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Higher 2nd life Lithium Titanate battery content in hybrid energy storage systems lowers environmental-economic impact and balances eco-efficiency

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Abstract

Energy exchange technologies will play an important role in the transition towards localised, sustainable energy supply. Hybrid energy storage systems, using different energy storage technologies, are currently under investigation to improve their technical performance and environmental sustainability. However, there is currently no exploration of the environmental benefits and economic feasibility of hybrid energy storage systems combining 1st and 2nd life batteries and battery electric vehicles. To determine the environmental and economic impacts of this type of hybrid energy storage system, this research employs a three-tier circularity assessment incorporating Life Cycle Assessment, Techno Economic Analysis and an Eco-Efficiency Index, from cradle-to-grave, of 43 techno-hybridisations of four 1st and 2nd life battery technologies; Lithium Titanate, Lead-acid, Lithium Iron Phosphate and Sodium-ion, with battery electric vehicles. The results of the life cycle assessment and techno-economic analysis show that a hybrid energy storage system configuration containing a low proportion of 1st life Lithium Titanate and battery electric vehicle battery technologies with a high proportion of 2nd life Lithium Titanate batteries minimises the environmental and economic impacts and provides a high eco-efficiency. The results of the eco-efficiency index show that a hybrid energy storage system configuration containing equal proportions of 1st and 2nd life Lithium Titanate and BEV battery technologies is the most eco-efficient. This research highlights the environmental and economic benefits of the use of Lithium Titanate battery technologies within novel hybrid energy storage systems.

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Highlights

- Three-tier circularity of a hybrid energy storage system (HESS) assessed
- High 2nd life battery content reduces environmental and economic impacts
- Eco-efficiency index results promote a high 2nd life battery content
- Lithium titanate (LTO) HESS has the lowest environmental and economic impacts
- LTO HESS balances eco-efficiency index

Key words: life cycle assessment, techno-economic analysis, eco-efficiency index, energy storage, circular economy

Word count: 7645

Abbreviations

Battery Electric Vehicle	BEV	Life cycle inventory	LCI
Eco-efficiency	EE	Lithium Iron Phosphate	LFP
Dynamic Frequency Response	DFR	Lithium Titanate	LTO
FDP	Fossil Depletion Potential	MEP	Marine Eutrophication Potential
FEP	Freshwater Eutrophication Potential	NPV	Net Present Value
GWP	Global Warming Potential	PV	Photo Voltaic
Hybrid Energy Storage System	HESS	SDG	Sustainable Development Goal
HTP	Human Toxicity Potential	Sodium-ion	Na-ion
Life cycle assessment	LCA	Techno-economic analysis	TEA

1 Introduction

Energy storage can effectively balance supply and demand at both the grid and smaller scales, storing excess energy at times of high generation for use later, ensuring energy security by minimising system volatility. The response time, storage time, and capacity of different energy storage technologies can vary substantially and scale from kW to MW based on user needs. However, when each is used in insolation, they may not be able to mitigate all types of destabilisation event and there are technical limitations to each technology, which can lead to an oversized installation, resulting in poor economics for the installation and long payback terms [1]. Utilisation of different technologies into a combined Hybrid Energy Storage System (HESS) can alleviate this and provide a system that meets the technical needs of the application or that can dynamically adapt to changing requirements. Different battery types can make up a HESS where each of the batteries characteristics are exploited to optimize the service delivery [2].

The ability to store energy and generate power from conventional energy production is of critical importance in a society where energy demand is increasing and, in turn, this technology has allowed for the development of hybrid and plug-in electric vehicles [3], [4]. Recently, battery usage has increased, while costs have been seen to decrease [5], [6], and production is expected to increase further as the number of Battery Electric Vehicles (BEVs) on the road rises from 1.2 million in 2016 to 44 million in 2030 [7], [8]. This rapid development of new electrochemical reactions and battery technologies, coupled with limited battery lifetimes, will result in a significant second-hand battery market, which can potentially provide new energy exchange services [9], [10].

Despite the prevalence of battery technologies in electrical energy storage systems [11] alternative technologies such as supercapacitors and fuel cells can also be utilised in electric hybrid vehicles. Supercapacitors have fast charge and discharge cycles, high power density, operate over a wide temperature range, have a high cycle life, and result in low maintenance costs [12]. Fuel cell technologies have a number of advantages over batteries for electric vehicles, including their light weight and small dimensions [13].

Battery technologies such as Lithium Titanate (LTO), Lead-acid, Lithium Iron Phosphate (LFP) and Sodium-ion (Na-ion) [14] have reliable performance, rapid response, are compact systems and have low costs [5] . However, 2nd life batteries and BEVs, could potentially be utilised as an alternative sustainable solution for battery energy storage systems as they can provide an additional service by acting as energy storage technology [15], [16]. For instance, Gough et al. [14] analysed the techno-economic feasibility of multiple vehicles taking into account electric vehicle electricity sale price, battery degradation cost and infrastructure costs [14]. Furthermore, Zhao et al. [15] analysed the environmental and economic benefits and found that BEV to grid systems can generate an economic revenue and greenhouse gas savings [15].

As BEV batteries reach their end of life at 80% capacity, there will be a considerable 2nd life battery market as the production of BEVs increases worldwide. Such batteries are ideal for stationary energy storage applications since they are low cost and provide relatively fast scale-up for large energy and power requirements [16].

Academic research utilising life cycle assessment (LCA) [9] and techno-economic analysis (TEA) [17] to determine the environmental and economic impacts of batteries is extensive.

Ahmadi et al. [9] utilised LCA to analyse the environmental impacts of 1st and 2nd life EV LIBs from a life cycle perspective and found that the 1st and 2nd use phase contributes the largest environmental impact [9]. However, there is still limited understanding on the environmental and economic benefits of such systems.

Although the LTO battery technology (utilising a LFP cathode) is not yet commercialised, it was chosen for this study as research [18] has shown that understanding the environmental impacts of a product at design stage may prevent an increase in its environmental burden throughout its lifecycle. LCA has been conducted to determine the environmental impacts of LTO and has shown the carbon footprint of LTO battery production to be 14.19 kg CO_2 kg^{-1}, compared to 16.11 kg CO_2 kg^{-1} for LFP batteries and only 2.33 kg CO_2 kg^{-1} for Lead-acid batteries [16]. Research into the economic impacts of batteries calculating the life cycle costing of LTOs, compared to Lead-acid batteries, has also been published; the total cost of ownership of LTO in an industrial application is 33% lower than that of Lead-acid batteries [19]. A study by Baumann et al. [16] compared the economic impact of a range of battery types and found the main contributor to the overall cost of a battery technology is its cycle life [16].

Peters et al. [20] found the average greenhouse gas emissions of lithium-ion batteries to be 110g CO_2-eq for the production of 1Wh of storage capacity [20]. The life spans of 2nd life lithium-ion batteries have shown promising results of over 30 years [21], but for the environmental benefits of 2nd life battery technologies to be realised they should utilise renewable power sources and not supported by grid services [21]. From an economic perspective, it has been shown that while 2nd life lithium-ion batteries can provide a cheaper alternative to 1st life lithium-ion batteries [22], there may not be sufficient stationary applications available to contain the large amount of 2nd life batteries expected to be available in the future.

In their research, Khan et al. [23] outline the TEA of different hybrid power system using the hybrid optimisation model electric renewable software. They report the lowest cost of energy for a Photo Voltaic (PV)-Wind-Diesel-Battery system at 0.162 $/kWh and the highest cost of energy for a PV-Diesel system at 0.709$/kWh [23]. Eltoumi et al. [24] outline that while PV is an essential energy source to enable the globe to achieve net-zero, its implementation for BEV charging is limited due to intermittency and limited contribution in the daytime [24].

Philippot et al. [25] depict the eco-efficiency of a LIB for EVs as a scatter plot on which the kg CO2-eq/kWh is shown on the y-axis and the manufacturing cost is shown on the x-axis. This research considers different manufacturing locations and concludes that electricity mix is an environmental hotspot, and that the eco-efficiency can be improved through increased manufacturing capacity and a low carbon energy source [25].

Similarly, Onat et al. [26] consider the eco-efficiency of electric vehicles across 50 states in the United States. Their research considered three environmental impacts; carbon emissions, energy consumption, and water use, and one economic impact, calculated through life cycle costing with respect to a range of electricity sources. The results show that utilising solar charging facilities led to the most promising result [26].

Despite increased attention on battery repurposing and recycling as part of a circular economy, with the rise of BEVs and energy demand, there is a gap in current literature in which no research has examined the hybridisation of 1st and 2nd life batteries with BEVs. Specifically, the combination of LTO, LFP, Na-ion and Lead-acid battery technologies within a Hybrid Energy Storage System (HESS), has not been explored for their optimised arrangement to reduce environmental impacts and economic costs. A HESS is a system that incorporates *"different generation, storage, and consumption technologies in a single system"* [27], the aim of which is to enhance the service provided by a single source [27]. This is becoming of increasing importance, as in the near future, the capacity of stationary battery storage systems is likely to rapidly increase [28]. This research presents a new model of energy exchange services, namely a HESS combining 1st and 2nd life batteries with BEVs. The study determines which technological combination of 1st and 2nd life batteries with BEVs provides the maximum environmental benefit and minimum economic cost according to a functional unit of 1MWh over 10,000 cycles. The combination of 1st life Lead-acid, LFP, Na-ion or LTO battery technologies, with 2nd life batteries of the same technology types and with BEVs are analysed, as part of a stationary storage system, using a three-tier circularity assessment of Life Cycle Assessment (LCA), Techno Economic Analysis (TEA) and an eco-efficiency (EE) index. The results were compared to a baseline system comprising of a 100% 1st life LFP battery. Furthermore, scenario analysis is employed to determine the change in environmental and economic impact to the HESS when the percentage contribution of each battery technology is altered.

Specifically, this study aims to determine the environmental impacts of novel HESS based on 1st and 2nd life batteries and BEVs. This research was conducted to address the gap in knowledge relating to HESS and therefore, it is intended that both the research community and battery-based industries, working on these types of systems, will use the results of this study to aid future decision making.

These four battery technologies were chosen for comparison as firstly, although LFP technology is likely to improve moving into the future, LTO and Na-ion technologies, with improved energy densities and cycle lives are likely to become available technologies for electric vehicles [29]. Secondly, Garche et al. [30] have outlined the deployment of Lead-acid batteries in hybrid applications and their applications in dual systems with Li-ion batteries.

The novelty of this research lies in its application of the LCA, TEA and an EE index, a three-tier circularity assessment, to a conceptualised HESS, utilising a range of battery technologies. Further novelty is provided through the use of scenario analysis to determine which percentage contribution of each battery technology leads to a HESS optimised to reduce the overall environmental impact and increase the economic benefit. This is the pioneering study extending beyond recycling into a circular economy [31] to generate power through battery life extension by enhancing the EE of battery energy storage using techno-hybridisation.

Accordingly, this manuscript is structured as follows: section 2 outlines the materials and methods utilised in the LCA, TEA and EE index and the associated scenario analysis for each HESS configuration; section 3 shows the results; section 4 provides the discussion; and section 5 presents a concise conclusion.

2 Materials and methods

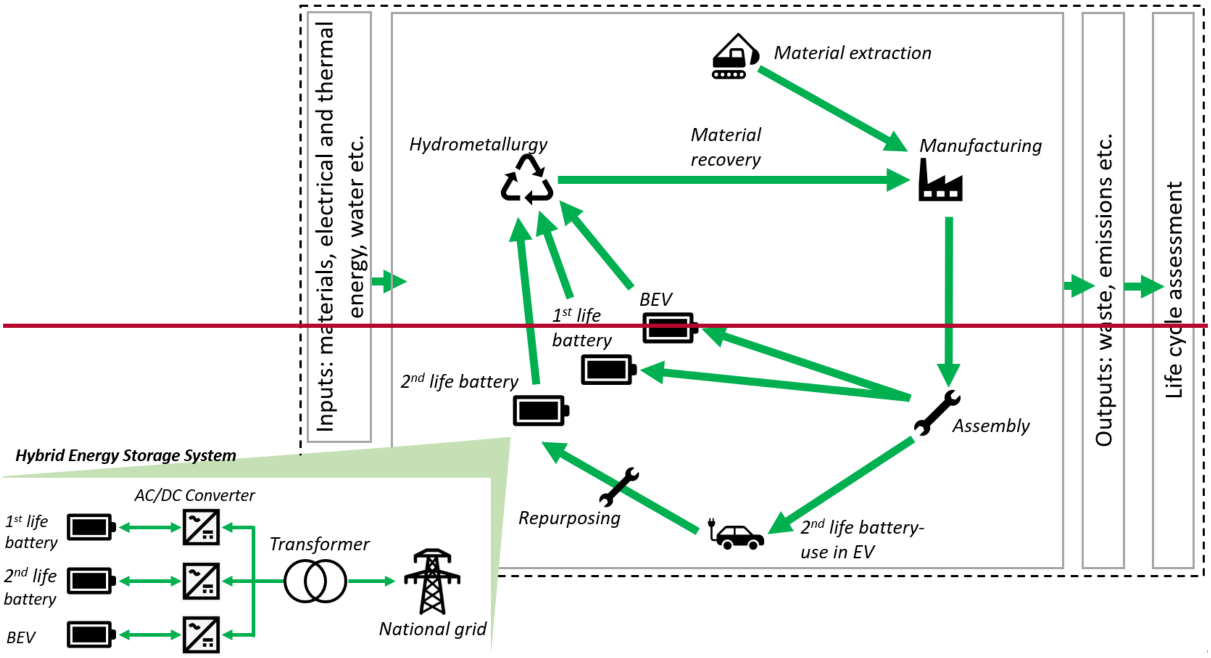
Three assessment methodologies, LCA, TEA and an EE index, were utilised in this study to determine the environmental and economic impacts of a HESS comprising of the combination of 1st life Lead-acid, LFP, Na-ion or LTO battery technologies, with 2nd life batteries of the same technology types and with BEVs. This section provides the methodological processes applied to each assessment type. The proposed structure of the HESS is provided in Appendix A and the LCI for each battery type can be found in Appendix B-E.

2.1 Life cycle assessment

The application of LCA began as far back as the 1960s, in a comparative context for products using a systematic methodology. Since then, the methodology has been developed to assess the whole life cycle of a product or service and as such, world governments support the use of the methodology throughout environmental policy [32], [33]. The production, use and disposal of products or services can be traced from a whole life cycle perspective to support informed decision-making and to provide mitigation strategies throughout the supply chain [34] and it is now the most commonly used tool to for the assessment of environmental impacts [35].

In this study, we adopted the process LCA methodology, which calculates the environmental impact of the unit process exchange and inputs within the supply chain, directly associated with the battery technologies under consideration [18]. According to ISO 14040 [36], the LCA methodology involves a four-step process: (1) goal and scope definition; (2) inventory analysis; (3) impact assessment and (4) interpretation, where step 4 runs concurrently with steps 1, 2 and 3 [32].

The LCA was performed on HESS consisting of 33.3% 1st life batteries, 33.3% 2nd life batteries and 33.3% BEVs (where the BEV was assumed to be of LFP battery technology). This was conducted to provide a baseline HESS configuration result against which variations of the percentage of battery technologies hybridisation can be compared using scenario analysis. As a comparative baseline, the environmental impacts of a 100% 1st life LFP battery were also tested. A functional unit of 1MWh over 10,000 cycles was applied. The system boundary and HESS implementation strategy are shown in Figure 1.



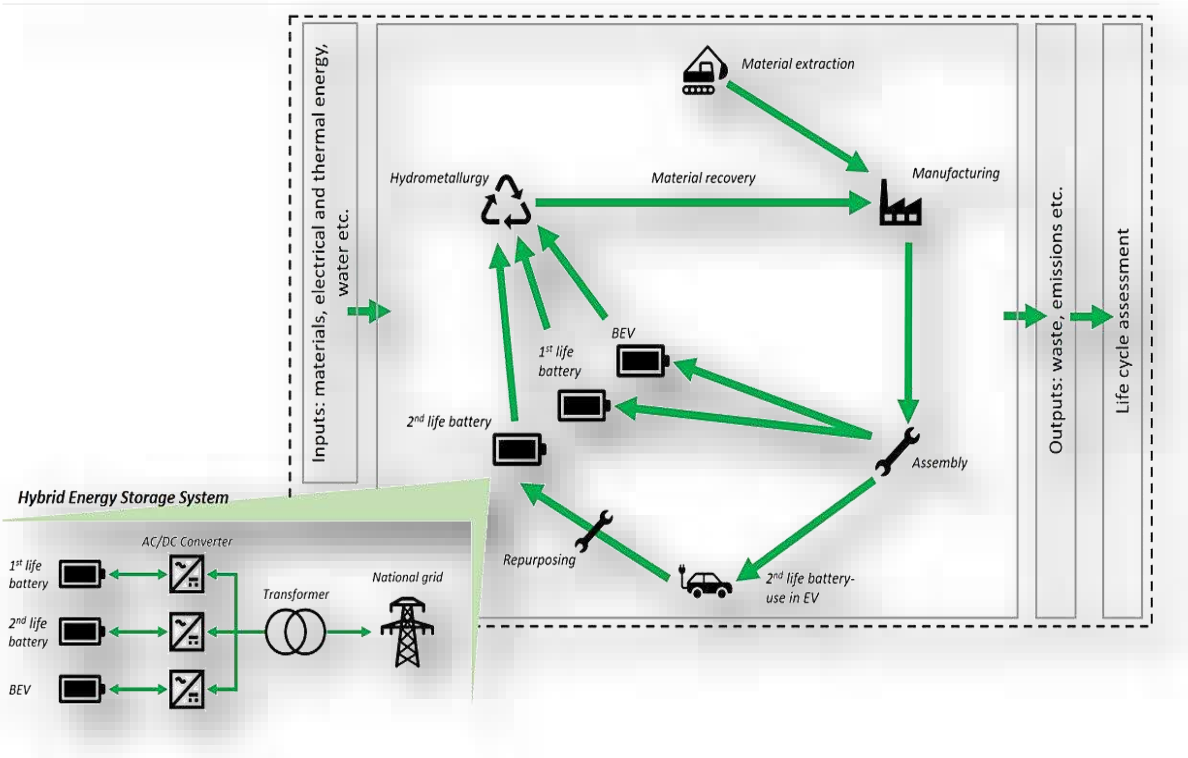


Figure 1: The system boundary applied to the LCA of the HESS consisting of 1st and 2nd life batteries and BEVs in this study. The system boundary includes the inputs and outputs relating to the raw material extraction, component manufacture, battery assembly, use phase and end of life management (i.e. hydrometallurgy). The repurposing and second use phase of the 2nd life battery is also assessed. The HESS implementation approach is shown in the bottom left-hand corner of this figure.

Each energy storage technology will have a different DC voltage range meaning that sharing a common DC bus would not be possible. Figure 1 shows an example configuration whereby each technology is connected via its own DC to AC electrical converter to an AC common bus allowing independent control of power flow to/from each one. The total import/export to the electrical grid is the net sum of the total power of all three converters, therefore, this configuration also allows for energy transfer between storage technologies.

To complete step 2 of the LCA methodology, the LCI for each battery supply chain was developed using data from primary and secondary sources [37]–[47]. Individual contributions of each battery were accounted for as shown by the system boundary in Figure 1.

The data relating to the bill of materials and process flows for each of the four battery technologies (LTO, Lead-acid, LFP and Na-ion) were taken from published literature [37]–[42], [48]. The bill of materials was validated by a mass and energy balance to ensure thermodynamic constraints of the systems were accurate [36]. The infrastructure, transportation and ancillary equipment, such as charging facilities, relating to certain types of battery manufacturing and assembly are negligible, compared to the remaining aspects, and therefore have been excluded from this study where appropriate [38], [39]. Furthermore, the impact of the power electronics is assumed to be equal across all battery types and therefore are not included in the comparative model. Prior to implementation in the HESS, the 2nd life battery is assumed to have been used in a BEV.

The use phase in the HESS is a 1MWh stationary system with an energy throughput of 6900MWh over a 15-year lifetime based on providing dynamic frequency response (DFR) services, leading to a daily consumption of 1.26MWh. The total service life is modelled as 10,000 cycles. Over the 10,000 cycle life, the effect of degradation will reduce the performance of each battery type, i.e. the ideal state of the battery will decrease, known as state of health. The cycle life of the LTO battery is assumed to be 18,000 cycles [19]; the cycle life of the LFP battery is assumed to be 2,500 cycles [49]; the cycle life of the Na-ion battery is assumed to be 2,000 cycles [50] and that of the Lead-acid battery is assumed to be 1,500 cycles [19]. The state of health of a battery is mainly governed by the thermodynamic instability of the materials used in the electrodes and this aging process requires a trade-off between usage and performance [51]–[53]. As noted above, the availability of 2nd life batteries is likely to outweigh the market for stationary applications moving into the future and therefore it is assumed that battery stock is abundant [22]. Research has shown that the average vehicle is only in use for 4% of its life, therefore the model assumes this to be negligible, making the BEV an appropriate addition to the HESS [54]. The "round trip energy efficiency" degradation of the system is assumed to be negligible over the one-year period assessed by the LCA and is not part of the TEA calculation and therefore has not been considered in this study.

Battery end of 1st life is assumed when 80% of its original energy capacity is reached [55]. It is assumed that at the end of its first use, the battery shows no sign of leakage, high internal impedance or internal short circuits and therefore is suitable for reuse. To repurpose the battery, it must be disassembled and tested, followed by the addition of new hardware and packaging [48]. As battery technology is continually improving, leading to increased capacitance; the results of this LCA provide the current environmental outlook relating to the implementation of a HESS over a 15-year period.

The HESS systems would aim to be 100% re-processed to recover materials when decommissioned. A number of different processes exist for battery end of life treatment, for instance, pyrometallurgical, hydrometallurgical (a combination of the pyrometallurgical and hydrometallurgical methods), direct cathode recycling and the use of deep eutectic solvents [43], [44], [56]–[58]. The pyrometallurgical and hydrometallurgical routes are the main methodologies for Li-ion battery recycling, each yielding different end products. For example, the Retriev hydrometallurgical process produces a cobalt cake, lithium carbonate and copper and aluminium foils, whilst the Xstrata Nickle process yields nickel, cobalt, and copper alloys [59]. Though it would not be unreasonable to assess the impact of the pyrometallurgy methodology for resource recovery, for this study, the hydrometallurgical recovery process was chosen for the assessment of all four technology types due to its most selective route to extract metals [45]. Hydrometallurgy involves leaching with sulphuric acid, neutralisation, the recovery of the required metals and wastewater treatment [57].

To provide a robust assessment, the life cycle impact assessment (step 3) was completed using the ReCiPe Life Cycle Impact Assessment [60] methodology based on the environmental impact indicators in Peters et al. [38]. In our study, five environmental mid-point impact categories were measured: Global Warming Potential (GWP), Human Toxicity Potential (HTP), Fossil Depletion Potential (FDP), Marine Eutrophication Potential (MEP) and Freshwater Eutrophication Potential (FEP) were analysed [31], [38]; environmental input data was sourced from Ecoinvent [61].

The environmental impact of climate change can be measured by the GWP, i.e., the global temperature change caused by the emissions of greenhouse gases. GWP can be ~~is~~ measured over 20, 100, or 500 years, ~~different time horizons,~~ though 100 years is~~us~~ the most commonly used, with the units kg CO_2-equivalent. The HTP is utilised to determine the potential harm to humans caused when a chemical is emitted to the environment; the calculation takes into account the toxicity and likely does of the chemical and is measured in kg 1,4-DB-equivalent [62].

In LCA, ~~F~~fossil fuel consumption is calculated by the FDP, ~~and measured in kg oil-equivalent~~ [59] and is measured in kg oil-equivalent [63], ~~;~~this method includes non-renewable resources (fossil fuels and minerals). The ReCiPe methodology quantifies this additional effort in economic terms (additional costs) For minerals, the marginal increase of costs due to the extraction of an amount of ore is the basis of the model. Furthermore, mineral depletion is based on depletion of ores, instead of elements. For fossil fuels, the marginal increase of oil production costs (due to the need to mine non-conventional oils) is used [65].

In this study, we emphasise the increasing role of renewable energy and electrification in the energy mix (and the reducing role of fossils) to power EVs, which aligns with global net zero, decarbonisation, and climate change strategies including the IPCC 2021 report approved by 195 member governments [66]and the IEA Net Zero by 2050 report [67]. As such, it is expected that the cost of batteries technologies and systems, both new and recycled, such as the ones proposed in this research, will drop as the energy supply and grid become cleaner and more affordable with the decrease of energy cost for renewable and electricity. Consequently, the FDP impact will reduce due to less reliance on the fossil-based energy supply chain.~~ Fossil fuel consumption is calculated by the FDP and measured in kg oil-equivalent~~ [59]~~.~~

Eutrophication is a phenomenon that occurs when chemical nutrients build up in an ecosystem, leading to increased productivity which in turn reduces water quality and biodiversity. This phenomenon is mainly affected by the release of ammonia, nitrates, nitrogen oxides, and phosphorous. The MEP is measured as k N-equivalent and the FEP is measured as kg P-equivalent [62].

The HESS systems lead to reduction in the environmental impacts of the combustion and processing of natural gas for energy production through lower peak load and load levelling [68].

The environmental impacts across the supply chain of each HESS configuration were calculated using equation 1.

$$Environmental\ Impact = \sum_{i=1}^{n} A_{p(i)} \times E_{p(i)} \quad (1)$$

where: A_p denotes the inputs (i) into a product's supply chain including raw material extraction, energy consumption, material production and manufacturing processes, etc.; n is the total number of process input (i) into the product's supply chain and E_p represents the emissions intensity across the chosen environmental and sustainability metrics (e.g. greenhouse gas emissions, land use etc.), for each input (i) into a product's supply chain emissions [18].

Throughout the LCA process, the data and results are assessed (step 4: interpretation). The aim of this step is to explain the results, derive conclusions and suggest recommendations with respect to the LCI and LCIA. The results of the LCA are disaggregated in Section 3, Table 2 and Figure 3, and discussed in full in section 4.

2.2 Techno-economic analysis

Techno-economic analysis (TEA) is a process used to evaluate the economic performance of a system, e.g., an industrial process, product, or service. The process parameters of a system are considered to enable the financial impact to be determined [69]–[71], e.g., process inputs and size of the technology, but in the main TEA is used to consider the economic impact [69].

TEA is a methodology used to determine the economic feasibility of a system; the process parameters of a system are considered to enable the financial impact to be determined. The TEA of a HESS is of paramount importance to researchers and industry to ensure the understanding of the economic viability of the system [72][64]. In this study, TEA was performed to analyse the costs associated with the hybrid energy storage technologies technical configurations during the operational phase. As such, this paper focuses on those technical parameters required for the TEA since a wide array of research papers on the technical batteries chemistry are available. The technical parameters considered in the current TEA are material requirements, battery cycle life, manufacturing and re-manufacturing processes, and end-of-life management processes.

Net Present Value (NPV) measures profitability by discounting the cash flow at a specific rate of return [73]. In line with the LCA methodology outlined above which provides the technical parameters of each HESS as part of the LCI, TEA was performed on HESS consisting of 33.3% 1st life batteries, 33.3% 2nd life batteries and 33.3% BEVs, the economically optimised technological configurations of each technology type (where the optimised HESS was taken to be the configuration resulting in the lowest economic impact) and the 100% LFP baseline. This was conducted to provide a baseline HESS configuration result against which variations of the percentage of battery technologies hybridisation can be compared.

The economic model is based on HESS revenue generation from a DFR service. Whilst DFR may not be the only market applicable to each battery technology, it is most suited to provide a representative baseline across the four technologies studied. Furthermore, Enhanced Frequency Response is no longer in use and the comparison of different energy trading models is outside of the scope of this research. Further work on these issues can be found in literature, for example [74].

The economic model adopted during the operational phase is where the revenue from HESS is generated by a DFR service. NPV is calculated at a discount rate of 3% to determine the profitability of the HESS in relation to the revenue generated over the full lifetime. The NPV formula is shown in equation 2.

$$NPV = -C_o + \frac{C_1}{1+r} + \frac{C_2}{(1+r)^2} + \cdots . + \frac{C_T}{(1+r)^T} \qquad (2)$$

where C_o represents cash outflow at time 0, C_T represents cash flow at time T and r represents the discount rate. A positive NPV result indicates that the investment leads to a profit over the period assessed (in this case, 15 years), whilst a negative result shows that the investment costs outweigh the overall economic benefit [73].

The cost data of each battery type was retrieved from the literature [17], [75] and adjusted to provide the result in GBP (exchange rate: \$1=£0.71, €1=£0.89). As the data provided by literature reflects battery costs in 2017, a cost reduction of 12% per year was modelled for each battery type to align with 2019 costs [76].

Table 1: Purchase cost of 1st and 2nd BEV technologies [17], [75], [76]. N/A: The BEV in this study is assumed to be of LFP battery technology and therefore only one BEV cost is provided.

~~Battery technology~~	~~1st life battery technology (£/kWh)~~	~~2nd life battery technology (£/kWh)~~	~~BEV (£/kWh)~~
~~LTO~~	~~827~~	~~414~~	~~N/A~~
~~LFP~~	~~217~~	~~73~~	~~683~~
~~Na-ion~~	~~278~~	~~139~~	~~N/A~~
~~Lead-acid~~	~~221~~	~~110~~	~~N/A~~

Battery technology	1st life battery technology (£/kWh)	2nd life battery technology (£/kWh)	BEV (£/kWh)
LTO	827	414	N/A
LFP	217	73	683

Na-ion	278	139	N/A
Lead-acid	221	110	N/A

Table 1 summarises the purchase costs of the 1st and 2nd life batteries and the BEVs examined in this study. Figure 4 shows these investment appraisal results based on the economic modelling for DFR based on an initial £6 DFR/MW/hr at 24 hours' service over 15 years, as maintenance periods of such systems are very short and therefore assumed to be negligible. The total cost of the HESS unit was calculated based on the percentage contribution of each battery technology and the number of replacement batteries required throughout the cycle life of the HESS unit. The results of the TEA are disaggregated in Section 3, Figure 4, and discussed in full in section 4.

2.3 Eco-efficiency index

The assessment of eco-efficiency is required to provide a consistent methodology against which the parameters of environmental and economic impacts can be assessed [25]. It also provides a robust decision-making tool for policy makers, enabling a range of environmental impacts to be targeted [26]. Therefore, to harmonise the environmental and economic analyses, we calculated the EE index depicting the investment per environmental impact category for one unit of the baseline HESS configurations, the environmentally and economically optimised configurations and the 100% 1st life LFP baseline. The EE index measures sustainability via integrating the environmental and economic performances of a product. This methodology was originated in the 1970s, and by the 1990s the process had become an industrial basis for sustainable development. EE is defined as a ratio between the environmental impact and economic performance or the ratio between economic impact and environmental performance. The higher the EE index, the higher the value of a product with improved use of resources associated with the product or service and reduced environmental impact. Therefore, EE can be improved by increasing the value of the product or reducing the environmental impact [77]. In this manner, we adopted an EE index to calculate the cost per environmental impact based on the World Business Council for Sustainable Development definition, shown in equation 3.

$$Eco-efficiency = \frac{Economic\ value}{Environmental\ impacts} \qquad (3)$$

where the $Economic\ value$ represents the NPV and the $Environmental\ impacts$ represents each of the five environmental impact categories assessed in the LCA, namely GWP, FDP, MEP, FEP and HTP.

The EE analysis relates to the investment and consequential environmental impact of one HESS unit. An energy storage system may require multiple HESS configurations to achieve the required storage capacity. Therefore, the investment cost per environmental impact would increase with the investment cost.

The economic value relates to the value-added benefit of the product or service, the cost associated with the environmental burden or, as in this case, the unit of the product i.e. cost of the HESS. The environmental impacts relate to the resources used, the cost associated with the environmental burden or, as in this case, the pollution emissions from the HESS. The five environmental impacts measured in the LCA (GWP, FDP, MEP, FEP and HTP) were assessed and therefore the "environmental impacts" in equation 3 relate to the total environmental impact of the HESS for each environmental impact category. The total cost of the HESS was calculated based on the data provided in Table 1 [78]. The results are illustrated in Figure 6.

2.4 Scenario analysis

In the 1970s, oil shocks shook global corporations and since then, there has been increasing use of "multiple scenario analysis". The aim of scenario analysis is largely to effectively manage uncertainties [79] and this is a robust methodology to model effects of experimentations with varied conditions and variables. Although numerous approaches of scenario analysis exist [80]–[83], this research utilises that provided by Bood and Postma [79] which requires the completion of the following steps: (1) problem identification and demarcation of its context; (2) description of the current situation and identification of relevant factors; (3) classification, valuation and selection of scenario-elements; (4) construction of scenarios; (5) analysis, interpretation and selection of scenarios and (6) supporting decision making with scenarios [79].

To satisfy step one of the process, the implications of the percentage contribution of each battery type was highlighted as a predetermined causal factor within the LCA and TEA (as the outcome can be predicated with sufficient precision) [84]. The "current situation" (step 2) is taken as the baseline HESS configuration (i.e. equal percentage contribution of each battery type within the HESS). Therefore, the relevant factors affecting the current situation relate to how a change in the HESS configuration affects the results of the LCA and TEA. The battery types were identified as the scenario-elements, are required by step 3 and the scenarios were constructed (step 4) by altering the contributions of each battery type according to Table 2 (showing the LTO 1st life battery, LTO 2nd life battery and BEV HESS configuration as an example). Whilst the percentage content of one battery type remained constant (33.3%), another of the component's contributions was increased (up to 65%) and the percentage contribution of the third battery type was decreased (to 2%). Steps 5 and 6 are addressed in sections 3 (results) and 4 of this manuscript where the results are provided, interpreted, and presented to aid decision making.

To determine the optimised percentage of 1st and 2nd life batteries and BEVs, we performed scenario analysis on 43 variations of each configuration, across all five environmental impact categories and the constraints of the TEA. The optimised HESS was taken to be the configuration resulting in the lowest environmental impact and/or the lowest economic impact. As shown in Table 2, the content of one battery type was held constant while the two other battery types were varied from 2% to 65%, e.g. 33% 1st life LTO, 2% 2nd life LTO and 65% BEV.

Table 2 illustrates the scenario analysis for a HESS configuration using a 1st and 2nd life battery technology of any of the four types and a BEV when the percentage contribution of the 1st life battery is held constant, that of the 2nd life battery is increased and that of the BEV decreased accordingly.

Table 2: The HESS configurations assessed during the scenario analysis using a 1st and 2nd life battery technology of any of the four types and a BEV configuration as an example. In this example, the 1st life LTO content remained constant, the 2nd life LTO content was increased, and the BEV content was decreased.

1st life battery technology	Battery content (%)	2nd life battery technology	Battery content (%)	BEV	Battery content (%)
LTO/LFP/Na-ion/ Lead-acid	33.33%	LTO/LFP/Na-ion/ Lead-acid	33.33%	BEV	33.33%
LTO/LFP/Na-ion/ Lead-acid	33.33%	LTO/LFP/Na-ion/ Lead-acid	36.67%	BEV	30.00%
LTO/LFP/Na-ion/ Lead-acid	33.33%	LTO/LFP/Na-ion/ Lead-acid	40.33%	BEV	26.33%
LTO/LFP/Na-ion/ Lead-acid	33.33%	LTO/LFP/Na-ion/ Lead-acid	44.37%	BEV	22.30%
LTO/LFP/Na-ion/ Lead-acid	33.33%	LTO/LFP/Na-ion/ Lead-acid	48.80%	BEV	17.86%
LTO/LFP/Na-ion/ Lead-acid	33.33%	LTO/LFP/Na-ion/ Lead-acid	53.68%	BEV	12.98%
LTO/LFP/Na-ion/ Lead-acid	33.33%	LTO/LFP/Na-ion/ Lead-acid	59.05%	BEV	7.61%
LTO/LFP/Na-ion/ Lead-acid	33.33%	LTO/LFP/Na-ion/ Lead-acid	64.96%	BEV	1.71%

1st life battery technology	%	2nd life battery technology	%	BEV	%
LTO/LFP/Na-ion/Lead-acid	33.33%	LTO/LFP/Na-ion/Lead-acid	33.33%	BEV	33.33%
LTO/LFP/Na-ion/Lead-acid	33.33%	LTO/LFP/Na-ion/Lead-acid	36.67%	BEV	30.00%
LTO/LFP/Na-ion/Lead-acid	33.33%	LTO/LFP/Na-ion/Lead-acid	40.33%	BEV	26.33%
LTO/LFP/Na-ion/Lead-acid	33.33%	LTO/LFP/Na-ion/Lead-acid	44.37%	BEV	22.30%
LTO/LFP/Na-ion/Lead-acid	33.33%	LTO/LFP/Na-ion/Lead-acid	48.80%	BEV	17.86%
LTO/LFP/Na-ion/Lead-acid	33.33%	LTO/LFP/Na-ion/Lead-acid	53.68%	BEV	12.98%
LTO/LFP/Na-ion/Lead-acid	33.33%	LTO/LFP/Na-ion/Lead-acid	59.05%	BEV	7.61%
LTO/LFP/Na-ion/Lead-acid	33.33%	LTO/LFP/Na-ion/Lead-acid	64.96%	BEV	1.71%

The representative results of the scenarios are shown in Figure 3 (environmental impact) and Figure 5 (economic impact) respectively to depict how, by maintaining a constant percentage content of one component and varying the other two components, the environmental and economic impacts are affected. Data relating to the results of the 43 scenarios tested per battery type are available from the corresponding author on request.

3 Results

The results shown in section 3.1 provide tabulated (Table 2) and graphical data (Figure 2) to evaluate the environmental impact of the four baseline HESS configurations and the 100% LFP HESS; the results of the scenario analysis to determine the environmentally optimised HESS are shown in Figure 3. Similarly, section 3.2 provides the results of the TEA in Figure 4 and the associated scenario analysis in Figure 5. Finally, the results of the EE index are shown in Figure 6 in section 3.3. These results are discussed in detail in section 4.

3.1 Environmental impact of HESS

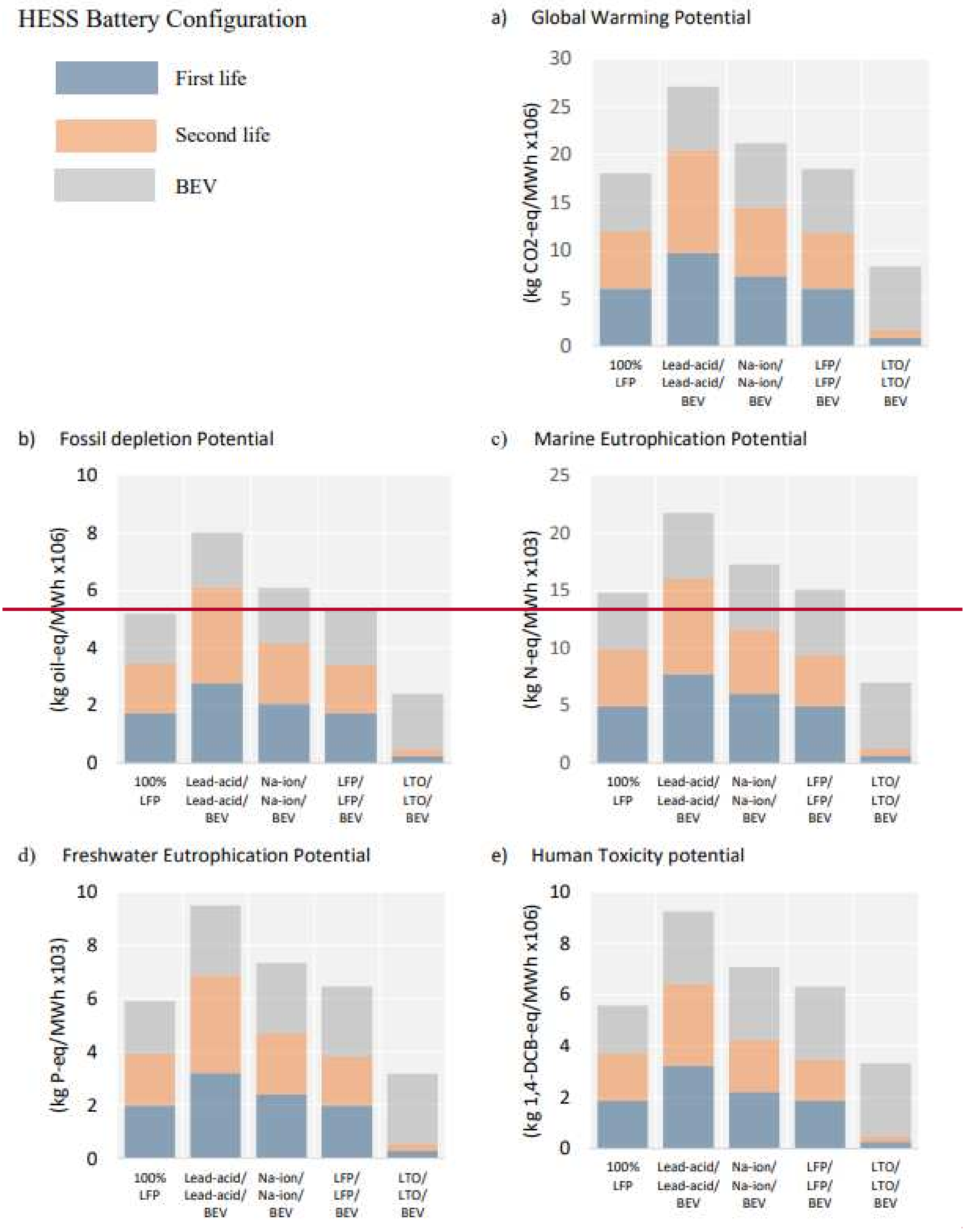
The total environmental impacts of each baseline HESS configuration (i.e. consisting of 33.3% 1st life batteries, 33.3% 2nd life batteries and 33.3% BEVs) and the 100% LFP HESS are shown in Table 3. These results were calculated according to the constraints of equation 1 in-line with the system boundary shown in Figure 1 which defines the inputs and outputs of the system that were considered as part of the LCA. The state of health of each battery type will decrease over the 10,000 cycle life, due to the effect of degradation which requires a trade-off between usage and performance and the battery end of life is assumed when 80% of its original energy capacity is reached [55]. Table 3 shows the results for all five environmental impact categories studied; GWP, FDP, MEP, FEP and HTP. As shown by Table 3, across all impact categories, the Lead-acid baseline HESS configuration leads to the highest environmental impact, whilst the LTO baseline HESS configurations results in the lowest environmental impact.

Table 3: Environmental impact of each baseline HESS configuration and the 100% LFP HESS for each environmental impact category; Global Warming Potential (GWP), Fossil Depletion Potential (FDP), Marine Eutrophication Potential (MEP), Freshwater Eutrophication Potential (FEP), Human Toxicity Potential (HTP).

~~HESS Configuration~~	~~GWP (kg CO_2-eq)~~	~~FDP (kg oil-eq)~~	~~MEP (kg N-eq)~~	~~FEP (kg P-eq)~~	~~HTP (kg 1,4-DCB-eq)~~
~~100% LFP~~	~~18,044,641~~	~~5,184,230~~	~~14,800~~	~~5,917~~	~~5,582,791~~
~~Lead acid/ Lead acid/ BEV~~	~~27,100,888~~	~~8,015,047~~	~~21,699~~	~~9,502~~	~~9,247,450~~
~~Na ion/ Na ion/ BEV~~	~~21,207,371~~	~~6,083,879~~	~~17,280~~	~~7,346~~	~~7,069,384~~
~~LFP/LFP/ BEV~~	~~18,488,654~~	~~5,329,166~~	~~15,085~~	~~6,452~~	~~6,309,777~~
~~LTO/LTO/ BEV~~	~~8,349,871~~	~~2,402,798~~	~~6,985~~	~~3,181~~	~~3,325,792~~

Configuration	GWP (kg CO_2-eq)	FDP (kg oil-eq)	MEP (kg N-eq)	FEP (kg P-eq)	HTP (kg 1,4-DCB-eq)
100% LFP	18,044,641	5,184,230	14,800	5,917	5,582,791
Lead-acid/ Lead-acid/BEV	27,100,888	8,015,047	21,699	9,502	9,247,450
Na-ion/ Na-ion/BEV	21,207,371	6,083,879	17,280	7,346	7,069,384
LFP/LFP/BEV	18,488,654	5,329,166	15,085	6,452	6,309,777
LTO/LTO/BEV	8,349,871	2,402,798	6,985	3,181	3,325,792

The results in Table 3 are disaggregated further in Figure 2 to show how the environmental impact of each battery type (1st life, 2nd life and BEV) contributes to the total environmental impact across all five environmental impact categories. Figure 2 shows that for the Lead-acid, Na-ion and LFP baseline HESS configurations, there are no overriding environmental hotspots, for example, the total GWP of the Na-ion baseline HESS configuration is comprised of 7.29 kg CO_2-eq/MWh (34.36%) attributed to the 1st life battery, 7.23 kg CO_2-eq/MWh (34.09%) attributed to the 2nd life battery and 6.69 kg CO_2-eq/MWh (31.55%) attributed to the BEV. Comparatively, for the LTO baseline HESS configuration, the environmental hotspot can be attributed to the BEV technology across all environmental impact categories, for example the MEP of the LTO baseline HESS configuration is comprised of 0.65 kg N-eq/MWh (9.26%) attributed to the 1st life battery, 0.63 kg N-eq/MWh (9.09%) attributed to the 2nd life battery and 5.70 kg N-eq/MWh (81.65%) attributed to the BEV.


HESS Battery Configuration
First life
Second life
BEV
a) Global Warming Potential
(kg CO2-eq/MWh x106)
b) Fossil depletion Potential
(kg oil-eq/MWh x106)
c) Marine Eutrophication Potential
(kg N-eq/MWh x103)
d) Freshwater Eutrophication Potential
(kg P-eq/MWh x103)
e) Human Toxicity potential
(kg 1,4-DCB-eq/MWh x106)
100% LFP
Lead-acid/ Lead-acid/ BEV
Na-ion/ Na-ion/ BEV
LFP/ LFP/ BEV
LTO/ LTO/ BEV

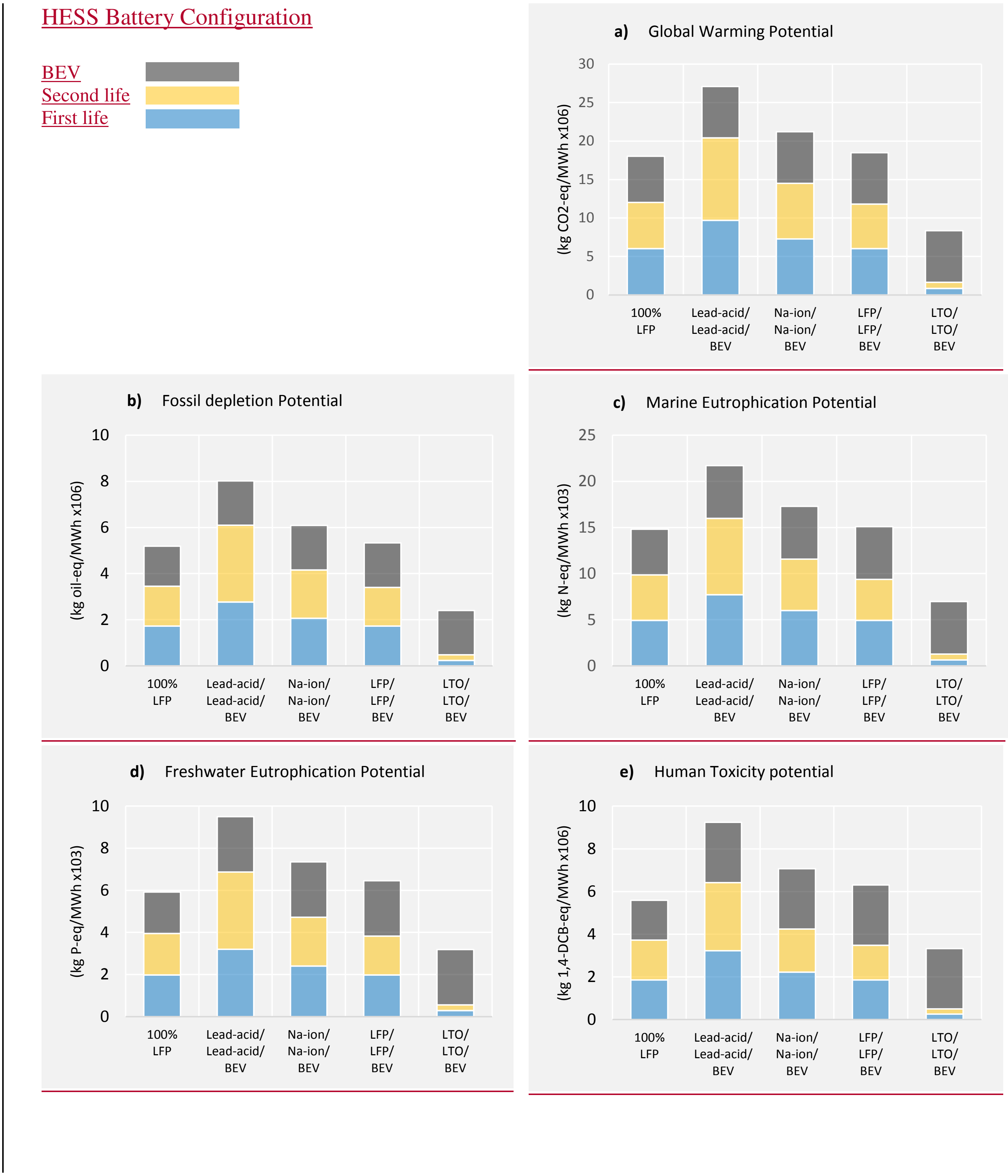
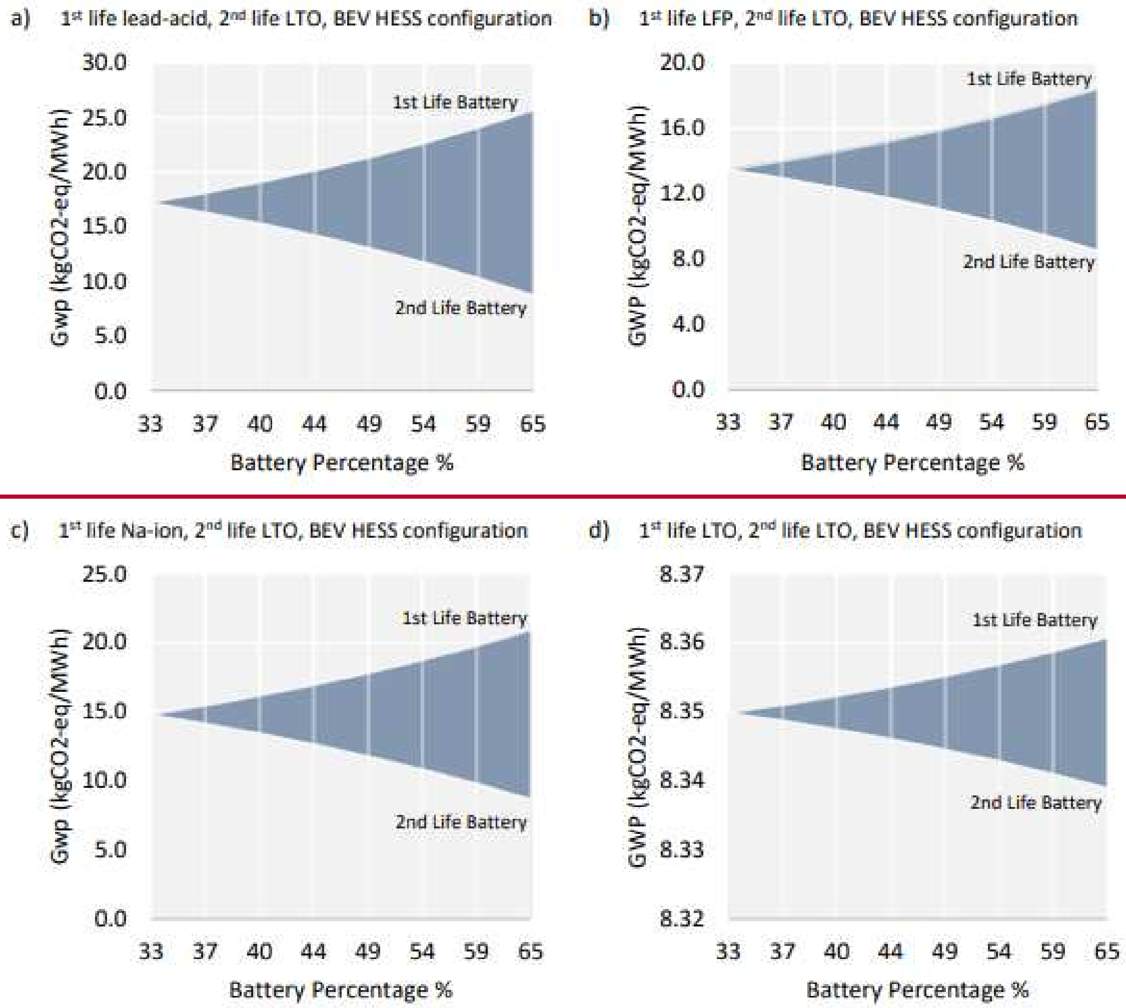


Figure 2: The environmental impact of each of the baseline HESS configurations and the 100% LFP baseline measured by a) Global Warming Potential; b) Fossil Depletion Potential; c) Marine Eutrophication Potential; d) Freshwater Eutrophication Potential; e) Human Toxicity Potential and broken down by contributions of the 1st life, 2nd life and BEV battery technologies.

Figure 3 shows the GWP results of the scenario analysis with respect to four HESS configurations using one of each of the four 1st life battery technologies, a LTO 2nd life battery and BEV. The chart shows the effect on the GWP impact category for four HESS configurations when the BEV content of the HESS remains constant and the content of 1st and 2nd life batteries vary (as one increases the other decreases). The y-axis depicts the GWP of the whole HESS as the percentage contributions of the 2nd life battery and BEV change with the x-axis. The results of the scenario analysis show that all HESS with a high proportion of 2nd life LTO battery technology (independent of the 1st life battery technology) leads to the lowest environmental impact i.e. the environmentally optimised HESS configuration.



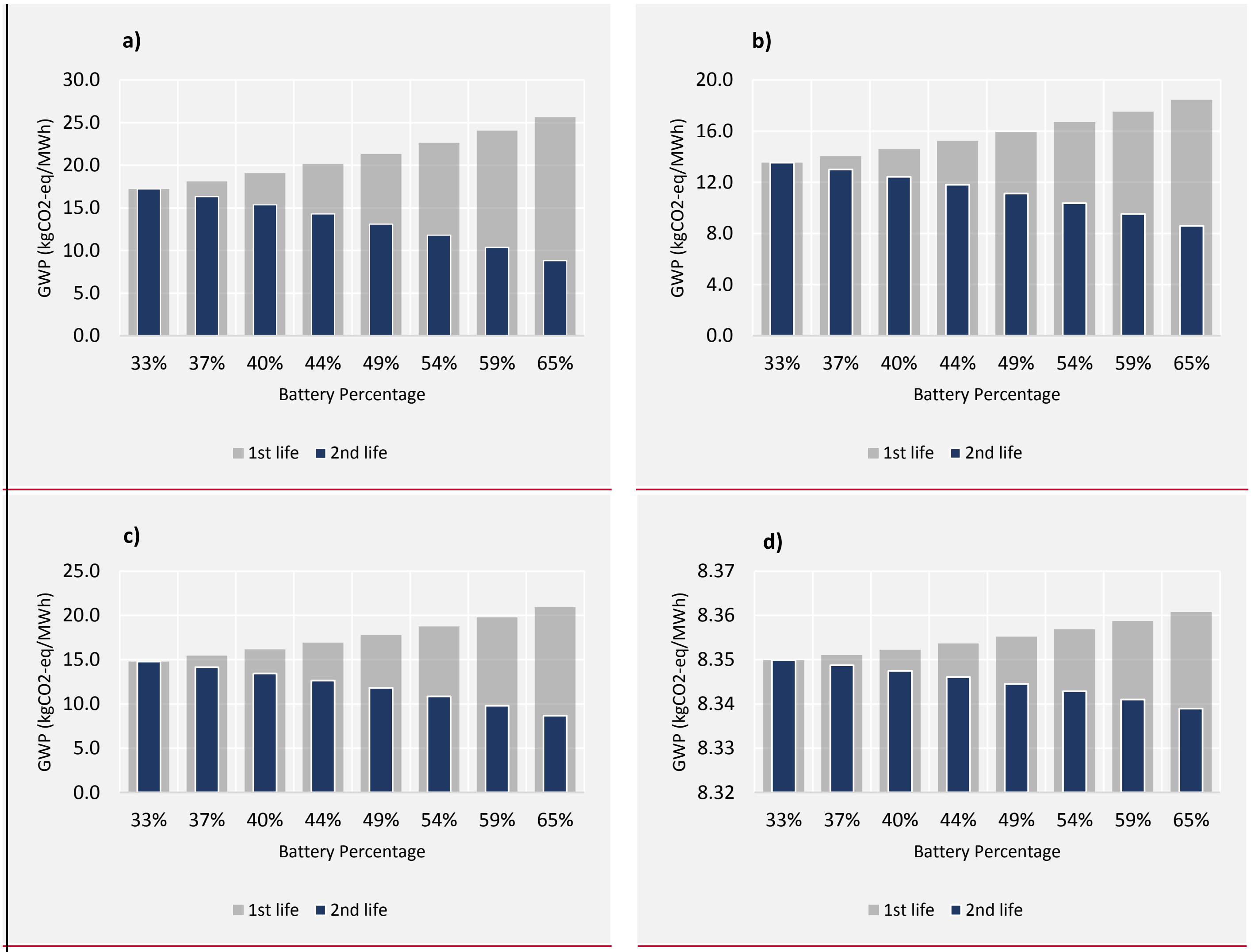


Figure 3: Scenario analysis of the GWP impact category for each baseline HESS configuration. The BEV content remains constant and the 1st and 2nd life battery contents are varied (as one increases the other decreases); a) 1st life Lead-acid battery, 2nd LTO life battery and BEV; b) 1st life LFP battery, 2nd life LTO battery, BEV; c) 1st life Na-ion battery, 2nd life LTO battery, BEV; d) 1st life LTO battery, 2nd life LTO battery, BEV.

As can be seen from Figure 3, independent of the 1st life battery technology, if the percentage contribution of the 1st life battery technology increases, the percentage contribution of the 2nd life battery technology decreases and the contribution of the BEV is held constant, the environmental impact increases, and vice-versa. Data relating to the results of the 43 scenarios tested per battery type are available from the corresponding author on request.

3.2 Techno-economic impact of HESS

An investment appraisal was performed using TEA on the baseline HESS configurations of each technology type (i.e. consisting of 33.3% 1st life batteries, 33.3% 2nd life batteries and 33.3% BEVs), the economically optimised technological configurations of each technology type (where the optimised HESS was taken to be the configuration resulting in the lowest economic impact) and the 100% LFP baseline. The economic model is based on HESS revenue generation from a DFR service. Figure 4 shows these investment appraisal results based on the economic modelling for DFR based on an initial £6 DFR/MW/hr at 24 hours' service over 15 years, as maintenance periods of such systems are very short and therefore assumed to be negligible. The results show that the economically optimised LTO HESS configuration has a NVP of £374,644 at £6 DFR/MW/hr, which increases to £2,884,275 at £30 DFR/MW/hr. Comparatively, the Lead-acid baseline HESS configuration has a NVP of -£508,436 at £6 DFR/MW/hr, which increases to £2,001,396 at £30 DFR/MW/hr.

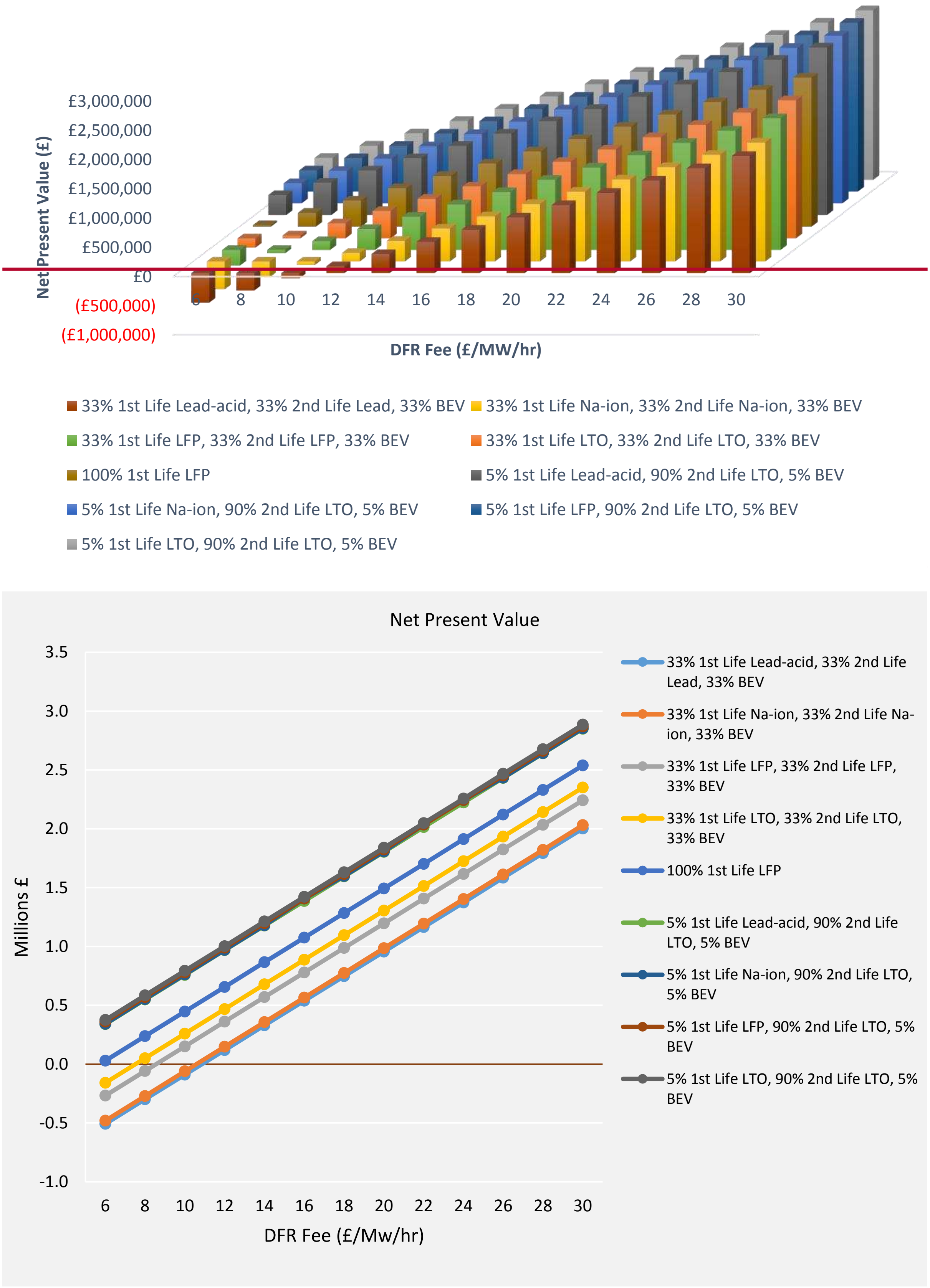
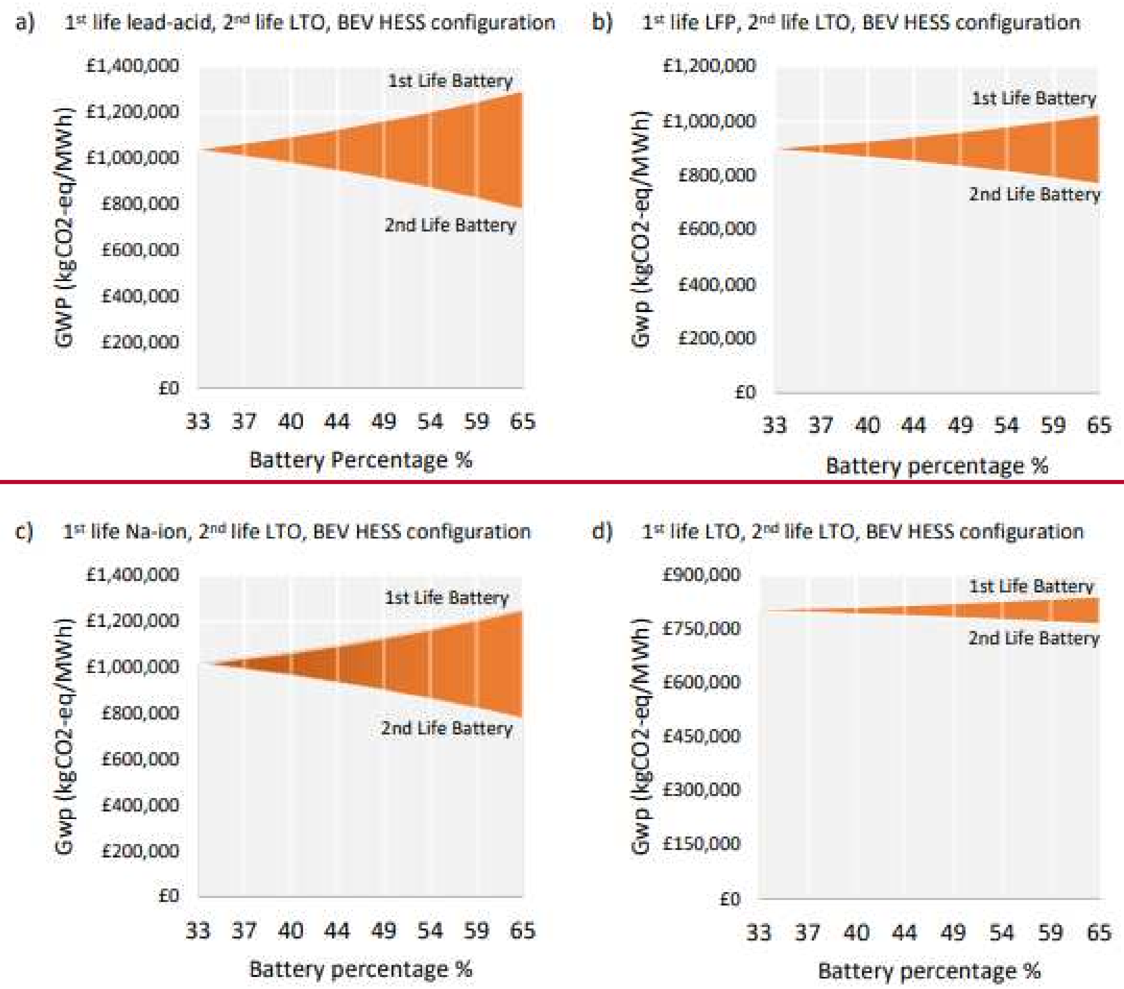


Figure 4: Net Present Value of the 100% 1st life LFP battery, all four baseline HESS configurations and the economically optimised HESS configurations economic based on the economic modelling for DFR which is based on an initial £6 DFR/MW/hr at 24 hours’

service over 15 years, as maintenance periods of such systems are very short and therefore assumed to be negligible.

The results of the scenario analysis show that all HESS with a high proportion of 2nd life LTO battery technology (independent of the 1st life battery technology) lead to the lowest economic impact i.e. an economically optimised HESS configuration. Figure 5 shows the TEA results of the scenario analysis with respect to four HESS configurations using one of each of the four 1st life battery technologies, a LTO 2nd life battery and BEV, where the BEV content is constant and the 1st and 2nd life battery contents vary (as one increases the other decreases). The y-axis depicts the GWP of the whole HESS as the percentage contributions of the 2nd life battery and BEV change with the x-axis. Data relating to the results of the 43 scenarios tested per battery type are available from the corresponding author on request.



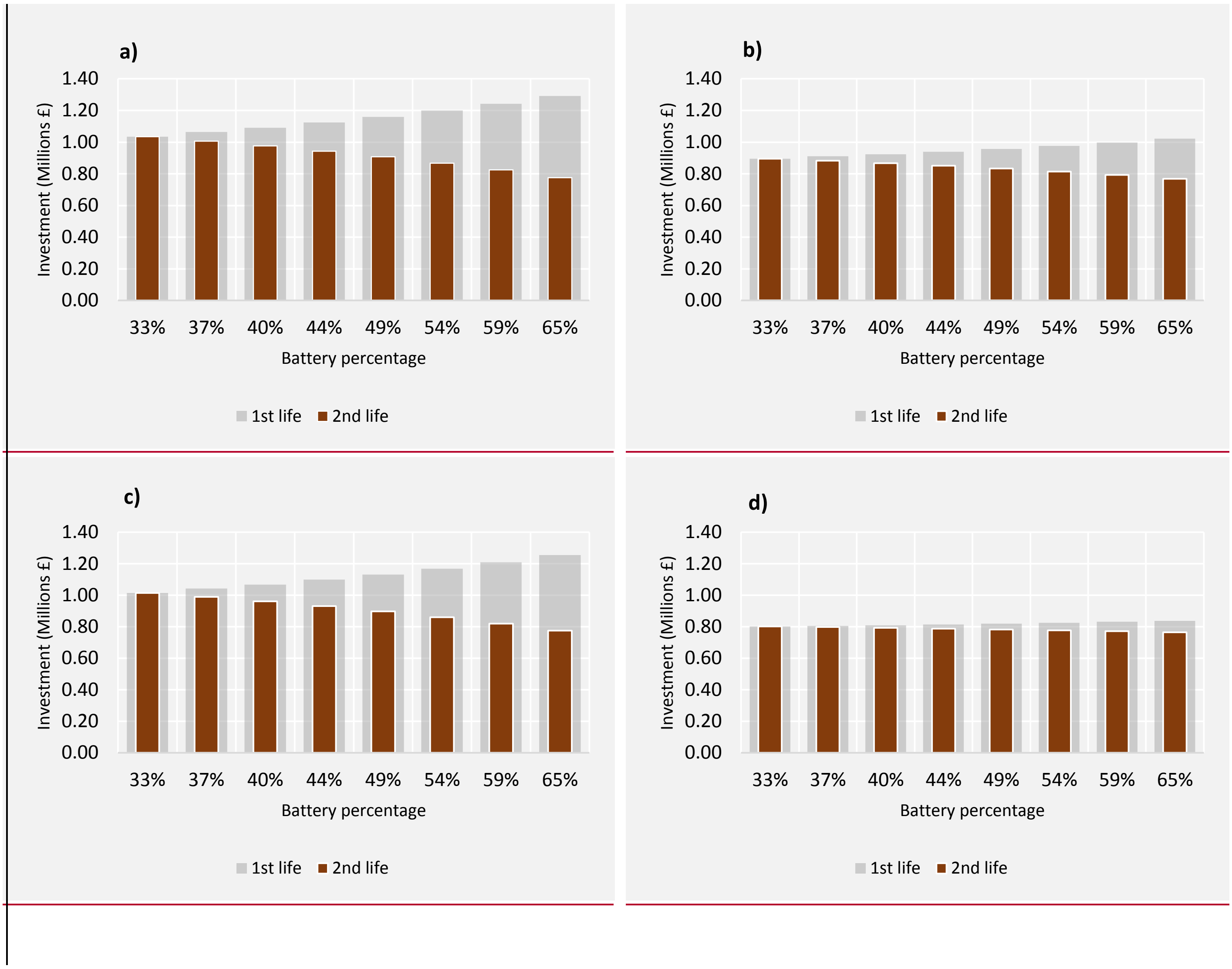
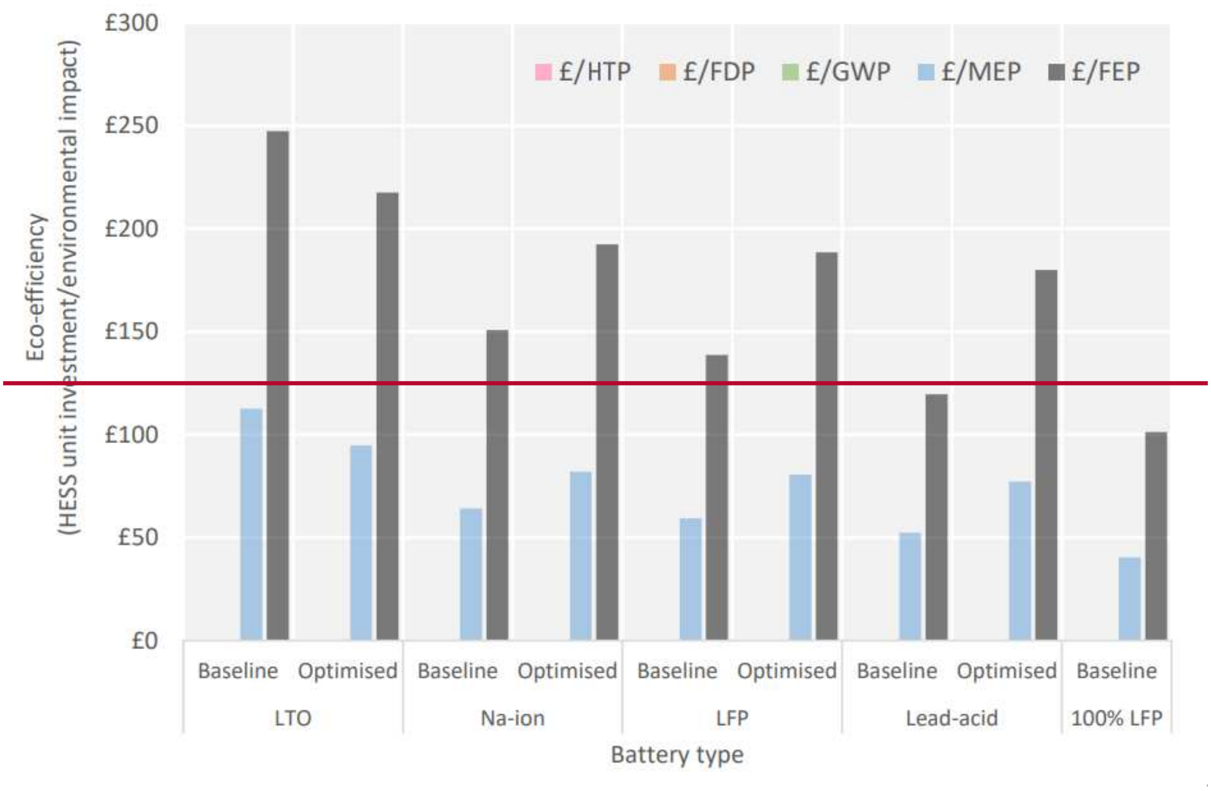


Figure 5: Scenario analysis of the economic impact for each baseline HESS configuration. The BEV content constant and the 1st and 2nd life battery contents are varied (as one increases the other decreases); a) 1st life LTO battery, 2nd life LTO battery and BEV; b) 1st life Na-ion battery, 2nd life LTO battery, BEV; c) 1st life LFP battery, 2nd life LTO battery, BEV; d) 1st life Lead-acid battery, 2nd life LTO battery, BEV.

3.3 Eco-efficiency of HESS

The EE analysis was calculated according to equation 3 to determine the cost per environmental impact for the baseline HESS configurations, the environmentally and economically optimised HESS configurations and the 100% LFP HESS. As shown by Figures 3 and 5, the HESS configurations with both the lowest environmental and economic impact are those containing a low proportion of 1st life battery, a high proportion of 2nd life LTO battery and a low proportion of BEV i.e. these are both the economically and environmentally optimised structures. Figure 6 shows the results of the EE, which was calculated according to equation 3 for each of the five environmental impact categories under consideration. The results clearly show that the 100% LFP HESS has the lowest cost per environmental impact, this system has an initial investment of £599,204 leading to 0.12 £/FDP, 0.03 £/GWP, 40.49 £/MEP, 101.26

£/FEP and 0.11 £/HTP. While baseline LTO HESS configuration (33.3% 1st life LTO, 33.3% 2nd life LTO, 33.3% BEV) has the highest cost per environmental impact, this system has an initial investment of £787,150 leading to 0.33 £/FDP, 0.09 £/GWP, 112.69 £/MEP, 247.49 £/FEP and 0.24 £/HTP.



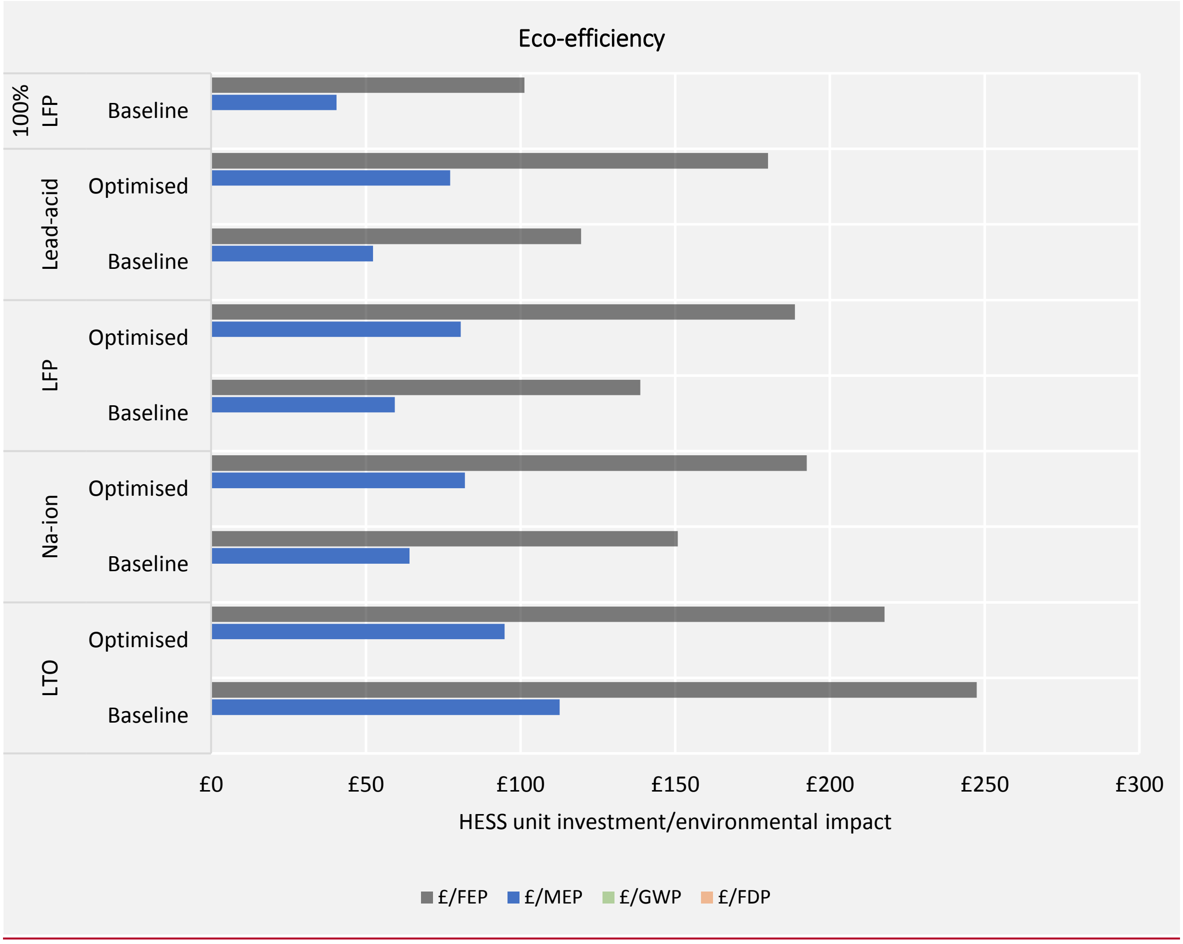


Figure 6: Result of the eco-efficiency analysis relating to the performance of one unit of the baseline HESS configurations (containing an equal distribution of each battery type), the environmentally and economically optimised HESS configurations based on the findings of the scenario analysis and the 100% 1st life LFP baseline. The environmental impact categories tested were the Fossil Depletion Potential (FDP), the Global Warming Potential (GWP), the Marine Eutrophication Potential (MEP), the Freshwater Eutrophication Potential (FEP) and the Human Toxicity Potential (HTP). The results relating to the £/HTP, £/ FDP, and £/GWP cannot be seen on this figure as they are negligible in comparison to the £/MEP and £/FEP results.

The results of this three-tiered assessment provide information relating to the environmental impacts, economic impact and eco-efficiency of each HESS configuration, which is pertinent to decision makers [79], [85], [86].

4 Discussion

4.1 Environmental impact of HESS

The environmental impacts of an equal proportion of 1st and 2nd life batteries and BEVs (i.e. 33.3% 1st life, 33.3% 2nd life, 33.3% BEV), referred to as the "baseline HESS configuration", were tested with respect to GWP, HTP, FDP, MEP and FEP. As a comparative baseline, the environmental impacts of a 100% 1st life LFP battery were also tested. The LCA is modelled over a 15-year period, assuming a total energy consumption of 6900 MWh. Table 3 shows the environmental impact of four baseline HESS configurations, where the 1st and 2nd life battery technology is the same, and environmental impacts of a 100% 1st life LFP battery. The aim of the HESS baseline configurations is to provide a reference point against which different HESS configurations can be benchmarked.

Table 3 details the results for all five environmental impact categories studied; GWP, FDP, MEP, FEP and HTP for each battery type and clearly shows that, over the five environmental impact categories studied, a HESS containing 1st and 2nd life Lead-acid batteries and a BEV has the highest environmental impact. These results are further disaggregated in Figure 2, where the individual contribution of each battery type (1st life, 2nd life and BEV) is shown. In equal proportions, the whole life cycle of a HESS with a 1st and 2nd life Lead-acid battery and BEV configuration leads to a GWP impact of 27,100,887 kg CO_2-eq/MWh, over three times that of the HESS containing an equal proportion of 1st and 2nd life LTO battery technology and a BEV which has a GWP impact of 8,349,871 kg CO_2-eq/MWh. The high environmental impact relating to the Lead-acid baseline HESS configuration does not relate to the environmental impact of the components of processing procedure of the battery itself, as cradle-to-gate this technology has the lowest environmental impact. Rather, the 1st life battery is hindered by the low cycle life of the Lead-acid battery (1,500 cycles, compared to 18,000 cycles for the LTO technology) and the 2nd life battery is hampered by the mass of the battery required for repurposing (64,433 kg, compared to 25,845 kg for the LTO technology).

Figure 2 further disaggregates the results shown in Table 3 to demonstrate how the environmental impact of each battery type (1st life, 2nd life and BEV) contributes to the total environmental impact across all five environmental impact categories. The results shown in Figure 2 show that for the Na-ion, LFP and LTO baseline HESS configurations, the GWP, MEP and FEP environmental impact of the second life battery is smaller than that of the 1st life battery. For example, the GWP impact category results of the Lead-acid baseline HESS configuration show 39.5% of the GWP environmental impact can be attributed to the 2nd life battery and 35.8% can be attributed to the 1st life battery. As mentioned above, the environmental impact of repurposing a battery for 2nd life is dependent on the mass of the battery and therefore, due to the increased mass of the Lead-acid battery compared to the other battery technologies, the environmental impact of repurposing the battery is higher.

Furthermore, when the life cycle of each battery type is inspected, it is the use phase that presents the highest impact across the five environmental impact categories studied. In each case, the use phase represents around 90% of the total environmental impact. This supports the results provided by Ahmadi et al. [9] who also report that the use phase provides the highest contribution to the overall impact.

On deeper inspection, the results show that the cradle-to-gate GWP of the LTO battery is 14.10 kg CO_2 kg^{-1}, and that of the Lead-acid batter is 2.42 kg CO_2 kg^{-1}, these results support those provided by Baumann et al. [16], which were given at 14.19 and 2.33 kg CO_2 kg^{-1}, respectively. Comparatively, the cradle-to-gate GWP for the LFP battery was found to be 30.01 kg CO_2 kg^{-1}, which is much higher than the 16.11 kg CO_2 kg^{-1} reported by Baumann et al. [16].

Across all five environmental impact categories, the contribution of the BEV to the baseline LTO HESS configuration provides the highest environmental impact. For example, the GWP impact of the BEV is 20,072,836 kg CO_2-eq/MWh, compared to only 2,505,607 kg CO_2-eq/MWh for the 1st life LTO battery technology and 2,471,172 kg CO2-eq/MWh for the 2nd life LTO battery technology. Therefore, when an equal percentage contribution of each battery type is assumed for the baseline LTO HESS configuration, the GWP impact of the BEV contributes almost 80% of the total impact.

Closer analysis of the environmental impact of each individual battery type shows the highest environmental impact, across all five environmental impact categories from cradle to gate, is related to the LFP. The results show the GWP of 1st life LFPs to be 301,317 kg CO_2-eq/MWh, compared to only 124,884 kg CO_2-eq/MWh for Lead-acid batteries. This impact is related to the mass of the battery required to deliver 1 MWh. The GWP of a 1kg Lead-acid battery is only 2.24 kg CO_2-eq/kg, but a total mass of 51,546 kg is required to deliver 1 MWh using a Lead-acid battery. Comparatively, the GWP of a 1 kg LFP battery is much higher at 30.01 kg CO_2-eq/kg, but only a total mass of 10,042 kg is required to deliver 1 MWh using a LFP.

The baseline HESS configuration with the lowest environmental impact across all five environmental impact categories, i.e. the most "environmentally friendly", is that containing 33.3% 1st life LTO, 33.3% 2nd life LTO, and 33.3% BEV. This HESS has a GWP impact of 8,349,871 kg CO_2-eq/MWh. The main contribution to the low environmental impact is due to the high cycle life of LTO technology. In comparison, a Na-ion battery would need to be replaced nine times to match the same cycle life of LTO technology.

When the environmental impacts of the baseline HESS configurations are compared to the 100% 1st life LFP battery baseline, Figure 2 shows that only the baseline LTO HESS configuration (33.3% 1st life LTO, 33.3% 2nd life LTO, and 33.3% BEV) has a lower environmental impact across all five environmental impact categories than using a 1st life LFP battery for energy storage. Interestingly, the results in Figure 2 show the use of 2nd life Lead-acid, Na-ion and LFP battery technologies, in the baseline HESS configurations, result in a higher environmental impact compared to a 100% 1st life LFP. In the case of the Lead-acid battery technology, this is due to the increased weight of this battery technology required for repurposing, therefore leading to a higher environmental impact. As the state of health of a 2nd life battery is lower than that of a 1st life battery, a higher number of 2nd life batteries are required to perform the same function and therefore the associated mass is higher.

Despite this increase in the required mass of the battery technologies, with the exception of the FDP environmental impact category, the environmental impact of both the repurposed 2nd life Na-ion and LFP battery technologies is lower than their 1st life counterparts and therefore the relative impact of the BEV in the HESS leads to a higher environmental impact compared to a 100% LFP HESS.

Battery recycling for each battery technology was modelled using the "treatment of used Li-ion battery, hydrometallurgical treatment, GLO" dataset from the Ecoinvent database [61] and adjusted for the weight of the different battery technologies. This recycling methodology was chosen as it is the most selective route to extract metals [45]. Recycling not only saves natural resources, but also it can lead to a reduction in the energy consumption and water required for primary production, whilst improving the quality of waste discharge. However, the economics of recycling necessitate the value of the recovered materials to exceed the costs of the input processes. Economically strategic materials include lithium, nickel, cobalt, manganese, zinc and rare earth elements; therefore, lithium-ion batteries may be preferentially recycled over Na-ion, Lead-acid or LTO technologies [87].

Scenario analysis was performed to determine how the percentage contribution of each battery type affects the environmental impact of each HESS. Figure 3 shows the GWP results of the scenario analysis for four HESS configurations using one of each of the four 1st life battery technologies, a LTO 2nd life battery and BEV, where the BEV content is constant, and the 1st and 2nd life battery contents vary (as one increases the other decreases).

The largest variation in the results relates to the Lead-acid/LTO/BEV HESS configuration in Figure 3a. This is caused by large difference in the GWP result for a 1st life lead-acid battery and a 2nd life LTO battery (29,122,957 kg CO_2-eq/MWh and 2,471,172 kg CO_2-eq/MWh, respectively). The factors affecting these results are discussed above.

Figure 2d shows the smallest level of variation between the different scenarios for the LTO/LTO/BEV baseline HESS configuration. In all cases, a HESS configuration containing a high percentage contribution of 2nd life LTO battery technology leads to the lowest environmental impact across all impact categories. Due to the current low technology readiness level of LTOs, sparse data is available with respect to their environmental impacts. Despite this, it has been shown that lithium iron phosphate utilised in LTOs provides a low contribution to the impact of other lithium based battery technologies [40]. The production of nano-scale titanium dioxide for LTO technology contributes to high nitrate concentrations in aquatic systems which contributes to the MEP impact [88].

Overall, taking the whole system into account, it is clear to see that a HESS configuration comprising of a low proportion of 1st life LTO battery technology and BEV with a high proportion of 2nd life LTO battery technology results in the lowest environmental impact across all environmental impact categories except FDP.

4.2 Techno-economic analysis

To determine the economic impact of the HESS, an investment appraisal was performed using TEA for each of the baseline HESS configurations, the economically optimised technological configurations of each technology type and the 100% LFP baseline. The optimised HESS was taken to be the configuration resulting in the lowest economic impact. The economic model is based on HESS revenue generation from a DFR service. Figure 4 shows the results of the investment appraisal according to the economic modelling for DFR based on an initial £6 DFR/MW/hr at 24 hours' service over 15 years, as maintenance periods of such systems are very short and therefore assumed to be negligible.

The results demonstrate that over a 15-year period only the 100% 1st life LFP baseline is economically viable across the whole range of DFR scenarios, while the baseline HESS configurations only become economically viable at: LTO = £8/MW/hr, LFP = £10/MW/hr, Na-ion = £12/MW/hr and Lead-acid = £12/MW/hr. The investment cost relating to a 100% 1st life LFP baseline is £599,204; the highest baseline investment cost relates to the Lead-acid baseline HESS at £1,135,894.

As illustrated in Figure 4, the most economically feasible HESS configuration, at any DFR fee, is 5% 1st life LTO, 90% 2nd life LTO, and 5% BEV. Although, as shown in Table 1, the price of a repurposed LTO battery is the highest of the four technologies, the high cycle life of the LTO battery technology results in fewer battery replacements over the 15-year period that was assessed, therefore leading to a lower environmental impact overall.

The TEA results of the scenario analysis are shown in Figure 5, four HESS configurations using one of each of the four 1st life battery technologies, a LTO 2nd life battery and BEV are shown. In this scenario the BEV content of the HESS remains constant, and the 1st and 2nd life battery contents vary (as one increases the other decreases). Figure 5 shows the change in investment (Capital expenditure) of the HESS configurations utilising a 1st life battery of each technology type combined with a 2nd life battery of LTO and BEV, when the BEV percentage remains constant and the 1st life battery and 2nd life battery vary (as one increases the other decreases). The y-axis depicts the investment of the whole HESS as the percentage contributions of the 1st and 2nd life battery changes with the x-axis.

Regardless of the 1st life battery technology used, as the content of this battery type is increased, the investment cost increases. The lowest investment cost of £252,814, can be attributed to the configuration containing 5% of 1st life LTO battery technology, 90% 2nd life LTO battery technology and 5% BEV technology. This is a reduction of £534,336 compared to the baseline LTO HESS configuration.

The most economically viable configuration is that of the 100% LFP battery technology, followed by the LTO battery technology. Overall, to support a low-cost HESS investment, in line with a low environmental impact, a HESS configuration comprising of a low proportion of 1st life LTO battery technology and BEV with a high proportion of 2nd life LTO battery technology should be supported.

4.3 Eco-efficiency

The Eco-efficiency (EE) analysis relates to the investment and consequential environmental impact of one HESS unit. An energy storage system may require multiple HESS configurations to achieve the required storage capacity. Therefore, the investment cost per environmental impact would increase with the investment cost.

Figure 6 provides the results of the EE analysis. The EE was calculated according to equation 3 for each of the five environmental impacts considered in this study and depicts the ratio between economic impact and environmental performance of the baseline and optimised HESS configurations. The results of the eco-efficiency index show that a hybrid energy storage system configuration containing equal proportions of 1st and 2nd life Lithium Titanate and BEV i.e., the baseline LTO HESS configuration, battery technologies is the most eco-efficient. This EE result has the highest cost per environmental impact; the initial investment of this system is £787,150, leading to the highest £/environmental impact across all impact categories. Specifically, the highest investment per HESS unit relates to the MEP and FEP impact categories; the eco-efficiency for the baseline LTO HESS configuration is £112.69/MEP and £247.49/FEP. In comparison, the eco-efficiency relating to the GWP (£0.09/GWP), FDP (£0.33/FDP) and HTP (£0.24/HTP) are much lower.

Although the optimised LTO HESS provides the highest EE result when compared to the other optimised systems, it is the only optimised HESS configuration that has a lower result than the corresponding baseline configuration. While the EE index presents a harmonised approach to evaluate the HESS from both the environmental impact categories and costs, therefore integrating the analysis from LCA and TEA perspectives, this result is contradictory to the findings of each of the individual environmental and economic assessment methodologies.

Overall, the lowest EE result can be attributed to the 100% LFP HESS, as the initial investment of this configuration is £599,204, the EE result could be improved both by reducing this investment cost and by decreasing the overall environmental impacts of the battery technology.

Figure 6 shows that the Lead-acid baseline HESS configuration has the lowest EE index, this can be attributed to the highest initial investment cost of £1,135,894 and the highest GWP of

27,100,888 CO_2-eq/MWh over the 15-year life cycle of the HESS of all of baseline systems considered.

This harmonised approach supports the findings of both the LCA and the TEA in that the most eco-efficient baseline HESS configuration contains LTO battery technology. Despite this the environmental and economically optimised LTO HESS configuration was found to have a lower EE result than the baseline configuration and therefore is not optimised for the EE index calculation due to the lower cost to environmental impact ratio of the environmental and economically optimised LTO HESS configuration.

4.4 Circular economy

The transition from a linear to a circular economy, in which waste and pollution are eliminated, products and materials remain within supply chains, and natural systems are regenerated, is beneficial not only to the economy, but also to the environment and society [89].

Batteries are a key tool in the global race to decarbonisation, which will directly lead to an increase in the depletion rates of those metals upon which the battery technologies rely. A batteries life span is dependent on its chemistry and cycling frequency and therefore both the designer and user have an impact on the total service life. To date, the collection mechanism for lead-acid batteries has proven to be successful, with high collection rates in developed countries. It is not therefore unconceivable to envisage this level of reuse or recycling for new battery technologies [90].

The HESS configuration directly contributes to a circular economy through the reuse of an end-of-life battery into a new energy storage solution, this is supported by the results which show a HESS configuration comprising of a high proportion of 2nd life battery technology results in the lowest environmental impact overall. Furthermore, this HESS promotes a circular economy through the utilisation of an asset that would usually be stood idle. This innovative study moves up the waste hierarchy to remanufacturing, in place of recycling, thereby supporting a circular economy. Furthermore, it has been shown that remanufacturing can result in a low carbon system with high efficiency and effectiveness, further enhancing the ideals of a circular economy [90].

4.5 Practical implications of this study

The practical implications relating to the implementation of this system, specifically utilising LTO batteries, would reduce the environmental impacts of 1st life battery manufacture through remanufacturing methodologies and reduce the overall economic impact. This is significant as the number of EVs on the road increases over the next ten years to approximately ~~10~~44 million [6]. Limited battery lifetimes will result in a significant second-hand battery market; therefore, the implementation of this hybrid system provides a key steppingstone to reducing resource consumption across the planet.

5 Conclusion

This research is the first to present a three-tier circularity assessment of a "Hybrid Energy Storage System" (HESS) which integrates 1st and 2nd life batteries and BEVs. Four different battery technologies were assessed, namely Lithium Titanate, Lead-acid, Lithium Iron Phosphate and Sodium-ion. These systems were evaluated based on analyses from three perspectives: (1) life cycle assessment, (2) techno-economic analysis and (3) eco-efficiency and scenario analysis was applied. Our findings show that the life cycle assessment and techno-economic analysis assessment methodologies support the implementation of a HESS consisting of 5% 1st life LTO, 90% 2nd life LTO and 5% BEV, while the eco-efficiency index shows that a HESS with equal proportions of 1st and 2nd life LTO and BEV battery technologies is the most eco-efficient.

This research shows that a HESS configuration comprising of a low proportion of 1st life LTO battery technology and BEV with a high proportion of 2nd life LTO battery technology results in the lowest environmental impact across all environmental impact categories except FDP.

The most economically viable baseline HESS configuration is that of the 100% LFP battery technology, followed by the LTO battery technology. To support a low cost HESS investment, a HESS configuration comprising of a low proportion of 1st life LTO battery technology and BEV with a high proportion of 2nd life LTO battery technology should be implemented.

The harmonised approach of the eco-efficiency index supports the findings of the LCA and the TEA by showing that the most eco-efficient baseline HESS configuration contains LTO battery technology. Comparatively to the LCA and TEA, the environmental and economically optimised LTO HESS configuration was found to have a lower EE result than the baseline configuration.

These results clearly support a circular economy through the remanufacture of 1st life batteries to be implemented into a useful system and the use of BEVs in this system further promotes a circular economy through their enhanced utilisation. ~~The implementation of this system, specifically utilising LTO batteries, would reduce the environmental impacts of 1st life battery manufacture through remanufacturing methodologies and reduce the overall economic impact. This is significant as the number of EVs on the road increases over the next ten years to approximately 10 million. Limited battery lifetimes will result in a significant second-hand battery market; therefore, the implementation of this hybrid system provides a key steppingstone to reducing resource consumption across the planet.~~

The main limitation to conducting the LCA, TEA, and consequently the EE of a HESS is the lack of primary data as this cannot be sourced directly from battery manufacturers due to confidentiality restrictions. To mitigate this limitation on the final results, robust published data was sourced for the completion of the LCI of each battery and is provided in detail in the appendix.

In all of the HESS models considered in this research, it was assumed that the BEV was a LFP battery. While this is currently the predominant battery technology for BEVs, this may change in the future due to the ongoing technological development in the battery arena. Consequently, the overall impact of the HESS may vary if the BEV battery technology is altered.

In addition, this study assumes the availability of the 2nd life batteries from EVs for the creation of the proposed HESS systems and the linearity of cost reduction conservatively, although the cost is expected to drop through scale up and more renewable mix and electrification in the energy supply chain. While in this study it is assumed that the 1st life of the 2nd life battery used in the HESS was in a BEV, to overcome potential availability issues, the 2nd life batteries could be collected from alternative sources.

Future research can address these in further scenario modelling, including the complexity and logistic of sourcing of secondary batteries, decarbonised energy supply (e.g., nuclear, hydrogen) and projected spatial time series of economic return and payback. Also, additional future work can consider the potential revenue streams for each HESS with the aim of clearly differentiating between the different chemistries and mixes.

Also, additional future work can consider the potential revenue streams for each HESS with the aim of clearly differentiating between the different chemistries and mixes.

This research supports the use of a three-tiered assessment to aid decision making. Although Sustainable Development Goal (SDG)12 aims to decouple resource use from economic growth, economic productivity is still important for society as demonstrated by SDG8. Reduced toxicological impacts are directly attributed to emission intensities reduction and clean production practices adoption [31], contributing to SDG13. Therefore, our harmonised approach integrating LCA, TEA and eco-efficiency index in the three-tier circularity assessment is key to ensure the sustainability of energy storage system for future energy security.

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Data availability

All data is available from the corresponding author on request.

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Higher 2nd life Lithium Titanate battery content in hybrid energy storage systems lowers environmental-economic impact and balances eco-efficiency

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Abstract

Energy exchange technologies will play an important role in the transition towards localised, sustainable energy supply. Hybrid energy storage systems, using different energy storage technologies, are currently under investigation to improve their technical performance and environmental sustainability. However, there is currently no exploration of the environmental benefits and economic feasibility of hybrid energy storage systems combining 1st and 2nd life batteries and battery electric vehicles. To determine the environmental and economic impacts of this type of hybrid energy storage system, this research employs a three-tier circularity assessment incorporating Life Cycle Assessment, Techno Economic Analysis and an Eco-Efficiency Index, from cradle-to-grave, of 43 techno-hybridisations of four 1st and 2nd life battery technologies; Lithium Titanate, Lead-acid, Lithium Iron Phosphate and Sodium-ion, with battery electric vehicles. The results of the life cycle assessment and techno-economic analysis show that a hybrid energy storage system configuration containing a low proportion of 1st life Lithium Titanate and battery electric vehicle battery technologies with a high proportion of 2nd life Lithium Titanate batteries minimises the environmental and economic impacts and provides a high eco-efficiency. The results of the eco-efficiency index show that a hybrid energy storage system configuration containing equal proportions of 1st and 2nd life Lithium Titanate and BEV battery technologies is the most eco-efficient. This research highlights the environmental and economic benefits of the use of Lithium Titanate battery technologies within novel hybrid energy storage systems.

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Highlights

- Three-tier circularity of a hybrid energy storage system (HESS) assessed
- High 2nd life battery content reduces environmental and economic impacts
- Eco-efficiency index results promote a high 2nd life battery content
- Lithium titanate (LTO) HESS has the lowest environmental and economic impacts
- LTO HESS balances eco-efficiency index

Key words: life cycle assessment, techno-economic analysis, eco-efficiency index, energy storage, circular economy

Word count: 7645

Abbreviations

Battery Electric Vehicle	BEV	Life cycle inventory	LCI
Eco-efficiency	EE	Lithium Iron Phosphate	LFP
Dynamic Frequency Response	DFR	Lithium Titanate	LTO
FDP	Fossil Depletion Potential	MEP	Marine Eutrophication Potential
FEP	Freshwater Eutrophication Potential	NPV	Net Present Value
GWP	Global Warming Potential	PV	Photo Voltaic
Hybrid Energy Storage System	HESS	SDG	Sustainable Development Goal
HTP	Human Toxicity Potential	Sodium-ion	Na-ion
Life cycle assessment	LCA	Techno-economic analysis	TEA

1 Introduction

Energy storage can effectively balance supply and demand at both the grid and smaller scales, storing excess energy at times of high generation for use later, ensuring energy security by minimising system volatility. The response time, storage time, and capacity of different energy storage technologies can vary substantially and scale from kW to MW based on user needs. However, when each is used in insolation, they may not be able to mitigate all types of destabilisation event and there are technical limitations to each technology, which can lead to an oversized installation, resulting in poor economics for the installation and long payback terms [1]. Utilisation of different technologies into a combined Hybrid Energy Storage System (HESS) can alleviate this and provide a system that meets the technical needs of the application or that can dynamically adapt to changing requirements. Different battery types can make up a HESS where each of the batteries characteristics are exploited to optimize the service delivery [2].

The ability to store energy and generate power from conventional energy production is of critical importance in a society where energy demand is increasing and, in turn, this technology has allowed for the development of hybrid and plug-in electric vehicles [3], [4]. Recently, battery usage has increased, while costs have been seen to decrease [5], [6], and production is expected to increase further as the number of Battery Electric Vehicles (BEVs) on the road rises from 1.2 million in 2016 to 44 million in 2030 [7], [8]. This rapid development of new electrochemical reactions and battery technologies, coupled with limited battery lifetimes, will result in a significant second-hand battery market, which can potentially provide new energy exchange services [9], [10].

Despite the prevalence of battery technologies in electrical energy storage systems [11] alternative technologies such as supercapacitors and fuel cells can also be utilised in electric hybrid vehicles. Supercapacitors have fast charge and discharge cycles, high power density, operate over a wide temperature range, have a high cycle life, and result in low maintenance costs [12]. Fuel cell technologies have a number of advantages over batteries for electric vehicles, including their light weight and small dimensions [13].

Battery technologies such as Lithium Titanate (LTO), Lead-acid, Lithium Iron Phosphate (LFP) and Sodium-ion (Na-ion) [14] have reliable performance, rapid response, are compact systems and have low costs [5] . However, 2nd life batteries and BEVs, could potentially be utilised as an alternative sustainable solution for battery energy storage systems as they can provide an additional service by acting as energy storage technology [15], [16]. For instance, Gough et al. [14] analysed the techno-economic feasibility of multiple vehicles taking into account electric vehicle electricity sale price, battery degradation cost and infrastructure costs [14]. Furthermore, Zhao et al. [15] analysed the environmental and economic benefits and found that BEV to grid systems can generate an economic revenue and greenhouse gas savings [15].

As BEV batteries reach their end of life at 80% capacity, there will be a considerable 2nd life battery market as the production of BEVs increases worldwide. Such batteries are ideal for stationary energy storage applications since they are low cost and provide relatively fast scale-up for large energy and power requirements [16].

Academic research utilising life cycle assessment (LCA) [9] and techno-economic analysis (TEA) [17] to determine the environmental and economic impacts of batteries is extensive.

Ahmadi et al. [9] utilised LCA to analyse the environmental impacts of 1st and 2nd life EV LIBs from a life cycle perspective and found that the 1st and 2nd use phase contributes the largest environmental impact [9]. However, there is still limited understanding on the environmental and economic benefits of such systems.

Although the LTO battery technology (utilising a LFP cathode) is not yet commercialised, it was chosen for this study as research [18] has shown that understanding the environmental impacts of a product at design stage may prevent an increase in its environmental burden throughout its lifecycle. LCA has been conducted to determine the environmental impacts of LTO and has shown the carbon footprint of LTO battery production to be 14.19 kg CO_2 kg^{-1}, compared to 16.11 kg CO_2 kg^{-1} for LFP batteries and only 2.33 kg CO_2 kg^{-1} for Lead-acid batteries [16]. Research into the economic impacts of batteries calculating the life cycle costing of LTOs, compared to Lead-acid batteries, has also been published; the total cost of ownership of LTO in an industrial application is 33% lower than that of Lead-acid batteries [19]. A study by Baumann et al. [16] compared the economic impact of a range of battery types and found the main contributor to the overall cost of a battery technology is its cycle life [16].

Peters et al. [20] found the average greenhouse gas emissions of lithium-ion batteries to be 110g CO_2-eq for the production of 1Wh of storage capacity [20]. The life spans of 2nd life lithium-ion batteries have shown promising results of over 30 years [21], but for the environmental benefits of 2nd life battery technologies to be realised they should utilise renewable power sources and not supported by grid services [21]. From an economic perspective, it has been shown that while 2nd life lithium-ion batteries can provide a cheaper alternative to 1st life lithium-ion batteries [22], there may not be sufficient stationary applications available to contain the large amount of 2nd life batteries expected to be available in the future.

In their research, Khan et al. [23] outline the TEA of different hybrid power system using the hybrid optimisation model electric renewable software. They report the lowest cost of energy for a Photo Voltaic (PV)-Wind-Diesel-Battery system at 0.162 $/kWh and the highest cost of energy for a PV-Diesel system at 0.709$/kWh [23]. Eltoumi et al. [24] outline that while PV is an essential energy source to enable the globe to achieve net-zero, its implementation for BEV charging is limited due to intermittency and limited contribution in the daytime [24].

Philippot et al. [25] depict the eco-efficiency of a LIB for EVs as a scatter plot on which the kg CO2-eq/kWh is shown on the y-axis and the manufacturing cost is shown on the x-axis. This research considers different manufacturing locations and concludes that electricity mix is an environmental hotspot, and that the eco-efficiency can be improved through increased manufacturing capacity and a low carbon energy source [25].

Similarly, Onat et al. [26] consider the eco-efficiency of electric vehicles across 50 states in the United States. Their research considered three environmental impacts; carbon emissions, energy consumption, and water use, and one economic impact, calculated through life cycle costing with respect to a range of electricity sources. The results show that utilising solar charging facilities led to the most promising result [26].

Despite increased attention on battery repurposing and recycling as part of a circular economy, with the rise of BEVs and energy demand, there is a gap in current literature in which no research has examined the hybridisation of 1st and 2nd life batteries with BEVs. Specifically, the combination of LTO, LFP, Na-ion and Lead-acid battery technologies within a Hybrid Energy Storage System (HESS), has not been explored for their optimised arrangement to reduce environmental impacts and economic costs. A HESS is a system that incorporates *"different generation, storage, and consumption technologies in a single system"* [27], the aim of which is to enhance the service provided by a single source [27]. This is becoming of increasing importance, as in the near future, the capacity of stationary battery storage systems is likely to rapidly increase [28]. This research presents a new model of energy exchange services, namely a HESS combining 1st and 2nd life batteries with BEVs. The study determines which technological combination of 1st and 2nd life batteries with BEVs provides the maximum environmental benefit and minimum economic cost according to a functional unit of 1MWh over 10,000 cycles. The combination of 1st life Lead-acid, LFP, Na-ion or LTO battery technologies, with 2nd life batteries of the same technology types and with BEVs are analysed, as part of a stationary storage system, using a three-tier circularity assessment of Life Cycle Assessment (LCA), Techno Economic Analysis (TEA) and an eco-efficiency (EE) index. The results were compared to a baseline system comprising of a 100% 1st life LFP battery. Furthermore, scenario analysis is employed to determine the change in environmental and economic impact to the HESS when the percentage contribution of each battery technology is altered.

Specifically, this study aims to determine the environmental impacts of novel HESS based on 1st and 2nd life batteries and BEVs. This research was conducted to address the gap in knowledge relating to HESS and therefore, it is intended that both the research community and battery-based industries, working on these types of systems, will use the results of this study to aid future decision making.

These four battery technologies were chosen for comparison as firstly, although LFP technology is likely to improve moving into the future, LTO and Na-ion technologies, with improved energy densities and cycle lives are likely to become available technologies for electric vehicles [29]. Secondly, Garche et al. [30] have outlined the deployment of Lead-acid batteries in hybrid applications and their applications in dual systems with Li-ion batteries.

The novelty of this research lies in its application of the LCA, TEA and an EE index, a three-tier circularity assessment, to a conceptualised HESS, utilising a range of battery technologies. Further novelty is provided through the use of scenario analysis to determine which percentage contribution of each battery technology leads to a HESS optimised to reduce the overall environmental impact and increase the economic benefit. This is the pioneering study extending beyond recycling into a circular economy [31] to generate power through battery life extension by enhancing the EE of battery energy storage using techno-hybridisation.

Accordingly, this manuscript is structured as follows: section 2 outlines the materials and methods utilised in the LCA, TEA and EE index and the associated scenario analysis for each HESS configuration; section 3 shows the results; section 4 provides the discussion; and section 5 presents a concise conclusion.

2 Materials and methods

Three assessment methodologies, LCA, TEA and an EE index, were utilised in this study to determine the environmental and economic impacts of a HESS comprising of the combination of 1st life Lead-acid, LFP, Na-ion or LTO battery technologies, with 2nd life batteries of the same technology types and with BEVs. This section provides the methodological processes applied to each assessment type. The proposed structure of the HESS is provided in Appendix A and the LCI for each battery type can be found in Appendix B-E.

2.1 Life cycle assessment

The application of LCA began as far back as the 1960s, in a comparative context for products using a systematic methodology. Since then, the methodology has been developed to assess the whole life cycle of a product or service and as such, world governments support the use of the methodology throughout environmental policy [32], [33]. The production, use and disposal of products or services can be traced from a whole life cycle perspective to support informed decision-making and to provide mitigation strategies throughout the supply chain [34] and it is now the most commonly used tool to for the assessment of environmental impacts [35].

In this study, we adopted the process LCA methodology, which calculates the environmental impact of the unit process exchange and inputs within the supply chain, directly associated with the battery technologies under consideration [18]. According to ISO 14040 [36], the LCA methodology involves a four-step process: (1) goal and scope definition; (2) inventory analysis; (3) impact assessment and (4) interpretation, where step 4 runs concurrently with steps 1, 2 and 3 [32].

The LCA was performed on HESS consisting of 33.3% 1st life batteries, 33.3% 2nd life batteries and 33.3% BEVs (where the BEV was assumed to be of LFP battery technology). This was conducted to provide a baseline HESS configuration result against which variations of the percentage of battery technologies hybridisation can be compared using scenario analysis. As a comparative baseline, the environmental impacts of a 100% 1st life LFP battery were also tested. A functional unit of 1MWh over 10,000 cycles was applied. The system boundary and HESS implementation strategy are shown in Figure 1.

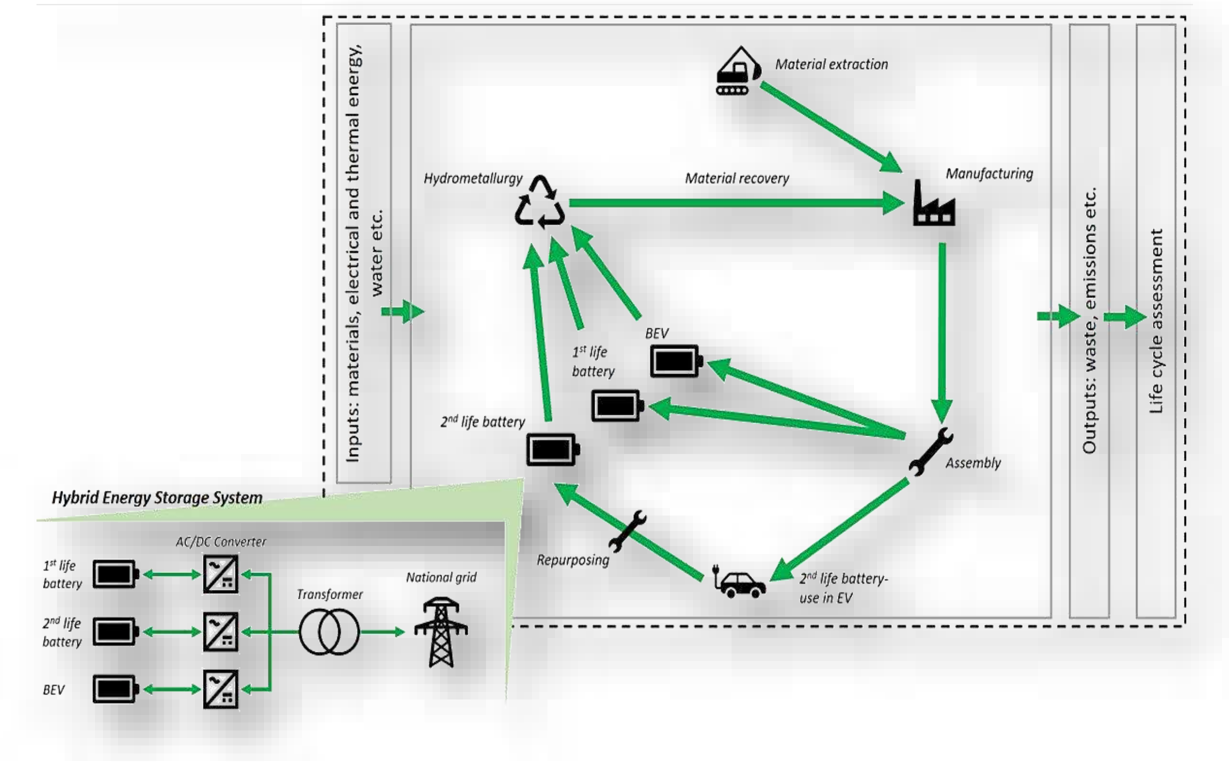

Figure 1: The system boundary applied to the LCA of the HESS consisting of 1st and 2nd life batteries and BEVs in this study. The system boundary includes the inputs and outputs relating to the raw material extraction, component manufacture, battery assembly, use phase and end of life management (i.e. hydrometallurgy). The repurposing and second use phase of the 2nd life battery is also assessed. The HESS implementation approach is shown in the bottom left-hand corner of this figure.

Each energy storage technology will have a different DC voltage range meaning that sharing a common DC bus would not be possible. Figure 1 shows an example configuration whereby each technology is connected via its own DC to AC electrical converter to an AC common bus allowing independent control of power flow to/from each one. The total import/export to the electrical grid is the net sum of the total power of all three converters, therefore, this configuration also allows for energy transfer between storage technologies.

To complete step 2 of the LCA methodology, the LCI for each battery supply chain was developed using data from primary and secondary sources [37]–[47]. Individual contributions of each battery were accounted for as shown by the system boundary in Figure 1.

The data relating to the bill of materials and process flows for each of the four battery technologies (LTO, Lead-acid, LFP and Na-ion) were taken from published literature [37]–[42], [48]. The bill of materials was validated by a mass and energy balance to ensure thermodynamic constraints of the systems were accurate [36]. The infrastructure, transportation and ancillary equipment, such as charging facilities, relating to certain types of battery manufacturing and assembly are negligible, compared to the remaining aspects, and therefore have been excluded from this study where appropriate [38], [39]. Furthermore, the impact of the power electronics is assumed to be equal across all battery types and therefore are not included in the comparative model. Prior to implementation in the HESS, the 2nd life battery is assumed to have been used in a BEV.

The use phase in the HESS is a 1MWh stationary system with an energy throughput of 6900MWh over a 15-year lifetime based on providing dynamic frequency response (DFR) services, leading to a daily consumption of 1.26MWh. The total service life is modelled as 10,000 cycles. Over the 10,000 cycle life, the effect of degradation will reduce the performance of each battery type, i.e. the ideal state of the battery will decrease, known as state of health. The cycle life of the LTO battery is assumed to be 18,000 cycles [19]; the cycle life of the LFP battery is assumed to be 2,500 cycles [49]; the cycle life of the Na-ion battery is assumed to be 2,000 cycles [50] and that of the Lead-acid battery is assumed to be 1,500 cycles [19]. The state of health of a battery is mainly governed by the thermodynamic instability of the materials used in the electrodes and this aging process requires a trade-off between usage and performance [51]–[53]. As noted above, the availability of 2nd life batteries is likely to outweigh the market for stationary applications moving into the future and therefore it is assumed that battery stock is abundant [22]. Research has shown that the average vehicle is only in use for 4% of its life, therefore the model assumes this to be negligible, making the BEV an appropriate addition to the HESS [54]. The "round trip energy efficiency" degradation of the system is assumed to be negligible over the one-year period assessed by the LCA and is not part of the TEA calculation and therefore has not been considered in this study.

Battery end of 1st life is assumed when 80% of its original energy capacity is reached [55]. It is assumed that at the end of its first use, the battery shows no sign of leakage, high internal impedance or internal short circuits and therefore is suitable for reuse. To repurpose the battery, it must be disassembled and tested, followed by the addition of new hardware and packaging [48]. As battery technology is continually improving, leading to increased capacitance; the results of this LCA provide the current environmental outlook relating to the implementation of a HESS over a 15-year period.

The HESS systems would aim to be 100% re-processed to recover materials when decommissioned. A number of different processes exist for battery end of life treatment, for instance, pyrometallurgical, hydrometallurgical (a combination of the pyrometallurgical and hydrometallurgical methods), direct cathode recycling and the use of deep eutectic solvents [43], [44], [56]–[58]. The pyrometallurgical and hydrometallurgical routes are the main methodologies for Li-ion battery recycling, each yielding different end products. For example, the Retriev hydrometallurgical process produces a cobalt cake, lithium carbonate and copper and aluminium foils, whilst the Xstrata Nickle process yields nickel, cobalt, and copper alloys [59]. Though it would not be unreasonable to assess the impact of the pyrometallurgy methodology for resource recovery, for this study, the hydrometallurgical recovery process was chosen for the assessment of all four technology types due to its most selective route to extract metals [45]. Hydrometallurgy involves leaching with sulphuric acid, neutralisation, the recovery of the required metals and wastewater treatment [57].

To provide a robust assessment, the life cycle impact assessment (step 3) was completed using the ReCiPe Life Cycle Impact Assessment [60] methodology based on the environmental impact indicators in Peters et al. [38]. In our study, five environmental mid-point impact categories were measured: Global Warming Potential (GWP), Human Toxicity Potential

(HTP), Fossil Depletion Potential (FDP), Marine Eutrophication Potential (MEP) and Freshwater Eutrophication Potential (FEP) were analysed [31], [38]; environmental input data was sourced from Ecoinvent [61].

The environmental impact of climate change can be measured by the GWP, i.e., the global temperature change caused by the emissions of greenhouse gases. GWP can be measured over 20, 100, or 500 years, though 100 years is the most commonly used, with the units kg CO_2-equivalent. The HTP is utilised to determine the potential harm to humans caused when a chemical is emitted to the environment; the calculation takes into account the toxicity and likely does of the chemical and is measured in kg 1,4-DB-equivalent [62].

In LCA, fossil fuel consumption is calculated by the FDP, [59] and is measured in kg oil-equivalent [63], this method includes non-renewable resources (fossil fuels and minerals). The ReCiPe methodology quantifies this additional effort in economic terms (additional costs) For minerals, the marginal increase of costs due to the extraction of an amount of ore is the basis of the model. Furthermore, mineral depletion is based on depletion of ores, instead of elements. For fossil fuels, the marginal increase of oil production costs (due to the need to mine non-conventional oils) is used [65].

In this study, we emphasise the increasing role of renewable energy and electrification in the energy mix (and the reducing role of fossils) to power EVs, which aligns with global net zero, decarbonisation, and climate change strategies including the IPCC 2021 report approved by 195 member governments [66]and the IEA Net Zero by 2050 report [67]. As such, it is expected that the cost of batteries technologies and systems, both new and recycled, such as the ones proposed in this research, will drop as the energy supply and grid become cleaner and more affordable with the decrease of energy cost for renewable and electricity. Consequently, the FDP impact will reduce due to less reliance on the fossil-based energy supply chain.

Eutrophication is a phenomenon that occurs when chemical nutrients build up in an ecosystem, leading to increased productivity which in turn reduces water quality and biodiversity. This phenomenon is mainly affected by the release of ammonia, nitrates, nitrogen oxides, and phosphorous. The MEP is measured as k N-equivalent and the FEP is measured as kg P-equivalent [62].

The HESS systems lead to reduction in the environmental impacts of the combustion and processing of natural gas for energy production through lower peak load and load levelling [68].

The environmental impacts across the supply chain of each HESS configuration were calculated using equation 1.

$$Environmental\ Impact = \sum_{i=1}^{n} A_{p(i)} \times E_{p(i)} \quad (1)$$

where: A_p denotes the inputs (i) into a product's supply chain including raw material extraction, energy consumption, material production and manufacturing processes, etc.; n is the total number of process input (i) into the product's supply chain and E_p represents the emissions intensity across the chosen environmental and sustainability metrics (e.g. greenhouse gas emissions, land use etc.), for each input (i) into a product's supply chain emissions [18].

Throughout the LCA process, the data and results are assessed (step 4: interpretation). The aim of this step is to explain the results, derive conclusions and suggest recommendations with respect to the LCI and LCIA. The results of the LCA are disaggregated in Section 3, Table 2 and Figure 3, and discussed in full in section 4.

2.2 Techno-economic analysis

Techno-economic analysis (TEA) is a process used to evaluate the economic performance of a system, e.g., an industrial process, product, or service. The process parameters of a system are considered to enable the financial impact to be determined [69]–[71], e.g., process inputs and size of the technology, but in the main TEA is used to consider the economic impact [69].

In this study, TEA was performed to analyse the costs associated with the hybrid energy storage technologies technical configurations during the operational phase. As such, this paper focuses on those technical parameters required for the TEA since a wide array of research papers on the technical batteries chemistry are available. The technical parameters considered in the current TEA are material requirements, battery cycle life, manufacturing and re-manufacturing processes, and end-of-life management processes.

Net Present Value (NPV) measures profitability by discounting the cash flow at a specific rate of return [73]. In line with the LCA methodology outlined above which provides the technical parameters of each HESS as part of the LCI, TEA was performed on HESS consisting of 33.3% 1st life batteries, 33.3% 2nd life batteries and 33.3% BEVs, the economically optimised technological configurations of each technology type (where the optimised HESS was taken to be the configuration resulting in the lowest economic impact) and the 100% LFP baseline. This was conducted to provide a baseline HESS configuration result against which variations of the percentage of battery technologies hybridisation can be compared.

The economic model is based on HESS revenue generation from a DFR service. Whilst DFR may not be the only market applicable to each battery technology, it is most suited to provide a representative baseline across the four technologies studied. Furthermore, Enhanced Frequency Response is no longer in use and the comparison of different energy trading models is outside of the scope of this research. Further work on these issues can be found in literature, for example [74].

The economic model adopted during the operational phase is where the revenue from HESS is generated by a DFR service. NPV is calculated at a discount rate of 3% to determine the profitability of the HESS in relation to the revenue generated over the full lifetime. The NPV formula is shown in equation 2.

$$NPV = -C_o + \frac{C_1}{1+r} + \frac{C_2}{(1+r)^2} + \cdots . + \frac{C_T}{(1+r)^T} \qquad (2)$$

where C_o represents cash outflow at time 0, C_T represents cash flow at time T and r represents the discount rate. A positive NPV result indicates that the investment leads to a profit over the period assessed (in this case, 15 years), whilst a negative result shows that the investment costs outweigh the overall economic benefit [73].

The cost data of each battery type was retrieved from the literature [17], [75] and adjusted to provide the result in GBP (exchange rate: $1=£0.71, €1=£0.89). As the data provided by literature reflects battery costs in 2017, a cost reduction of 12% per year was modelled for each battery type to align with 2019 costs [76].

Table 1: Purchase cost of 1st and 2nd BEV technologies [17], [75], [76]. N/A: The BEV in this study is assumed to be of LFP battery technology and therefore only one BEV cost is provided.

Battery technology	1st life battery technology (£/kWh)	2nd life battery technology (£/kWh)	BEV (£/kWh)
LTO	827	414	N/A
LFP	217	73	683
Na-ion	278	139	N/A
Lead-acid	221	110	N/A

Table 1 summarises the purchase costs of the 1st and 2nd life batteries and the BEVs examined in this study. Figure 4 shows these investment appraisal results based on the economic modelling for DFR based on an initial £6 DFR/MW/hr at 24 hours' service over 15 years, as maintenance periods of such systems are very short and therefore assumed to be negligible. The total cost of the HESS unit was calculated based on the percentage contribution of each battery technology and the number of replacement batteries required throughout the cycle life of the HESS unit. The results of the TEA are disaggregated in Section 3, Figure 4, and discussed in full in section 4.

2.3 Eco-efficiency index

The assessment of eco-efficiency is required to provide a consistent methodology against which the parameters of environmental and economic impacts can be assessed [25]. It also provides a robust decision-making tool for policy makers, enabling a range of environmental impacts to be targeted [26]. Therefore, to harmonise the environmental and economic analyses, we calculated the EE index depicting the investment per environmental impact category for one unit of the baseline HESS configurations, the environmentally and economically optimised configurations and the 100% 1st life LFP baseline. The EE index measures sustainability via integrating the environmental and economic performances of a product. This methodology was originated in the 1970s, and by the 1990s the process had become an industrial basis for sustainable development. EE is defined as a ratio between the environmental impact and economic performance or the ratio between economic impact and environmental performance. The higher the EE index, the higher the value of a product with improved use of resources associated with the product or service and reduced environmental impact. Therefore, EE can be improved by increasing the value of the product or reducing the environmental impact [77]. In this manner, we adopted an EE index to calculate the cost per environmental impact based on the World Business Council for Sustainable Development definition, shown in equation 3.

$$Eco-efficiency = \frac{Economic\ value}{Environmental\ impacts} \qquad (3)$$

where the $Economic\ value$ represents the NPV and the $Environmental\ impacts$ represents each of the five environmental impact categories assessed in the LCA, namely GWP, FDP, MEP, FEP and HTP.

The EE analysis relates to the investment and consequential environmental impact of one HESS unit. An energy storage system may require multiple HESS configurations to achieve the required storage capacity. Therefore, the investment cost per environmental impact would increase with the investment cost.

The economic value relates to the value-added benefit of the product or service, the cost associated with the environmental burden or, as in this case, the unit of the product i.e. cost of the HESS. The environmental impacts relate to the resources used, the cost associated with the environmental burden or, as in this case, the pollution emissions from the HESS. The five environmental impacts measured in the LCA (GWP, FDP, MEP, FEP and HTP) were assessed and therefore the "environmental impacts" in equation 3 relate to the total environmental impact of the HESS for each environmental impact category. The total cost of the HESS was calculated based on the data provided in Table 1 [78]. The results are illustrated in Figure 6.

2.4 Scenario analysis

In the 1970s, oil shocks shook global corporations and since then, there has been increasing use of "multiple scenario analysis". The aim of scenario analysis is largely to effectively manage uncertainties [79] and this is a robust methodology to model effects of experimentations with varied conditions and variables. Although numerous approaches of scenario analysis exist [80]–[83], this research utilises that provided by Bood and Postma [79] which requires the completion of the following steps: (1) problem identification and demarcation of its context; (2) description of the current situation and identification of relevant factors; (3) classification, valuation and selection of scenario-elements; (4) construction of scenarios; (5) analysis, interpretation and selection of scenarios and (6) supporting decision making with scenarios [79].

To satisfy step one of the process, the implications of the percentage contribution of each battery type was highlighted as a predetermined causal factor within the LCA and TEA (as the outcome can be predicated with sufficient precision) [84]. The "current situation" (step 2) is taken as the baseline HESS configuration (i.e. equal percentage contribution of each battery type within the HESS). Therefore, the relevant factors affecting the current situation relate to how a change in the HESS configuration affects the results of the LCA and TEA. The battery types were identified as the scenario-elements, are required by step 3 and the scenarios were constructed (step 4) by altering the contributions of each battery type according to Table 2 (showing the LTO 1st life battery, LTO 2nd life battery and BEV HESS configuration as an example). Whilst the percentage content of one battery type remained constant (33.3%), another of the component's contributions was increased (up to 65%) and the percentage contribution of the third battery type was decreased (to 2%). Steps 5 and 6 are addressed in sections 3 (results) and 4 of this manuscript where the results are provided, interpreted, and presented to aid decision making.

To determine the optimised percentage of 1st and 2nd life batteries and BEVs, we performed scenario analysis on 43 variations of each configuration, across all five environmental impact categories and the constraints of the TEA. The optimised HESS was taken to be the configuration resulting in the lowest environmental impact and/or the lowest economic impact. As shown in Table 2, the content of one battery type was held constant while the two other battery types were varied from 2% to 65%, e.g. 33% 1st life LTO, 2% 2nd life LTO and 65% BEV.

Table 2 illustrates the scenario analysis for a HESS configuration using a 1st and 2nd life battery technology of any of the four types and a BEV when the percentage contribution of the 1st life battery is held constant, that of the 2nd life battery is increased and that of the BEV decreased accordingly.

Table 2: The HESS configurations assessed during the scenario analysis using a 1st and 2nd life battery technology of any of the four types and a BEV configuration as an example. In this example, the 1st life LTO content remained constant, the 2nd life LTO content was increased, and the BEV content was decreased.

1st life battery technology	%	2nd life battery technology	%	BEV	%
LTO/LFP/Na-ion/Lead-acid	33.33%	LTO/LFP/Na-ion/Lead-acid	33.33%	BEV	33.33%
LTO/LFP/Na-ion/Lead-acid	33.33%	LTO/LFP/Na-ion/Lead-acid	36.67%	BEV	30.00%
LTO/LFP/Na-ion/Lead-acid	33.33%	LTO/LFP/Na-ion/Lead-acid	40.33%	BEV	26.33%
LTO/LFP/Na-ion/Lead-acid	33.33%	LTO/LFP/Na-ion/Lead-acid	44.37%	BEV	22.30%
LTO/LFP/Na-ion/Lead-acid	33.33%	LTO/LFP/Na-ion/Lead-acid	48.80%	BEV	17.86%
LTO/LFP/Na-ion/Lead-acid	33.33%	LTO/LFP/Na-ion/Lead-acid	53.68%	BEV	12.98%
LTO/LFP/Na-ion/Lead-acid	33.33%	LTO/LFP/Na-ion/Lead-acid	59.05%	BEV	7.61%
LTO/LFP/Na-ion/Lead-acid	33.33%	LTO/LFP/Na-ion/Lead-acid	64.96%	BEV	1.71%

The representative results of the scenarios are shown in Figure 3 (environmental impact) and Figure 5 (economic impact) respectively to depict how, by maintaining a constant percentage content of one component and varying the other two components, the environmental and economic impacts are affected. Data relating to the results of the 43 scenarios tested per battery type are available from the corresponding author on request.

3 Results

The results shown in section 3.1 provide tabulated (Table 2) and graphical data (Figure 2) to evaluate the environmental impact of the four baseline HESS configurations and the 100% LFP HESS; the results of the scenario analysis to determine the environmentally optimised HESS are shown in Figure 3. Similarly, section 3.2 provides the results of the TEA in Figure 4 and the associated scenario analysis in Figure 5. Finally, the results of the EE index are shown in Figure 6 in section 3.3. These results are discussed in detail in section 4.

3.1 Environmental impact of HESS

The total environmental impacts of each baseline HESS configuration (i.e. consisting of 33.3% 1st life batteries, 33.3% 2nd life batteries and 33.3% BEVs) and the 100% LFP HESS are shown in Table 3. These results were calculated according to the constraints of equation 1 in-line with the system boundary shown in Figure 1 which defines the inputs and outputs of the system that were considered as part of the LCA. The state of health of each battery type will decrease over the 10,000 cycle life, due to the effect of degradation which requires a trade-off between usage and performance and the battery end of life is assumed when 80% of its original energy capacity is reached [55]. Table 3 shows the results for all five environmental impact categories studied; GWP, FDP, MEP, FEP and HTP. As shown by Table 3, across all impact categories, the Lead-acid baseline HESS configuration leads to the highest environmental impact, whilst the LTO baseline HESS configurations results in the lowest environmental impact.

Table 3: Environmental impact of each baseline HESS configuration and the 100% LFP HESS for each environmental impact category; Global Warming Potential (GWP), Fossil Depletion Potential (FDP), Marine Eutrophication Potential (MEP), Freshwater Eutrophication Potential (FEP), Human Toxicity Potential (HTP).

Configuration	GWP (kg CO_2-eq)	FDP (kg oil-eq)	MEP (kg N-eq)	FEP (kg P-eq)	HTP (kg 1,4-DCB-eq)
100% LFP	18,044,641	5,184,230	14,800	5,917	5,582,791
Lead-acid/ Lead-acid/BEV	27,100,888	8,015,047	21,699	9,502	9,247,450
Na-ion/ Na-ion/BEV	21,207,371	6,083,879	17,280	7,346	7,069,384
LFP/LFP/BEV	18,488,654	5,329,166	15,085	6,452	6,309,777
LTO/LTO/BEV	8,349,871	2,402,798	6,985	3,181	3,325,792

The results in Table 3 are disaggregated further in Figure 2 to show how the environmental impact of each battery type (1st life, 2nd life and BEV) contributes to the total environmental impact across all five environmental impact categories. Figure 2 shows that for the Lead-acid, Na-ion and LFP baseline HESS configurations, there are no overriding environmental hotspots, for example, the total GWP of the Na-ion baseline HESS configuration is comprised of 7.29 kg CO_2-eq/MWh (34.36%) attributed to the 1st life battery, 7.23 kg CO_2-eq/MWh (34.09%) attributed to the 2nd life battery and 6.69 kg CO_2-eq/MWh (31.55%) attributed to the BEV. Comparatively, for the LTO baseline HESS configuration, the environmental hotspot can be attributed to the BEV technology across all environmental impact categories, for example the MEP of the LTO baseline HESS configuration is comprised of 0.65 kg N-eq/MWh (9.26%) attributed to the 1st life battery, 0.63 kg N-eq/MWh (9.09%) attributed to the 2nd life battery and 5.70 kg N-eq/MWh (81.65%) attributed to the BEV.

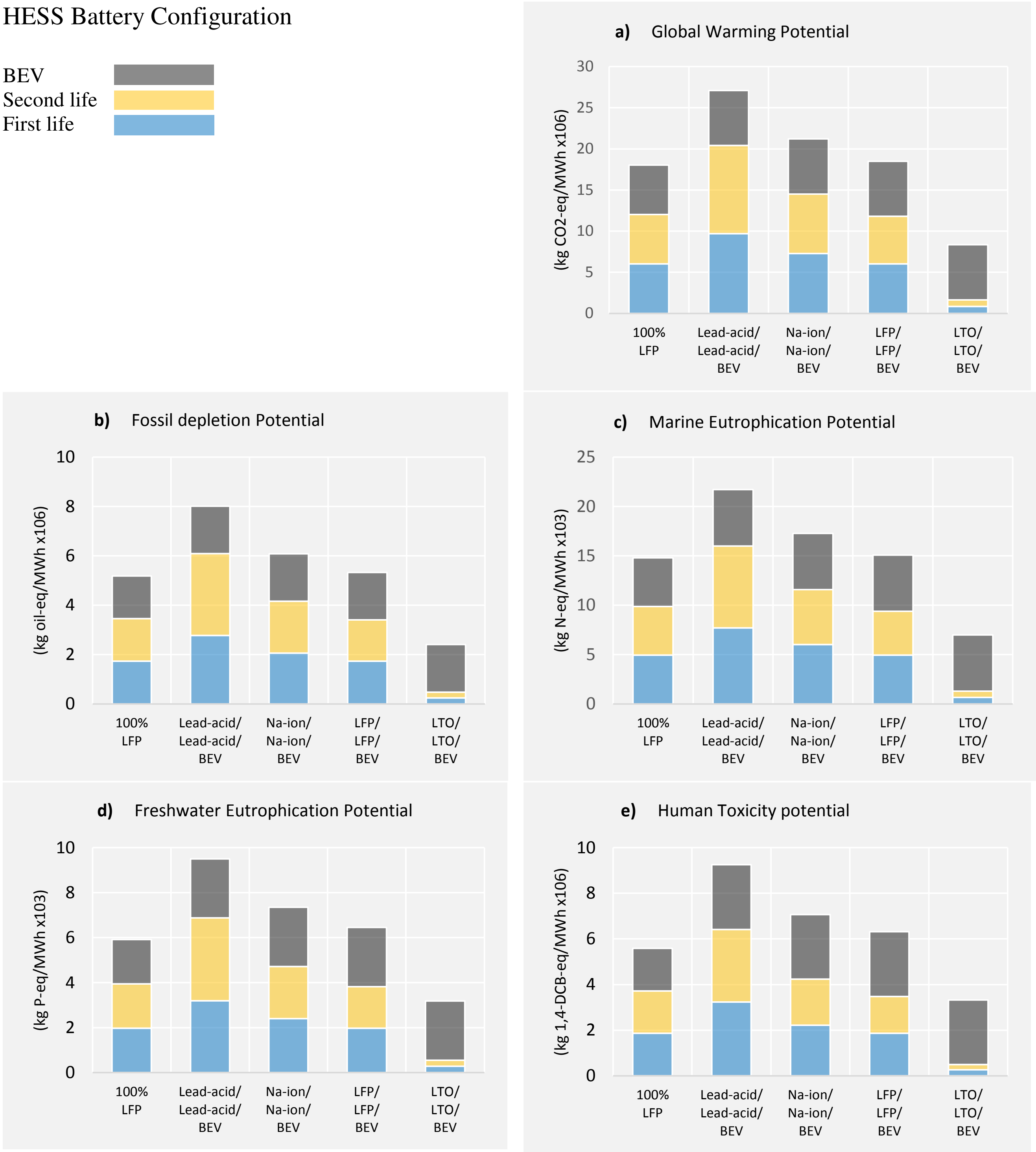

Figure 2: The environmental impact of each of the baseline HESS configurations and the 100% LFP baseline measured by a) Global Warming Potential; b) Fossil Depletion Potential; c) Marine Eutrophication Potential; d) Freshwater Eutrophication Potential; e) Human Toxicity Potential and broken down by contributions of the 1st life, 2nd life and BEV battery technologies.

Figure 3 shows the GWP results of the scenario analysis with respect to four HESS configurations using one of each of the four 1st life battery technologies, a LTO 2nd life battery and BEV. The chart shows the effect on the GWP impact category for four HESS configurations when the BEV content of the HESS remains constant and the content of 1st and 2nd life batteries vary (as one increases the other decreases). The y-axis depicts the GWP of the whole HESS as the percentage contributions of the 2nd life battery and BEV change with the x-axis. The results of the scenario analysis show that all HESS with a high proportion of 2nd life LTO battery technology (independent of the 1st life battery technology) leads to the lowest environmental impact i.e. the environmentally optimised HESS configuration.

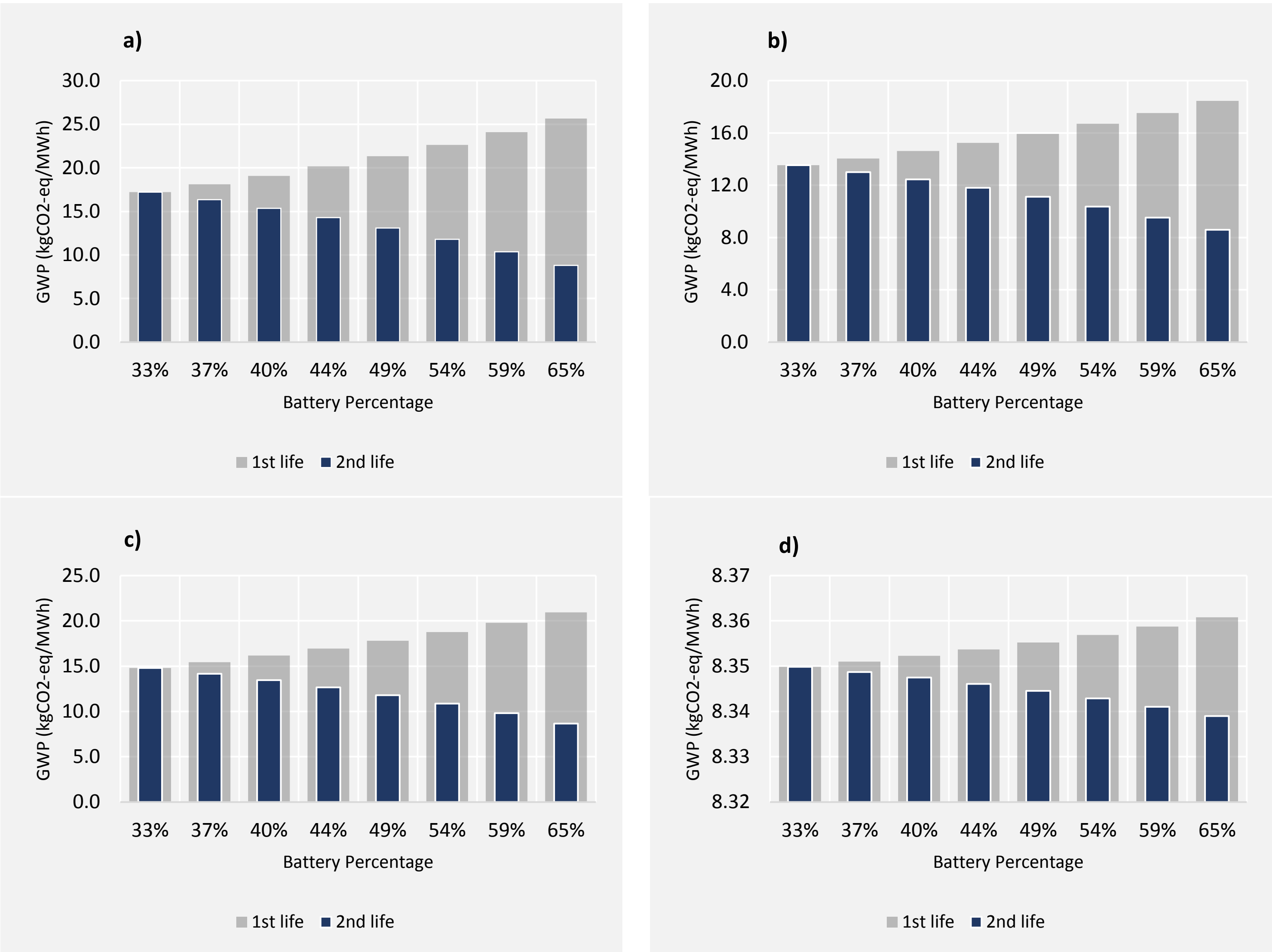

Figure 3: Scenario analysis of the GWP impact category for each baseline HESS configuration. The BEV content remains constant and the 1st and 2nd life battery contents are varied (as one increases the other decreases); a) 1st life Lead-acid battery, 2nd LTO life battery and BEV; b) 1st life LFP battery, 2nd life LTO battery, BEV; c) 1st life Na-ion battery, 2nd life LTO battery, BEV; d) 1st life LTO battery, 2nd life LTO battery, BEV.

As can be seen from Figure 3, independent of the 1st life battery technology, if the percentage contribution of the 1st life battery technology increases, the percentage contribution of the 2nd life battery technology decreases and the contribution of the BEV is held constant, the environmental impact increases, and vice-versa. Data relating to the results of the 43 scenarios tested per battery type are available from the corresponding author on request.

3.2 Techno-economic impact of HESS

An investment appraisal was performed using TEA on the baseline HESS configurations of each technology type (i.e. consisting of 33.3% 1st life batteries, 33.3% 2nd life batteries and 33.3% BEVs), the economically optimised technological configurations of each technology type (where the optimised HESS was taken to be the configuration resulting in the lowest economic impact) and the 100% LFP baseline. The economic model is based on HESS revenue generation from a DFR service. Figure 4 shows these investment appraisal results based on the economic modelling for DFR based on an initial £6 DFR/MW/hr at 24 hours' service over 15 years, as maintenance periods of such systems are very short and therefore assumed to be negligible. The results show that the economically optimised LTO HESS configuration has a NVP of £374,644 at £6 DFR/MW/hr, which increases to £2,884,275 at £30 DFR/MW/hr. Comparatively, the Lead-acid baseline HESS configuration has a NVP of -£508,436 at £6 DFR/MW/hr, which increases to £2,001,396 at £30 DFR/MW/hr.

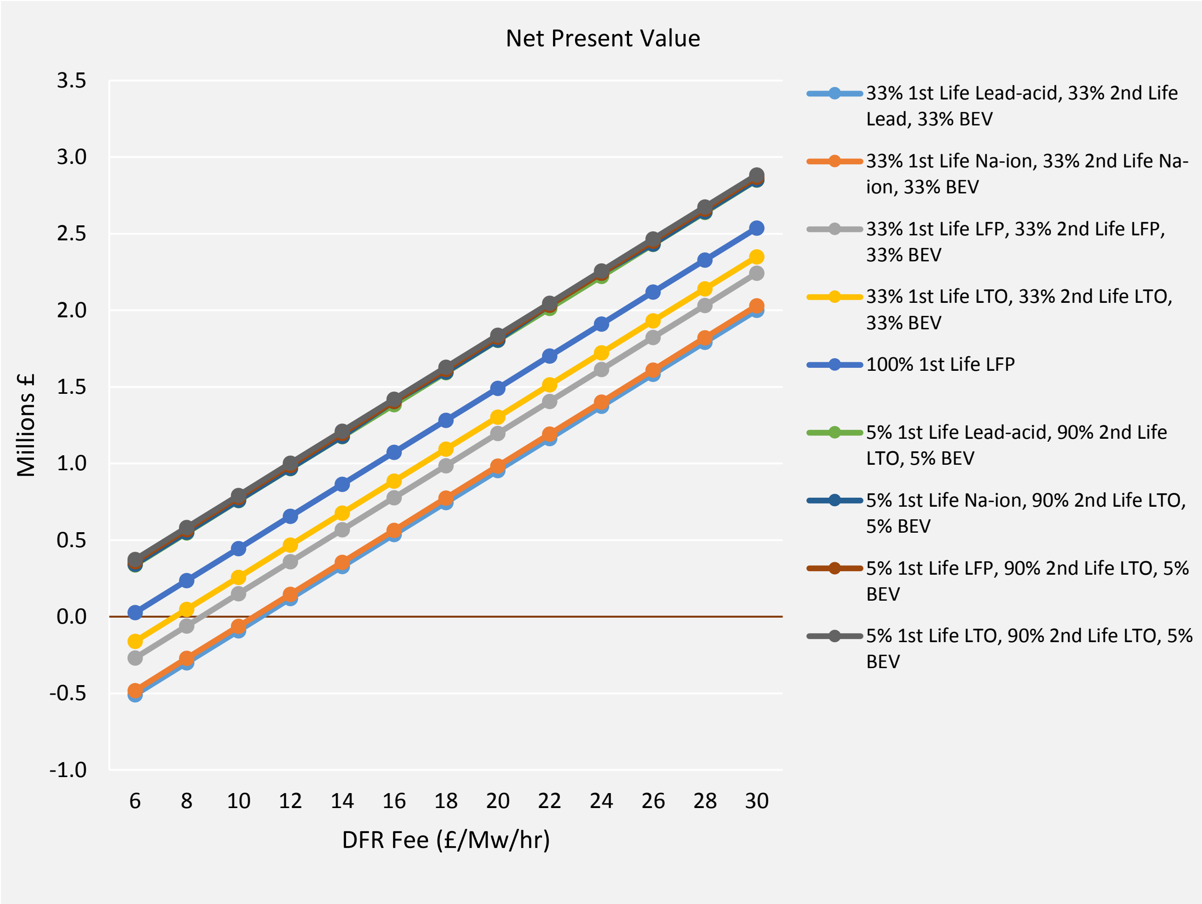

Figure 4: Net Present Value of the 100% 1st life LFP battery, all four baseline HESS configurations and the economically optimised HESS configurations economic based on the economic modelling for DFR which is based on an initial £6 DFR/MW/hr at 24 hours' service over 15 years, as maintenance periods of such systems are very short and therefore assumed to be negligible.

The results of the scenario analysis show that all HESS with a high proportion of 2nd life LTO battery technology (independent of the 1st life battery technology) lead to the lowest economic impact i.e. an economically optimised HESS configuration. Figure 5 shows the TEA results of the scenario analysis with respect to four HESS configurations using one of each of the four 1st life battery technologies, a LTO 2nd life battery and BEV, where the BEV content is constant and the 1st and 2nd life battery contents vary (as one increases the other decreases). The y-axis depicts the GWP of the whole HESS as the percentage contributions of the 2nd life battery and BEV change with the x-axis. Data relating to the results of the 43 scenarios tested per battery type are available from the corresponding author on request.

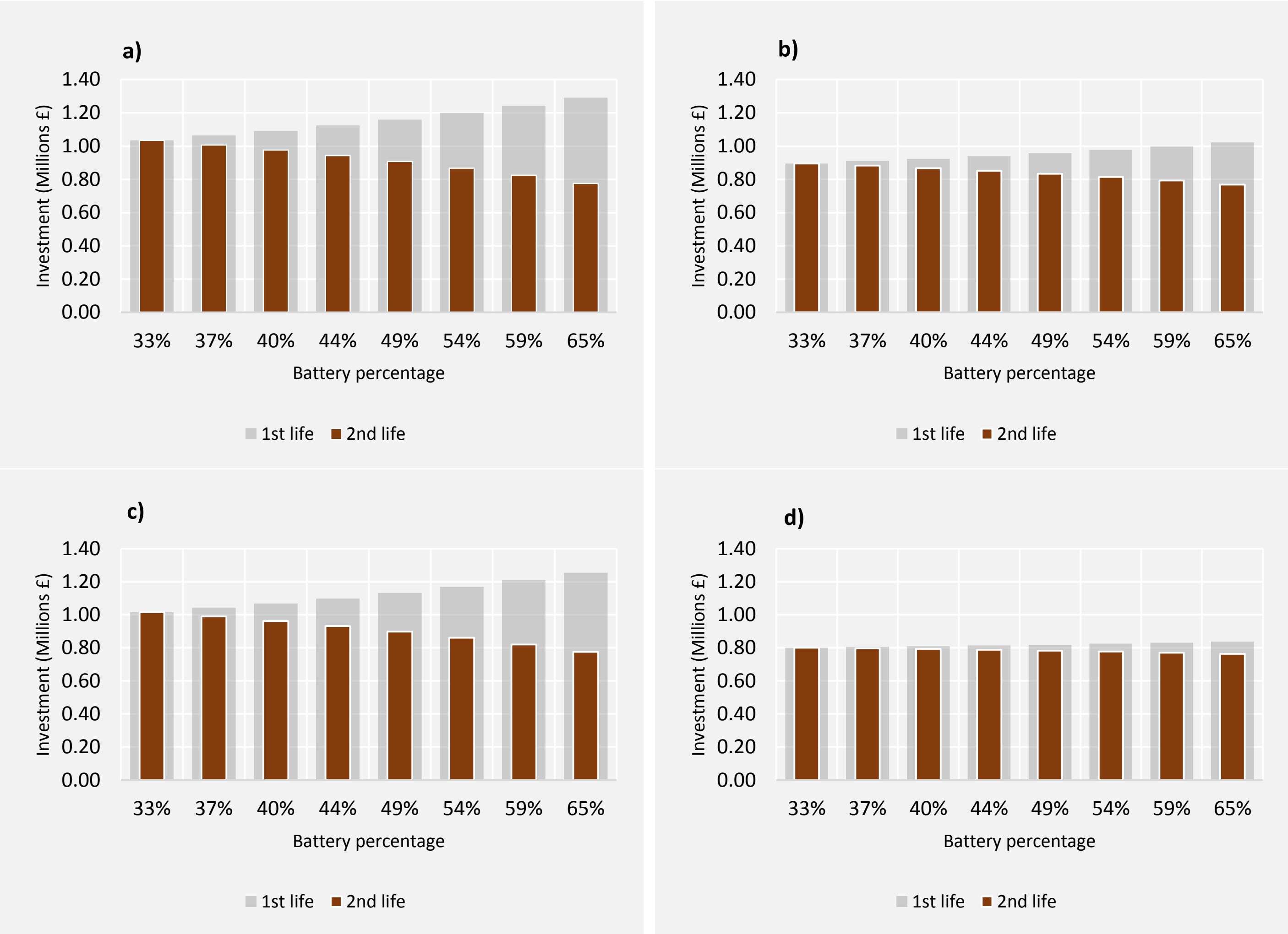

Figure 5: Scenario analysis of the economic impact for each baseline HESS configuration. The BEV content constant and the 1st and 2nd life battery contents are varied (as one increases the other decreases); a) 1st life LTO battery, 2nd life LTO battery and BEV; b) 1st life Na-ion battery, 2nd life LTO battery, BEV; c) 1st life LFP battery, 2nd life LTO battery, BEV; d) 1st life Lead-acid battery, 2nd life LTO battery, BEV.

3.3 Eco-efficiency of HESS

The EE analysis was calculated according to equation 3 to determine the cost per environmental impact for the baseline HESS configurations, the environmentally and economically optimised HESS configurations and the 100% LFP HESS. As shown by Figures 3 and 5, the HESS configurations with both the lowest environmental and economic impact are those containing a low proportion of 1st life battery, a high proportion of 2nd life LTO battery and a low proportion of BEV i.e. these are both the economically and environmentally optimised structures. Figure 6 shows the results of the EE, which was calculated according to equation 3 for each of the five environmental impact categories under consideration. The results clearly show that the 100% LFP HESS has the lowest cost per environmental impact, this system has an initial investment of £599,204 leading to 0.12 £/FDP, 0.03 £/GWP, 40.49 £/MEP, 101.26 £/FEP and 0.11 £/HTP. While baseline LTO HESS configuration (33.3% 1st life LTO, 33.3%

2nd life LTO, 33.3% BEV) has the highest cost per environmental impact, this system has an initial investment of £787,150 leading to 0.33 £/FDP, 0.09 £/GWP, 112.69 £/MEP, 247.49 £/FEP and 0.24 £/HTP.

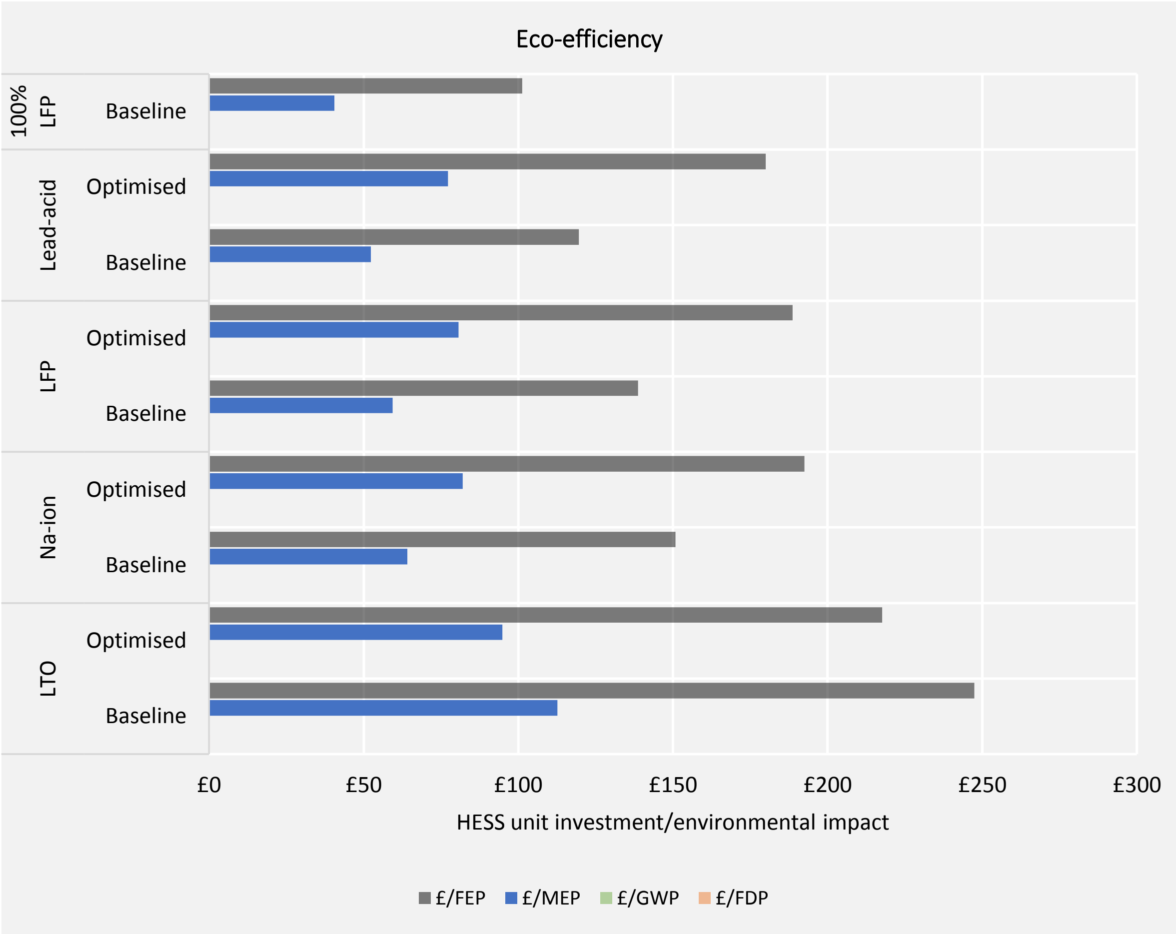

Figure 6: Result of the eco-efficiency analysis relating to the performance of one unit of the baseline HESS configurations (containing an equal distribution of each battery type), the environmentally and economically optimised HESS configurations based on the findings of the scenario analysis and the 100% 1st life LFP baseline. The environmental impact categories tested were the Fossil Depletion Potential (FDP), the Global Warming Potential (GWP), the Marine Eutrophication Potential (MEP), the Freshwater Eutrophication Potential (FEP) and the Human Toxicity Potential (HTP). The results relating to the £/HTP, £/ FDP, and £/GWP cannot be seen on this figure as they are negligible in comparison to the £/MEP and £/FEP results.

The results of this three-tiered assessment provide information relating to the environmental impacts, economic impact and eco-efficiency of each HESS configuration, which is pertinent to decision makers [79], [85], [86].

4 Discussion

4.1 Environmental impact of HESS

The environmental impacts of an equal proportion of 1st and 2nd life batteries and BEVs (i.e. 33.3% 1st life, 33.3% 2nd life, 33.3% BEV), referred to as the "baseline HESS configuration", were tested with respect to GWP, HTP, FDP, MEP and FEP. As a comparative baseline, the environmental impacts of a 100% 1st life LFP battery were also tested. The LCA is modelled over a 15-year period, assuming a total energy consumption of 6900 MWh. Table 3 shows the environmental impact of four baseline HESS configurations, where the 1st and 2nd life battery technology is the same, and environmental impacts of a 100% 1st life LFP battery. The aim of the HESS baseline configurations is to provide a reference point against which different HESS configurations can be benchmarked.

Table 3 details the results for all five environmental impact categories studied; GWP, FDP, MEP, FEP and HTP for each battery type and clearly shows that, over the five environmental impact categories studied, a HESS containing 1st and 2nd life Lead-acid batteries and a BEV has the highest environmental impact. These results are further disaggregated in Figure 2, where the individual contribution of each battery type (1st life, 2nd life and BEV) is shown. In equal proportions, the whole life cycle of a HESS with a 1st and 2nd life Lead-acid battery and BEV configuration leads to a GWP impact of 27,100,887 kg CO_2-eq/MWh, over three times that of the HESS containing an equal proportion of 1st and 2nd life LTO battery technology and a BEV which has a GWP impact of 8,349,871 kg CO_2-eq/MWh. The high environmental impact relating to the Lead-acid baseline HESS configuration does not relate to the environmental impact of the components of processing procedure of the battery itself, as cradle-to-gate this technology has the lowest environmental impact. Rather, the 1st life battery is hindered by the low cycle life of the Lead-acid battery (1,500 cycles, compared to 18,000 cycles for the LTO technology) and the 2nd life battery is hampered by the mass of the battery required for repurposing (64,433 kg, compared to 25,845 kg for the LTO technology).

Figure 2 further disaggregates the results shown in Table 3 to demonstrate how the environmental impact of each battery type (1st life, 2nd life and BEV) contributes to the total environmental impact across all five impact categories. The results shown in Figure 2 show that for the Na-ion, LFP and LTO baseline HESS configurations, the GWP, MEP and FEP environmental impact of the second life battery is smaller than that of the 1st life battery. For example, the GWP impact category results of the Lead-acid baseline HESS configuration show 39.5% of the GWP environmental impact can be attributed to the 2nd life battery and 35.8% can be attributed to the 1st life battery. As mentioned above, the environmental impact of repurposing a battery for 2nd life is dependent on the mass of the battery and therefore, due to the increased mass of the Lead-acid battery compared to the other battery technologies, the environmental impact of repurposing the battery is higher.

Furthermore, when the life cycle of each battery type is inspected, it is the use phase that presents the highest impact across the five environmental impact categories studied. In each case, the use phase represents around 90% of the total environmental impact. This supports the results provided by Ahmadi et al. [9] who also report that the use phase provides the highest contribution to the overall impact.

On deeper inspection, the results show that the cradle-to-gate GWP of the LTO battery is 14.10 kg CO_2 kg^{-1}, and that of the Lead-acid batter is 2.42 kg CO_2 kg^{-1}, these results support those provided by Baumann et al. [16], which were given at 14.19 and 2.33 kg CO_2 kg^{-1}, respectively. Comparatively, the cradle-to-gate GWP for the LFP battery was found to be 30.01 kg CO_2 kg^{-1}, which is much higher than the 16.11 kg CO_2 kg^{-1} reported by Baumann et al. [16].

Across all five environmental impact categories, the contribution of the BEV to the baseline LTO HESS configuration provides the highest environmental impact. For example, the GWP impact of the BEV is 20,072,836 kg CO_2-eq/MWh, compared to only 2,505,607 kg CO_2-eq/MWh for the 1st life LTO battery technology and 2,471,172 kg CO2-eq/MWh for the 2nd life LTO battery technology. Therefore, when an equal percentage contribution of each battery type is assumed for the baseline LTO HESS configuration, the GWP impact of the BEV contributes almost 80% of the total impact.

Closer analysis of the environmental impact of each individual battery type shows the highest environmental impact, across all five environmental impact categories from cradle to gate, is related to the LFP. The results show the GWP of 1st life LFPs to be 301,317 kg CO_2-eq/MWh, compared to only 124,884 kg CO_2-eq/MWh for Lead-acid batteries. This impact is related to the mass of the battery required to deliver 1 MWh. The GWP of a 1kg Lead-acid battery is only 2.24 kg CO_2-eq/kg, but a total mass of 51,546 kg is required to deliver 1 MWh using a Lead-acid battery. Comparatively, the GWP of a 1 kg LFP battery is much higher at 30.01 kg CO_2-eq/kg, but only a total mass of 10,042 kg is required to deliver 1 MWh using a LFP.

The baseline HESS configuration with the lowest environmental impact across all five environmental impact categories, i.e. the most "environmentally friendly", is that containing 33.3% 1st life LTO, 33.3% 2nd life LTO, and 33.3% BEV. This HESS has a GWP impact of 8,349,871 kg CO_2-eq/MWh. The main contribution to the low environmental impact is due to the high cycle life of LTO technology. In comparison, a Na-ion battery would need to be replaced nine times to match the same cycle life of LTO technology.

When the environmental impacts of the baseline HESS configurations are compared to the 100% 1st life LFP battery baseline, Figure 2 shows that only the baseline LTO HESS configuration (33.3% 1st life LTO, 33.3% 2nd life LTO, and 33.3% BEV) has a lower environmental impact across all five environmental impact categories than using a 1st life LFP battery for energy storage. Interestingly, the results in Figure 2 show the use of 2nd life Lead-acid, Na-ion and LFP battery technologies, in the baseline HESS configurations, result in a higher environmental impact compared to a 100% 1st life LFP. In the case of the Lead-acid battery technology, this is due to the increased weight of this battery technology required for repurposing, therefore leading to a higher environmental impact. As the state of health of a 2nd life battery is lower than that of a 1st life battery, a higher number of 2nd life batteries are required to perform the same function and therefore the associated mass is higher.

Despite this increase in the required mass of the battery technologies, with the exception of the FDP environmental impact category, the environmental impact of both the repurposed 2nd life Na-ion and LFP battery technologies is lower than their 1st life counterparts and therefore the relative impact of the BEV in the HESS leads to a higher environmental impact compared to a 100% LFP HESS.

Battery recycling for each battery technology was modelled using the "treatment of used Li-ion battery, hydrometallurgical treatment, GLO" dataset from the Ecoinvent database [61] and adjusted for the weight of the different battery technologies. This recycling methodology was chosen as it is the most selective route to extract metals [45]. Recycling not only saves natural resources, but also it can lead to a reduction in the energy consumption and water required for primary production, whilst improving the quality of waste discharge. However, the economics of recycling necessitate the value of the recovered materials to exceed the costs of the input processes. Economically strategic materials include lithium, nickel, cobalt, manganese, zinc and rare earth elements; therefore, lithium-ion batteries may be preferentially recycled over Na-ion, Lead-acid or LTO technologies [87].

Scenario analysis was performed to determine how the percentage contribution of each battery type affects the environmental impact of each HESS. Figure 3 shows the GWP results of the scenario analysis for four HESS configurations using one of each of the four 1st life battery technologies, a LTO 2nd life battery and BEV, where the BEV content is constant, and the 1st and 2nd life battery contents vary (as one increases the other decreases).

The largest variation in the results relates to the Lead-acid/LTO/BEV HESS configuration in Figure 3a. This is caused by large difference in the GWP result for a 1st life lead-acid battery and a 2nd life LTO battery (29,122,957 kg CO_2-eq/MWh and 2,471,172 kg CO_2-eq/MWh, respectively). The factors affecting these results are discussed above.

Figure 2d shows the smallest level of variation between the different scenarios for the LTO/LTO/BEV baseline HESS configuration. In all cases, a HESS configuration containing a high percentage contribution of 2nd life LTO battery technology leads to the lowest environmental impact across all impact categories. Due to the current low technology readiness level of LTOs, sparse data is available with respect to their environmental impacts. Despite this, it has been shown that lithium iron phosphate utilised in LTOs provides a low contribution to the impact of other lithium based battery technologies [40]. The production of nano-scale titanium dioxide for LTO technology contributes to high nitrate concentrations in aquatic systems which contributes to the MEP impact [88].

Overall, taking the whole system into account, it is clear to see that a HESS configuration comprising of a low proportion of 1st life LTO battery technology and BEV with a high proportion of 2nd life LTO battery technology results in the lowest environmental impact across all environmental impact categories except FDP.

4.2 Techno-economic analysis

To determine the economic impact of the HESS, an investment appraisal was performed using TEA for each of the baseline HESS configurations, the economically optimised technological configurations of each technology type and the 100% LFP baseline. The optimised HESS was taken to be the configuration resulting in the lowest economic impact. The economic model is based on HESS revenue generation from a DFR service. Figure 4 shows the results of the investment appraisal according to the economic modelling for DFR based on an initial £6 DFR/MW/hr at 24 hours' service over 15 years, as maintenance periods of such systems are very short and therefore assumed to be negligible.

The results demonstrate that over a 15-year period only the 100% 1st life LFP baseline is economically viable across the whole range of DFR scenarios, while the baseline HESS configurations only become economically viable at: LTO = £8/MW/hr, LFP = £10/MW/hr, Na-ion = £12/MW/hr and Lead-acid = £12/MW/hr. The investment cost relating to a 100% 1st life LFP baseline is £599,204; the highest baseline investment cost relates to the Lead-acid baseline HESS at £1,135,894.

As illustrated in Figure 4, the most economically feasible HESS configuration, at any DFR fee, is 5% 1st life LTO, 90% 2nd life LTO, and 5% BEV. Although, as shown in Table 1, the price of a repurposed LTO battery is the highest of the four technologies, the high cycle life of the LTO battery technology results in fewer battery replacements over the 15-year period that was assessed, therefore leading to a lower environmental impact overall.

The TEA results of the scenario analysis are shown in Figure 5, four HESS configurations using one of each of the four 1st life battery technologies, a LTO 2nd life battery and BEV are shown. In this scenario the BEV content of the HESS remains constant, and the 1st and 2nd life battery contents vary (as one increases the other decreases). Figure 5 shows the change in investment (Capital expenditure) of the HESS configurations utilising a 1st life battery of each technology type combined with a 2nd life battery of LTO and BEV, when the BEV percentage remains constant and the 1st life battery and 2nd life battery vary (as one increases the other decreases). The y-axis depicts the investment of the whole HESS as the percentage contributions of the 1st and 2nd life battery changes with the x-axis.

Regardless of the 1st life battery technology used, as the content of this battery type is increased, the investment cost increases. The lowest investment cost of £252,814, can be attributed to the configuration containing 5% of 1st life LTO battery technology, 90% 2nd life LTO battery technology and 5% BEV technology. This is a reduction of £534,336 compared to the baseline LTO HESS configuration.

The most economically viable configuration is that of the 100% LFP battery technology, followed by the LTO battery technology. Overall, to support a low-cost HESS investment, in line with a low environmental impact, a HESS configuration comprising of a low proportion of 1st life LTO battery technology and BEV with a high proportion of 2nd life LTO battery technology should be supported.

4.3 Eco-efficiency

The Eco-efficiency (EE) analysis relates to the investment and consequential environmental impact of one HESS unit. An energy storage system may require multiple HESS configurations to achieve the required storage capacity. Therefore, the investment cost per environmental impact would increase with the investment cost.

Figure 6 provides the results of the EE analysis. The EE was calculated according to equation 3 for each of the five environmental impacts considered in this study and depicts the ratio between economic impact and environmental performance of the baseline and optimised HESS configurations. The results of the eco-efficiency index show that a hybrid energy storage system configuration containing equal proportions of 1st and 2nd life Lithium Titanate and BEV i.e., the baseline LTO HESS configuration, battery technologies is the most eco-efficient. This EE result has the highest cost per environmental impact; the initial investment of this system is £787,150, leading to the highest £/environmental impact across all impact categories. Specifically, the highest investment per HESS unit relates to the MEP and FEP impact categories; the eco-efficiency for the baseline LTO HESS configuration is £112.69/MEP and £247.49/FEP. In comparison, the eco-efficiency relating to the GWP (£0.09/GWP), FDP (£0.33/FDP) and HTP (£0.24/HTP) are much lower.

Although the optimised LTO HESS provides the highest EE result when compared to the other optimised systems, it is the only optimised HESS configuration that has a lower result than the corresponding baseline configuration. While the EE index presents a harmonised approach to evaluate the HESS from both the environmental impact categories and costs, therefore integrating the analysis from LCA and TEA perspectives, this result is contradictory to the findings of each of the individual environmental and economic assessment methodologies.

Overall, the lowest EE result can be attributed to the 100% LFP HESS, as the initial investment of this configuration is £599,204, the EE result could be improved both by reducing this investment cost and by decreasing the overall environmental impacts of the battery technology.

Figure 6 shows that the Lead-acid baseline HESS configuration has the lowest EE index, this can be attributed to the highest initial investment cost of £1,135,894 and the highest GWP of 27,100,888 CO_2-eq/MWh over the 15-year life cycle of the HESS of all of baseline systems considered.

This harmonised approach supports the findings of both the LCA and the TEA in that the most eco-efficient baseline HESS configuration contains LTO battery technology. Despite this the environmental and economically optimised LTO HESS configuration was found to have a lower EE result than the baseline configuration and therefore is not optimised for the EE index calculation due to the lower cost to environmental impact ratio of the environmental and economically optimised LTO HESS configuration.

4.4 Circular economy

The transition from a linear to a circular economy, in which waste and pollution are eliminated, products and materials remain within supply chains, and natural systems are regenerated, is beneficial not only to the economy, but also to the environment and society [89].

Batteries are a key tool in the global race to decarbonisation, which will directly lead to an increase in the depletion rates of those metals upon which the battery technologies rely. A batteries life span is dependent on its chemistry and cycling frequency and therefore both the designer and user have an impact on the total service life. To date, the collection mechanism for lead-acid batteries has proven to be successful, with high collection rates in developed countries. It is not therefore unconceivable to envisage this level of reuse or recycling for new battery technologies [90].

The HESS configuration directly contributes to a circular economy through the reuse of an end-of-life battery into a new energy storage solution, this is supported by the results which show a HESS configuration comprising of a high proportion of 2nd life battery technology results in the lowest environmental impact overall. Furthermore, this HESS promotes a circular economy through the utilisation of an asset that would usually be stood idle. This innovative study moves up the waste hierarchy to remanufacturing, in place of recycling, thereby supporting a circular economy. Furthermore, it has been shown that remanufacturing can result in a low carbon system with high efficiency and effectiveness, further enhancing the ideals of a circular economy [90].

4.5 Practical implications of this study

The practical implications relating to the implementation of this system, specifically utilising LTO batteries, would reduce the environmental impacts of 1st life battery manufacture through remanufacturing methodologies and reduce the overall economic impact. This is significant as the number of EVs on the road increases over the next ten years to approximately 44 million [6]. Limited battery lifetimes will result in a significant second-hand battery market; therefore, the implementation of this hybrid system provides a key steppingstone to reducing resource consumption across the planet.

5 Conclusion

This research is the first to present a three-tier circularity assessment of a "Hybrid Energy Storage System" (HESS) which integrates 1st and 2nd life batteries and BEVs. Four different battery technologies were assessed, namely Lithium Titanate, Lead-acid, Lithium Iron Phosphate and Sodium-ion. These systems were evaluated based on analyses from three perspectives: (1) life cycle assessment, (2) techno-economic analysis and (3) eco-efficiency and scenario analysis was applied. Our findings show that the life cycle assessment and techno-economic analysis assessment methodologies support the implementation of a HESS consisting of 5% 1st life LTO, 90% 2nd life LTO and 5% BEV, while the eco-efficiency index shows that a HESS with equal proportions of 1st and 2nd life LTO and BEV battery technologies is the most eco-efficient.

This research shows that a HESS configuration comprising of a low proportion of 1st life LTO battery technology and BEV with a high proportion of 2nd life LTO battery technology results in the lowest environmental impact across all environmental impact categories except FDP.

The most economically viable baseline HESS configuration is that of the 100% LFP battery technology, followed by the LTO battery technology. To support a low cost HESS investment, a HESS configuration comprising of a low proportion of 1st life LTO battery technology and BEV with a high proportion of 2nd life LTO battery technology should be implemented.

The harmonised approach of the eco-efficiency index supports the findings of the LCA and the TEA by showing that the most eco-efficient baseline HESS configuration contains LTO battery technology. Comparatively to the LCA and TEA, the environmental and economically optimised LTO HESS configuration was found to have a lower EE result than the baseline configuration.

These results clearly support a circular economy through the remanufacture of 1st life batteries to be implemented into a useful system and the use of BEVs in this system further promotes a circular economy through their enhanced utilisation.

The main limitation to conducting the LCA, TEA, and consequently the EE of a HESS is the lack of primary data as this cannot be sourced directly from battery manufacturers due to confidentiality restrictions. To mitigate this limitation on the final results, robust published data was sourced for the completion of the LCI of each battery and is provided in detail in the appendix.

In all of the HESS models considered in this research, it was assumed that the BEV was a LFP battery. While this is currently the predominant battery technology for BEVs, this may change in the future due to the ongoing technological development in the battery arena. Consequently, the overall impact of the HESS may vary if the BEV battery technology is altered.

In addition, this study assumes the availability of the 2nd life batteries from EVs for the creation of the proposed HESS systems and the linearity of cost reduction conservatively, although the cost is expected to drop through scale up and more renewable mix and electrification in the energy supply chain. While in this study it is assumed that the 1st life of the 2nd life battery used in the HESS was in a BEV, to overcome potential availability issues, the 2nd life batteries could be collected from alternative sources.

Future research can address these in further scenario modelling, including the complexity and logistic of sourcing of secondary batteries, decarbonised energy supply (e.g., nuclear, hydrogen) and projected spatial time series of economic return and payback. Also, additional future work can consider the potential revenue streams for each HESS with the aim of clearly differentiating between the different chemistries and mixes.

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This research supports the use of a three-tiered assessment to aid decision making. Although Sustainable Development Goal (SDG)12 aims to decouple resource use from economic growth, economic productivity is still important for society as demonstrated by SDG8. Reduced toxicological impacts are directly attributed to emission intensities reduction and clean production practices adoption [31], contributing to SDG13. Therefore, our harmonised approach integrating LCA, TEA and eco-efficiency index in the three-tier circularity assessment is key to ensure the sustainability of energy storage system for future energy security.

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Data availability

All data is available from the corresponding author on request.

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Figure 1

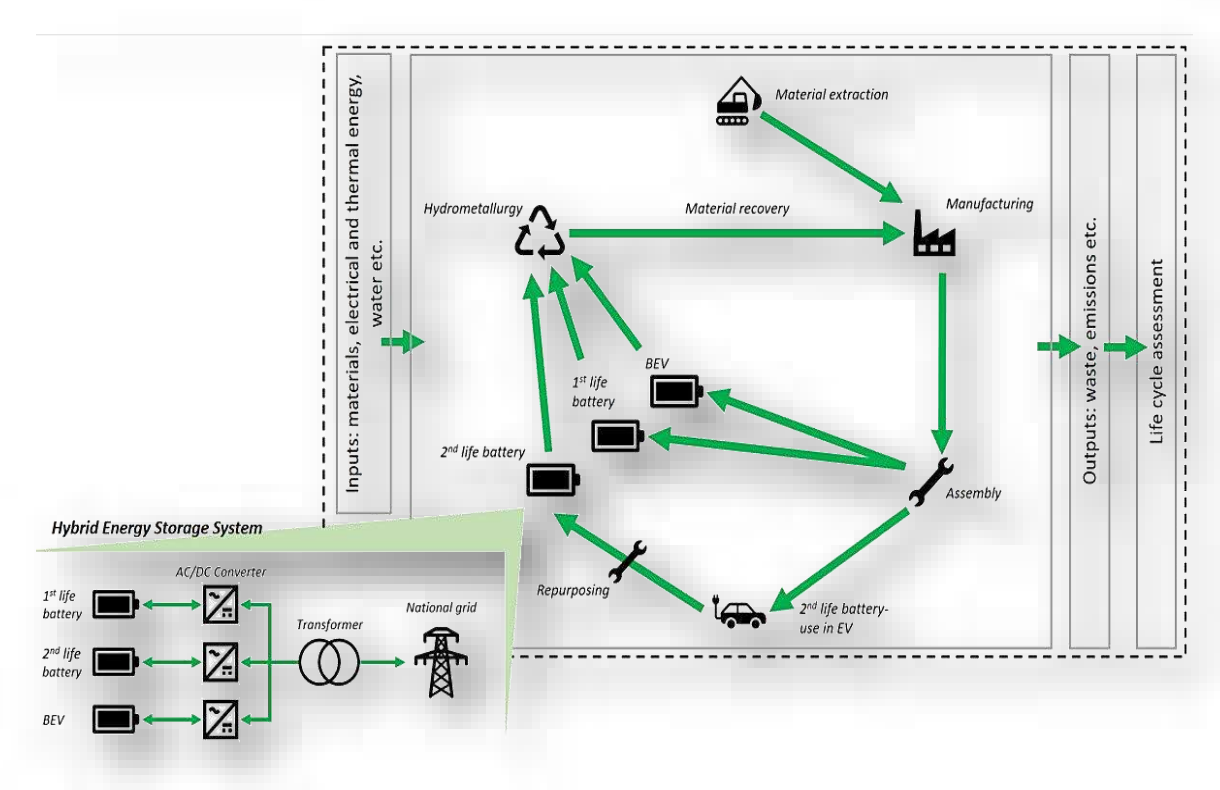

Figure 1: The system boundary applied to the LCA of the HESS consisting of 1st and 2nd life batteries and BEVs in this study. The system boundary includes the inputs and outputs relating to the raw material extraction, component manufacture, battery assembly, use phase and end of life management (i.e. hydrometallurgy). The repurposing and second use phase of the 2nd life battery is also assessed. The HESS implementation approach is shown in the bottom left-hand corner of this figure.

Figure 2

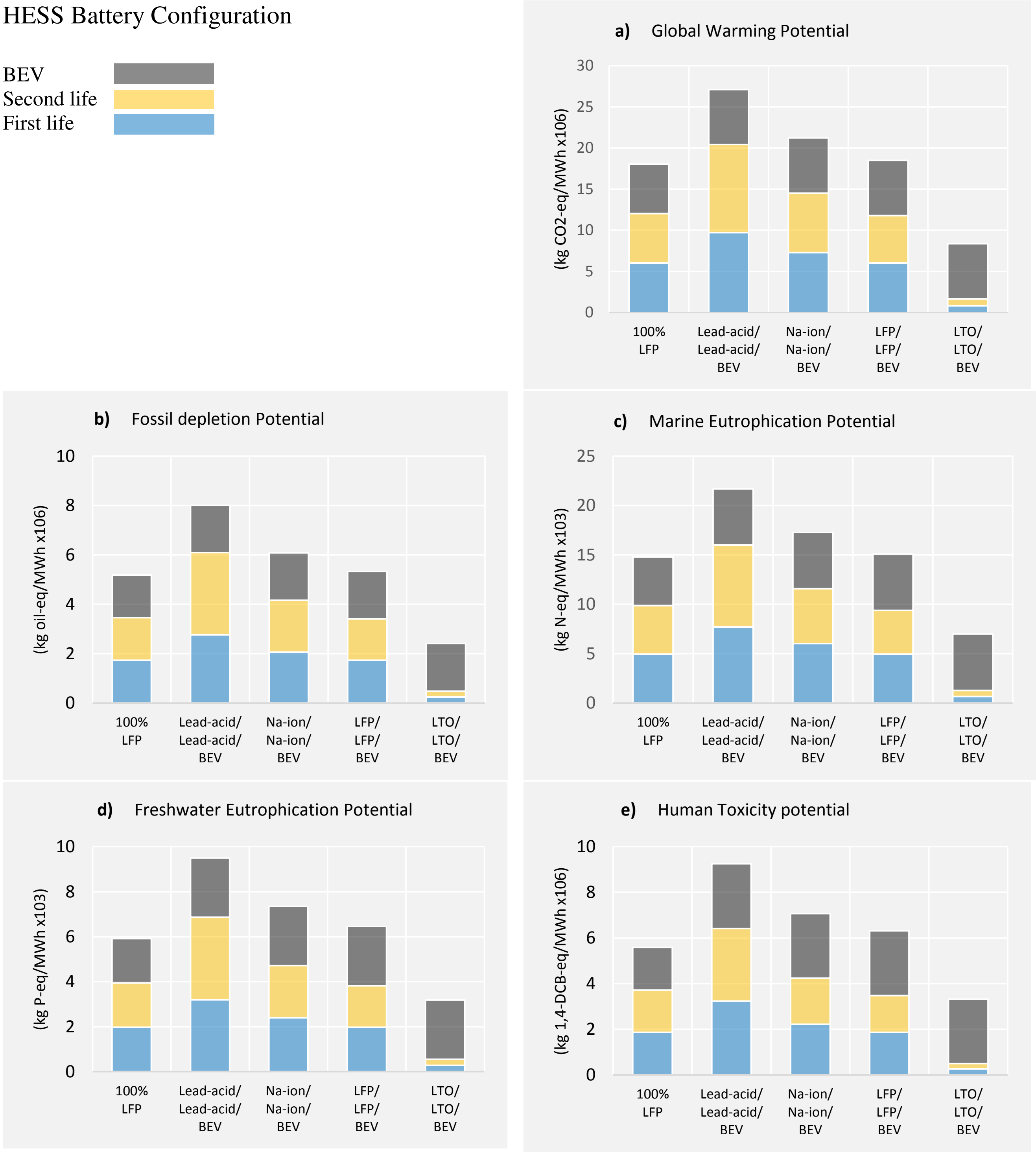

Figure 2: The environmental impact of each of the baseline HESS configurations and the 100% LFP baseline measured by a) Global Warming Potential; b) Fossil Depletion Potential; c) Marine Eutrophication Potential; d) Freshwater Eutrophication Potential; e) Human Toxicity Potential and broken down by contributions of the 1st life, 2nd life and BEV battery technologies.

Figure 3

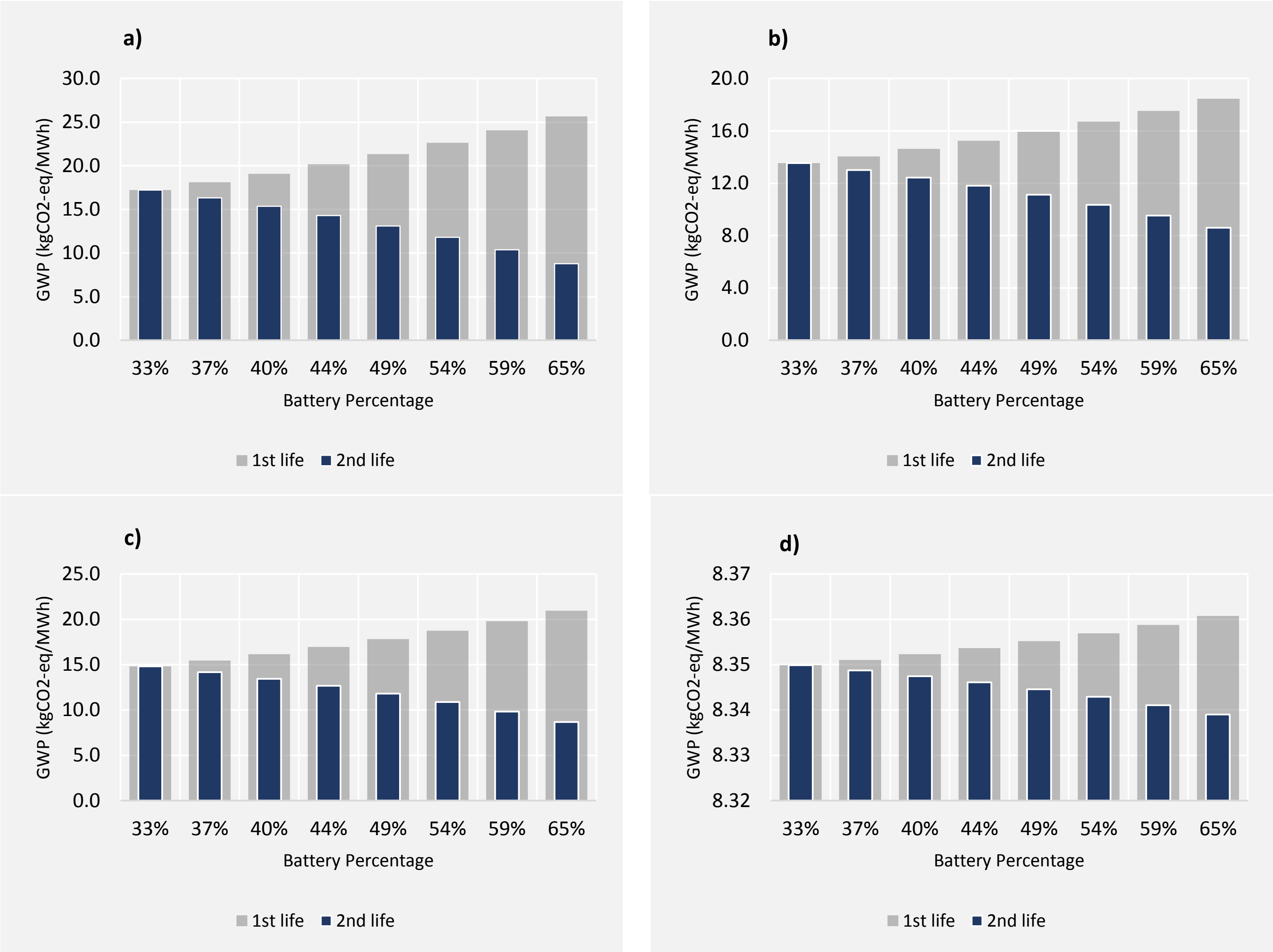

Figure 3: Scenario analysis of the GWP impact category for each baseline HESS configuration. The BEV content remains constant and the 1st and 2nd life battery contents are varied (as one increases the other decreases); a) 1st life Lead-acid battery, 2nd LTO life battery and BEV; b) 1st life LFP battery, 2nd life LTO battery, BEV; c) 1st life Na-ion battery, 2nd life LTO battery, BEV; d) 1st life LTO battery, 2nd life LTO battery, BEV.

Figure 4

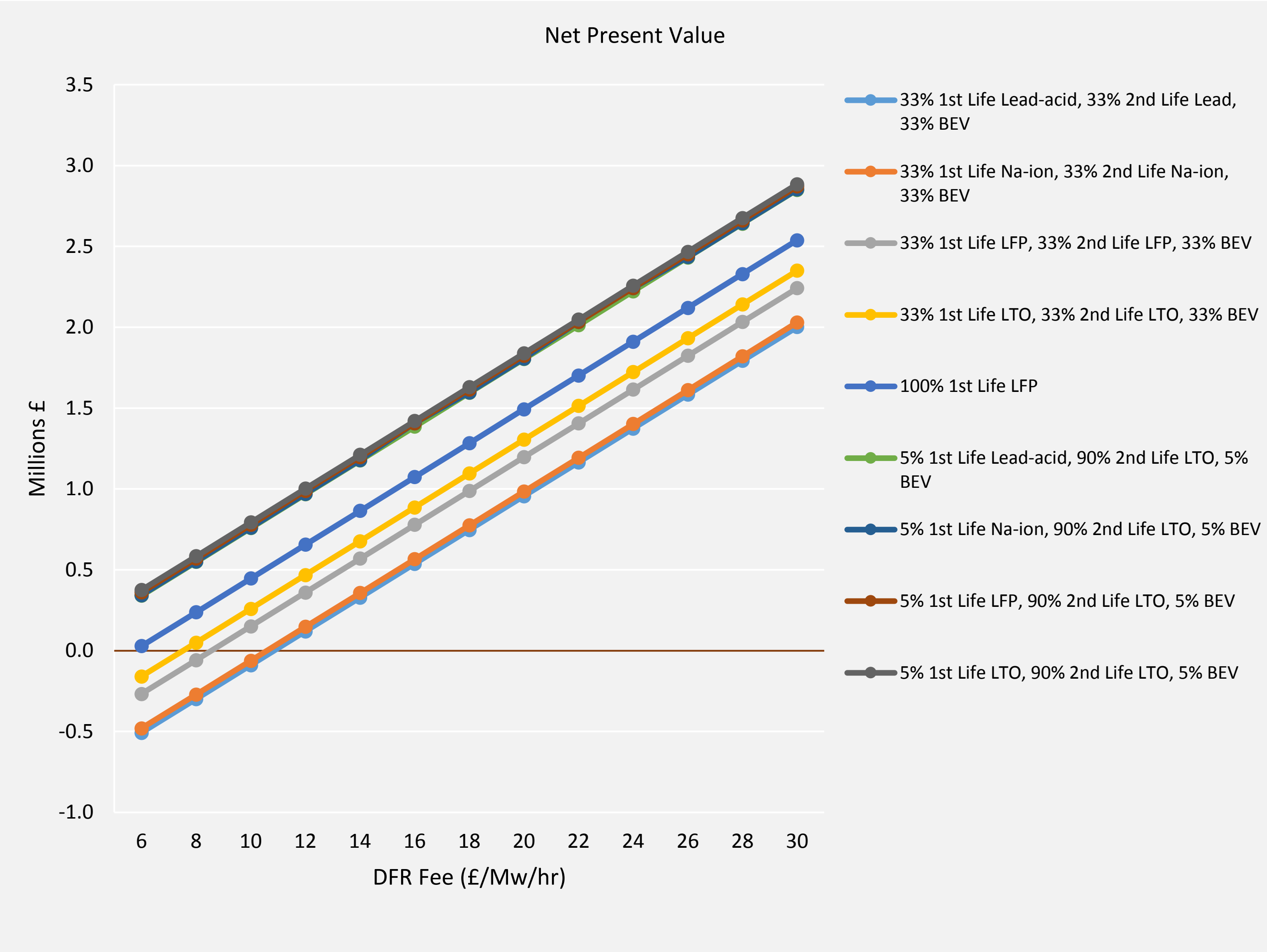

Figure 4: Net Present Value of the 100% 1st life LFP battery, all four baseline HESS configurations and the economically optimised HESS configurations economic based on the economic modelling for DFR which is based on an initial £6 DFR/MW/hr at 24 hours' service over 15 years, as maintenance periods of such systems are very short and therefore assumed to be negligible.

Figure 5

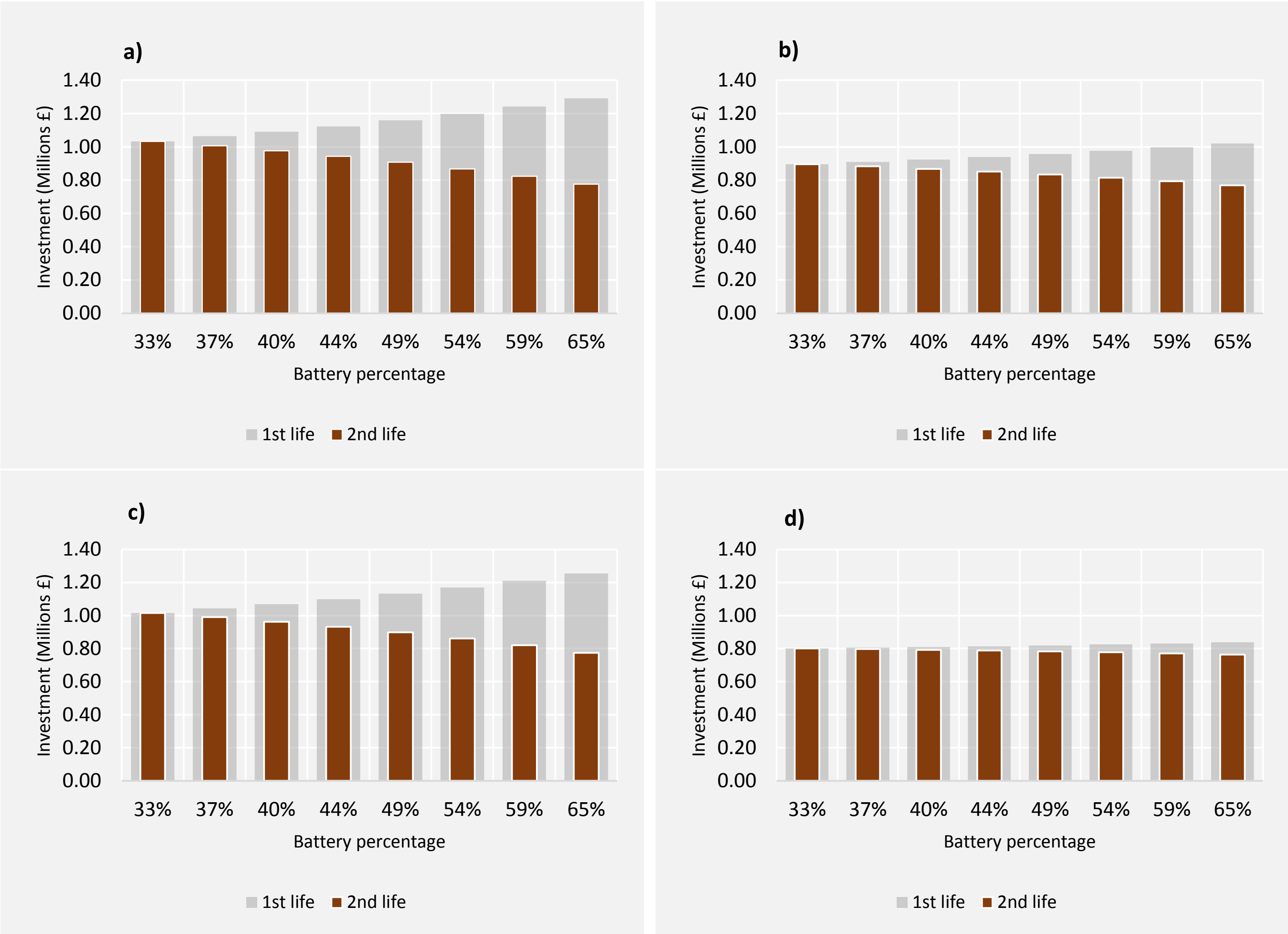

Figure 5: Scenario analysis of the economic impact for each baseline HESS configuration. The BEV content constant and the 1st and 2nd life battery contents are varied (as one increases the other decreases); a) 1st life LTO battery, 2nd life LTO battery and BEV; b) 1st life Na-ion battery, 2nd life LTO battery, BEV; c) 1st life LFP battery, 2nd life LTO battery, BEV; d) 1st life Lead-acid battery, 2nd life LTO battery, BEV.

Figure 6

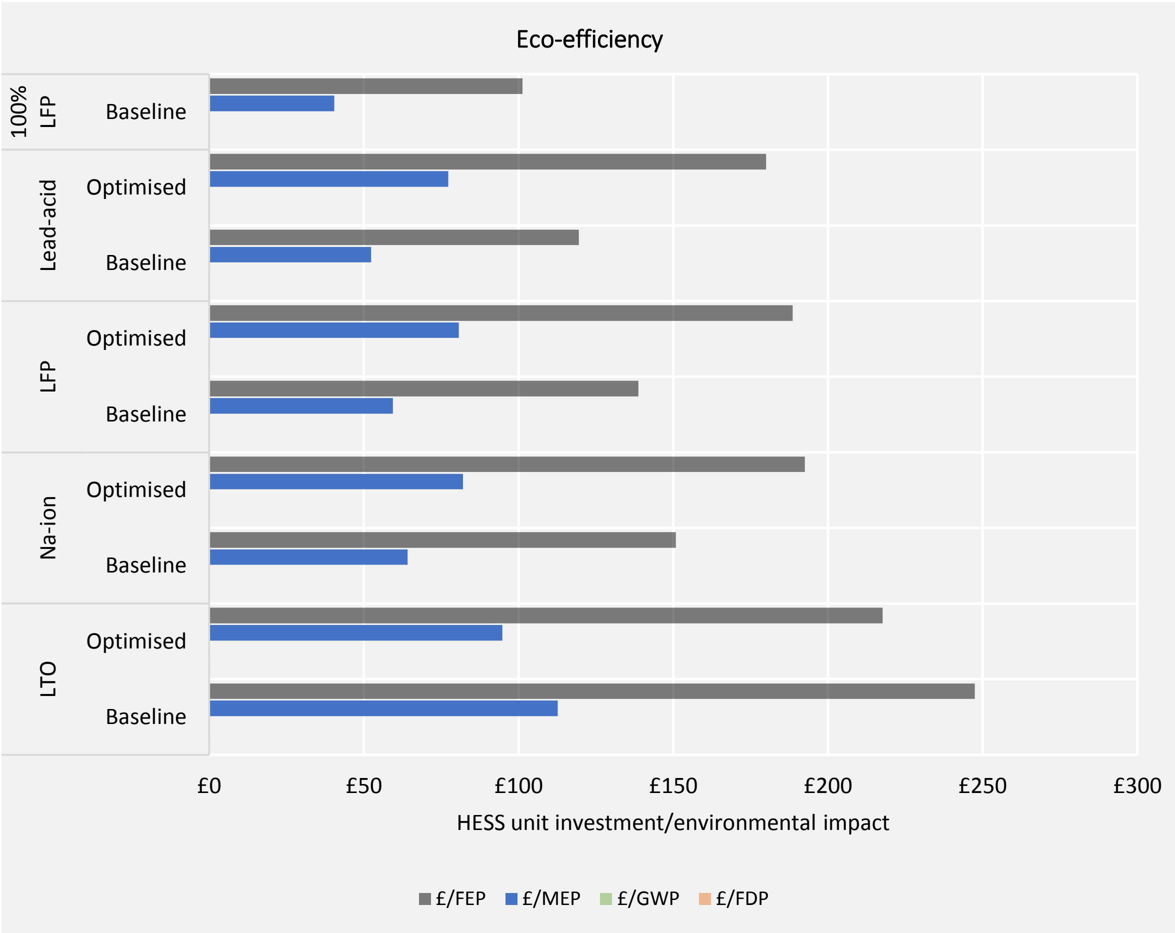

Figure 6: Result of the eco-efficiency analysis relating to the performance of one unit of the baseline HESS configurations (containing an equal distribution of each battery type), the environmentally and economically optimised HESS configurations based on the findings of the scenario analysis and the 100% 1st life LFP baseline. The environmental impact categories tested were the Fossil Depletion Potential (FDP), the Global Warming Potential (GWP), the Marine Eutrophication Potential (MEP), the Freshwater Eutrophication Potential (FEP) and the Human Toxicity Potential (HTP).