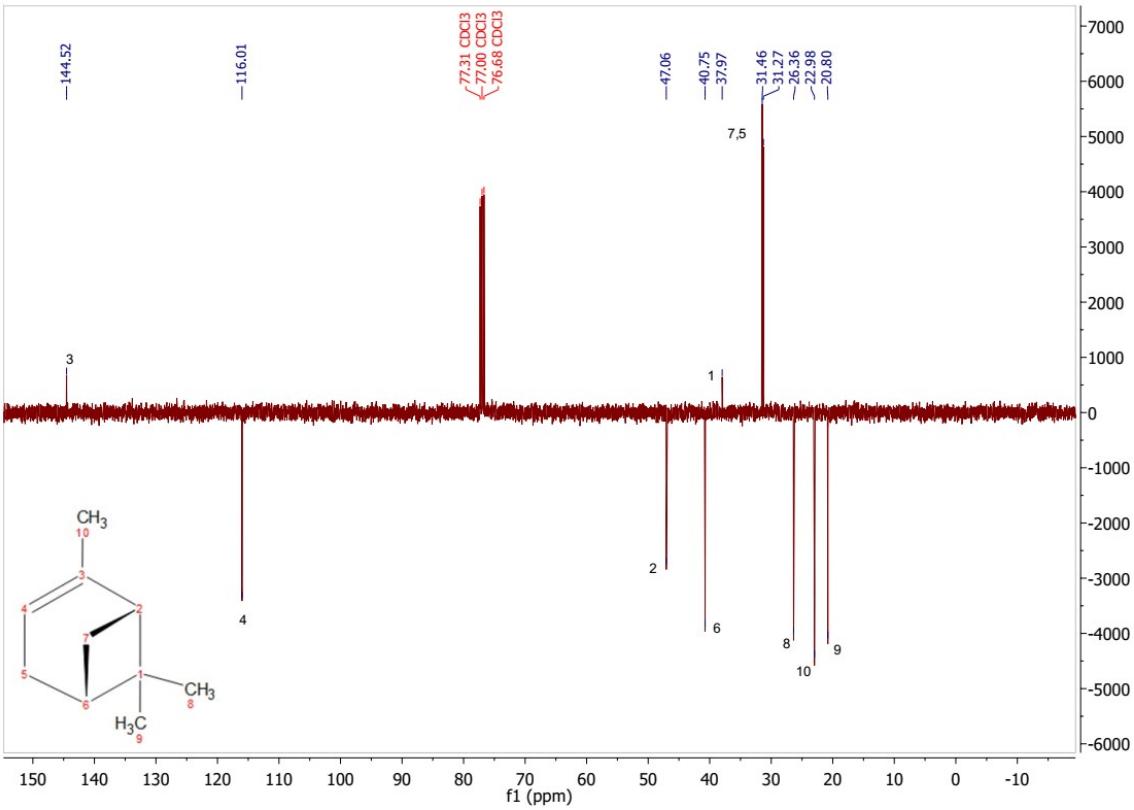

Figure S26 - [13]C NMR spectra of recovered α-pinene after 3 consecutive uses.

2.9. Process simulation

The dissolution and precipitation operations were performed in RSTOIC reactors (DISSOL and PRECIP, respectively), assuming both steps are complete, and thus 100% of the polymer leaves the precipitation vessel in the solid state. For these steps, the amounts of α-pinene and ethanol entering the system were specified according to the experimental conditions chosen: 3wt% of HDPE in the dissolution, at 110ºC, and a mass ratio of 2/1 between the antisolvent and the solvent.

The stream resulting from the precipitation step is then filtered, in FILTER, modeled with the block Filter. To match the solvent recovery attained for this step in the laboratory, it was assumed that 55% of the liquid phase is separated from the polymer.

The polymer stream is washed using 2 kg/hr of ethanol, in the equipment WASH (model SWash), removing the remaining solvent, and the polymer is finally dried at 80ºC (DRIER). Both the liquid outlet stream from the filter (10) and the washing solution (14) are mixed with water and decanted (DECANTER). The amount of water was defined so that it corresponds to 50wt% of the mixed stream. According to the liquid-liquid equilibrium estimated in the decanter model, it is possible to recover α-pinene with a mass purity of 98.5%, in stream 18. A purge was inserted in the simulation to mimic the loss of solvent observed experimentally, and thus only 70% of the α-pinene is recycled back to the dissolution vessel (stream 21), and the utility cost was corrected with the assumption that this amount was lost through evaporation.

The second liquid phase, composed mainly of ethanol and water, is distilled at atmospheric pressure, using a distillation column modeled as RADFRAC (DIST COLUMN), allowing the recovery of ethanol with 95% mass purity (stream 24), and water with 99.4% purity (stream 22). Both streams can be recycled back to their respective operations.

2.10. PET and HDPE separation

Table S15 - HDPE, PET, α-pinene and thymol:carvacrol (1:1) recovery from selective dissolution and precipitation.

	HDPE	**PET**
Polymer	79.77 ± 1.27	84.16 ± 5.26
Solvent from precipitation step	34.47 ± 12.39	68.11 ± 8.70
Solvent from washing step	20.38 ± 12.81	--
Total solvent	54.85 ± 7.60	68.11 ± 8.70

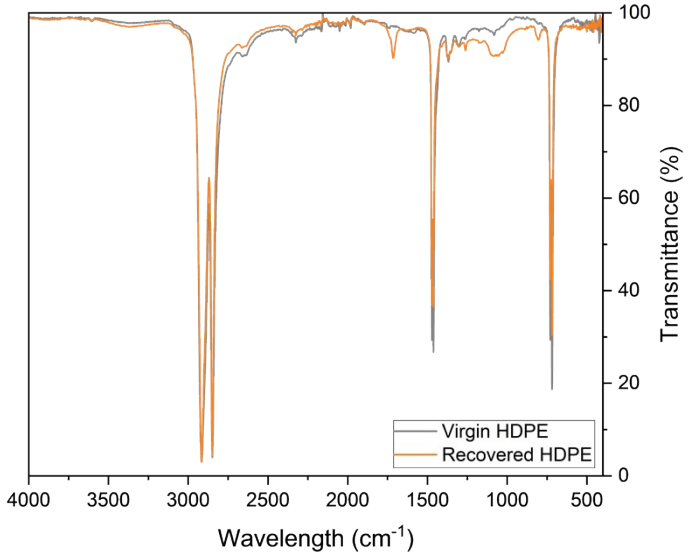

Figure S27 - FTIR spectra of virgin and recovered HDPE from HDPE/PET mixture.

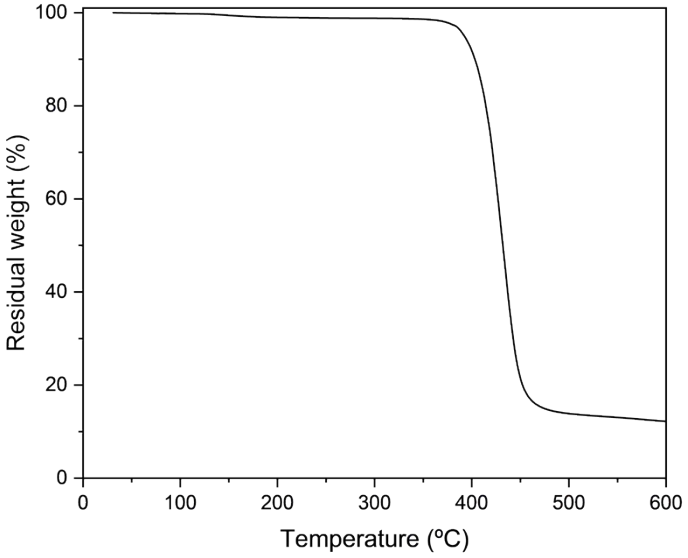

Figure S28 - Variation of recovered PET's residual weight with temperature, resulting from TGA analysis.

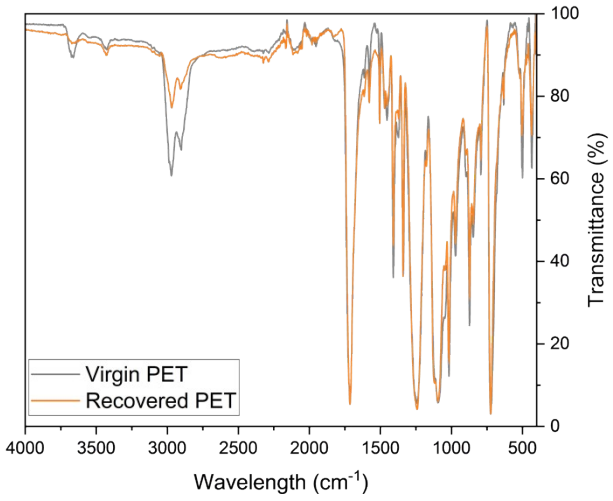

Figure S29 - FTIR spectra of virgin and recovered PET.

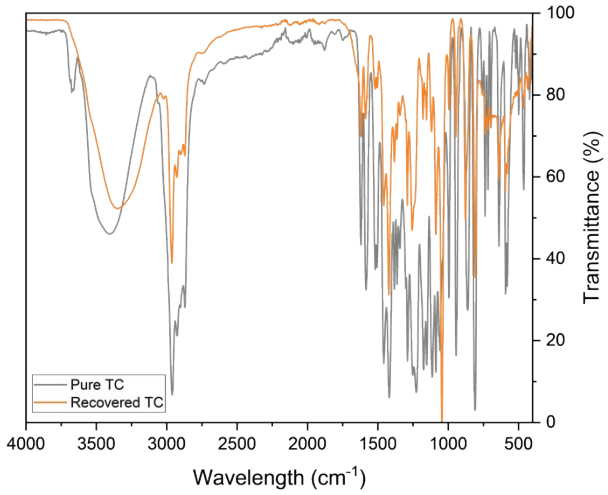

Figure S30 - FTIR spectra of pure and recovered thymol:carvacrol NaDES (1:1).

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