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Prospective life cycle assessment of hydrogen production by waste photoreforming

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ABSTRACT

Identifying sustainable energy vectors is perhaps one of the most critical issues that needs addressing to achieve a climate-neutral society by 2050. In this context, the hydrogen economy has been proposed as a solution to mitigate our current fossil-based energy system while the concept of the circular economy aims to boost the efficient use of resources. Photoreforming offers a promising opportunity for recycling and transforming widely available biomass-derived wastes (e.g., crude glycerol from biodiesel) into clean hydrogen fuel. This processing technology may be a versatile method that can be performed not only under UV light but also under visible light. However, this approach is currently at the lab-scale and some inherent challenges must be overcome, not least the relatively modest hydrogen production rates for the lamps' substantial energy consumption. This study aims to assess the main environmental impacts, identifying the hotspots and possible trade-off in which this technology could operate feasibly. We introduce an assessment of the windows of opportunity using seven categories of environmental impact with either artificial light or sunlight as the source of photocatalytic conversion. We compared the environmental indicators from this study with those of the benchmark water electrolysis and steam–methane reforming (SMR) technologies, which are currently operating at a commercial scale. The results obtained in this study situate biowaste photoreforming within the portfolio of sustainable H_2 production technologies of interest for future development in terms of target H_2 production rates and lifetimes of sustainable operation.

1. Introduction

Since the industrial revolution, society's ever-increasing consumption of traditional fossil fuels has caused significant damage to the environment, including global warming and resource depletion. The international community is currently trying to implement ambitious policies and sustainable goals that should be reached in the next few decades. The European Green Deal (European Commission, 2019) represents the biggest commitment to climate change mitigation. The main goal is to transform Europe into a carbon-neutral economy by 2050. The current energy production model is leading to increased greenhouse gas (GHG) emissions and fossil resource depletion. Hence, it is essential that we transition to a sustainable and low-carbon energy market over the coming years. In 2020, a year marked by the COVID-19 pandemic, the European Commission announced an important hydrogen (H_2) strategy (European Commission, 2020) as part of the European Green Deal that could play a substantial role in the recovery from the socioeconomic implications of the pandemic. In a decarbonized future scenario, hydrogen is earmarked as one of the most promising energy carrier candidates thanks to its high energy density, being its lower heating value (LHV) ~120 kJ g^{-1} and therefore high energy density. Furthermore, green hydrogen opens up a sustainable pathway for conversion into other energy carriers, such as ammonia, methanol, methane and liquid hydrocarbons. It can be also used in fuel cells or a wide range of transport applications. As a chemical, green hydrogen can reduce GHG emissions from sectors where fossil-H_2 is widely used today, including refining oil and methanol and ammonia production. Finally, hydrogen can be stored and transported by various means (IRENA, 2020a).

Within this context, hydrogen could replace exhaustible fossil fuels and help decarbonise energy-intensive sectors (e.g., chemical, petrochemical, metallurgy, etc.) as its combustion produces just pure water. However, although hydrogen combustion is carbon-free, current production methods are still related to CO_2 emissions and fossil fuel consumption. Today, the vast majority of hydrogen is produced by steam–methane reforming (SMR) of natural gas, which accounts for around 48% of global production (Staffell et al., 2019), 30% is from oil

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(mostly consumed in refineries), 18% from coal and the remaining 4% from water electrolysis. In a carbon-neutral economy, the conventional routes must be gradually replaced by greener technologies. The recent trend of using hydrogen as an energy carrier in chemical and transport industries has led to considerable research efforts to find clean production alternatives to traditional fossil fuels. Several water-splitting, such as thermolysis, electrolysis, photolysis (e.g., photocatalytic, photobiological and photoelectrochemical processes), and thermochemical technologies can be applied to transform different feedstocks into hydrogen and other by-products (El-Emam and Özcan, 2019; Martinez-Burgos et al., 2021; Razi and Dincer, 2020). These clean technologies are currently at different stages of maturity in terms of technology readiness levels (TRLs) (European Commission, 2015), with splitting water through electrolysis the most mature (TRL 8, at small scale), while others, such as photocatalysis or thermolysis, are still in their infancy (TRL < 4). The shift towards green hydrogen production will not happen overnight and the synergy of all these technologies will be needed in the near future. Furthermore, they can boost renewable energy's market growth and may help create new export opportunities for countries rich in renewable energy resources (IRENA, 2019).

Photocatalytic water splitting is an environmentally friendly approach. It was first proposed in the 1970s by Fujishima and Honda (Fujishima and K. Honda, 1972); since then various strategies have been explored to enhance photocatalytic efficiency (Toe et al., 2021), including photocatalytic hydrogen production through organic reforming, i.e., photoreforming. The process was originally put forward in 1980 (Kawai and Sakata, 1980) as an interesting option to exploit biomass-derived substrates. It is currently considered an important route to cost-effective, clean and sustainable hydrogen production under room conditions (Aydin et al., 2021), thus contributing to the circular economy (Patsoura et al., 2007). It relies on the use of organic biomass-derived waste as the sacrificial agent to resolve the undesired electron-hole recombination reaction. Although many other compounds have been reported as suitable sacrificial reagents, such as methanol, ethanol, ethylenediaminetetraacetic acid (EDTA), Na_2S, Na_2SO_4, or ions such as I^-, IO_3^-, CN^- and Fe^{3+} (Galińska and Walendziewski, 2005), most of them are non-renewable. Nowadays, one of the most promising sacrificial agents is glycerol, the main by-product of biodiesel production, which has been shown to enhance hydrogen production yields (Ribao et al., 2019; Yasuda et al., 2018). Given that biodiesel production levels are expected to increase rapidly, this approach could help mitigate its oversupply and benefit the biodiesel industry by reducing disposal costs.

Nevertheless, hydrogen production through glycerol photoreforming remains unfeasible because of the insufficient light absorption and modest production rates (Corredor et al., 2019). Titanium dioxide (TiO_2) has generally been considered the most promising light-harvesting material for the production of hydrogen from water because it is low-cost, innocuous, chemically and thermally stable, and long-lasting (Pelaez et al., 2012). Research efforts are now focusing on the development of alternative smart photocatalysts with operational flexibility under both sunlight and artificial light (Younis and Kim, 2020) and catalytic materials that can exploit the full spectrum of sunlight (Kubacka et al., 2021). From an environmental perspective, sunlight-driven photoreforming hydrogen production seems the most sustainable option, but it is only attractive in areas where the availability of biomass waste supply coincides with high solar irradiance. Moreover, most photocatalysts (e.g., TiO_2, ZrO_2, etc.) are only activated by ultraviolet light, with the UV light used corresponding to about 5% of the sunlight spectrum (Sang et al., 2015). While photocatalytic activity can be improved with nanomaterials or metal doping (Ribao et al., 2017), this may introduce additional environmental impacts that would require assessment. Of course, the main limitation of sunlight-driven photoreactors as compound parabolic collectors (CPC) is their low efficiency on cloudy days and at night. Therefore, an alternative design using artificial light, for example, light-emitting diodes (LEDs), could improve the production efficiency of common photocatalysts such as TiO_2. The rapid progress of LED technology, in terms of a longer useful life and more affordable prices (Rasoulifard et al., 2015), has opened a new frontier for its application in photoreactors. LED-driven photocatalysis not only improves the efficiency of hydrogen production but the reactor is also more compact. However, the technology is only a clean option when it is powered by renewable energy sources (photovoltaic solar panels, wind, etc.). Although several advances in lab-scale photoreforming hydrogen production have been made in recent years (Corredor et al., 2019), the technology is still low on the TRL scale and there is a lack of studies focusing on a sustainable early-stage design.

The present study aims to identify the main hotspots and possible trade-offs in which photoreforming technology can operate sustainably. For this purpose, we have applied the so-called ex-ante LCA, specifically a prospective LCA, which is one of the better guidance tools for emerging technologies (Cucurachi et al., 2018) seeking to incorporate externalities that have major implications for long-term sustainability (Aldaco et al., 2019; Butnar et al., 2010; Guinée et al., 2002; Ita-Nagy et al., 2020; Rumayor et al., 2020).

Although the literature contains several studies on hydrogen production LCAs, most of them addressed the technologies in terms of global warming and/or their acidification potential (Aydin et al., 2021; Bhandari et al., 2014; Dufour et al., 2012; El-Emam and Özcan, 2019). To the best of our knowledge, this study is the first to assess the window of opportunity for photoreforming from a complete environmental perspective, including additional indicators, such as resource depletion or water stress. Water electrolysis is used as the benchmark technology, given its high TRL and potential, while conventional fossil-based steam–methane reforming (SMR) was included to demonstrate the full window of opportunity for improvement.

The study uses a sensitivity analysis to look at some key performance parameters, such as light source (LEDs or sunlight), energy efficiency and hydrogen production rate. We assess their influence in several environmental impact categories, including global warming potential, acidification potential, water scarcity, and resource depletion, among others. This study supports design decision-making and situates waste photoreforming in the portfolio of green hydrogen technologies.

2. Methodology

In this study, a waste photoreforming hydrogen production route was assessed through a prospective ex-ante life cycle assessment (LCA) (Cucurachi et al., 2018). LCAs are generally used to study the environmental impacts of supply chains, production systems and consumption systems, as defined in ISO standards 14040 (International Organization for Standardization, 2006a) and 14044 (International Organization for Standardization, 2006b). The procedure quantifies how much raw material and energy is used and the emissions and waste produced in the context of a life cycle thinking. Here, the LCA, performed using GaBi Professional software (Sphera, 2019), will help identify hotspots affecting the emerging technology. First, we determined which key performance parameters (KPPs) have the greatest environmental impact. KPPs include the light source (either an artificial LED source or sunlight) and hydrogen production rate. Then, we defined the best performance scenario for feasible hydrogen production from an environmental perspective. The datasets of the background processes (e.g., water production, electricity production, etc.) were obtained from Ecoinvent v3.7 database (Swiss Centre for Life Cycle Inventories, 2020). The environmental impacts were determined using the CML 2001 (Guinée et al., 2002) and AWARE (WULCA, 2007) methods, which include several midpoint categories based on common mechanisms (e.g., climate change, acidification potential, abiotic resource depletion) and water stress, respectively (see Supporting Information). We applied a cradle-to-gate approach (Fig. 1) that only included the upstream processes and hydrogen production. The hydrogen exploitation and end-of-life stages would be identical to other alternative routes and were

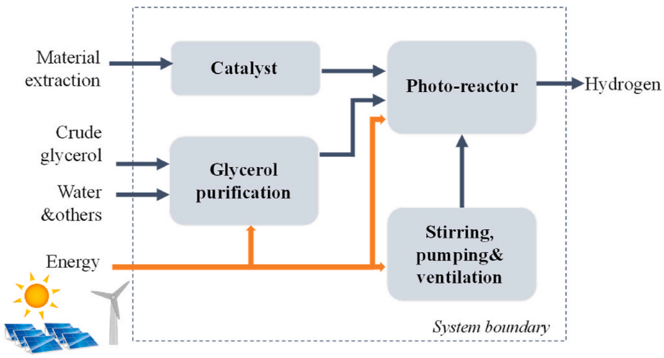


Fig. 1. System boundary.

therefore neglected. The functional unit (FU) established for the study was 1 kg of hydrogen. We used an inter-technology LCA comparison based on proton exchange membrane (PEM) electrolysis as the renewable benchmark technology given its good TRL position.

2.1. Photocatalytic hydrogen production route: scale-up for future application

Briefly, the photocatalytic production route involves a photocatalyst that absorbs photons from a light source, thereby inducing the promotion of an electron from the semiconductor's valence band to its conduction band, creating an electron–hole pair. Water is then oxidised by the photo-generated holes to produce O_2 and H^+. The holes can oxidise H_2O or the organic compound acting as the sacrificial agent (waste glycerol), depending on the semiconductor band gap. Any unreacted electrons and holes recombine mutually of their own accord. This study analysed two reactor designs: (i) a photoreactor using an artificial LED light source (scenario Sc. 1); and (ii) a conventional solar CPC reactor (scenario Sc. 2).

The emerging technology has already undergone a systematic lab-to-industrial scale-up procedure (Thonemann and Schulte, 2019). It is well-known within the field that the main issue when conducting a prospective LCA is the scale-up of the emerging technology (Thonemann et al., 2020). Nevertheless, scale-up is a vital step when performing a prospective LCA based on an inter-technology comparison, which, as its name suggest, involves comparing an emerging technology against a conventional or another mature technology that occupies a different TRL. Both technologies should be modelled and analysed at the same point in time. Therefore, the baseline scenario should consider future conditions to a certain degree (temporal development); otherwise, it could negatively affect the comparison due to different time-related background systems (different TRLs). According to the literature (Thonemann and Schulte, 2019), the first scale-up step during a prospective LCA must assume ideal conditions (e.g., ideal lamp efficiency, 100% quantum yield under artificial or solar radiation, and so on). A comparison then provides a projection of the emerging technology's potential to compete with the benchmark from an environmental perspective. Here, we assessed realistic conditions in a series of sensitivity analyses.

Fig. 2 shows the scale-up of the photocatalytic reactor. The reactor volume, number of LEDs and reactor configuration were decided based on our experience and knowledge considering the typical size of commercial photocatalytic reactors, expert interviews and process simulations. Note that any engineering design parameters (e.g., lamp tube distances, CPC inclination angles, tube ratios, etc.) for these photoreactors are out of the scope of the present study. Only, the overall amount of material used and electricity consumed have a significant influence on the environmental impact.

Hydrogen was assumed to be produced according to Eq. (1) in a photocatalytic reactor with a capacity to irradiate 100 L per batch (Fig. 2).

$$C_3H_8O_3 + 3\ H_2O \rightarrow 3\ CO_2 + 7\ H_2 \tag{1}$$

In Scenario 1 (Fig. 2a), the LED photoreactor vessel is surrounded by 19 LED tubes with an overall radiation of 1.75 kW. The baseline scenario assumes the LEDs are 100% efficient. We also used a fan in Sc. 1 to keep the reactor within a suitable temperature range (20.0–30.0 °C) and therefore maintain constant radiation over the reactor's lifetime. In both Sc. 1 and Sc. 2, a 150 L mixing tank was kept under stirring and filled with 140 L of a diluted organic waste (20 vol% glycerol solution as the sacrificial agent) and 0.5 g L^{-1} of the TiO_2 photocatalyst. The suspension was continuously pumped into the photoreactors and hydrogen exited the tanks through a pressure valve. Crude glycerol could be assumed to be free of environmental burdens if burdens are allocated to the biodiesel as the process main product. However, for a fair environmental assessment, we have attributed the corresponding burdens to waste crude glycerol from biodiesel production through a mass allocation based on an LCA study found in the literature (Dufour and Iribarren, 2012). This crude glycerol, which derives from biodiesel production using waste vegetable oils, needs to be purified before entering the reservoir tank. Crude glycerol consists of 80% glycerol, 7% NaCl, 2% matter organic non-glycerol (MONG) and 11% water. The extraction of NaCl or KCl is a priority during the purification process. According to the literature (Menezes et al., 2013), in the present study we have included a step that upgrades the glycerol concentration to 99%. The inventory of the glycerol derived from waste vegetable oils and the crude glycerol purification is detailed in the Supporting Information. The glycerol solution and photocatalyst were assumed to be replaced after 10,000 working hours in the baseline scenarios. This durability is optimistic; however, according to other LCA studies in the literature, such a lifetime can be assumed for the baseline scenarios as objective in medium-term developments (Dufour et al., 2012). Scenario 2 (Fig. 2b) only relies on a renewable electricity input for pumping and stirring.

The study was based on the following hypotheses: i) the hydrogen plant was in the vicinity of the biodiesel plant supplying the crude glycerol, thus nullifying any transport impact; ii) the plant's electricity

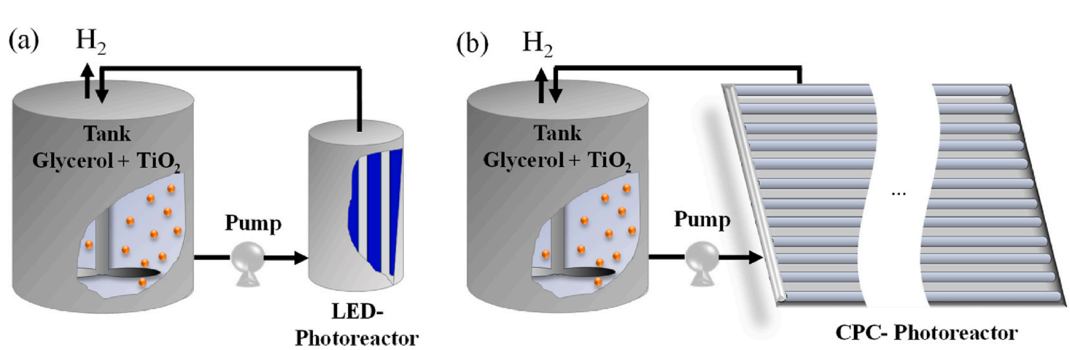


Fig. 2. Scale-up configurations: (a) LED photoreactor (in Sc. 1); (b) solar CPC photoreactor (in Sc. 2).

source was considered renewable (i.e., wind and solar photovoltaic (PV)); iii) the average solar irradiance in Sc. 2 was considered to be 41.5 W m^{-2} for photons below 400 nm (Arzate Salgado et al., 2016); and iv) the plant's infrastructure is disregarded as the expected real lifetimes at industrial scale are long enough and therefore, it has a negligible impact compared to the impact of the operational phase. Remember that photoreforming hydrogen production is still at a low TRL and a long way from large scale exploitation. Of course, the impact of infrastructure would have to be considered in any more detailed, future studies. We used the Ecoinvent database to obtain EU (RER) proxies of the background processes (e.g., water production, titanium dioxide production, etc.). The impacts of European renewable electricity (solar PV and wind) were calculated using GaBi Software with the latest renewable energy statistics report for EU-27 (IRENA, 2020b). Although this sort of technology is better suited to countries with a high solar radiation potential, we regionalised the proxies to EU to apply LCA consistently. Note that the use of renewable proxies from high solar radiation countries (e.g., Spain, Portugal, etc.) could have a negative impact on other categories, especially, water scarcity. The background data used to calculate environmental categories for EU solar PV/wind electricity can be found in the Supporting Information. The influence of location, downstream purification and the development of renewables falls outside the scope of the current study given the technology's low TRL.

2.2. Benchmark processes for a prospective inter-technology LCA comparison

Here we perform an inter-technology LCA comparison using water electrolysis as the benchmark because it is the renewable hydrogen route with the highest TRL at the time of writing. Water electrolysis can be achieved through alkaline electrolysis (AEL), proton exchange membrane (PEM), anion exchange membrane (AEM) and solid oxide electrolysis cell (SOEL) systems. Of these, AEL and PEM are considered the most mature, while SOEL is still at the demonstration stage (Burton et al., 2021). Although AEL is currently a commercially available option, in this study we have considered a PEM set-up powered by renewable electricity (solar PV/wind) as the benchmark process. PEM processes produce purer hydrogen and the technology is more compact and benefits from a quick start-up compared to AEL (Burton et al., 2021). With respect to technology readiness levels (TRL), SMR and AEL electrolysis are currently the only commercially available gigawatt-scale technologies (TRL 9). PEM electrolysis has been commercialised but at a smaller, megawatt scale (TRL 6–8), with large scale (GW) systems currently at TRL 4 (Pinsky et al., 2020).

Briefly, PEM-based H_2 production involves splitting water into H_2 and O_2 by applying an electric current (Eq. (2)). The electrolysis cell is the basic element of electrolytic H_2 production systems.

$$H_2O + \text{direct current electricity} \rightarrow H_2 + ½O_2 \quad (2)$$

Several cells are often connected in parallel or in series to form the electrolyser module. The gas products (H_2 and O_2) generated are cooled, purified, compressed and stored (Zhang et al., 2015). Bear in mind that water entering the unit must be treated (deionised) to prevent mineral deposition and undesired electrochemical reactions in the cells. Stoichiometrically, 9 kg of water are required per kg of H_2; however, deionisation means that 18–24 kg of water is required per kg of H_2. This includes some inefficiencies in the upstream process (IRENA, 2020a). On the other hand, a significant advantage of PEM is its flexibility and capacity to work at differential pressures (IRENA, 2020a). The scenario labelled as Sc-PEM is modelled using GaBi Software and according to the best performance parameters found in the latest publications (Burton et al., 2021; IRENA, 2019). According to the latest report by IRENA, current PEM electricity consumption ranges between 50 and 83 kWh per kg of H_2 and typical water consumption is 18–24 kg per kg of H_2 (IRENA, 2020a). Here we have considered the lowest values in these ranges to model the Sc-PEM scenario in order to consider a certain degree of improvement. Note that 50 kWh per kg of H_2 is an optimistic value and close to the target fixed for 2050 (42 kWh per kg of H_2) (IRENA, 2020a). Comparing the environmental indicators from the LCA for the photocatalytic process against the benchmark process (Sc-PEM) will allow us to identify hotspot performance parameters in the emerging photoreforming technology studied here.

Furthermore, our comparative assessment also included conventional fossil-based steam–methane reforming (SMR) from natural gas. This scenario will frame the window of opportunity for improvement, especially for certain impact categories, such as reduced use of fossil resources, carbon footprint, etc. It is important to clarify that we had no intention of comparing the conditions or H_2 production rates against the thermal process because it is already at a full industrial scale (TRL 9). However, fossil-based routes are commonly included as a benchmark in environmental assessments (Bhandari et al., 2014; Cetinkaya et al., 2012; Dufour et al., 2012; Mehmeti et al., 2018).

According to the SMR dataset from the Ecoinvent database, this route requires natural gas (0.921 m^3 per kg of H_2), fossil fuels (coal, oil, etc.) and catalysts (e.g., nickel) (Swiss Centre for Life Cycle Inventories, 2020). The first step involves reacting methane (CH_4) with steam at 750–800 °C (1380–1470 °F) to produce syngas, a mixture of hydrogen (H_2) and carbon monoxide (CO) (Eq. (3)). In the second step, known as a water–gas shift reaction (Eq. (4)), the CO reacts with steam over a catalyst to form hydrogen and carbon dioxide (CO_2).

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \quad (3)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \ (+\text{heat}) \quad (4)$$

2.3. Sensitivity assessment

We performed a sensitivity assessment to determine the influence of the most significant KPPs on the selected environmental impact categories. In this regard, sensitivity assessments represent an important tool when studying the robustness of results and trying to provide some target values to guide future technology developments. The KPPs that are expected to change in the short-to-midterm include the catalyst lifetime and hydrogen production rate. Note that the environmental impacts of reference processes, such as renewable electricity production, have remained unchanged in this study. Some impact categories for renewable electricity (wind and solar PV) are expected to decrease in the near future because of efficiency improvements in PV modules, new recycling processes, and so on. However, their consequential assessment is out of the scope of the present study because they will impact the indicators of both the studied technology and the benchmark technology (water electrolysis) depending on electricity consumption. For a fair comparison, we have also assumed a certain degree of improvement in Sc-PEM technology. We also modelled an additional scenario, called Sc-PEM-2050, considering an energy consumption of 40 kWh per kg of H_2, which agrees with the latest PEM figures of merit proposed by IRENA to meet the 1.5 °C climate goal (IRENA, 2020a).

3. Results

3.1. Inventory

The inventories were built up by determining the mass and energy balances per FU. Table 1 includes the most relevant input and output data for the scenarios in the separate unit processes. The values were calculated according to the equations shown in the Supporting Information. On one hand, there is a very marked difference in electricity consumption of 105 kWh per kg of H_2 and 2.61 kWh per kg of H_2 for scenarios 1 and 2, respectively. The main contributor to electricity consumption in Sc. 1 is the LED lamps, while Sc. 2 needs electricity for

Table 1
Inventory of H_2 production via glycerol photoreforming in the baseline scenarios.

Performance parameters	Unit	Sc. 1	Sc. 2
Inputs			
Electricity			
Photoreactor	kWh	87.5	*sunlight*
Pump	kWh (10^{-5})	0.79	9.51
Stirring	kWh	0.22	2.61
Refrigeration	kWh	17.5	–
Water	kg	0.40	4.82
Glycerol [a]	kg	0.13	1.52
Catalyst, TiO_2	kg (10^{-3})	0.25	3.00
Outputs			
Hydrogen	kg	1.00	1.00

[a] Crude glycerol from biodiesel (see Supporting Information).

stirring and pumping. On the other hand, Sc. 2 has a lower hydrogen production rate because direct sunlight is less intense than the artificial light provided by the LEDs in Sc. 1. This means more glycerol and catalyst are required to produce 1 kg of hydrogen in Sc. 2 compared to Sc. 1.

3.2. Life cycle impact assessment

This section discusses the impact of scenarios 1 and 2 in seven environmental categories: i) global warming potential (GWP), ii) abiotic depletion potential (ADP)-fossil, iii) available water remaining (AWARE), iv) acidification potential (AP), v) photochemical oxidant creation potential (POCP), vi) eutrophication potential (EP), and vii) ADP-elements. We compared the results with the Sc-PEM benchmark and SMR reference to discover the potential opportunities of the photocatalytic technology from an environmental perspective.

Global warming impact. The GWP impact category measures the possible warming effect at the earth's surface due to the emission of GHGs. GWP is the most frequently quantified category in environmental studies exploring different hydrogen production routes (Aydin et al., 2021; Bhandari et al., 2014; Cetinkaya et al., 2012; Galera and Gutiérrez Ortiz, 2015; Razi and Dincer, 2020). Fig. 3 shows the GWP impact values for Sc. 1, Sc. 2 and Sc-PEM, as well as the influence of the renewable electricity source (solar PV or wind). The GWP value for SMR is shown as the reference value. When the electricity source is solar, the results for Sc. 1 and Sc-PEM are slightly higher than those for wind electricity. The GWP impact of Sc. 1/solar is almost double that of the benchmark Sc-PEM/solar. As mentioned previously, Sc. 1 doubles the electricity consumption of Sc-PEM (per kg of H_2). If the electricity needs were met by wind turbines, we would obtain GWP values of 4.73 and 1.18 kg CO_2-eq per kg of H_2 for Sc. 1 and Sc-PEM respectively. Solar PV energy is known for higher GWP values than wind turbines because of the emissions associated with the production of PV modules involving energy-demanding processes such as metal deposition under vacuum conditions and high temperatures in sputtering and layer deposition (Chatzisideris et al., 2016). The GWP values we calculated are lower than the GWP reference value for the conventional fossil route (SMR). It is evident that the main environmental issue with both renewable processes of hydrogen production occurs in their operational phase, i.e., electricity supply. In the case of the reference Sc-PEM, less than 20% is attributed to the technology's heating needs (to operate the electrolyser). Scenario 2 involved very little electricity consumption, just enough for pumping and stirring. Hence, the GWPs obtained in Sc. 2 are noticeably lower depending on the electricity source, 0.15 (wind) and 0.32 kg CO_2-eq per kg of H_2 (solar). Although, we are considering a 100% quantum yield at the baseline for Sc. 1 and Sc. 2, Sc. 2 exhibits a wider window of opportunity than Sc. 1 in terms of competing with the benchmark technology, Sc-PEM. Other minor contributions, such as catalyst or glycerol impacts, can have an important role in the case of sunlight-driven Sc. 2.

Fossil resource and water consumption. Fossil resource consumption is determined in the abiotic depletion potential-fossil (ADP-fossil) impact category, while the available water remaining (AWARE) category shows the potential for water scarcity. Fig. 4 shows the values for these categories when 1 kg of H_2 is produced by photocatalysis in scenarios 1 and 2 and via the benchmark water electrolysis (Sc-PEM). It also highlights the influence of the renewable electricity source (wind or solar PV). Due to the low hydrogen production rate of Sc. 1, the system requires long reaction times resulting in high electricity consumption. When electricity is derived from solar PV, the photocatalysis route has an even greater impact on ADP-fossil than SMR (Fig. 4a). However, when wind power is used, the magnitude of this impact category is in the

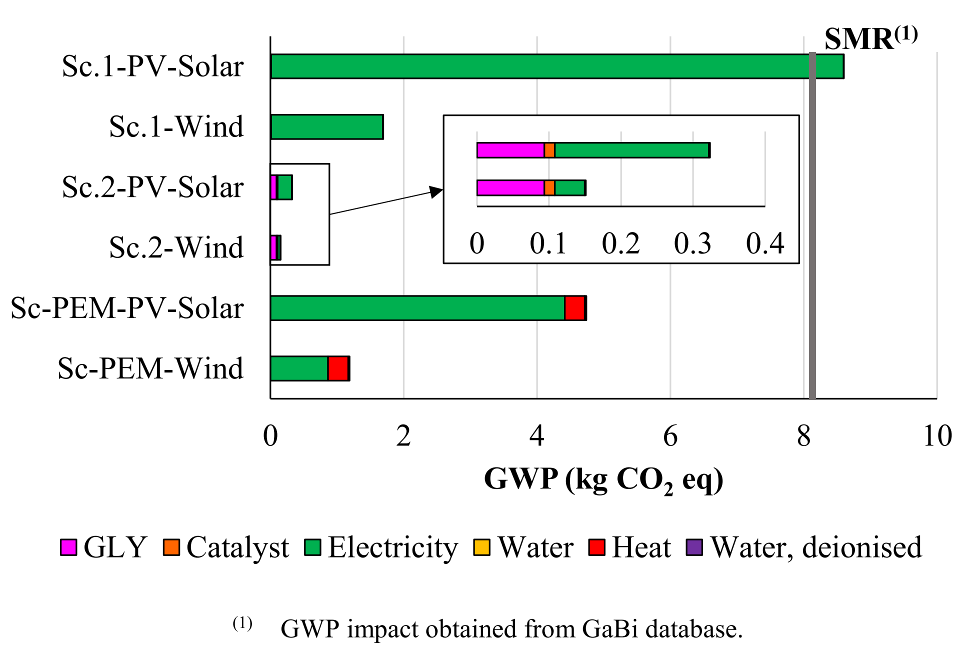
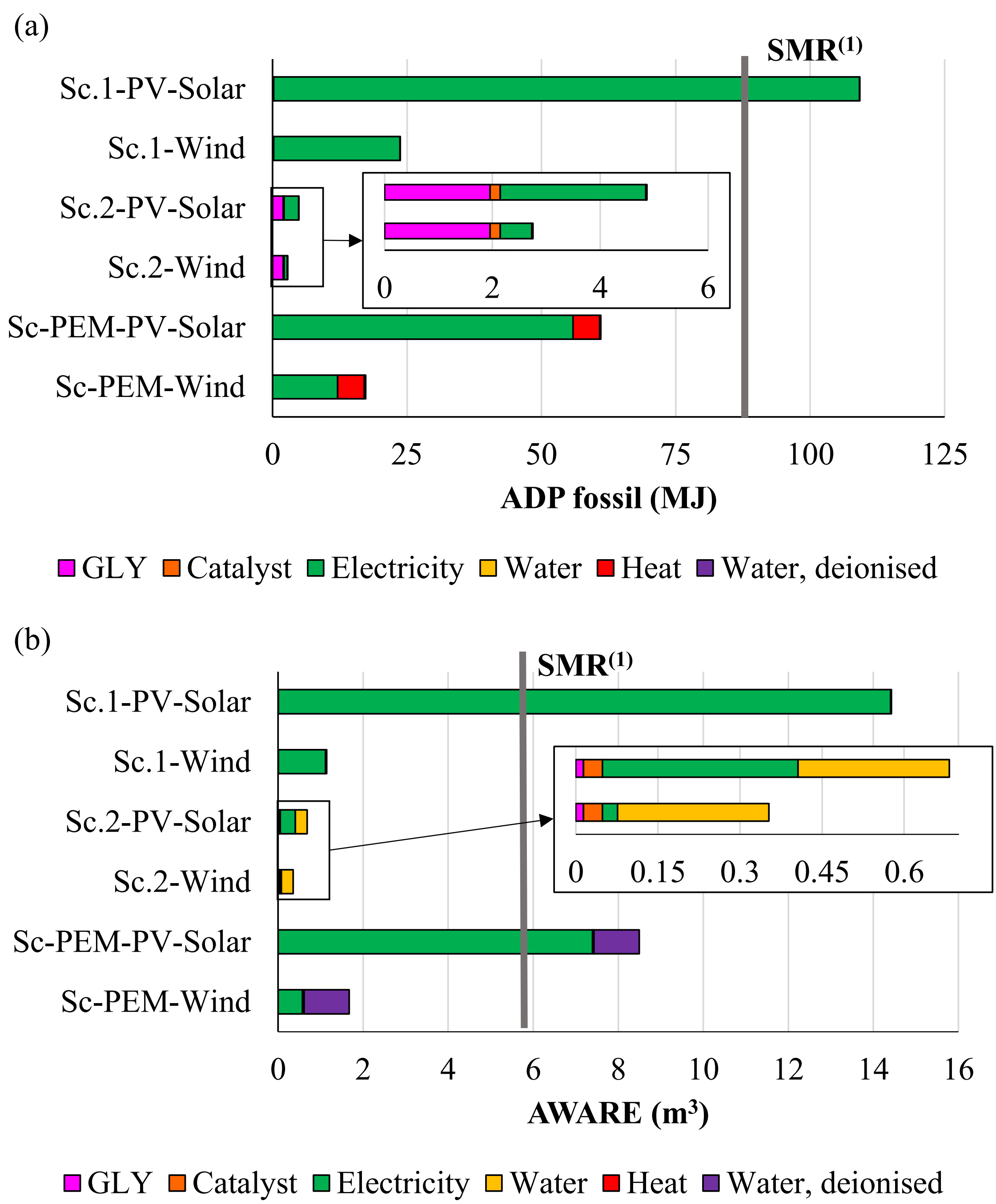


Fig. 3. LCA results of GWP impact category in baseline scenarios Sc. 1 and Sc. 2 and reference scenario Sc-PEM per functional unit (1 kg of H_2).
(1) GWP impact obtained from GaBi database.



(1) ADP-fossil and AWARE impact value obtained from GaBi database.

Fig. 4. LCA results for ADP-fossil (a) and AWARE (b) impact categories in Sc. 1, Sc. 2 and Sc-PEM (reference) per functional unit (1 kg of H_2). (1) ADP-fossil and AWARE impact value obtained from GaBi database.

same order as that of Sc-PEM. Note that our baseline scenarios consider ideal conditions (100% quantum yields and 100% LED efficiency), as our aim was to demonstrate the window of opportunity or margin of environmental feasibility. We should also point out that 91% of the impact on ADP-fossil is from solar PV consumption in Sc. 1/solar, while this percentage falls to 74% in the Sc-PEM/solar reference process. The results for the AWARE impact category are shown in Fig. 4b. One would expect water electrolysis to have a higher impact on water scarcity as deionised water is the main raw material, whereas photocatalysis is fed with a glycerol-based waste. However, as can be seen in Fig. 4b, the high electricity consumption associated with photocatalysis, almost double the consumption of electrolysis, outweighs the benefits of using glycerol waste instead of deionised water in the AWARE category. We found a significant reduction in the water scarcity for 1 kg of hydrogen production from electrolysis and photocatalysis: from 8.5 m^3 to 14 m^3 when using solar power, to 1.7 m^3 and 1.1 m^3 for wind power. This analysis also suggested that there may be a trade-off between water impact and emissions, as it has been found that water-related impacts tend to be higher in technologies with relatively low GWP and fine particulate matter scores, such as solar PV (Mehmeti et al., 2018). In any case, Sc.

1/wind and both Sc. 2 scenarios are environmentally positive compared to the Sc-PEM scenario and even the fossil route (SMR).

Acidification impact. The acidification potential (AP) quantifies the amount of chemicals released into the atmosphere that would cause acidification. AP is the second-most analysed impact category after GWP (Häfele et al., 2016; Suleman et al., 2015; Valente et al., 2017; Wang et al., 2019). Unlike for the case of GWP, solar PV has a relatively high value in the AP impact category – almost double that of the SMR route – mainly due to emissions associated with PV cell production. As shown in Fig. 5, only the Sc. 2 and Sc-PEM/wind scenarios had lower AP values than the SMR route. Efforts must be made to reduce the electricity consumed in the photocatalytic hydrogen production process if an LED-based design is preferred (e.g., because of the sunlight conditions, geographical location, etc.). Our results show that almost 99% of the AP contribution in Sc. 1 comes from the electricity impact regardless of the renewable energy source. However, in the case of Sc-PEM, other contributions from heat and even water consumption stand out in the results breakdown. Electricity sourced from wind turbines would be the most advantageous choice. As in the previous impact categories, Sc. 2 exhibits the best window of opportunity, and the hotspots in this case, namely glycerol purification or even the catalyst production related to the lifetime, should be studied further in a sensitivity analysis.

Photochemical smog. Photochemical oxidant creation potential (POCP) quantifies the release of chemicals that may contribute to ozone (O_3) formation in the troposphere. The POCP breakdown for the chosen hydrogen production routes are shown in Fig. 6. The POCP value was only higher when sunlight was used as the photocatalytic energy source (Sc 1/solar), as it returned a result of 0.0046 compared to 0.0035 kg of ethene$_{eq}$ perkg of H_2 for the fossile route (SMR). The POCP values for both life cycle routes (photocatalytic and the benchmark) were similar due to comparable amounts of life cycle NO_x emissions. Once again, the high rate of electricity consumed by photocatalysis explains the differences with the reference route (Sc-PEM).

Other impact categories. Fig. 7 shows the life cycle eutrophication potential (EP) and mineral abiotic depletion potential (ADP-elements). The eutrophication of ecosystems may promote algae growth and damage marine life. EP mainly derives from the phosphate emissions associated with mining the materials used in turbines and PV modules. Our assessment of EP (Fig. 7a) returned much higher levels for Sc. 1 and the benchmark, Sc-PEM, than for the fossil route (SMR). Renewable electricity consumption (both wind and solar PV) had the largest influence on EP. This finding is in agreement with the results of a recent study (Siddiqui and Dincer, 2019) that emphasised the need to decrease the EP associated with renewable hydrogen production routes, such as water electrolysis, to achieve a fully sustainable hydrogen economy. A similar trend was observed in the ADP-elements category. The photocatalytic, especially Sc. 1, and benchmark (water electrolysis) routes studied here have greater impacts on ADP-elements than the SMR route, being the main impact resulting from renewable electricity consumption. No doubt these impact categories, which are dominated by metal consumption, are expected to decrease in the coming years, which would result in an overall improvement in the results for the EP and ADP-elements categories. As shown in Fig. 7, at the current rate of renewable development, only Sc. 2 which uses direct sunlight can compete with the SMR fossil route in the mentioned environmental categories.

4. Discussion

4.1. Sensitivity assessment

We conducted a sensitivity assessment of Sc. 2 to evaluate the influence of some KPPs related to the photocatalytic technology. We intended to determine the target values for the selected KPPs necessary for an environmentally positive implementation of the studied technology. These KPPs included the minimum catalyst lifetime and the hydrogen production rate. These targets may help guide future developments in this area of photocatalytic technology. As mentioned in the list of limitations and assumptions, the performance of baseline scenarios, examined in the previous section, was close to ideal conditions (e.g., long catalyst lifetime, 100% quantum yield, etc.) according to the suggestions from prospective LCAs conducted on emerging technologies (Thonemann and Schulte, 2019; Zimmermann et al., 2018). Note that we do not discuss Sc. 1 in this section because it was an electricity-intensive process with power consumption being the main contributor in all impact categories (over 90%). This overshadowed all other impact contributors (e.g., catalyst production, sacrificial agent, etc.). Even though Sc. 1 is excluded from the discussion, it is worth

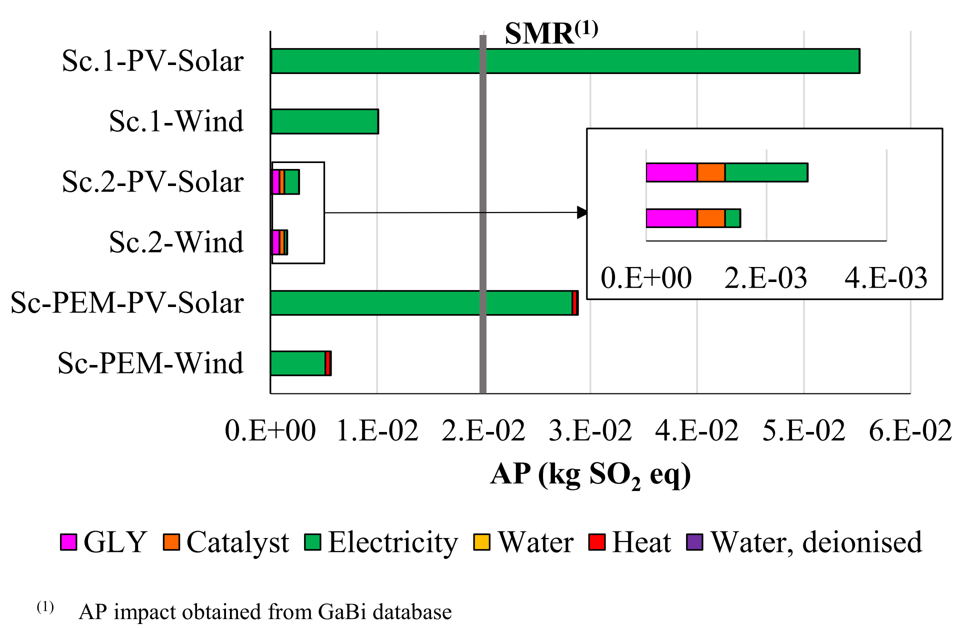


Fig. 5. LCA results for the AP impact category in baseline scenarios Sc. 1 and Sc. 2 and reference scenario Sc-PEM per functional unit (1 kg of H_2). (1) AP impact obtained from GaBi database.

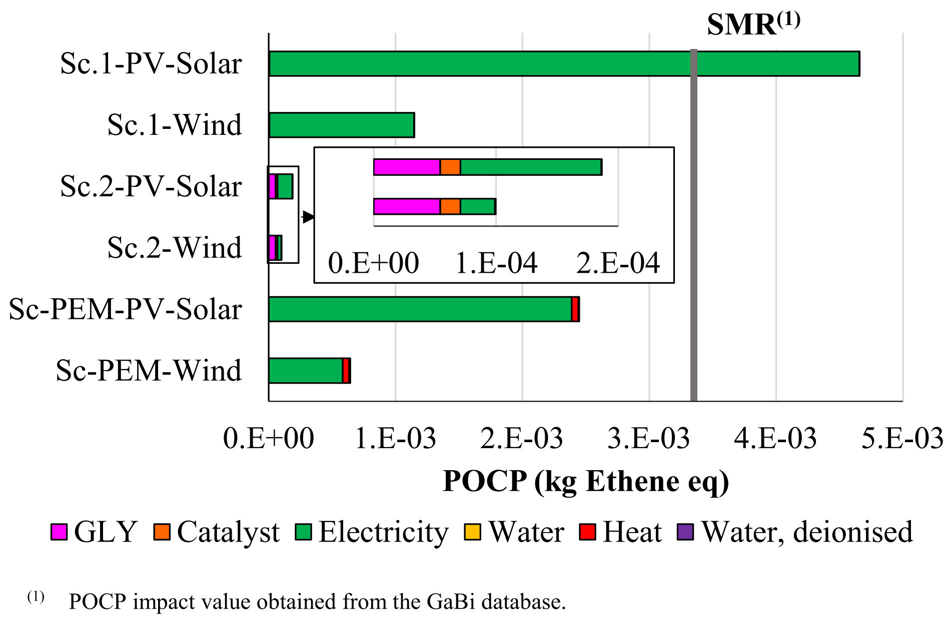


Fig. 6. LCA results for the POCP impact category in baseline scenarios Sc. 1 and Sc. 2 and reference scenario Sc-PEM per functional unit (1 kg of H_2). (1) POCP impact value obtained from the GaBi database.

bearing in mind that Sc. 1 is expected to improve in the short-to-midterm due to the predicted reductions in impact categories related to renewable electricity production. Despite the reductions expected in the coming years in solar PV and wind impacts (e.g., because of a module design and efficiency improvements, recycling processes, etc.) (Ludin et al., 2018), any reductions in these environmental indicators will impact proportionally to the energy consumed in Sc. 1 and Sc-PEM.

Fig. 8 depicts bivariate sensitivity analyses performed to assess the impact of lifetime and hydrogen production rate on the environmental categories which may significantly benefit from waste photoreforming – GWP, ADP-fossil, AP and AWARE. Combinations of lifetimes longer than 5000 h and hydrogen production rates above $1{\cdot}10^{-3}$ kg h^{-1} would be enough to ensure environmental competitiveness with technologically mature water electrolysis. According to the results, the GWP category offers the widest window of opportunity for environmentally positive improvements (compared to SMR) in hydrogen production through waste photoreforming even with low hydrogen production rates and short catalyst lifetimes. The figure also presents the analyses for Sc-PEM/solar PV (*state of the art*) and Sc-PEM 2050 using the impacts of wind-sourced electricity for a fair comparison. Considering the on-going progress and forecasted PEM-2050 scenario, hydrogen production with waste photo-reforming technology would need longer service life, above 8000 h, and higher hydrogen production rates, above $1.4{\cdot}10^{-3}$ kg h^{-1}, to guarantee its environmental competitiveness.

If photocatalysts can be developed to the performance levels assumed in this work, i.e., high durability and resistance, then the use of direct sunlight in Sc. 2 would be the most sustainable means of producing hydrogen for the impact categories studied here. However, Sc. 1 should be explored further given the benefits that can be obtained from the use of artificial light. Scenario 1 may offer some advantages, such as its compact design for indoor applications and continuous operation (i.e., hydrogen production in Sc. 1 does not have to stop at night or during cloudy conditions). The pathway selection between these configurations would depend on the particular practical solution, wherein the location, irradiation conditions and availability of renewable electricity play an important role in the decision-making.

4.2. Influence of methodological changes

Clean hydrogen is expected to play a key role in any future climate-neutral economies. We have used water electrolysis as the benchmark because it is the only mature technology to date that produce clean hydrogen. We used an ex-ante LCA study design to assess the impacts related to the emerging waste photoreforming technology and identify the potential opportunities for improvement from an environmental perspective. The results have highlighted the potential opportunities for the direct conversion of solar radiation into hydrogen (scenario 2) in six of the seven categories studied (GWP, ADP-fossil, AWARE, POCP, AP and EP). Sc. 2 reduced the dependence on electricity as an intermediate carrier in comparison with Sc. 1. By contrast, Sc. 1 supplied by wind-sourced electricity was positive in five of the categories (GWP, ADP-fossil, AWARE and POCP) compared to the SMR fossil route. Sc. 1, Sc. 2 and Sc-PEM revealed higher impacts on ADP-elements than the SMR route. It has already been shown that ADP-elements for solar and wind electricity can be around 50 and 6 times higher, respectively, than the values for electricity from a coal-fired power plant (Lieberei and Gheewala, 2017). The construction of PV plants and wind turbines consumes a lot of metals. Future work on renewable electricity should focus on the development of sustainable collector systems and, of course, recycling processes to recover the materials from existing turbines and PV modules.

The present study has identified electricity consumption as the main hotspot, as well as the possible trade-offs in which photoreforming technology may operate sustainably. However, it should be noted that certain assumptions and limitations affecting this study should be dealt with in further research. These assumptions include:

- The TRL of hydrogen production through waste photoreforming technology (TRL <4) is well below that of PEM water electrolysis (TRL 8) and the conventional SMR process (TRL 9). The application of an ex-ante LCA in this study relies on limited data. To overcome this issue, we have made some assumptions, such as a long catalyst lifetime and 100% quantum yield.
- We have disregarded downstream hydrogen purification because we do not consider it to be a significant bottleneck at the current stage of development of photoreforming technology. However, it should be

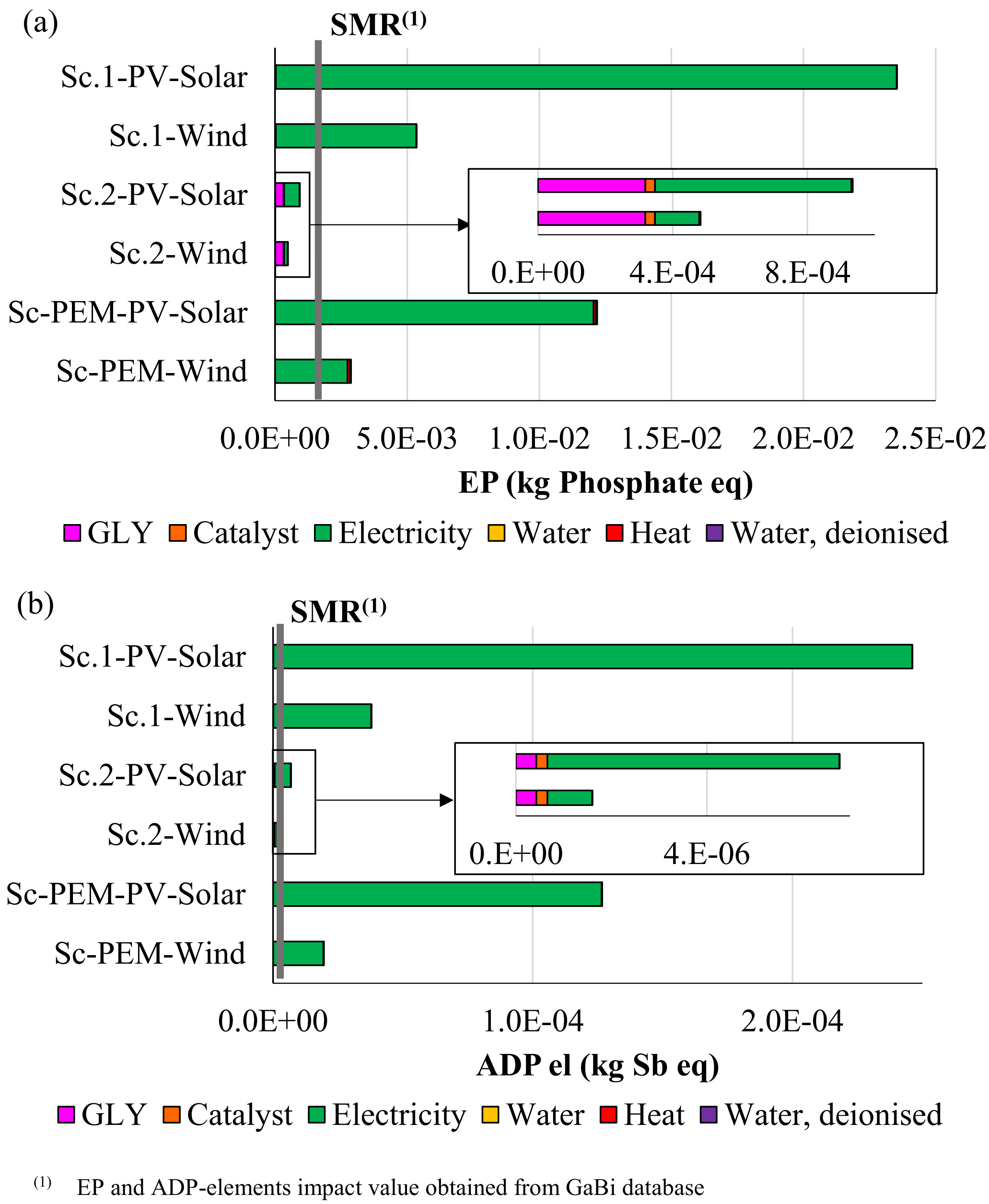


Fig. 7. LCA results for the EP (a) and ADP-elements (b) impact categories in Sc. 1, Sc. 2 and Sc-PEM (benchmark) per functional unit (1 kg of H_2). (1) EP and ADP-elements impact value obtained from GaBi database.

noted that ongoing developments in PEM water electrolysis are more flexible, as this technology can work at differential pressures. Downstream purification can be expected in a more detailed LCA.

- Sc. 1 and Sc. 2 assume the best-case performance because our aim was to identify the potential environmental benefits of waste photoreforming technology by assessing its main bottlenecks and challenges. Therefore, our results and findings should be considered as a particular case study, rather than definitive evidence.
- The scenarios presented in this study are a simplification of a complex reality. Of course, complementary scenarios are possible. Given the low TRL of the technology studied here, we conducted a prospective ex-ante LCA as a first approach. However, consequential and/or dynamic LCAs are a crucial task to be carried out in the future in order to evaluate other physical and economic causalities related to clean hydrogen penetration, renewables penetration and/or the expected development of each technology.

5. Conclusions

The development of green hydrogen recovery from organic waste photoreforming could provide many environmental benefits, particularly as regards to the mitigation of global warming, water stress and resource depletion compared with conventional fossil-based routes (e.g., steam–methane reforming). However, this emerging technology currently occupies a low TRL level (TRL 3–4) and its hotspots need to be assessed in order to find possible trade-offs for sustainable operation. In this study, a prospective LCA was successfully applied to determine the environmental impacts and target values for the key performance parameters (KPPs) that should be achieved in short-to-midterm developments. Decision-making is also supported by the technology's resource savings achieved through recycling waste glycerol in the context of the circular economy. Low hydrogen production rates and short catalyst lifetimes have been identified as the main challenges to

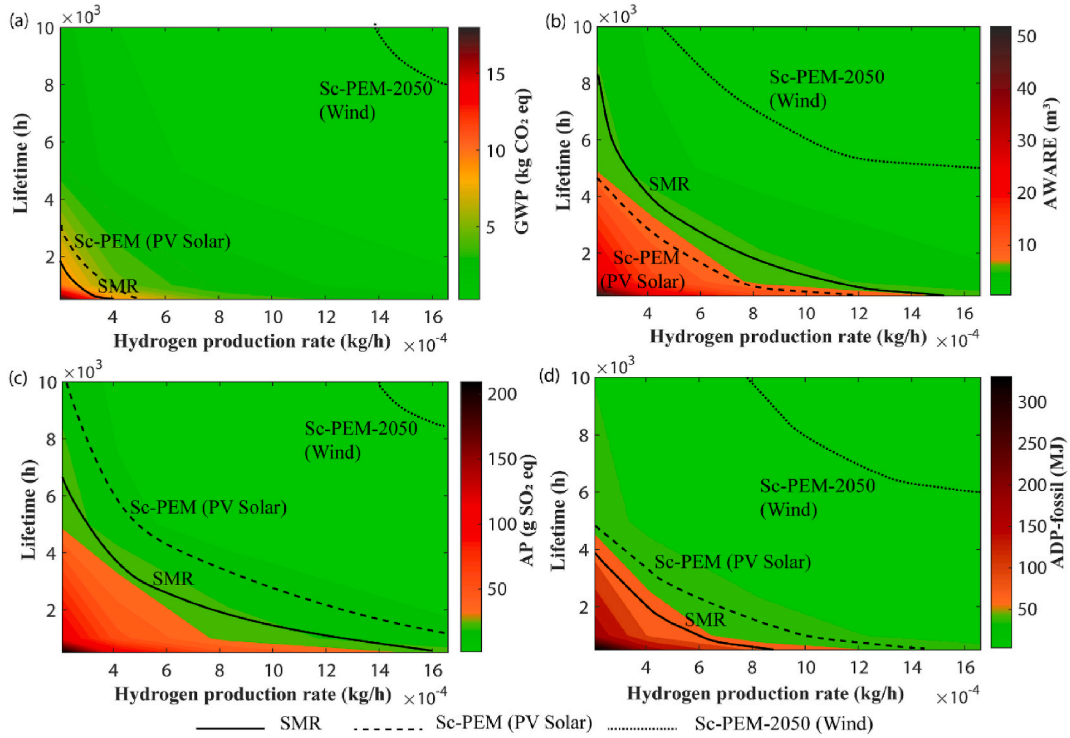


Fig. 8. Sensitivity of impact categories with respect to the KPPs (lifetime and hydrogen production rate): (a) GWP, (b) AWARE, (c) AP and (d) ADP-fossil.

this technology, especially when the process is driven by artificial light (e.g., LED lamps). In such a case, the production of electricity from solar PV or wind for the LED lamps was found to be the main contributor to all the environmental impact categories. We have identified direct sunlight-based photoreforming (using CPCs), followed by wind-powered photo-reforming (using LED lamps), as the most sustainable pathways to renewable hydrogen production. We assessed the influence of KPPs on selected impact categories through several sensitivity analyses and found that GWP presented the widest window of opportunity. Even under conditions of low production rates ($\sim 5 \cdot 10^{-4}$ kg h^{-1}) and short lifetimes (<10 h), this emerging technology can provide green hydrogen with a GWP in the range of other potential renewable technologies, such as water electrolysis (<4 kg of CO_2-eq per kg of H_2). The results of this study may be used in decision-making to guide future research into the promising waste glycerol photoreforming technology for sustainable hydrogen production.

CRediT authorship contribution statement

M. Rumayor: Conceptualization, Methodology, Software, Investigation, Writing – original draft. **J. Corredor:** Conceptualization, Methodology. **M.J. Rivero:** Conceptualization, Validation, Writing – review & editing, Supervision, Project administration, Funding acquisition. **I. Ortiz:** Conceptualization, Validation, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jclepro.2022.130430.

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