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## Sustainability spotlight Statement

The presented paper relates to Goal 12 (Sustainable Consumption and Production). The need for battery recycling exists and will undoubtedly become even more important in the future to enable the transition to a more sustainable and circular economy. Solvent extraction is often used for the recovery of critical metals. However, many processes rely on unsustainable, petroleum-derived diluents, often with low boiling points and low flash points, increasing the risk of accidents. In this paper, we demonstrate the application of two aromatic compounds with excellent physiochemical properties that are required for a suitable diluent and are made from feedstocks that can be obtained from renewable resources.



## ARTICLE

## Safer aromatic process diluents for solvent extraction of critical metals from spent batteries

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Accepted 00th April 2026

DOI: 10.1039/x0xx00000x

This Paper presents the demonstration of two aromatic compounds 1,4-di-tert-pentylbenzene and 1-methyl-4-(tert-pentyl)benzene as safer alternative process diluents in the application of critical metal recovery. Recycling of batteries is needed and within the hydrometallurgy recycling route, solvent extraction (SX) offers a highly efficient, highly selective and low energy separation technique. Besides available options for sustainable, aliphatic diluents like HVO100, aromatic alternatives, suitable for both laboratory and industrial use, are deficient. Synthesis and characterization (NMR and GC-MS) are provided and important process parameters (boiling point, flash point, viscosity, solubility, density, surface tension and inter-surface tension) were measured. Eligibility of the aromatic diluent candidates were investigated by solvent extraction using Aliquat 336, DEHPA and Cyanex 272 as extractants with various experimental conditions and metal compositions of typical battery metals like nickel (Ni), copper (Cu), cobalt (Co), manganese (Mn) and rare earth elements (REEs). Performance was compared against commercially used diluents.

### 1 Introduction

Energy consumption and the demand for energy storage has increased significantly in the past decades.<sup>1,2</sup> This trend can be attributed not only to the increasing use of portable electronic devices (mobile phones, laptops, smart watches, etc.), electrical vehicles (EV) and hybrid electrical vehicles (HEV), but also to a higher demand for renewable energy sources. All this energy needs to be stored for portable applications or for later use.<sup>3,4</sup> The two most important types of rechargeable storage systems (secondary batteries) are nickel-metal hydride (Ni-MH) batteries and Lithium-Ion batteries (LIBs).<sup>5–8</sup> According to Eurostat around 244 000 tonnes of portable batteries and accumulators were sold in 2022 in the European market and it is estimated that the demand of batteries will increase 14-fold globally by the year 2030 and the trend continues.<sup>9,10</sup> With an average cycle life of 400–1200 for LIBs and around 500 for Ni-MH batteries it is expected that an increasing number of end-of life batteries will enter the waste stream. According to an estimation of the International Energy Agency a total amount of LIB waste generated by the year 2040 could be around 8 million tons, that, if not recycled and reused will have a detrimental environmental impact.<sup>1,11</sup> Considering the uneven distribution and limited world reserves of materials resources like nickel (Ni), cobalt (Co), lithium (Li), rare earth elements (REEs) and graphite as well as ongoing worldwide geopolitical tensions, mining conditions, and market

fluctuations, it becomes more and more important to properly recycle the growing number of spent batteries.<sup>11</sup> In addition to the aspects mentioned, the EU has listed many elements that are present in batteries as critical raw materials.<sup>12</sup> For example Ni-MH batteries are rich in Ni, Co and REEs and an average HEV battery contains around 3.5 kg REEs.<sup>2</sup> LIBs on the other hand contain elements like Li, Ni, Co, as well as manganese (Mn), and graphite. In addition, other parts of the battery like copper (Cu) and aluminium (Al), which are used as the current collectors, are listed as critical materials as well. Therefore, spent end-of-life batteries are valuable secondary resources.<sup>2,6,12–15</sup>

Two processes are commonly used in the field of recycling: pyrometallurgy and hydrometallurgy. While pyrometallurgy is a relatively simplified process with high process capacities and high applicability, the main disadvantages are high energy consumption, loss of lithium, and secondary contamination of processed material. Hydrometallurgy, on the other hand, has a very low energy consumption, is highly efficient and can produce high purity products. Moreover, this route does not produce harmful dust emissions.<sup>16</sup> The main disadvantage of a hydrometallurgy process is its high consumption of chemicals and the production of large amounts of waste.<sup>17,18</sup> Among the variety of hydrometallurgy recycling routes, liquid-liquid extraction (more commonly known as solvent extraction or SX) is a well-established and widely applied separation technology due to its ability of high selectivity, high efficiency, mild operating conditions as well as low losses of the desired target compound.<sup>19–21</sup> Introduced as a large scale process for uranium purification during the U.S. Manhattan project in the 1940s, solvent extraction can nowadays be found in various areas like the pharmaceutical and food industry, as well as in the chemical

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Supplementary Information available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x



industry or in waste treatment for example battery recycling, where it is used to recover and produce high purity metals. Moreover, solvent extraction can also be used in basic research for investigation of equilibrium and kinetics of complex formation reactions.<sup>19,22–27</sup>

The International Union of Pure and Applied Chemistry (IUPAC) defines solvent extraction as a separation technique in which a dissolved substance is transferred from any sort of matrix to an immiscible or partially miscible liquid phase, which is in contact with the first phase. If both phases are liquids, the term solvent extraction is synonymous to liquid-liquid extraction.<sup>28–30</sup> In a hydrometallurgy process for example, solvent extraction is used to selectively recover and purify valuable metals from spent batteries. A complex, powdered mixture of graphite, cathode and anode materials, electrolyte and current collectors, known as black mass (BM) is dissolved in acid, often sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) or hydrochloric acid (HCl).<sup>2,31,32</sup> In order to recover and separate the dissolved metals, the acidic, aqueous phase (leachate) is contacted with an appropriate solvent. Note here, that in the field of solvent extraction, IUPAC refers to the term solvent as the whole initial phase. This phase is composed of a diluent (often organic) in which the extractant (the active compound responsible for complexation and transfer of the substance of interest from one phase to another) is dissolved. Both compounds together form the solvent.<sup>25,27,28</sup> Extractants such as the acidic di-(2-ethylhexyl) phosphoric acid (DEHPA)<sup>33,34</sup> and di-2,4,4-trimethylpentylphosphinic acid (Cyanex 272)<sup>22,34</sup> or the lipophilic ionic liquid Aliquat 336 (a quaternary amine salt) which consists of *N,N,N*-trialkyl-*N*-methyl ammonium (mainly *N,N,N*-octyl-*N*-methyl ammonium) cations and chloride anions have been used to extract metals from aqueous solutions.<sup>34,35</sup>

The diluent makes up much of the solvent phase and must be mutually miscible with the used extractant (and possible additives like phase modifiers) and able to dissolve the extracted metal complex, while simultaneously being insoluble in the aqueous phase and exhibit adequate surface tension. Moreover, another significant requirement for a diluent is low volatility and a high flashpoint to decrease solvent loss during operation and reduce fire hazards. This is especially important for larger industrial operations. A good diluent should also be relatively cheap and readily available.<sup>27,34</sup> The majority of diluents are produced from fossil fuels, many of them bulk industrial chemicals with other purposes like Isopar L, Kerosine, Solvesso 150ND or Shellsol A100.<sup>27,36,37</sup> Many of these are harmful for organisms and environment. Therefore, the need to develop safer and more sustainable process chemicals for solvent extraction is growing and many suitable candidates have been developed so far. For example it has not only been demonstrated that hydrogenated vegetable oil (HVO100) is a suitable replacement for aliphatic petroleum derived kerosine<sup>21,38</sup> but also that two bio-sourced aliphatic diluents (DEV2139, made from used cooking oil) and (DEV2063, made from tall oil) can be used for solvent extraction of LIBs.<sup>39</sup> However, it is not possible to use either HVO100 or other aliphatic kerosene as the diluent for all solvent extraction work. A

need exists to be able to form a homogenous solution of the extractant in the diluent and after contact with the aqueous phase. Separation of the organic phase into multiple phases when loaded with metals must be avoided. Although some natural compounds like *p*-Cymene,  $\alpha$ -Pinene or *D*-Limonene have been discussed as potential replacements for aromatic compounds such as xylene or toluene, they are volatile and have low flashpoints.<sup>40</sup> Therefore, a clear need for an alternative aromatic process diluent was identified.

In this work, we demonstrate the application of the two aromatic compounds 1,4-di-*tert*-pentylbenzene and 1-Methyl-4-(*tert*-pentyl)benzene as safer alternative process diluents for solvent extraction of valuable metals from spent batteries. With an industrial process in mind, we focused on upscaling of the reaction as well as measurements of physical chemical properties that are important for a solvent extraction process and have not been reported in the literature yet. We compared these two diluent candidates with existing and commonly used diluents in combination with the extractants Cyanex 272, DEHPA and Aliquat 336 with a broad spectrum of aqueous systems compositions and extraction conditions.

## 2 Experimental

### 2.1 Chemicals and Methods

Unless stated otherwise, all chemicals were purchased from Sigma-Aldrich and were used without further purification. Purities are given in brackets. Methanol (MeOH,  $\geq 99.8\%$ ), Benzene ( $>99\%$ ), Toluene ( $>99\%$ ), *tert*-Butylbenzene, 2-Methyl-2-butene (83% - 89%), Ethylbenzene, 1,3-Diisopropylbenzene, Eucalyptol ( $\geq 99\%$ ), (3-butoxypropyl)benzene, Solvesso<sup>TM</sup> 150ND (Exxon Mobile), Solvesso<sup>TM</sup> 200ND (Exxon Mobile), HVO100 (produced by Neste and purchased from a petrol station in Vara, Sweden. HVO100 was stored over basic alumina before use), DEHPA (97%), Aliquat 336 (Fisher Scientific, 97%), Cyanex 272 (Cytec Canada,  $>90\%$ ), nitric acid (HNO<sub>3</sub>) (65% -67%), nitric acid superpure (69%), hydrochloric acid (HCl) (37% w/w), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) (95% - 98%), Oxalic acid (99%), sodium sulfate ( $\geq 99\%$  anhydrous), sodium bicarbonate (NaHCO<sub>3</sub>) ( $\geq 99.7\%$ ), MilliQ deionized water (resistivity  $> 18\text{ M}\Omega\cdot\text{cm}$ ), sodium chloride (NaCl) ( $\geq 99\%$ ), CuSO<sub>4</sub> · 5H<sub>2</sub>O ( $\geq 99\%$ ), cobalt sulphate (CoSO<sub>4</sub> · 7H<sub>2</sub>O,  $\geq 99\%$ ), magnesium sulfate (MgSO<sub>4</sub> · 7H<sub>2</sub>O,  $\geq 89\%$ ), zinc sulfate (ZnSO<sub>4</sub> · 7H<sub>2</sub>O, 99%), aluminium chloride (AlCl<sub>3</sub> · 6H<sub>2</sub>O, 99%), cobalt chloride (CoCl<sub>2</sub> · 6H<sub>2</sub>O, 98%), manganese chloride (MnCl<sub>2</sub> · 4H<sub>2</sub>O,  $\geq 98\%$ ), nickel chloride (NiCl<sub>2</sub> · 6H<sub>2</sub>O,  $\geq 98\%$ ), copper chloride (CuCl<sub>2</sub>, 99%), zinc chloride (ZnCl<sub>2</sub>,  $\geq 98\%$ ), cadmium nitrate (Cd(NO<sub>3</sub>)<sub>2</sub> · 4H<sub>2</sub>O, 98%), potassium permanganate (KMnO<sub>4</sub>,  $\geq 99\%$ ), Emulsifier-safe<sup>TM</sup> LSC-cocktail (Perkin Elmer) were used throughout the experiments and analytics reported in this work. Nuclear Magnetic Resonance (NMR) spectra were recorded at room temperature on a Bruker AvanceNeo 600 device. Chromatography with Mass Spectrometry (GC-MS) experiments were performed on an Agilent Technologies 7890A GC System coupled with an Agilent Technologies 5977A MSD mass detector (EI). The data was processed using the



MassHunter software and detected compounds were identified by comparison of the recorded MS spectra with the NIST Mass Spectral Library (NIST 20). UV/Vis spectra and Infrared (IR) spectra were recorded on a Jasco V-730 UV/VIS Spectrophotometer and on a Perkin Elmer Spectrum 3 Tri-Range MIR/NIR/FIR with a PIKE Technology Monolithic diamond ATR, respectively. An Inductively Coupled Plasma Mass Spectrometer (ThermoScientific iCAP Q equipped with a ASX520 autosampler) and Inductively Coupled Plasma Optical Emission Spectrometer (ThermoScientific iCAP Pro equipped with a ASX560 autosampler) were used to measure the concentrations of metals in aqueous solutions. Further information about analytical equipment, methods and parameters are given in the ESI.

## 2.2 Synthesis and Characterisation

**Warning:** Benzene is carcinogenic. Exposure to benzene is associated with acute myeloid leukemia, myelodysplastic syndrome, aplastic anemia, and lymphomas. Avoid inhalation and skin contact.<sup>41,42</sup>

### 2.2.1 Synthesis of 1,4-di-tert-pentylbenzene

1,4-di-tert-pentylbenzene was synthesized according to a procedure reported by Ipatieff et al.<sup>43–45</sup> A 2l 3-neck round bottom flask was equipped with a thermometer, a 250 ml dripping funnel and a Dimroth condenser. The flask was charged with conc. sulfuric acid (100 ml) and the flask was cooled down to around 5 °C with an ice bath. After reaching the temperature, benzene (418 ml, 4,7 mol) was added, and the mixture was stirred for 10 min until the temperature dropped below 10 °C. Then 2-Methyl-2-butene (1000 ml, 9,41 mol, 660 g) was slowly added via the dripping funnel. The rate of addition was adjusted, that the temperature of the stirring mixture was hold in a range between 10 °C and 15 °C. After completion, the ice bath was removed, and the reaction mixture was allowed to warm up to room temperature. Water (100 ml) was added, and the pale, yellowish organic phase was separated from the aqueous phase. The separated organic phase was first washed with saturated aqueous sodium hydrogen carbonate solution (NaHCO<sub>3</sub>, 3 x 100 mL) and later with brine (sat. NaCl solution, 1 x 100 ml). The organic phase was dried over anhydrous sodium sulfate (NaSO<sub>4</sub>), filtered and unreacted benzene was removed by distillation under atmospheric conditions (1 atm). The product mixture was then further purified via vacuum distillation, and the product was obtained as a colorless and odorless liquid.

**Yield:** 68 % (GC calculated yield)

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>): δ = 7.26 (s, 4H), 1.65 (q, <sup>3</sup>J = 7.4 Hz, 4H), 1.29 (s, 12H), 0.70 (t, <sup>3</sup>J = 7.4 Hz, 6H) ppm.

**<sup>13</sup>C-NMR** (600 MHz, CDCl<sub>3</sub>): δ = 146.33 (s, 2C), 125.57 (s, 4C), 37.56 (s, 2C), 37.09 (s, 2C), 28.53 (s, 4C), 9.33 (s, 2C) ppm.

**MS** (GC-MS): m/z = calculated for C<sub>16</sub>H<sub>26</sub> = 218,20, found = 218,20.

### 2.2.2 Synthesis of 1-methyl-4-(tert-pentyl) benzene

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DOI: 10.1039/D6SU00096G

1-methyl-4-(tert-pentyl)benzene was synthesized in a similar way as 1,4-di-tert-pentylbenzene accordance to a procedure that was reported by Ipatieff et al.<sup>43–45</sup>

A 500 ml 3-neck round bottom flask was equipped with a thermometer, a 250 ml dripping funnel and a dimroth condenser. The flask was charged with conc. sulfuric acid (10 ml) and the flask was cooled down to around 5 °C with an ice bath. After reaching the temperature, toluene (150 ml, 1,41 mol, 1 eq.) was added and the mixture was stirred for 10 min until the temperature dropped below 10 °C. Then, 2-Methyl-2-butene (150 ml, 1,41 mol, 1 eq.) was slowly added via the dripping funnel. The rate of addition was adjusted, that the temperature of the stirring mixture was hold in a range between 10 °C and 15 °C. During the addition, the reaction mixture turned from colorless to slightly pale yellow. After completion, the ice bath was removed, and the reaction mixture was allowed to warm up to room temperature. Water was added and the aqueous phase and organic phase were separated. The organic phase was washed with saturated aqueous sodium hydrogen carbonate solution (NaHCO<sub>3</sub>, 3 x 100 mL until the solution was neutral and then with brine (1 x 100 ml). The combined organic phases were dried over anhydrous sodium sulfate (NaSO<sub>4</sub>), and filtered. To remove remaining traces of unreacted toluene the crude mixture was purified by distillation under atmospheric conditions (1 atm). After toluene was removed, the crude product was further purified by vacuum distillation. 1-methyl-4-(tert-pentyl) benzene was obtained as a colourless liquid.

**Yield:** 94 % (GC calculated yield)

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>): δ = 7.28 – 7.24 (m, 1H), 7.15 (d, *J* = 7.9 Hz, OH), 2.36 (s, 1H), 1.67 (q, *J* = 7.4 Hz, 1H), 1.31 (s, 2H), 0.73 (t, *J* = 7.4 Hz, 1H) ppm.

**<sup>13</sup>C-NMR** (600 MHz, CDCl<sub>3</sub>): δ = 146.60 (s, 1C), 134.79 (s, 1C), 128.82 (s, 2C), 125.97 (s, 2C), 37.66 (s, 1C), 36.98 (s, 1C), 28.66 (s, 2C), 20.99 (s, 1C), 9.29 (s, 1C) ppm.

**MS** (GC-MS): m/z = calculated for C<sub>12</sub>H<sub>18</sub> = 162,14, found = 162,14.

## 2.3 Physicochemical properties measurements

### 2.3.1 Viscosity

The viscosity of the two synthesised compounds was measured with an Ostwald viscometer (Fungilab, Viseometer U-Tube BS/U Size E). A 2L Erlenmeyer flask was filled with deionised water and was then heated up to 25 °C. The viscometer was placed in the water. After the temperature stabilized, the analyte was filled into the viscometer until the calibration mark was reached. The system was allowed to heat up for 15 minutes before the first measurement. The temperature of the water bath was measured with a thermometer before the experiment was performed. Each compound was measured 6 times and between each measurement the tube was cleaned with water and acetone before being dried and readjusted. Viscosity was measured against water as a reference.



### 2.3.2 Solubility

**Aqueous in organic:** The solubility of water in the two diluents 1,4-di-tert-pentylbenzene and 1-methyl-4-(tert-pentyl)benzene was determined with liquid scintillation counting (LSC) of tritium ( $^3\text{H}$ ) using a liquid scintillation counter (PerkinElmer life sciences, Wallac Guardian 1414).

**Warning:** At this point it should be noted that tritium is a beta emitting radionuclide which should only be used by a trained radioactive worker in a facility licensed and equipped for work with open radioactive sources. Note that tritium cannot be detected with a Geiger-Müller detector due to its low decay energy.

Glass vials (3.5 ml) were filled with 1 ml of tritiated water and with 1 ml of diluent. The vials were carefully closed with polyethylene push-in caps to prevent accidental leakage and contamination. The vials were further sealed with parafilm before shaking for 1 min by hand and centrifuged for 1 min. The caps were carefully removed, and 0.5 ml of the organic phase was pipetted into a scintillation vial (7 ml) that already contained the LSC cocktail. To investigate potential quenching effects during measurement, a set of calibration vials was prepared by loading 100  $\mu\text{l}$ , 200  $\mu\text{l}$ , 300  $\mu\text{l}$  and 400  $\mu\text{l}$  of diluent, with equal amounts of tritium (100  $\mu\text{l}$ ) into a scintillation vial and filled up to volume (7 ml) with LSC cocktail. In total 4 quenching vials, 2 blank vial and 3 measurement vials were prepared for each diluent. The 3 measurement vials were prepared in order to always measure in triplicates. LSC parameters were chosen in a way that each measurement lasted either until 10000 counts were reached or until a duration of 1 hour was reached.

**Organic in Aqueous:** The solubility the two diluents 1,4-di-tert-pentylbenzene and 1-methyl-4-(tert-pentyl)benzene in water was determined by UV/Vis using high precision quartz glass cuvettes with 10 mm pathlength (Hellma Analytics). Screw top head space glass vials were filled with 4 ml of water and 1 ml of organic phase and sealed with headspace screwcaps. The closed vials were shaken violently for 1 min and were left overnight before they were centrifuged (4000 rpm, 5 min). After that, 3 ml of the aqueous phase was carefully removed with a syringe through the septum from the lower end of the vial with was hold upside down. In this way, it was possible to remove the aqueous phase without contamination from the organic layer. A full spectrum of each compound with a concentration of 2 mM was measured within the range from 300 nm to 230 nm with a scan rate of 40 nm/min. This was done to evaluate the Wavelength at which maximum absorption occurs ( $\lambda_{\text{max}}$ ). After the determination of ( $\lambda_{\text{max}}$ ) a calibration curve was measured ranging from 2 mM to 0,016 mM at a fixed wavelength of  $\lambda_{\text{max}}$ . After that the samples were measured as triplets and the concentration was calculated.

### 2.3.3 Flash point

Flash points of 1,4-di-tert-pentylbenzene and 1-methyl-4-(tert-pentyl)benzene were measured according to ASTM D 92 (ASTM International test method) for materials with a flash point above 79 °C and below 400 °C.<sup>46</sup> The measurements were performed with a Herzog OptiFlash Nerzoo PAC (Cleveland Open Cup Tester). The sample (ca. 75 ml) was placed in an open cup sample holder, that was heated up from room temperature. A heated wire was present above the surface of the liquid sample that was oscillating over the surface. When the flash point was reached, a lid descended onto the sample holder and the experimental rig was allowed to cool down to room temperature before the next sample was measured.

### 2.3.4 Surface tension and Inter-surface tension

Surface tension of the two diluents 1,4-di-tert-pentylbenzene and 1-methyl-4-(tert-pentyl)benzene were measured using a force tensiometer (attention Sigma 701) and a Du Noüy Ring. The system was first calibrated with a calibration weight and then the liquids were measured at room temperature (22 °C). The method started by immersing the ring 3 mm into the liquid. Then the ring was lifted very slowly until it reached the end position which was set to be 5 mm above the surface. Within each experiment, the sequence was repeated 3 times and 30 measurement points were collected. Both diluents were measured in triplicates. The Inter-surface tension was measured against water as the denser phase and the set up and experimental procedure was similar to the one described for the surface tension measurement.

### 2.3.5 Density

The densities of 1,4-di-tert-pentylbenzene and 1-methyl-4-(tert-pentyl)benzene were measured using pycnometers (2 ml). Each sample was measured 3 times, and the average was calculated. All measurements were performed at room temperature (22 °C).

### 2.3.6 Stability against radiation

The stability of both diluents against radiation was investigated using a shielded irradiator (Gammacell 220, Atomic Energy Canada Limited) that was equipped with a 12 GIK-7-4 type cobalt-60 source. At the time of the experiments, the activity was around 143 TBq. Two glass ampoules were prepared by sealing the bottoms of two glass Pasteur pipettes using a propane torch and then filled with around 1 ml of the diluent. After that, the half-sealed ampoules were placed in liquid nitrogen and cooled down while a vacuum was applied. The top parts were sealed, and the ampoules were transferred to the exposure chamber of the irradiator and were irradiated with  $\gamma$ -radiation for a total time of 140 hours and 32 minutes. The received  $\gamma$ -dose rate at the time of measurement was 3 kGy/h. After exposure, the diluents were compared with reference samples of the non-irradiated diluent by GC-MS to investigate if the radiation caused decomposition.

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DOI: 10.1039/D6PY00006E



## 2.4 Solvent extraction

Distribution ratios ( $D$ ) were obtained by solvent extraction experiments. The distribution ratio ( $D$ ) is defined as the ratio of the total analytical concentration of an element in one phase (the organic phase,  $\overline{[c]}$ ) to its total analytical concentration in the other phase (the aqueous phase,  $[c]$ ) as described in equation (1).<sup>27,28</sup>

$$D = \frac{\overline{[c]}}{[c]} \quad (1)$$

In these experiments equal volumes (700  $\mu$ l) of aqueous and organic phases were pipetted into a glass vial (3.5 ml) and sealed with polyethylene push-in caps. To prevent accidental leakages each vial was further sealed with parafilm to cover the joints between glass vial and plastic cap. Prepared vials were transferred to a shaker (IKA VXR basic Vibrax®) equipped with a temperature-controlled vial holder. Unless noted otherwise, all liquid-liquid experiments were performed at a set temperature (25 °C) for a shaking time of 1 hour to reach equilibrium and at a constant speed of 1500 shakes per minute. After one hour of shaking the vials were transferred to a centrifuge (Thermo Scientific Heraeus Labofuge 200) and were centrifuged at 4000 rpm for a set time of 5 minutes to achieve a quick phase separation. The caps were removed carefully, and a sample (400  $\mu$ l) of the aqueous layer (almost always the lower layer) was transferred into a polyethylene ICP vial (15 ml) by pipetting. It is important to avoid taking any droplets of organic phase and make sure that no residue of organic phase is stuck on the pipette tip. The samples were diluted with hydrochloric acid (1 M, containing 1 ppm of either ruthenium or rhodium as the internal standard). If samples containing refractory metals in high oxidation states (such as Zr(IV), Nb(V) or Ta(V)), 1 % oxalic acid was added to the hydrochloric acid, and the used internal standard was always rhodium. In an early experiment it was found that oxalic acid causes ruthenium to disappear from the aqueous solutions in the analysis, rhodium was chosen as a replacement as it has a lower rate of ligand substitution. Analysis was performed by ICP-OES. An overview of the conditions and compositions of the solvent extraction experiments is listed in table 1. More information about the preparation of the individual aqueous phases and organic phases used for the experiments are listed in the ESI.

## 3 Results and Discussion

### 3.1 Synthesis and Characterization

The aim of this research was the development of a safer alternative aromatic diluent that is suitable for a solvent extraction process on laboratory scale but also for a potential industrial scale application. To improve environmental compatibility and workplace safety, we focused especially on a diluent with low volatility and a high flash point, to reduce exposure for workers as well as diluent loss due to evaporation and fire hazards. Moreover, a low solubility of the diluent in the

**Table 1:** Conditions for solvent extraction experiments with various metals and the variation of process parameters. DOI: 10.1039/D6SU00096G

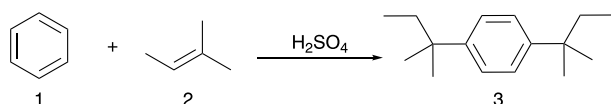
| Extractant             | Diluent   | Metals in aqueous solution                            | Experimental conditions  |
|------------------------|---|---|--|
| Aliquat 336 (30 % v/v) | TBB, Ethylbenzene, (3-butoxypropyl)benzene, Eucalyptol, Solvesso 150ND, Solvesso 200ND, 1,3-diisopropylbenzene, 1,4-di-tert-pentylbenzene 1-methyl-4-(tert-pentyl)benzene | Al, Cd, Co, Cu, Mn, Ni, Zn                            | NaCl concentration (5,3 M) <b>Condition a</b>                                  |
| Aliquat 336 (30 % v/v) | Eucalyptol, Ethylbenzene, 1,4-di-tert-pentylbenzene 1-methyl-4-(tert-pentyl)benzene, Solvesso150ND  | Cu, Zn, Co, Mg  | NaCl concentration (0,5M – 100M) <b>Condition b</b>                            |
| Aliquat 336 (10 % v/v) | 1,4-di-tert-pentylbenzene, methyl-4-(tert-pentyl)benzene, Ethylbenzene Solvesso 150ND   | 1- Nb, Co   | NaCl concentration (0,5M – 100M) <b>Condition c</b>                            |
| Cyanex 272 (30 % v/v)  | HVO100, 1,4-di-tert-pentylbenzene, TBB  | Al, Co, Zn, Cd, La, Fe, Mn, V, Cr, Sm, Nd, Pr, Ce, Li | H <sub>2</sub> SO <sub>4</sub> concentration (0,5 % - 10 %) <b>Condition d</b> |
| DEHPA (30 % v/v)       | HVO100, 1,4-di-tert-pentylbenzene   |   |  |
| DEHPA (30 % v/v)       | HVO100, 1-methyl-4-(tert-pentyl)benzene,  | Al,Cd, Co, Cu, Mn, Ni, Zn                             | H <sub>2</sub> SO <sub>4</sub> concentration (0 % - 0.2 %) <b>Condition e</b>  |
| Cyanex 272 (30 % v/v)  | 1,4-di-tert-pentylbenzene, methyl-4-(tert-pentyl)benzene, Solvesso 150, HVO100  | 1- Zn   |  |

aqueous phase was preferable to minimize diluent loss during solvent extraction operation. Following the principles of green chemistry that were first developed by Paul Anastas and John Warner<sup>47-49</sup> we aimed to focus especially on the design of safer chemicals to minimize their toxicity (green chemistry principle 4), and on introduction of inherently safer chemistry to reduce

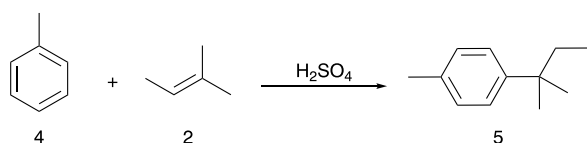


the likelihood and severities of accidents such as explosions, fires and unwanted releases into the environment (green chemistry principle 12). Additionally, we aimed for the usage of renewable feedstocks for the starting material of the compounds (green chemistry principle 7).<sup>48</sup> Based on these necessities, the two compounds 1,4-di-tert-pentylbenzene (**3**) and 1-methyl-4-(tert-pentyl)benzene (**5**) were selected as target molecules. The lab scale synthesis is shown in scheme 1.

a) Synthesis of 1,4-di-tert-pentylbenzene



b) Synthesis of 1-methyl-4-(tert-pentyl) benzene

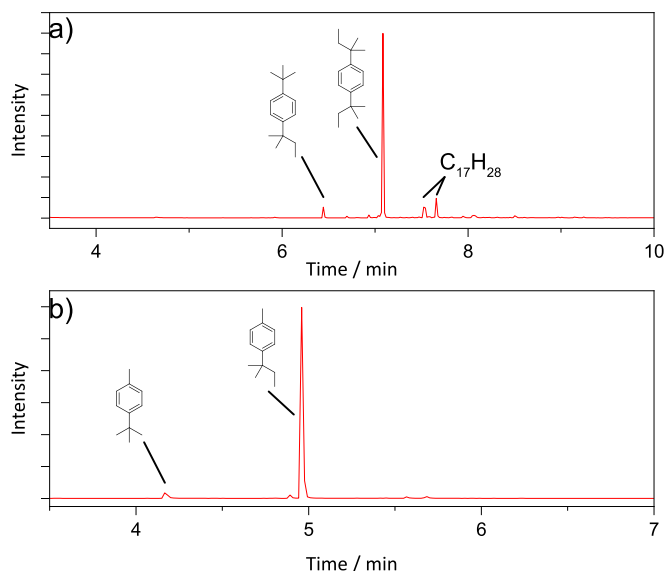


**Scheme 1:** a) Synthesis of 1,4-di-tert-pentylbenzene (**3**) from benzene (**1**) and 2-methylbut-2-ene (**2**) with catalytic amounts of acid (here sulfuric acid), b) Synthesis of 1-methyl-4-(tert-pentyl) benzene (**5**) from toluene (**4**) and 2-methylbut-2-ene (**2**) with catalytic amounts of acid (here sulfuric acid). Synthesis based on the work reported by Ipatieff et al.<sup>43-45</sup>

Although benzene (**1**) and toluene (**4**) were traditionally derived from non-renewable sources, and it is now widely accepted that there is no such thing as an *a priori* green diluent, the greenness factor of a diluent and the sustainability of a process is not just determined by the amount of non-benign chemicals, but a complex combination of inherent properties. In fact, if a more toxic chemical like benzene is used as a starting material, but is derived from renewable feedstocks, it can lead to a safer solvent extraction process, less waste production, less environmental pollution, if handled correctly at a well-designed plant, and reduced health impact, it aligns with the principles of green chemistry and has potential to be the greenest option for a given process according to Lancaster.<sup>48</sup> It has been shown that both benzene and toluene can be obtained from lignin.<sup>50-52</sup> Moreover, the used alkene 2-methylbut-2-ene can be synthesized from the natural compound isoprene or the corresponding alcohol can be obtained via fermentation. Although not yet produced commercially on a large industrial scale, the pathway and chemistry is available and bulk production might be possible in the future. This would satisfy the green chemistry principle to use renewable feedstocks for the synthesis of 1,4-di-tert-pentylbenzene and 1-methyl-4-(tert-pentyl)benzene.<sup>53-55</sup>

Purification of the raw material was done by distillation in two steps. The first distillation was performed at atmospheric pressure (760 Torr) to distill unreacted benzene ( $T_{\text{bp}} = 80\text{ }^\circ\text{C}$ )<sup>56</sup> or toluene ( $T_{\text{bp}} = 109\text{ }^\circ\text{C}$ )<sup>56</sup> from the product mixture which can be reused. The second distillation was performed under

reduced pressure and 1,4-di-tert-pentylbenzene was distilled with a boiling point of  $T_{\text{bp}} = 96\text{--}98\text{ }^\circ\text{C}$  at  $8.9 \cdot 10^{-4}\text{ mbar}$  (Lit<sup>57</sup>:  $T_{\text{bp}} = 262\text{--}265\text{ }^\circ\text{C}$  at 740 Torr). The compound 1-methyl-4-(tert-pentyl)benzene was distilled with a boiling point of  $T_{\text{bp}} = 80\text{--}82\text{ }^\circ\text{C}$  at  $4.9 \cdot 10^0\text{ mbar}$  (Lit<sup>58</sup>:  $T_{\text{bp}} = 212\text{--}215\text{ }^\circ\text{C}$  at 760 Torr). GC-MS analysis showed that the distilled products contained small amounts of side products. The two Chromatograms are shown in figure 1.



**Figure 1:** Chromatograms of **a**: 1,4-di-tert-pentylbenzene sample containing 1-(tert-butyl)-4-(tert-pentyl)benzene and two unidentified side products and **b**: 1-methyl-4-(tert-pentyl)benzene sample containing 1-(tert-butyl)-4-methylbenzene as a side product in small quantities.

In **a**) 1,4-di-tert-pentylbenzene was detected with a retention time of 7.085 min. 1-(tert-butyl)-4-(tert-pentyl)benzene was identified as a side product with a retention time of 6.444 min. However, two other signals were detected eluting at 7.525 min and 7.659 min respectively, that could not be identified with confidence. These two signals relate to two isomers with the chemical formula C<sub>17</sub>H<sub>28</sub>. In **b**) 1-methyl-4-(tert-pentyl)benzene was detected at 4.959 min. A minor side product signal was detected at 4.166 min and was identified as 1-(tert-butyl)-4-methylbenzene.

A full techno-economic analysis is outside of the scope of this work, however some key parameters like starting material availability and costs, synthetic complexity (including workup), and scalability potential of the production route, that govern economic feasibility should be qualitatively discussed to assess a potential industrial implementation. All feedstocks (benzene, toluene and 2-methyl-2-butene) are well established, readily available petrochemical platform chemicals that are produced on a large scale.<sup>59,60</sup> In contrast, the availability of the feedstocks from an alternative production route using renewable sources has not yet been implemented and remains at an early development stage. At present, any near-term production is more realistic from a basis of petrochemical sourcing. However, the potential alternative pathway is given, and the importance might grow in the near future taking



into account the limitation of the non-renewable feedstocks, political decision making as well as stricter regulations.<sup>40</sup> As shown in scheme 1, both diluent candidates were obtained through a Friedel-Crafts alkylation reaction.<sup>61</sup> This reaction is already implemented on an industrial scale to synthesize other alkylated aromatic compounds like tert-butylbenzene using a Friedel-Crafts catalyst like aluminum chloride (AlCl<sub>3</sub>), hydrofluoric acid (HF) or Boron trifluoride (BF<sub>3</sub>) or zeolites.<sup>62–64</sup> This indicates that scale-up production would not require a new reaction technology and that the primary cost drivers are predicted to arise from the selection of the feedstock source and the workup procedure. Downstream processing can be achieved by distillation and is expected to influence the process economics depending on the desired purity of the finished product. In consideration of the fact that many process diluents used in active solvent extraction processes like Solvesso 150ND or IsoparL are complex hydrocarbon mixtures (the chromatograms can be found in the ESI, figure S3), the downstream process does not need to produce high-purity, single compound diluents which may reduce purification requirements and associated costs. From a scalability perspective it can be assumed that the reaction can be performed in existing plants making use of well implemented industrial infrastructure. Additionally, we were able to successfully upscale the reaction from small lab scale volumes up to 5L in this study. In contrast to existing low-price diluents that are profiting from existing infrastructure and large production volumes, the cost of the new diluents might be higher per produced unit but they compensate this disadvantage by displaying improved safety-related properties, which is an extremely important parameter in the design of a solvent extraction process<sup>27,62,65,66</sup>

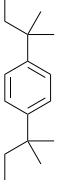
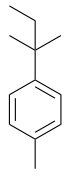
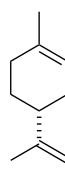
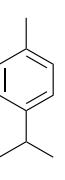
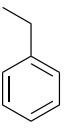
### 3.2 Physicochemical properties

The choice of a suitable diluent for a solvent extraction process is a crucial step and can be as important as the selection of a suitable extractant since diluents are not inert and can have a synergetic effect on metal extraction. Apart from some extractants like TBP that can be used without an additional diluent, extractants like Cyanex 921 or Aliquat 336 are either a solid or simply too viscous and require a diluent. Moreover, the use of a diluent in the organic phase can improve its hydrodynamic properties. Diluent use enables the adjustment of the extractant concentration, thus giving a distribution ratio suitable for the separation process. A list of important process related diluent parameters is displayed in table 2. The properties of the two diluent candidates that were investigated in this study were compared with ethylbenzene and Solvesso 150ND, which are used in laboratory and industrial-scale solvent extraction applications as aromatic diluents. *D*-Limonene and *p*-Cymene were compared as an example of bio-derived diluents. Additionally, HVO100 is compared as an example of a green sustainable aliphatic diluent shown to be effective in gold extraction.<sup>27,67</sup> The density values of 1,4-di-tert-pentylbenzene and 1-methyl-4-(tert-pentyl)benzene are within the range of those compounds, reported in table 2 as well as for other

commonly used solvent extraction diluents like Shellsol A100 (0.875 g/ml), Shellsol A150 (0.883 g/ml) and Shellsol A200 (0.992 g/ml).<sup>27</sup> In general, the density should be different enough from the used aqueous phase to ensure phase separation. In consideration of work safety and accident prevention, flash points and boiling points are vital. Especially on an industrial scale application, where large quantities of low volatility, flammable liquids are handled, the mix of diluent vapor and air can result in an explosion if ignited due to technical issues or human error.<sup>68</sup> Choosing a diluent with a high flash point therefore decreases risk of fire. Comparing the values in table 2 it is clear that the two investigated compounds (**3**) and (**5**) have far higher flash points than ethylbenzene, Solvesso 150ND and also HVO100. A similar trend is observable when comparing the values of Shell's Shellsol diluents A100 and A150 with flash points of 43 °C and 64 °C respectively.<sup>27</sup> Although distilled under vacuum, the boiling point of (**3**) and (**5**) can be estimated around 285 °C – 288 °C and 228 °C – 230 °C respectively when using the Clausius-Clapeyron equation. The boiling points exceed the ones from *D*-Limonene and *p*-Cymene, HVO100 as well as Solvesso 150ND and ethylbenzene. Only Shellsol A200 (T<sub>bp</sub> = 233–271 °C) shows a similar temperature range. A high boiling point decreases diluent loss during operation when the plant is running mixer settlers without being enclosed. Although this might be less problematic in a central european climate, in other areas like Australia or Africa the temperature becomes a important parameter. This aspect of reducing material loss not only aligns with environmental requirements to reduce pollution, but also with the green chemistry principle to use safer solvents and auxiliaries (green chemistry principle 5). Moreover, from an economic point of view, reducing the material loss decreases the cost to refill, and the organic phase can be used in more cycles. For many systems, viscosity increases with the concentration of extractant as well as with higher loading of metal. When viscosity problems occur, it might be necessary to operate the plant at higher temperatures, which results again in higher plant and operation costs.<sup>27</sup> Typical viscosities are within the range of 0.6 for ethylbenzene and can reach values up to 5.9 for Shellsol D120. Both investigated compounds are within the range of in-use diluents with 1,4-di-tert-pentylbenzene located on the higher end, while 1-methyl-4-(tert-pentyl)benzene is in the middle range, without significant deviations indicating a potential substitution possibility. We further investigated the solubility of the organic phase in water and of water in the organic phase. Solubility values should be small or negligible to prevent significant partitioning and reducing process efficiency and product recovery as well as operation costs. For both compounds (**3**) and (**5**) solubility values are small, indicating a negligible partitioning into the other phase. This means the organic phase can be recycled several times without being too dilute to hold the initial extractant concentration. The last two parameters that are important are surface tension and inter-surface tension. It is advantageous to use a diluent with a low surface tension because it will result in smaller droplets that have a larger contact area, thus making



**Table 2:** Properties of 1,4-di-tert-pentylbenzene and 1-methyl-4-(tert-pentyl) benzene as safer alternative diluents compared to two potential bio-derived natural diluents *D*-Limonene and *p*-Cymene, the sustainable biodiesel HVO100 as well as commercially applied diluents Solvesso 150ND and Ethylbenzene. Solubilities are measured as content of water (w) in organic (o), and as organic (o) in water (w).

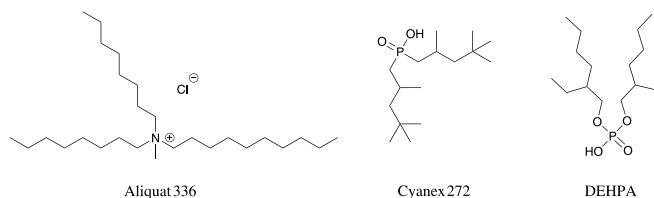
| Properties                              | 1,4-di-tert-pentylbenzene   | 1-methyl-4-(tert-pentyl) benzene  | <i>D</i> -Limonene <sup>40</sup>  | <i>p</i> -Cymene <sup>40</sup>  | HVO100 <sup>67,69</sup>                   | Solvesso 150ND <sup>65,67</sup>                                | Ethylbenzene <sup>36</sup>  |
|---|---|---|---|---|---|--|---|
| Chemical structure                      |  |  |  |  | Mixture of alkanes with up to 18 carbons. | Mixture of highly naphthalene-depleted C10 aromatic compounds. |  |
| Density (g/ml)                          | 0.8711 ± 0.0004 (at 22 °C)  | 0.8652 ± 0.0032 (at 22 °C)  | 0.841 (at 25 °C)  | 0.853 (at 25 °C)  | 0.780                                     | 0.898 (at 15 °C)   | 0.87 (at 20 °C)   |
| Boiling point (°C)                      | 96 – 98 (at 8.9 · 10 <sup>-1</sup> mbar)  | 80 – 82 (4.9 · 10 <sup>0</sup> mbar)  | 176   | 177   | 180-320                                   | 175  | 136.1   |
| Flash point (°C)                        | 133.7 ± 3.1   | 98.7 ± 3.1  | 48  | 47  | > 61                                      | 62   | 23  |
| Viscosity (mPa·s)                       | 3.84 ± 0.09 (at 25 °C)  | 0.96 ± 0.02 (at 25 °C)  | 0.897 (at 25 °C)  | 0.82 (at 25 °C)   | ≤ 5                                       | 1.198 (at 25 °C)   | 0.6725 (at 20 °C)   |
| Solubility w in o (mg·L <sup>-1</sup> ) | 709.9 ± 28.6 (at 22 °C)   | 578.3 ± 6.3 (at 22 °C)  |   |   | 34.2±2.5 ppm (v/v)                        | 386±95 ppm (v/v)   | 380 <sup>a</sup> (at 25 °C)   |
| Solubility o in w (mg·L <sup>-1</sup> ) | 13.94 ± 0.26 (at 22 °C)   | 4.20 ± 0.08 (at 22 °C)  | 20 (at 25 °C)   | 51 (at 25 °C)   | 0.075 mg/l (Calculated for 25 °C)         | Negligible   | 150 <sup>a</sup> (at 25 °C)   |
| Surface tension (mN/m)                  | 23.427 ± 0.028 (at 22 °C)   | 24.093 ± 0.013 (at 22 °C)   | 25.8 (at 25 °C)   | 28.5 (at 25 °C)   |   |  | 71.2 (at 23 °C)   |
| Inter-surface tension (mN/m)            | 25.250 ± 0.213 (at 22 °C)   | 28.743 ± 0.007 (at 22 °C)   |   |   |   |  |   |

<sup>a</sup> calculated from wt% values according to Rydberg *et al.*<sup>36</sup>

mass transfer between the two phases easier and faster. While the values for surface tension for (3) and (5) respectively are comparable with the values of *D*-Limonene and *p*-Cymene, ethylbenzene shows a higher value. It can be argued that in this case 1,4-di-tert-pentylbenzene and 1-methyl-4-(tert-pentyl) benzene might show a better performance in droplet size and mass transfer speed. For inter-surface tension no valid data could be found for comparison under suitable conditions without deviating too far from diluent-only values. However, the values for 1,4-di-tert-pentylbenzene and 1-methyl-4-(tert-pentyl) benzene are in the same order of magnitude as their corresponding surface tension, indicating the absence of significant interfacial effects. Investigation of the compound stability against radiation resulted in no detectable change by GC-MS. This result indicates that both compounds are stable against radiation within the experimental parameters. Additionally, UV/Vis and FT-IR spectra of the two compounds 1,4-di-tert-pentylbenzene and 1-methyl-4-(tert-pentyl)benzene have been recorded and available in the ESI.

### 3.3 Solvent extraction

Based on the evaluation of the physicochemical properties, both investigated compounds were considered as potential safer alternative process diluent substitutes, and the decision was made to evaluate their performance in a solvent extraction experiment. All structures of extractants used in this study are displayed in chart 1. Experimental conditions were listed in table 1.



**Chart 1:** Chemical structures of the extractants that were used in this study (from left to right): Aliquat 336, Cyanex 272 and DEHPA.



**Information:** Calculated D-Values are only reasonable in within the range of around 0.1 to around 100. At very low ( $D < 0.1$ ) or very high ( $D > 100$ ) distribution ratios, the extraction system approaches limiting conditions. Under such conditions, calculated D-values become highly sensitive to analytical uncertainty and provide no mechanistic or process relevant data and therefore are not shown<sup>70</sup>.

### 3.3.1 Aliquat 336 extractions

**Table 3:** Distribution ratios (D-Values) obtained from the extraction experiment of Aliquat 336 with different diluents (30 % v/v) for the manganese, copper and cobalt under experimental condition a.

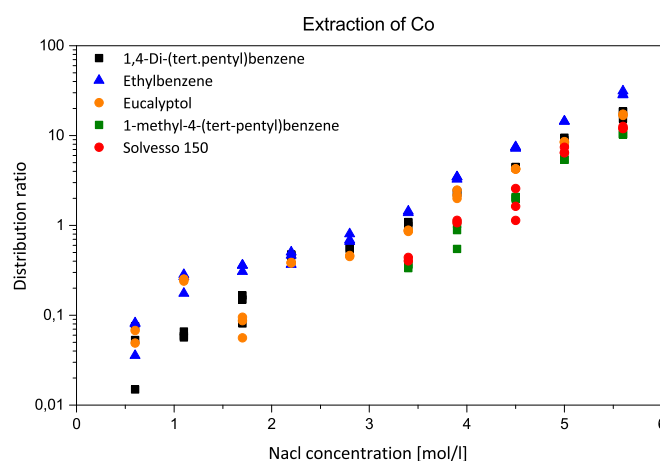
| Diluent name                    | Distribution ratios |          |          |
|---------------------------------|---------------------|----------|----------|
|                                 | $D_{Mn}$            | $D_{Cu}$ | $D_{Co}$ |
| 1,4-di-tert-pentylbenzene       | 1.597               | 61.134   | 13.810   |
| Solvesso 150ND                  | 1.975               | 71.513   | 16.248   |
| Solvesso 200ND                  | 3.418               | 108.472  | 27.299   |
| Ethylbenzene                    | 1.841               | 65.758   | 15.493   |
| 1,3-diisopropylbenzene          | 0.840               | 33.533   | 6.908    |
| TBB                             | 2.442               | 88.424   | 20.836   |
| (3-butoxypropyl) benzene        | 17.864              | 64.401   | 15.366   |
| Eucalyptol                      | 1.325               | 48.576   | 11.065   |
| 1-methyl-4-(tert-pentyl)benzene | 1.161               | 43.867   | 10.287   |

To evaluate the applicability of the new diluents under conditions relevant for battery recycling, a stepwise experimental strategy was employed. Initial experiments focused on the solvent performance compared to a wide variety of commonly used diluents under fixed conditions. For this purpose, Aliquat 336 was selected, and the aqueous phase was spiked with 5,3 M NaCl solution. The aqueous phase contained Al, Cd, Co, Cu, Mn, Ni and Zn (condition a). However, only Mn, Co and Cu exhibited distribution ratios within the analytical meaningful range and therefore only calculated D-Values of these metals are listed in table 3. The extraction behaviour of Mn across the tested systems showed that the D-value using 1,4-di-tert-pentylbenzene and 1-methyl-4-(tert-pentyl)benzene can be compared to those of commonly used diluents with 1,3-diisopropylbenzene having the lowest, and Solvesso 200ND the highest D-Value. The same trend can be observed for Co and Cu, indicating that diluent choice has no significant effect on the extraction efficiency. Comparing the D-Values within one system shows that extraction follows the trend of  $Mn < Co < Cu$ . This result is consistent with the well-known Irving-Williams series, according to which the stability of a metal complex only

depends on the metal ion and is largely independent of the choice of complexing agent, as widely observed in many different systems.<sup>71,72</sup>

Since both compounds showed satisfying results in the first initial experiment on the extraction performance under fixed conditions, the experimental design was extended by investigating the extraction performance as a function of NaCl concentration and extractant concentration according to condition b and c, respectively.

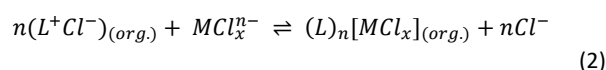
Figure 2 and figure 3 are showing D-values for Co and Cu extraction as a function of NaCl concentration. The solvent contained 30 % Aliquat 336 (condition b).



**Figure 2:** Distribution ratios (D-values) of Co in the form of  $[CoCl_4]^{2-}$  as a function of NaCl-concentration in a range between 0.5 M - 6 M for 1,4-di-tert-pentylbenzene, ethylbenzene, eucalyptol, Solvesso 150 and 1-methyl-4-(tert-pentyl)benzene according to condition b.

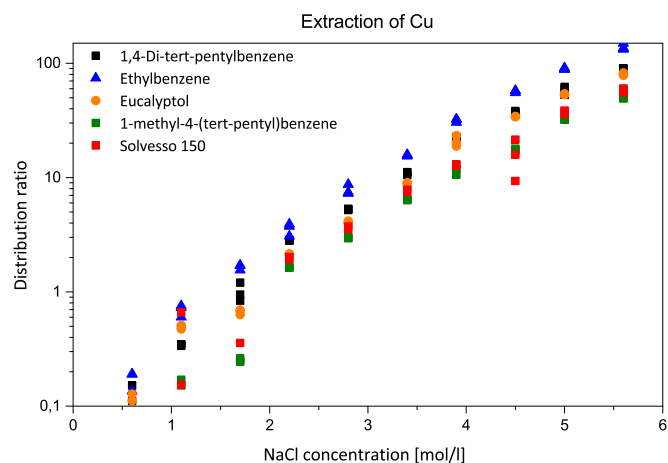
The results showed that D-values are increasing with increasing NaCl concentration and the trends are comparable between all used diluents. The reason for this trend is that Aliquat 336 is a tertiary ammonium salt and carries a permanent positive charge with chloride ( $Cl^-$ ) being the anion. Extraction occurs due to the formation of a neutral assembly (also referred to as an ion pair), and a higher chloride concentration in the aqueous phase favours the formation of stable anionic chloride species like  $[CuCl_4]^{2-}$ , or  $[CoCl_4]^{2-}$  that can be extracted by Aliquat 336.<sup>27,71</sup>

Equation 2 shows the extraction reaction where M is the metal cation and L the extractant cation.



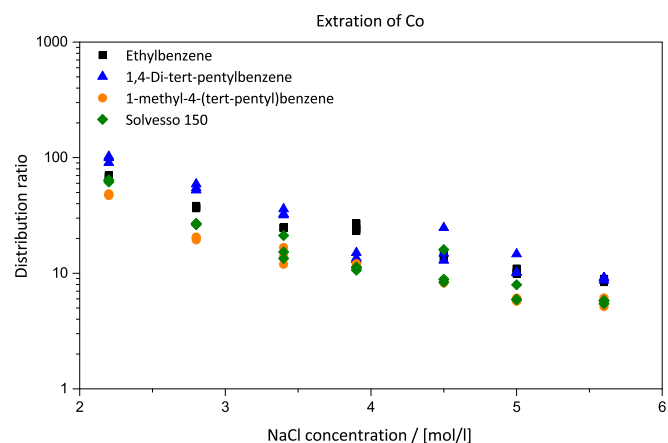
However, if the chloride concentration exceeds a certain limit, the chloride anion is competing with the chloro-complex for the remaining Aliquat cation, and the equilibrium is shifted to the reactant side resulting in decreasing distribution ratios. The beginning of this trend can be seen in figure 3, where the curve is flattening out at a chloride concentration around 4 M.





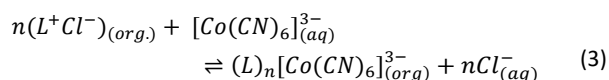
**Figure 3:** Distribution ratios (D-values) of Cu in the form of  $[\text{CuCo}_4]^{2-}$  as a function of NaCl-concentration in a range between 0.5 M - 6 M for 1,4-di-tert-pentylbenzene, ethylbenzene, eucalyptol, Solvesso 150 and 1-metyl-4-(tert-pentyl)benzene according to condition b.

Further experiments were performed with a lower extraction concentration of Aliquat 336 (10 %, condition c). Results are shown in figure 4 and in figure 5.



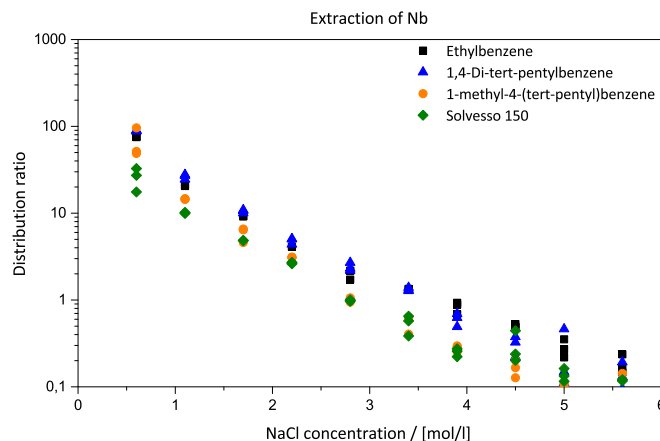
**Figure 4:** Distribution ratios (D-values) of Co in the form of  $[\text{Co}(\text{CN})_6]^{3-}$  as a function of NaCl-concentration (2 M - 6 M) for 1,4-di-tert-pentylbenzene, ethylbenzene, Solvesso 150 and 1-metyl-4-(tert-pentyl)benzene according to condition c.

Contrary to the previous results, an increase of NaCl concentration resulted in a decrease of the D-values. Although this seems to be counterintuitive at first, the observed trend can be explained by considering the present complex species. In figure 4 Co is present as the very stable species  $[\text{Co}(\text{CN})_6]^{3-}$ . Since the stability constant of  $[\text{Co}(\text{CN})_6]^{3-}$  is high, ligand exchange with chloride anions is kinetically disfavoured and no chloro-complex is formed.



According to the extraction mechanism in equation 3, the extraction of  $[\text{Co}(\text{CN})_6]^{3-}$  as the neutral species will release chloride anions. With increasing chloride concentration in the aqueous phase, the extraction equilibrium shifts to the reactant side, and as a result the

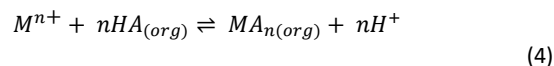
distribution ratio decreases as observed.<sup>71</sup> Similar system behaviour was observed for Nb extraction, where Nb was present in the form of  $[\text{Nb}(\text{O})(\text{C}_2\text{O}_4)]^{3-}$  and was extracted with Aliquat 336. Notably, it could be observed that 1,4-di-tert-pentylbenzene showed the same trends for extraction of various metals as the compared systems, indicating that it could be used as a greener alternative to common diluents. It should be noted here that only elements are shown that had D-values within the analytical reasonability as stated before. For elements that were included in the aqueous phase but not shown, D-Values were either too low ( $D < 0,1$ ) or significantly higher than the upper threshold around ( $D > 100$ ).



**Figure 5:** Distribution ratios (D-Values) of Nb in the form of  $[\text{Nb}(\text{O})(\text{C}_2\text{O}_4)_2]^{3-}$  as a function of NaCl-concentration (0.5 M - 6 M) 1,4-di-tert-pentylbenzene, ethylbenzene, Solvesso 150 and 1-metyl-4-(tert-pentyl)benzene according to condition c.

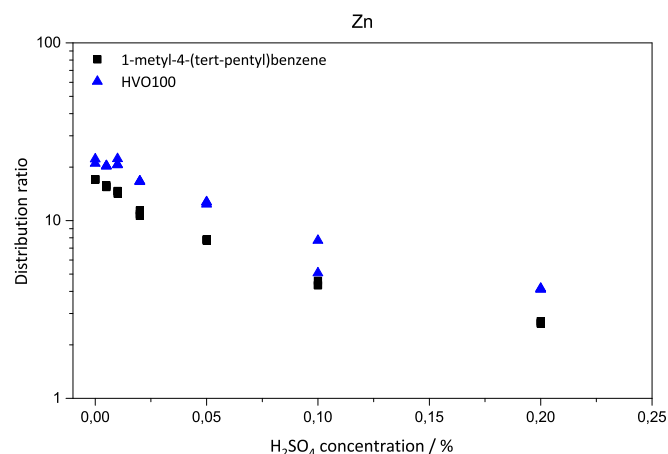
### 3.3.2 DEHPA extraction

DEHPA belongs to the class of acidic extractants (or cationic extractants), so they extract metals via a cationic exchange mechanism, where protons from the extractant are exchanged for the metal cation. This means the extraction for cationic extractants is pH dependant. Figure 6 shows the extraction of Zn with DEHPA in 1-methyl-4-tert-pentylbenzene and HVO100 according to experimental condition e. The extraction reaction is shown below in equation 4.



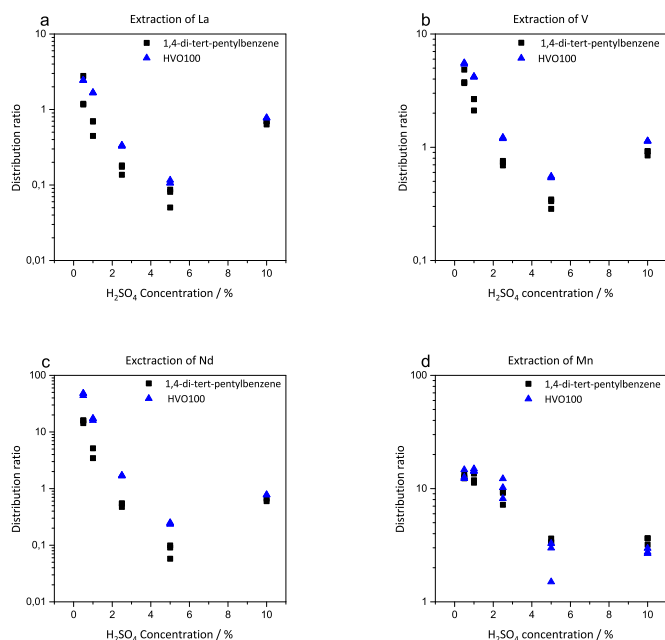
With increasing acid concentration, the equilibrium will shift to the left side and extraction is expected to decrease. This trend was observed and both used solvent systems showed comparable results. Distribution values for HVO100 are higher compared to values for 1-methyl-4-tert-pentylbenzene which was expected for aliphatic diluents. Although the aqueous phase contained Al, Co, Cu, Mn, Ni and Zn, only Zn showed distribution ratios within the reasonable range under the used experimental conditions. Further comparison experiments (experimental condition d) are shown in Figure 7.





**Figure 6:** Distribution ratios (D-values) of Zn as a function of various sulfuric acid concentrations (0% - 0.20%) for 1-methyl-4-(tert-pentyl)benzene and HVO100 according to experimental condition e.

In experiments a-d, 1,4-di-tert-pentylbenzene and HVO100 showed a similar trend in terms of extraction behaviour with HVO100 showing slightly higher distribution ratios, as commonly seen with aliphatic diluents. It can be observed that the distribution ratio is increasing at 10% acid concentration, which is counterintuitive at first. However, a change in pH to a certain level can also change the dominant extraction mechanism that can lead to more favoured formation of different species.<sup>73</sup> Since the aim of this work was to investigate comparability of the two new diluents, we did not investigate the extraction mechanism in detail.

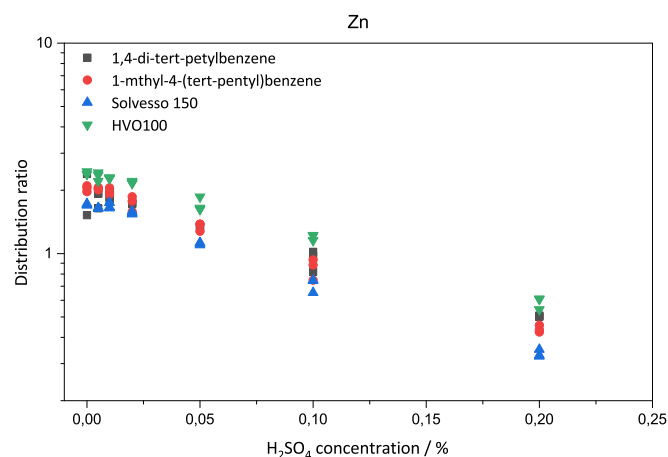


**Figure 7:** Distribution values (D-Values) of La (a), V (b), Nb (c) and Mn (d) as a function of various sulfuric acid concentrations (0.5% - 10%) for 1,4-di-tert-pentylbenzene and HVO100 according to experimental condition d.

### 3.3.3 Cyanex 272 extraction

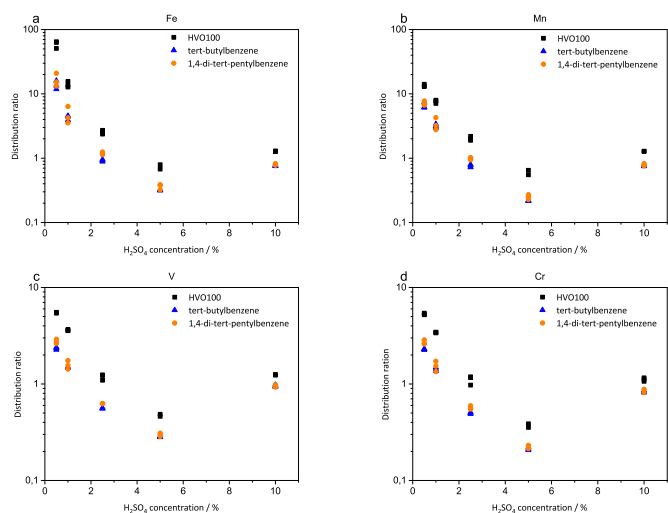
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DOI: 10.1039/D6SU00096G

Finally, Cyanex 272 was selected as an extractant as well due to its wide application in research and industry. The experiment was performed in a similar way as described for DEHPA and experimental condition d was used. The results are shown in figure 8 and figure 9.



**Figure 8:** Distribution ratios (D-values) of Zn as a function of various sulfuric acid concentrations (0% - 0.20%) for 1,4-di-tert-pentylbenzene, 1-methyl-4-(tert-pentyl)benzene, Solvesso 150 and HVO100 according to experimental condition e.

The results are comparable to the results with DEHPA shown in figure 6, following the same trend, and D-values are decreasing with higher acid concentration. Figure 9 shows the extraction of Fe, Mn, V and Cr where 1,4-di-tert-pentylbenzene, HVO100 and tert-Butylbenzene were used as diluents to make up the organic phase. Similar to the results from the DEHPA experiments, distribution ratios are decreasing with higher acid concentration before increasing again at 10% acid concentration. Additionally, HVO100 shows slightly higher D-values as often observed for aliphatic diluents.



**Figure 9:** Distribution ratios (D-Values) of Fe (a), Mn (b), V (c) and Cr (d) as a function of various sulfuric acid concentrations (0.5% - 10%) for 1,4-di-tert-pentylbenzene, HVO100 and tert-Butylbenzene according to experimental condition d.



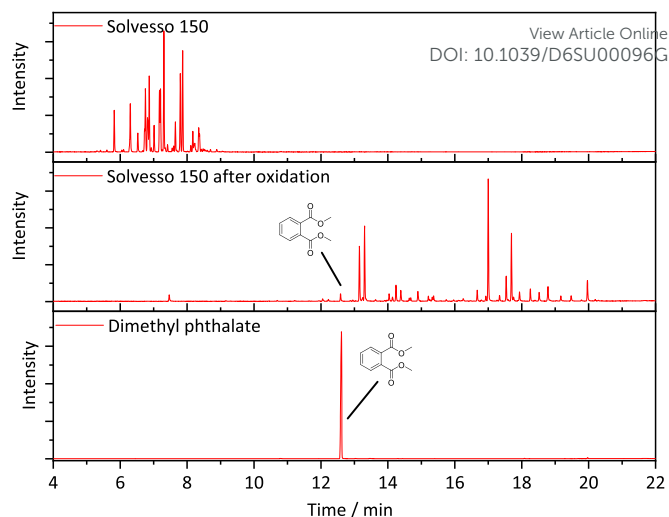
Overall, the general trend for both tested diluent candidates is consistent across all compared systems. It is important to mention that the quality of a process chemical is not proportional to the distribution ratio. In fact, excessive distribution ratios can frustrate the metal separation by impeding the removal of impurities (known as scrubbing) and the recovery of the extracted target (stripping stage) from the organic phase.<sup>74</sup> In summary, the results presented above show that the two investigated diluents not only possess properties that are very much like the properties for commercially and research-used diluents, but also perform identically in practical solvent extraction experiments, under various conditions and with a broad range of metals that are present in LIBs and Ni-MH batteries and are considered valuable for recovery.

Moreover, the different organic phases made up of different extractants that are widely used in research and industry showed no significant difference between the used diluents. The trends were comparable, indicating a good fit with various extractants.

## 4 Environmental and Workplace Safety Aspects

### 4.1 chronic neurotoxicity potential

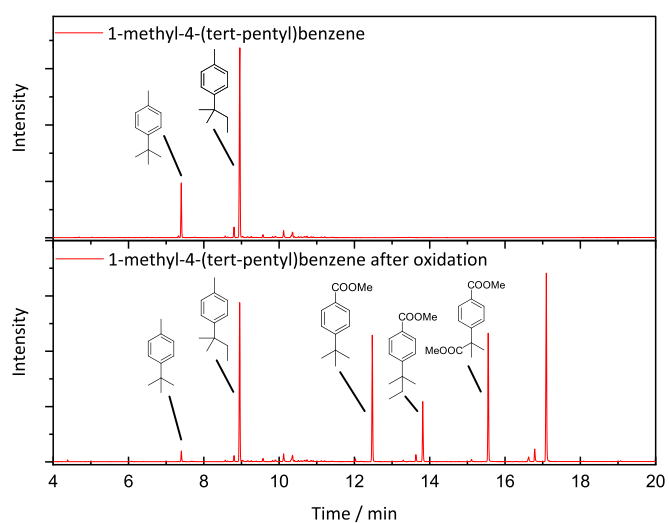
To evaluate further aspects of workplace safety, a possible neurotoxic potential was investigated. Both diluents 1,4-di-*tert*-pentyl benzene and 1-methyl-4-*tert*-pentylbenzene show potential to be safer by design (principle 4) compared to Solvesso 150 and other similar aromatic diluents like *o*-xylene, 1,2-diethylbenzene or 1,2-diisopropylbenzene.<sup>75</sup> It is well known that *n*-hexane is metabolised by cytochrome P450 into hexane-2-ol which is further oxidized into hexane-2,5-dione. In a similar way 1,2-alkylated aromatic compounds can be metabolized to the corresponding  $\gamma$ -diketones like 1,2-diacetylbenzene (1,2-DAB). These  $\gamma$ -diketones can undergo a Paal-Knorr reaction with the  $\epsilon$ -amino group of lysine or sulfhydryl groups in proteins to form pyrrole adducts, which is a key step in toxicity that promotes protein cross-linking, polymerization, and misfolding.<sup>76,77</sup> These processes disrupt proteostasis, including altered expression of protein disulfide isomerase and gelsolin, and lead to neurofilament accumulation in proximal axons and the formation of axonal spheroids—features consistent with central-peripheral axonopathy and early markers of neurodegeneration such as those observed in amyotrophic lateral sclerosis (ALS). The reaction with lysin also forms a blue pigment that results in blue-greenish discoloration of urine and tissues in rats. If 1,2-dialkylbenzenes precursors such as 1,2-diethylbenzene are present in aviation fuels and industrial solvents, they can then form 1,2-phenylene *bis*-alkylmethanones *in vivo*. These 1,2-phenylene *bis*-alkylmethanones are more neurotoxic than the hexane-2,5-dione formed from *n*-hexane.<sup>75,77</sup> A reference sample of Solvesso 150 was examined with GC-MS, and was



**Figure 10:** GC-Chromatograms for Solvesso 150 (**top**), Solvesso 150 after the oxidation and derivatisation (**middle**) and Dimethyl phthalate (**bottom**) as an authentic reference sample.

found to be predominately isomers of  $C_{10}H_{18}$ . If we confine ourselves to compounds with a single benzene ring with *n*-alkyl groups, it is possible to have at least seventeen different isomers. Many of these isomers are able to form 1,2-phenylene-*bis*-alkylmethanones. To investigate the formation of these neurotoxic compounds, 1,4-di-*tert*-pentyl benzene, 1-methyl-4-*tert*-pentylbenzene and Solvesso 150 were treated with potassium permanganate to form carboxylic acids according to a well-known mechanism.<sup>78</sup> The experimental procedure for the oxidation and the following esterification needed for GC-MS analysis is described in detail in the ESI.

Figure 10 shows GC-chromatograms from an unmodified Solvesso 150 sample (Top), a Solvesso 150 sample after oxidation and derivatisation (middle) and dimethyl phthalate as an authentic sample (retention time  $T_R = 12.612$  min). The results show that oxidation of Solvesso 150 lead to formation of small amounts of dimethyl phthalate and might have the

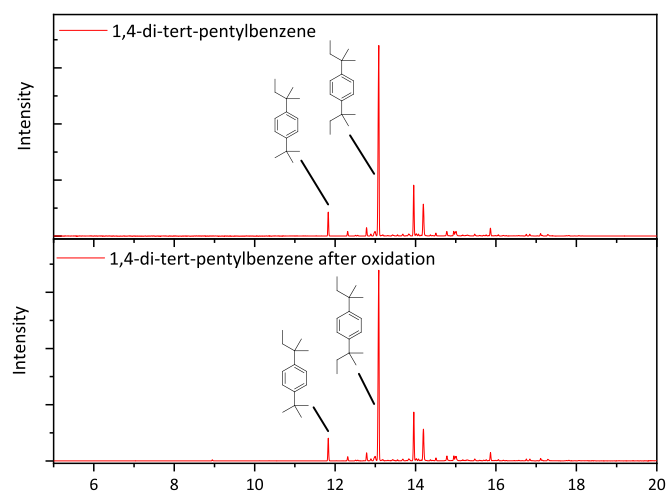


**Figure 11:** GC-Chromatograms of 1-methyl-4-(*tert*-pentyl)benzene (**Top**), and of 1-methyl-4-(*tert*-pentyl)benzene after oxidation and derivatisation (**bottom**).



potential to show neurotoxic effects typical for 1,2-DAB motifs as described. It can be deduced that many other isomers in Solvesso 150 with a 1,2 configuration will form 1,2-diketones and therefore might have neurotoxic potential as well.

In contrast oxidation of 1-methyl-4-(tert-pentyl)benzene does not indicate the formation of 1,2-diketones. Figure 11 shows a comparison of a sample of 1-methyl-4-(tert-pentyl)benzene (top) and a sample after oxidation. The oxidation leads to the appearance of 4 new significant signals that are related to methyl 4-(tert-butyl)benzoate ( $T_R = 12.457$  min), methyl 4-(tert-pentyl)benzoate ( $T_R = 13.814$  min), methyl 4-(1-methoxy-2-methyl-1-oxopropan-2-yl)benzoate ( $T_R = 15.522$  min) and another signal with a retention time of  $T_R = 15.522$  min, that might be attributed to methyl 4-(4-methoxy-2,3-dimethyl-4-oxobutan-2-yl)benzoate or a similar isomer with a molecular weight of 264.32 g/mol. None of the oxidation products relates to a 1,2-diketone. No conversion was observed for 1,4-di-tert-pentylbenzene an only starting material was recovered from the oxidation reaction as shown in figure 12. It can be argued that both diluents are therefore safer by design (principle 4) and increase the safety of the workplace for a process that is using either 1-methyl-4-(tert-pentyl)benzene or 1,4-di-tert-pentylbenzene as a process diluent.



**Figure 12:** GC-chromatograms of 1-methyl-4-(tert-pentyl)benzene (top) and 1-methyl-4-(tert-pentyl)benzene after oxidation (bottom). Only starting material was recovered and no chemical change could be observed.

#### 4.2 Simulation of evaporation rates

Another important process parameter that was investigated attributes to the evaporation rate of a given diluent. Since there is no process related data available, the evaporation rate and the air contamination was evaluated using a detailed modelling approach according to the work of Arnold and Engel.<sup>79</sup> This model allows an estimation of the evaporating rates from spills or open surface operations. The only parameters required are vapour pressure, molecular weight, the ambient air temperature and velocity of the wind as well as the area of the

**Table 4:** simulated values for the evaporation rate in  $\text{mg s}^{-1} \text{m}^{-2}$  and the air contamination in  $\text{mg m}^{-3}$  calculated for para-diethylbenzene, tert-butylbenzene, 1-methyl-4-(tert-pentyl)benzene and 1,4-di-tert-pentylbenzene.

|                                 | Evaporation rate<br>/ [ $\text{mg s}^{-1} \text{m}^{-2}$ ] | Air contamination<br>/ [ $\text{mg m}^{-3}$ ] |
|---------------------------------|--|---|
| para-diethylbenzene             | 67   | 669   |
| tert-butylbenzene               | 62   | 621   |
| 1-methyl-4-(tert-pentyl)benzene | 34   | 345   |
| 1,4-di-tert-pentylbenzene       | 2.3  | 23  |

liquid pool. Liquid pools are not just a potential risk for accidents but can also possess a health risk for potential plant workers, that are exposed to diluent fumes evaporated from the pool. In this simulation it is assumed that a mixer-settler with a length of 10 m is used in a solvent extraction process. The process is operated at 293 K (19,85 °C) and an assumed wind velocity of 1 m/s. Vapor pressure was estimated by the Clausius-Clapeyron-equation. The model was tested with para-diethylbenzene, tert-butylbenzene, 1-methyl-4-(tert-pentyl)benzene and 1,4-di-tert-pentylbenzene. Results are listed in table 4. Under the given simulated parameters, both diluent candidates perform better than the comparing systems. The evaporation rate of 1-methyl-4-(tert-pentyl)benzene is almost half the value of para-diethylbenzene or tert-butylbenzene. The evaporation rate of 1,4-di-tert-pentylbenzene is almost 30 times smaller than para-diethylbenzene and tert-butylbenzene and around 17 times smaller than 1-methyl-4-(tert-pentyl)benzene. The same trend can be found for the concentration in the contaminated air. The low evaporation indicates clearly a reduction in fire risk and a safer process (principle 12). According occupational exposure limit values from 2018, published by the Swedish Work Environment Authority (Arbetsmiljöverket) the recommendation for jet fuel and diesel fuel was reported to be  $350 \text{ mg/m}^3$  (value is expressed as time-weighted average value over a regular working day).<sup>80</sup>

Based on the Swedish air limits it is possible to compute the highest number of moles of ethylbenzene, toluene, and xylene per cubic meter of workplace which is reasonable. If we consider an unventilated room with an open container of one of our diluents then the air will be far less contaminated with the arene than it would be for either 1,4-diethylbenzene or tert-butylbenzene. This method was used to estimate if the aliphatic diluent HVO100 exceeds the Swedish air limits.<sup>67</sup> It turns out that para-diethylbenzene and tert-butylbenzene exceed the limit by 88 times and 82 times, respectively. 1-methyl-4-(tert-pentyl)benzene exceeds the limit only by 39 times while 1,4-di-tert-pentylbenzene is only about a factor of 2 over the limits. In summary, both diluents exhibit a clear reduction in fire and accident risk as well as an increase in human health and a



decrease in environmental pollution due to the lower evaporation rates.

## 5 Conclusions

This work successfully demonstrates the use of two aromatic compounds 1,4-di-tert-pentylbenzene and 1-methyl-4-(tert-pentyl)benzene as safer alternatives to commonly used diluents like toluene, ethylbenzene and Solvesso 150. Guided by the 12 principles of green chemistry proposed by Warner and Anastas, this study contributes to the implementation of safer diluents for solvent extraction processes (green chemistry principle 4) and presents a synthesis route that can, in principle, be based on renewable feedstocks (green chemistry principle 7). Owing to their high boiling points and flash points, combined with favourable physicochemical properties required for good diluents, the use of these compounds could enable the design of an inherently safer process and thereby reduce the risk of accidents (green chemistry principle 12). Additionally, both diluents are unable to form neurotoxic 1,2-diketones and show low evaporation rates. These aspects are particularly relevant in a large-scale application, where safety, robustness, and technical feasibility are decisive parameters. The concept of “greenness” can vary between academic research and industrial practice, and researchers might have different opinions, but the simultaneous implementation of all 12 principles is rarely achievable in complex industrial systems. Green chemistry in real-world applications therefore requires prioritisation and trade-offs, and incremental improvements rather than theoretical perfection. By integrating selected green chemistry principles into a technically viable solvent extraction system, this work represents a pragmatic and application-oriented contribution to the development of safer process diluents. In this sense, it demonstrates how green chemistry can be translated from conceptual guidelines into industrially relevant solutions for a sector that is rapidly growing. To assess the sustainability and environmental impact of 1,4-di-tert-pentylbenzene and 1-methyl-4-(tert-pentyl)benzene a full life cycle assessment is needed. However, due to the lack of published process data this might be challenging.

## Conflicts of interest

The authors declare no conflict of interest

## Data availability

All data supporting the findings of this research as well as additional information for methods, procedures and spectra can be found in the main article and in the ESI.

## Acknowledgements

This research was financed by the Swedish Energy Agency - Battery fund (Grant No: 2023-200431). The authors would like to acknowledge the Swedish NMR Centre at the University of Göteborg for its support. We would also like to acknowledge Scanlube AB for its support and help.

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View Article Online  
DOI: 10.1039/D6SU00096G

Open Access Article. Published on 07 May 2026. Downloaded on 5/8/2026 10:07:18 PM.  
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## Data availability statement

The data supporting this article as well as additional information for methods, procedures and spectra have been included in the main article and in the Supplementary Information (ESI)

