

Supplementary Information for: Amine-free CO₂-switchable hydrophilicity solvents and their application in extractions and polymer recycling

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Table of Contents

S1. Experimental Methods and Materials.....	1
S1.1. Evaluation of the switching behaviour of ASHS systems	1
S1.2. Evaluation of the switching behaviour of ASHS systems under elevated pressures of CO ₂	2
S1.3. Recovery of polystyrene from polystyrene foam	2
S1.4. Removal of motor oil from contaminated bottles.....	3
S2. Systems with a stoichiometric amount of base.....	4
S3. Systems with a substoichiometric amount of base	5
S4. Additional data for the carboxylic acid:NaOH:H ₂ O systems presented in Figure 3	7
S5. Additional data for the EHA:NaOH:H ₂ O systems	8
S6. Additional data for the recycling of polystyrene foam.....	9
S7. Additional data for the recovery of motor oil from used bottles	11
S8. Initial economic comparison between ASHS and CSHS	11
S9. References.....	12

S1. Experimental Methods and Materials

Chemicals were used as received. The following materials were obtained from commercial sources (Sigma-Aldrich, Fisher): 2-ethylhexanoic acid (EHA), 2-propylpentanoic acid (PPA), 3-cyclopentylpropionic acid (CPPA), octanoic acid (OA), oleic acid (OLA), linoleic acid (LA), 2-hexyldecanoic acid (HAD), 10-undecenoic acid (UA), nonanoic acid (NA), 2-phenylpropionic acid (PHPA), hexanoic acid (HA), 2-methylbutyric acid (MBA), isobutyric acid (IBA), triethanolamine (TEA), *N*-methyldiethanolamine (MDEA), *N,N*-dimethylethanolamine (DMEA), 3-dimethylamino-1-propanol (3-DMAP), polyoxypropylenediamine (Jeffamine D-230), sodium hydroxide, potassium hydroxide, ammonium hydroxide, pyridine and sodium dodecyl sulphate (SDS). Solvents used were: hexanes and tetrahydrofuran (THF). Water with a conductivity of 18.2 MΩ before exposure to air was obtained from a Milli-Q® purification system (Synergy UV). Gum mastic was obtained from Sigma.

For the ¹H NMR (Bruker spectrometer) spectroscopy, either d₆-C₆D₆ or d₁-CDCl₃ (Cambridge Isotope Laboratories) were used as the solvent.

S1.1. Evaluation of the switching behaviour of ASHS systems

Base solutions were prepared by combining the desired base and water (mass for components measured in an analytical scale) into either a 10 or 25 mL graduated cylinder (containing a magnetic stir bar) depending on the final volume of the mixture obtained. The carboxylic acid (mass measured using an analytical balance prior to addition) being studied was added to the base solution, and the mixture was mixed with the help of a magnetic stir plate. The amount of base and water used were selected based on the acid:base:water ratio desired. Experiments were carried out using

stoichiometric and substoichiometric amounts of the base relative to the number of mols of acid added. In addition, the quantity of water used was adjusted based on the acid:water mass ratio desired. A typical experiment would contain 1 g of the carboxylic acid; between 0.4 and 1 mol of base per mol of acid; and a water mass varying from 1 to 9.5 g.

After the components of the mixture were properly mixed (approximately 5 min of stirring), the pH of the monophasic mixture was measured and recorded using a semi-micro pH probe (Thermo Scientific model 9103BNWP) attached to a pH meter (Thermo – Orion Star Series). The stir bar was removed, and the solution was then slowly bubbled (no evaporation was visually noticed) with CO₂ (bone dry 3.0, 99.9%) via a sparge tube (ace gas dispersion tube with porous fritted glass tip Fit #7 Ace-Thred, O.D. × L 7 mm × 135 mm, porosity 145-174 μm). During a typical experiment, CO₂ would be added for approximately 2 h at atmospheric pressure. At the end of the 2 h, the sparge tube would be removed, and the number and volume of the phases obtained would be recorded. The pH was once again recorded. For mixtures with only 1 phase, the pH of that phase was recorded. While for mixtures with 2 phases, the pH of the aqueous phase was recorded. Loss of volume due to evaporation was not significantly noticeable.

In the systems in which the base:acid mole ratio and the water:acid mass ratio were being studied, a slight modification from this method was used. The acid being tested (1 g) was mixed with 1 g of water and the required amount of NaOH (based on the acid:base molar ratio desired) to prepare the mixture. To mixtures that were initially biphasic under air, water was added dropwise under agitation (using a magnetic stir plate). These systems remained biphasic under air, and this behaviour was highlighted in the graphs prepared.

For the tests with different carboxylic acids and the fixed 1:2 mass ratio of carboxylic acid:H₂O, the carboxylic acid:base ratio was determined for each sample, the required mass of NaOH was weighed in an analytical balance and solubilised with the appropriate mass of H₂O. The base solution was then added to the carboxylic acid, and the next steps followed the procedure previously described.

During the experiments where EHA was mixed with different bases, the EHA:H₂O mass ratio was fixed at 1:2. The EHA:base ratio was determined for each sample, the required mass of NaOH, KOH or pyridine was weighed in an analytical balance and solubilised with the appropriate mass of H₂O. For the systems containing NH₄OH, a 30 wt% solution in water (obtained from Sigma) was used instead, and additional water was added to achieve the 1:2 EHA:H₂O mass ratio. The base solution was then added to the carboxylic acid, and the next steps followed the procedure previously described.

S1.2. Evaluation of the switching behaviour of ASHS systems under elevated pressures of CO₂

The base (NaOH), water and acid (2-ethylhexanoic acid (EHA)) mixtures were prepared following the same procedure previously described. After obtaining the pH of the mixture prior to the addition of CO₂, the solutions were transferred to a high-pressure liquid level sight gauge (hereafter referred to as the “sight gauge”) manufactured by Inferno Manufacturing Co. (modified 11A-TL-B model, T316 stainless steel, with a pressure rating of 345 bar at 38 °C, 36.5 mL internal volume), equipped with a stainless steel dip-tube. The sight gauge was kept at a constant temperature (20 °C) in a water bath. The solutions were maintained under stirring due to a magnetic stir bar controlled by a magnetic stir plate. To maximise the stirring, the vessel was placed on its side (horizontal position).

The mixture was then pressurised to 10 bar of CO₂ in the sight gauge. In order to determine the volume of the phases obtained, measurements of the height of the water-rich and the carboxylic acid phase were obtained using a cathetometer while the vessel was in a vertical position. The relationship between height and internal volume on the sight gauge is known. The vessel was then slowly depressurised. The phases were collected using a glass pipette.

S1.3. Recovery of polystyrene from polystyrene foam

In a typical experiment, 1.0 g chunks of polystyrene (PS) foam packing material (Uline Peanuts S-1128 white anti-static) were weighted in a beaker, and 2.5 g (0.017 mol, 2.5 mL) of 3-

cyclopentylpropionic acid (CPPA) was added to the chunks. The beaker was placed in an oven at 60 °C to dissolve the foam. After dissolution was complete, the mixture was cooled down to room temperature (23 ± 1 °C), a magnetic stir bar was added, and the mixture was stirred at 450 rpm. To this mixture, 5.0 g of water was slowly added using a syringe. The addition of water before adding the base solution allowed the polymer to precipitate as a powder at the end of the process. In a separate vial, 0.45 g of NaOH flakes were added to 1.25 g of water. The mixture was cooled down with the help of an ice bath. Once at room temperature, the base solution was dripped into the polystyrene mixture. After the complete addition of the base solution, the pH of the mixture was measured using the same pH probe/meter previously described. The new mixture was stirred for 2 h (using a stir plate).

After the 2 h of stirring, the styrofoam precipitated polystyrene powder was collected by filtration. To remove any remaining acid in the polystyrene, the powder was washed 3x with a saturated sodium bicarbonate aqueous solution (3 x 100 mL washes) and DI water and finally air-dried.

The dry powder was submitted to double-screw extrusion in order to prepared pellets from the recovered styrofoam. The procedure was carried out at 150 °C at 100 rpm with 1 min retention time into the chamber (Micro 5CC Twin Screw Compounder, DSM Research Netherlands).

The original polystyrene foam and the extruded polystyrene were characterised by gel permeation chromatography (GPC). The GPC analyses were performed using tetrahydrofuran (THF) as the eluent. Samples at a 4 mg/mL concentration in THF were passed through a 0.2 µm filter prior to injection. The samples were analysed on a Waters 2695 separation module equipped with a Waters 410 differential refractometer and Waters Styragel HR (4.6 × 300 mm) 4, 3, 1 and 0.5 separation columns at 32 °C and 1 mL/min flow rate. The GPC was calibrated using PS monodisperse standards.

The PS foam, the recovered PS and the PS pellets were characterised via ¹H NMR and ATR-FTIR. ¹H NMR spectra were recorded at 298 K with a Bruker Advance 400.30 MHz NMR spectrometer using d₆-C₆D₆ as the solvent. ATR-FTIR spectra were measured using a Bruker ALPHA FT-IT Spectrometer with attenuated total reflectance (ATR) sampling module.

S1.4. Removal of motor oil from contaminated bottles

A 10DW30 motor oil bottle was emptied by pouring the oil until flow ceased, but without any rinsing, and the bottle was cut into small (1 cm²) pieces. The pieces still contaminated with the motor oil were transferred to a glass vial. A typical experiment used 2.0 g of bottle pieces. To the vial containing the pieces, approximately 3.0 g of the extraction solvent (either hexanes or 2-ethylhexanoic acid (EHA)) was added. To this mixture, a magnetic stir bar was added, and the mixture was stirred at 500 rpm for 1 h. After that time, the solvent was recovered with a glass pipette, its mass was measured, and the solvent was set aside for the next steps. To the vial containing the pieces, an additional 3 g of fresh extraction solvent was added, and the mixture was once again left under stirring for 1 h. After that time, the solvent was once again recovered and the mass measured. The two solvent fractions were combined.

The bottle pieces which were in contact with the hexanes were left to air dry. The hexanes/motor oil mixture recovered from the bottle pieces was also left under air (24 h) to allow the hexanes to evaporate, and the mass of oil removed from the bottle pieces was measured.

The bottle pieces which had been washed with EHA were then washed with a NaOH aqueous solution. This base solution contained 0.63 mol of NaOH for every mole of EHA that had been used, and 2.5 g of water for every gram of EHA that had been used. Next, the base solution was recovered using a glass pipette and mixed with the recovered EHA/motor oil mixture. The NaOH:EHA mixture was stirred for 30 min, after which the pH was measured using the same pH meter and probe previously described. After that, the mixture was centrifuged (Thermo Scientific IEC Medilite Microcentrifuge) at 3100 rpm for 15 min. After that time, the motor oil fraction was collected and the mass measured to determine the recovery. The recovered motor oil was analysed to identify any carboxylic acid contamination via ¹H NMR spectroscopy (Bruker 300.13 MHz

spectrometer) using CDCl_3 as solvent and ethanol (99.9%) as internal standard. To remove any remaining acid in the motor oil, the oil was washed 3x with a saturated sodium bicarbonate aqueous solution (3 x 10 mL washes). And the oil was analysed via ^1H NMR spectroscopy (Bruker 300.13 MHz spectrometer) using CDCl_3 as solvent.

The aqueous phase containing the deprotonated carboxylic acid was transferred to the sight gauge and pressurised to 10 bar. This reprotonated the carboxylic acid and caused it to form a separate organic liquid phase, which was recovered and weighed. The carboxylic acid was analysed via ^1H NMR spectroscopy (Bruker 300.13 MHz spectrometer) to determine whether it contained any water or leftover oil. CDCl_3 was used as solvent and ethanol (99.9%) as internal standard. The aqueous solution obtained after the addition of CO_2 was discarded. The recovered EHA was mixed with fresh EHA (to account for the mass loss to the aqueous solution) and used in a second extraction cycle with extra bottle pieces contaminated with motor oil. The processes performed in the first extraction were repeated to this second extraction. The EHA was once again recovered by adding a fresh mixture aqueous of NaOH and pressurising the aqueous solution to 10 bar of CO_2 . The mass of EHA recovered was measured and used to determine the overall recovery after the extractions.

S2. Systems with a stoichiometric amount of base

These tests evaluated the use of less basic amines. The original work by Chen *et al.*¹ made use of an ecotoxic and relatively basic amine, Jeffamine D-230. Decreasing the initial pH of the acid/base/water mixture could facilitate the separation once CO_2 is added, since the protonation of the carboxylic acid occurs at lower pH values. Following the procedure used by Chen *et al.* in which the base:acid mole ratio was 1:1 and the water:acid mass ratio was 15:1, mixtures containing octanoic acid, EHA, PPA, or CPPA as the acid and either Jeffamine D-230, TEA, MDEA, DMEA or 3DMAP as the base were prepared. In addition, attempts were made at different water:acid mass ratios (Table S1). Upon addition of 1 bar of CO_2 , no phase separation was observed, meaning the %protonation of the carboxylic acid was not sufficient to initiate the formation of the acid-phase. As a result, a series of modifications were attempted to obtain a successful ASHS combination.

Table S1. Comparison among the carboxylic acid and bases combinations at varying water:acid mass ratios. The pH and the behaviour of the system are presented.

Base	Carboxylic acid	H ₂ O:acid mass ratio	pH under air	pH under 1 bar of CO ₂	Behaviour of the system after CO ₂ addition
Jeffamine D-230	Octanoic acid	1:1 - 9.5:1	Between 7.60 - 7.90	Between 6.85 - 7.60	No phase separation
Jeffamine D-230	Octanoic acid ^a	15:1	7.55	6.70	Partial phase separation ^b
Jeffamine D-230	CPPA	12:1	7.00	6.55	No phase separation
Jeffamine D-230	CPPA	15:1	6.94	6.45	No phase separation
Jeffamine D-230	PPA	12:1	7.86	6.84	Partial phase separation
Jeffamine D-230	PPA	15:1	8.43	6.73	Partial phase separation
Jeffamine D-230	EHA	12:1	6.98	6.94	Partial phase separation
Jeffamine D-230	EHA	15:1	8.34	6.74	Partial phase separation
TEA, MDEA, DMEA or 3-DMAP	Octanoic acid	12:1 - 15:1	7.60 - 7.70	6.70 - 6.90	No phase separation
TEA, MDEA, DMEA or 3-DMAP	EHA	1:1	7.50 – 8.30	7.50 – 8.05	No phase separation
TEA, MDEA, DMEA or 3-DMAP	EHA	2:1	8.00 – 8.15	7.20 – 7.60	No phase separation
TEA, MDEA, DMEA or 3-DMAP	EHA	6:1	7.50 - 8.10	6.20 - 6.70	No phase separation
TEA, MDEA, DMEA or 3-DMAP	EHA	15:1	6.80 - 7.90	6.60 - 6.80	No phase separation

The temperature was maintained at 20 °C. The CO₂ pressure used for all the experiments was 1 bar (CO₂ was added via a dispersion tube). The base:acid mol ratio was maintained at 1:1, except for the systems containing Jeffamine D-230. Because it has two basic sites, two moles of carboxylic acid were used per mole of D-230.

^a Sample was prepared following the same ratios described by Chen *et al.*¹ The results obtained were also similar.

^b The “partial phase separation” label was used for systems where the amount of carboxylic acid recovered after the addition of CO₂ was smaller than the mass of carboxylic acid added.

S3. Systems with a substoichiometric amount of base

The next series of tests varied the base:acid ratio. In the previous examples,^{1,2} the base:acid mole ratio was maintained at 1:1. For the systems described here, this ratio was decreased, and different base:acid ratios were explored. Base was added until a monophasic mixture was obtained under air.

The results with different amounts of base can best be understood by comparing the pH of the solution under air (pH_{air}) to the system midpoint. For a system to be successful, the pH_{air} must be above the system midpoint pH to ensure that the acid is primarily in the anionic form. The system midpoint pH refers to the pH at which 50% of the acid has been protonated, regardless of the location of the acid in the system.^{3,4} Because phase separation occurs, the system midpoint is not

equal to the pK_a of the acid. The pH_{air} needs to be close enough to the system midpoint that the addition of 1 bar of CO_2 can lower the pH below the system midpoint. For most base/acid combinations, a 1:1 mole ratio produced a pH_{air} so far above the system midpoint that the addition of 1 bar of CO_2 could not lower the pH enough. We observed that the addition of substoichiometric amounts of base created solutions with pH_{air} values only slightly above the system midpoint. Only for those samples was the addition of CO_2 able to trigger the formation of a separate liquid acid phase. Table S2 compiles the acid:alkanolamines combinations attempted.

Although phase separation was observed with the systems containing substoichiometric amounts of alkanolamines, there were still issues with some of the combinations. A threshold of 50% volume recovered was set to identify the successful systems. Some of the combinations crossed that threshold. However, even though a switchable behaviour was observed, the carboxylic acid (organic) phase was in some cases significantly larger in volume than the amount of carboxylic acid initially added to the system. This observation, when it occurred, was an indication that both base and water were being drawn from the aqueous phase into the acid phase (confirmed via GC-FID). This issue had to be addressed because reusing the acid was not possible due to the excessive contamination with water and amine. This contamination impacted any attempts made to deprotonate the acid using a fresh aqueous base solution. Although full recovery of the carboxylic acid was not achieved, the utilisation of substoichiometric amounts of the base led to substantial acid recovery for combinations of CPPA, PPA or EHA with one or more of the amines.

During the experiments with substoichiometric amounts of the base, another modification was also successfully attempted. As previously pointed out, past ASHS required very large volumes of water, at least 9.5 g of water per g of carboxylic acid. All of our attempts at using less water failed when the base:acid mole ratio was 1:1. The pH under CO_2 was too high, and no phase separation was observed. However, once we decreased the base:acid molar ratio, it became possible to use less water. For the same systems presented in Table S1, we were able to decrease the water:acid mass ratio to 2.5:1 and still observe phase separation upon CO_2 addition. Unfortunately, the volume of the acid-phase was still above the initial volume of acid added.

Table S2. Comparison among the carboxylic acid and bases combinations with a substoichiometric amount of base. The pH and the behaviour of the system are presented.

Carboxylic acid	Base	base:acid mole ratio	pH under air	pH under 1 bar of CO_2	Behaviour of the system after CO_2 addition
Octanoic acid	TEA	0.65:1	6.68	6.75	No phase separation
Octanoic acid	MDEA	0.65:1	6.69	6.65	No phase separation
Octanoic acid	DMEA	0.60:1	6.86	6.71	Phase separation below 50 vol%
Octanoic acid	3DMAP	0.55:1	6.34	6.46	Phase separation below 50 vol%
CPPA	TEA	0.40:1	5.98	6.04	No phase separation
CPPA	MDEA	0.50:1	6.16	6.23	No phase separation
CPPA	DMEA	0.50:1	6.22	6.25	No phase separation
CPPA	3DMAP	0.45:1	6.06	6.02	Phase separation above 50 vol%
PPA	TEA	0.60:1	6.51	6.72	No phase separation
PPA	MDEA	0.55:1	6.59	6.69	Phase separation above 50 vol%
PPA	DMEA	0.55:1	6.70	6.78	Phase separation above 50 vol%
PPA	3DMAP	0.60:1	6.63	6.70	Phase separation above 50 vol%
EHA	TEA	0.55:1	6.48	6.53	No phase separation
EHA	MDEA	0.55:1	6.50	6.61	No phase separation
EHA	DMEA	0.55:1	6.57	6.69	Phase separation above 50 vol%
EHA	3DMAP	0.50:1	6.53	6.64	Phase separation above 50 vol%

The temperature was maintained at 20 °C. The CO_2 pressure used for all the experiments was 1 bar (CO_2 was added via a dispersion tube). The H_2O :acid mass ratio was maintained at 2.5:1.

S4. Additional data for the carboxylic acid:NaOH:H₂O systems presented in Figure 3

We are presenting additional data for the carboxylic acid:NaOH:H₂O systems presented in Figure 3. We included the mole ratio between carboxylic acid:NaOH and the mass ratio between carboxylic acid:H₂O that resulted in the behaviours showed.

Table S3. Additional data for the ASHS presented in Figure 3. The carboxylic acid:H₂O mass ratio, the carboxylic acid:NaOH mol ratio and the behaviour of the systems under these conditions is presented.

ASHS	Carboxylic acid:H ₂ O mass ratio	Carboxylic acid:NaOH mol ratio	Behaviour of the system
2-ethylhexanoic acid	1:2.5	1:0.6	Switchable
2-hexyldecanoic acid	1:12	1:1	Biphasic under air
2-methylbutyric acid	1:2.5	1:0.5 - 1:1	Biphasic under air
2-phenylpropionic acid	1:2.5	1:0.5 and 1:0.6	Monophasic under 1 bar of CO ₂
2-propylpentanoic acid	1:2.5	1:0.8	Switchable
3-cyclopentylpropionic acid	1:2.5	1:0.8	Switchable
10-undecenoic acid	1:2.5	1:1	Switchable
Hexanoic acid	2:1	1:0.6	Monophasic under 1 bar of CO ₂
Isobutyric acid	1:2.5	1:0.6	Monophasic under 1 bar of CO ₂
Linoleic acid	1:5	1:1	Biphasic under air
Nonanoic acid	1:2.5	1:0.7	Switchable
Octanoic acid	1:1.5 and 1:2.5	1:0.9	Switchable
Oleic acid	1:10	1:1	Biphasic under air

S5. Additional data for the EHA:NaOH:H₂O systems

We are presenting Fig. 4 with the pH obtained for the mixtures prior to the addition of CO₂.

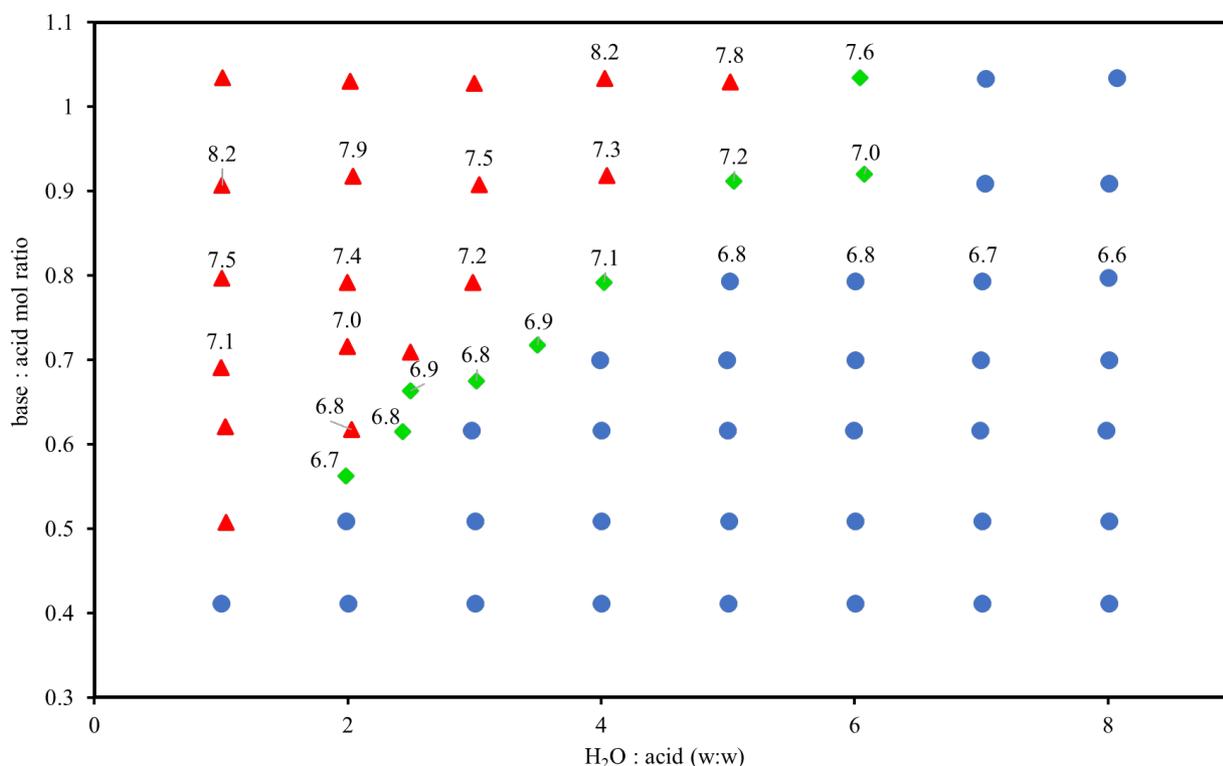


Fig. S1 ASHS behaviour for systems with varying EHA:NaOH:H₂O ratios. The molar ratio for NaOH:EHA is used and for the H₂O:EHA the mass ratio is used. The blue ● denote conditions where the ratio used resulted in a system that remained biphasic under air. The green ◆ are attributed to the systems where a switchable behaviour for the ASHS was observed (monophasic under air and biphasic under CO₂). The red ▲ represents the systems that remained monophasic upon addition of 1 bar of CO₂. In addition to the pH obtained to the mixture prior to the addition of CO₂.

The pH of some of the EHA:NaOH:H₂O mixtures was also obtained before the addition of CO₂ (SI Fig. S1). The goal was to determine if there was a dependency of the switchable behaviour in regards to the pH of the solution. If that was to be the case, instead of having to prepare solutions with precise ratios, the pH of the solution under air could serve as an indication to predict the behaviour of the system. Unfortunately, as the data presented demonstrated, that was no correlation between the pH and a switchable behaviour. For example, the sample with the 0.8:1 NaOH:EHA mole ratio and 3:1 H₂O:EHA mass ratio which did not present a switchable behaviour had the same pH (7.2) as the sample with a 0.9:1 NaOH:EHA mole ratio and 5:1 H₂O:EHA mass ratio, which presented a switchable behaviour. Similar behaviour was observed for other mixtures tested. However, when comparing the pH of samples with the same EHA:NaOH mol ratio, it was observed that with an increase in the amount of water added to the system, there is a decrease in the pH observed under air. For the samples with NaOH:EHA mole ratio of 0.9:1, the samples with H₂O:EHA mass ratio from 1:1 to 3:1 do not present a switchable behaviour under 1 bar of CO₂, and the pH varies from 7.5 to 7.2 respectively. For the sample with a 4:1 mass ratio, the pH observed was 7.1. Once extra water is added, the systems become biphasic under air, and the pH

decreases from 7.1 to 6.6. These results might indicate a threshold pH in which the aqueous solution becomes too acidic (because the NaOH is being diluted), and the carboxylic is not deprotonated by the base under air. Further investigation needs to be carried over to determine if this behaviour is replicated for other systems, but the preliminary data suggests a correlation of the behaviour of the system, at least when the same EHA:NaOH mol ratio is maintained.

S6. Additional data for the recycling of polystyrene foam

During the recycling of polymers using CSHS, one of the issues faced was the contamination of the polymer obtained with the solvent; this was not an issue for the ASHS tested. Fig. S2 shows the ^1H NMR spectra obtained for the initial EPS foam (a), the recovered EPS powder after treatment with CPPA (b) and the polymer obtained after extrusion (c). As Figs S1b and S1c show, no peaks associated with CPPA were detected. This demonstrates that the addition of the aqueous solution of NaOH and subsequent rinsing cycles of the EPS powder with the NaHCO_3 solution successfully removed the residual CPPA below the detection limit of NMR spectroscopy.

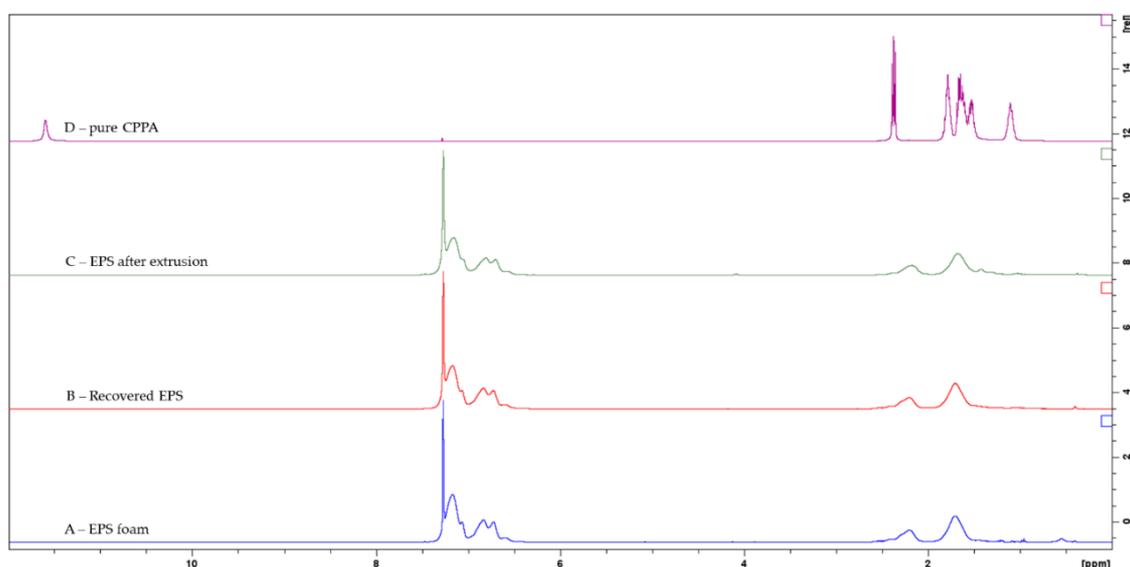


Fig. S2 ^1H NMR spectra demonstrated that there was no detectable contamination of the EPS powder obtained after recycling using CPPA as the solvent or after the extrusion process. The spectra was obtained using a 400 Hz NMR and $\text{d}_6\text{-C}_6\text{D}_6$ as the solvent. Spectra A was obtained for the EPS foam; spectra B was obtained for the EPS powder after the ASHS recycling process; spectra C was obtained for the polymer pieces after the powder was submitted to extrusion; and spectra D was obtained for pure CPPA.

Aiming to confirm the importance of the NaHCO_3 washes, ATR-FTIR spectra were obtained for the original EPS foam, the recovered polystyrene powder after treatment with the NaOH aqueous solution; and the powder after rinsing with the sodium bicarbonate solution to remove residual CPPA (Fig. S3).

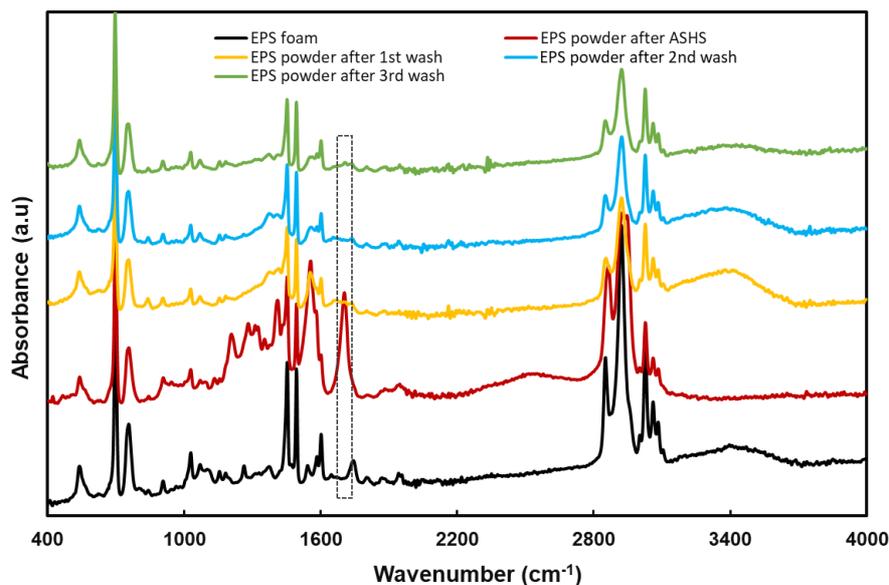


Fig. S3 FTIR-ATR spectra for EPS foam (in black), the recovered EPS powder after the NaOH aqueous solution was added (in red) and the EPS powder after subsequent washes with the NaHCO₃ solution (in yellow, blue and green). The carbonyl peak at 1719 cm⁻¹ (grey box) which is associated with the presence of CPPA disappeared after the EPS was submitted to additional rinses with a NaHCO₃ solution. Demonstrating that the rinses are a necessary step to remove any leftover ASHS even after the addition of the NaOH solution.

The peak at 1719 cm⁻¹ is associated with the presence of a carbonyl stretch in the CPPA solvent. This peak is still present in the EPS powder, even after the CPPA solvent was deprotonated by the addition of the NaOH aqueous solution but not after the powder was further washed with a NaHCO₃ aqueous solution. As evidenced by the FTIR spectra presented in Fig. S3, even after a first rinsing cycle, the peak at 1719 cm⁻¹ completely disappears, indicating that the CPPA contaminating the EPS powder was deprotonated and washed out by the basic bicarbonate solution. The rinsing solution could potentially be treated to recover the CPPA dissolved on it in order to maximise the CPPA recovery.

EHA was also tested as a possible solvent to dissolve the EPS foam. Different from CPPA, when EHA was mixed with the EPS foam, a very viscous mixture was obtained. The maximum EPS loading that could be attained and still allow for the next steps to occur was 5 wt%. In addition, the dissolution of the EPS into EHA was slower, and upon heating, the solution attained a rubber-like consistency which impeded the continuation of the process. Upon addition of the NaOH solution to this rubbery mixture, the polymer does not precipitate. Instead, an oil with a lower density than the aqueous solution is formed. For these reasons, EHA was ruled out as a possible solvent for this specific application.

S7. Additional data for the recovery of motor oil from used bottles

The ASHS was able to remove the motor oil from the bottle pieces as efficiently as a VOS; however, the oil recovered was still contaminated by EHA. NMR spectra were obtained for the oil recovered with the ASHS. As can be seen, the ^1H NMR (Fig. S4) shows that the oil recovered was still contaminated by a small amount of EHA. The spectrum obtained for the recovered oil still presented peaks from EHA around 5.40 ppm, 2.10 ppm and overlapping with the motor oil peaks. Aiming to quantify the amount of EHA still mixed with the oil recovered, we added an internal standard to the mixture (EtOH); however, due to the overlap in the peaks for the oil and EHA, quantification was not possible. To address this issue, the oil recovered was washed with a saturated solution of NaHCO_3 (3×10 mL). After that, the oil was recovered and analysed via ^1H NMR. As can be seen, after the washes, there are no peaks associated with EHA, demonstrating that the washing procedure was efficient to remove any carboxylic acid remaining in the oil.

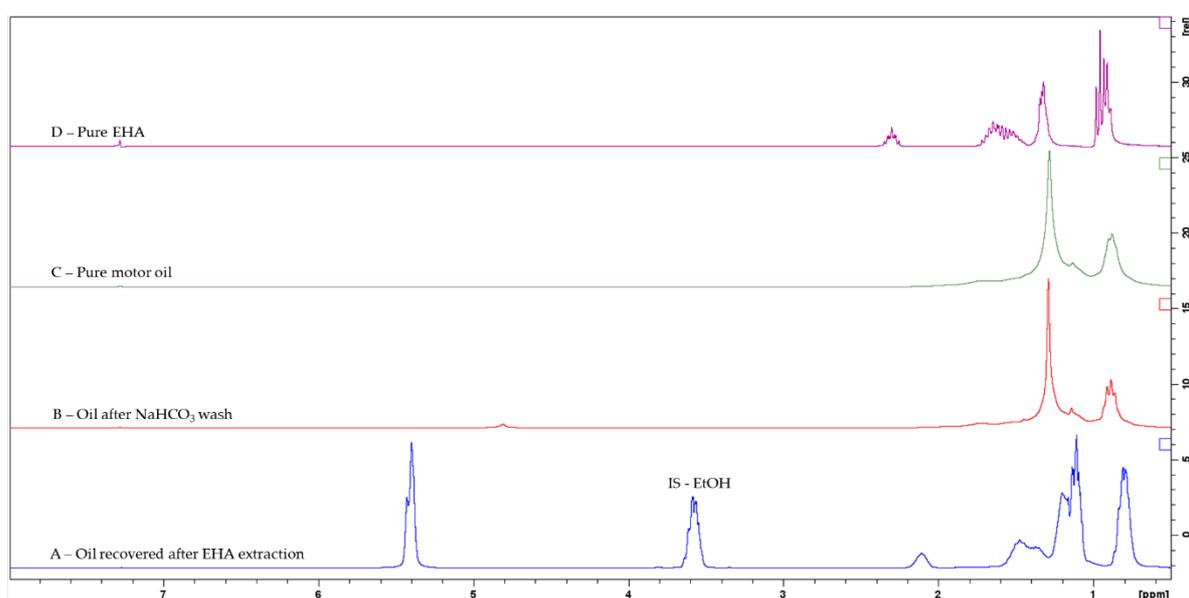


Fig. S4 ^1H NMR spectra obtained for the oil recovered after extraction with ASHS, the oil extracted after washes with saturated NaHCO_3 , pure motor oil and pure EHA. As observed in the spectra obtained for the recovered oil, there is still EHA mixed with the oil, as confirmed by the peaks at 5.40 and 2.10 ppm, and the overlap with the oil peaks. However, after the washes with NaHCO_3 the spectra obtained demonstrated that the acid was almost removed to completion, but there is still a small amount present.

S8. Initial economic comparison between ASHS and CSHS

An accurate estimate of economic improvements provided by the ASHS over CSHS would require a thorough simulation of costs, resources and equipment required. However, based on the changes promoted by the utilization of ASHS, we hypothesize that lower costs when a lower base to acid ratio is adopted can be expected from:

1. The capital cost differential arises from the larger equipment required. According to the aim of the process, this will be a mixer and/or a separator, the relevant pumps and piping.

In general, the cost of tanks, pumps, piping and valves scale with the power 0.6 of their size/capacity. For instance, for the separator tank volume, V_T :

$$V_T = \frac{V_s + V_{H_2O}}{\varepsilon} = \frac{V_s + r \cdot V_s}{\varepsilon} = \frac{(1 + r)}{\varepsilon} V_s$$

where V_s is the volume of solvent required by the process, which is a result of the liquid to solid (L/S) of the contact process at the scaled upsize, r is the water to solvent ratio (which in turn depends upon the base to acidic solvent ratio), and ε is the voidage ratio of the separator at its operating filling. It should be noted here that while processes are often studied in a single stage at a fairly high L/S at the small scale, L/S can be reduced by adopting multi-stage, countercurrent processes and staged equipment with reduced solvent usage generally represent the most convenient solution at the industrial scale. For instance, for the separator case:

$$\left(\frac{C'}{C_o}\right) = \left(\frac{V'_T}{V_{T_o}}\right)^{0.6} = \left(\frac{1 + r'}{1 + r_o}\right)^{0.6} \sim \left(\frac{3}{10.5}\right)^{0.6} \sim 0.47$$

Therefore, the cost of the separator would be halved if a reduced base/acid ratio is adopted, with entailed reduction of the water/fatty acid ratio. Similar gains can be expected for pumps, piping, and valves.

2. The operating cost differential arising from the lower amount of water turnover, which accounts for the lower cost of pumping, and a lower make-up for unavoidable losses of reactants in water purge streams. This concerns the fatty acids, whose loss to the water stream is proportional to the water volume required, and amine/alkali.
3. The cost differential arising from the management of substances which have a different impact on the human health and/or the environment, any intervening regulatory implication.

S9. References

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