Sustainability analysis of hydrogen production processes

Andrea Mio [a,c], *Elena Barbera* [b,e,*], *Alessandro Massi Pavan* [a,c], *Alberto Bertucco* [b,d], *Maurizio Fermeglia* [a,c]

[a] *Department of Engineering and Architecture, University of Trieste, Italy*
[b] *Department of Industrial Engineering (DII), University of Padova, Italy*
[c] *Center for Energy, Environment and Transport Giacomo Ciamician, University of Trieste, Italy*
[d] *Centro Studi "Levi Cases" for Energy Economics and Technology, University of Padova, Italy*
[e] *Department of Civil, Environmental and Architectural Engineering, University of Padova, Italy*

HIGHLIGHTS

- Process simulation provides data to design hydrogen production processes.
- Green hydrogen has larger return of energy invested than natural gas-based routes.
- Floating photovoltaic production is competitive for green hydrogen production.
- Life cycle assessment shows excellent results for green hydrogen.
- Indicators are evaluated for hydrogen use in the maritime industry.

ARTICLE INFO

Keywords:
Hydrogen production
Ferryboats
Floating photovoltaics
EROEI
LCOH
LCA

ABSTRACT

Hydrogen is a versatile energy carrier and storage medium that is expected to have a key role in the energy transition, as it can be employed in a variety of applications. Hydrogen can be produced from different feedstocks and using different processes. Based on the production technology used, hydrogen is conventionally identified by a color. In this work, we compare different hydrogen generation processes: (i) green hydrogen, obtained by electrolysis of water using electricity from floating photovoltaic platforms, (ii) grid hydrogen, also obtained by electrolysis but using grid electricity, (iii) grey hydrogen, produced from natural gas using steam reforming and (iv) blue hydrogen, which is similar to grey hydrogen, but uses hot potassium carbonate as the solvent for carbon capture and storage. The paper considers the production of hydrogen necessary for 2 trips per day of a medium size ferryboat to navigate full electric for 7 h in the Adriatic Sea. Process simulation is applied to solve material and energy balances for each process investigated, as well as for the evaluation of capital and operating costs. Process simulation outcomes are then used to estimate three key performance indicators focused on energetic, economic, and environmental sustainability issues: the energy return on energy invested, the levelized cost of hydrogen, and the life cycle assessment. The energy indicator for grid and green hydrogen has a value of 13.39–14.29, versus a value of 4.59–5.48 for other hydrogen production methods from natural gas. The cost for green hydrogen is slightly higher (8.76) compared to the blue hydrogen (5.50) however green hydrogen has a much lower impact to the environment. Considering the combined results obtained by all the indicators, it is concluded that the most sustainable hydrogen production method is green hydrogen.

---

[*] *Corresponding author.*
E-mail address: elena.barbera@unipd.it (E. Barbera).

Introduction

Over the past few decades, there has been a sharp growth in energy demand, placing increasing pressure on the energy sector. The global average primary energy consumption rate increased significantly from 2000 to 2020 by nearly 53%, namely from 104,722 TWh in 2000 to 160,833 TWh in 2020 [1]. These consumption rates vary by nation and area. To attain the 2030 greenhouse gas emission targets, a significant decrease in the usage of fossil fuels is required, according to recent reports from the Intergovernmental Panel for Climate Changes (IPCC) [2] and International Energy Agency (IEA) [3]. With this goal in mind, hydrogen (H_2) is a viable energy carrier to be directly used in many applications such as heavy transportation, logistics and “hard-to-abate sectors” [4].

Several papers have been published in this journal in the last years dealing with environmental impact of hydrogen production: Noh et al. [5] addressed the environmental and energy efficiency of hydrogen supply chains comparing gaseous and liquid organic hydrogen carriers; Ahmadi and Khoshnevisan [6] performed life cycle assessment of hydrogen fuel cell electric vehicles considering various hydrogen production methods; Liu et al. [7] focused their attention on green hydrogen standards in China; Dilshani et al. [8] reported life cycle net energy and global warming impact assessment for hydrogen production via decomposition of ammonia; Zhang et al. [9] compared the environmental impact of three types of hydrogen production methods using solar energy; Iannuzzi et al. [10] compared hydrogen fuel cell buses vs diesel engine buses in the city of Rosario.

Numerous European member countries, including France, Germany and Spain, have already started ambitious plans on hydrogen, in accordance with the European Hydrogen Strategy [11]. Research on H_2 has also been given 3.2 billion euros under the Italian National Recovery and Resilience Plan [12], which should support Italy's decarbonization efforts. H_2 is anticipated to eventually be able to power ships and trucks, but it also could decarbonize high energy consumption industry and stabilize the operation of the electricity grid. However, in order to achieve these goals, the production of H_2 must be considerably increased, by adopting only clean and sustainable routes to avoid emission of greenhouse gases (GHG). Unfortunately, currently, 95% of the H_2 is produced worldwide by steam methane reforming (SMR), while only 5% comes from other sources [13].

The consensus among experts is that H_2 should play a specialized role in the transition to direct electrification, helping to decarbonize “hard-to-abate” sectors. For these industries where H_2 is crucial, it is essential to carefully assess the H_2 manufacturing procedures. To do this, any evaluation has to be based on thoughtful process design and widely accepted indicators.

A variety of indicators can be found in the literature to be used by decision-makers. One of them is the Energy Return on Energy Invested (EROEI) [14], which compares the amount of net energy stored in an energy vector (in this case, the H_2) and the one that is required to produce it. The US Energy Information Administration (EIA) has recently suggested using EROEI as a benchmark tool in the recommended approach for the net energy analysis [15].

The Levelized Cost of Hydrogen (LCOH), which is computed as the ratio between the net discounted H_2 production costs over the amount of H_2 produced throughout the plant lifetime, is another important performance metric [16]. Inputs to LCOH include plant lifetime costs, annual operating and maintenance costs and capital and investment costs.

Although EROEI and LCOH, which focus on the energy use and economic analysis of H_2 manufacturing processes, are certainly two key performance indicators to be assessed, they are insufficient to estimate the process' overall environmental impact. A Life Cycle Assessment (LCA) study [17] can actually give a comprehensive overview of the environmental burdens of a particular process or product [18–20].

Among the sectors where H_2 could provide a significant contribution towards decarbonization, the management of maritime transportations and port operations may be of great interest. In this paper we focus on the use of hydrogen in medium size ferryboats traveling in the Adriatic Sea. Due to the high energy intensity needed for shipping, which batteries cannot provide, this industry still uses marine diesel fuel, emitting 1.2–1.25 billion tons of carbon dioxide equivalent each year (i.e., 3% of the global anthropogenic emissions) [21]. The solutions being currently investigated in the maritime transportation sector include not just H_2, but also ammonia and methanol, of which hydrogen is a building block [22]. The naval industry is expected to require 46 million tons of green H_2 by 2050, with the vast majority (73%) being used to produce ammonia, accounting for more than half of the total naval energy consumption. However, 183 million tons of ammonia would be required, which equals today's total worldwide production.

The performance of hydrogen production methods has been evaluated and compared in a number of recent articles from an energetic, economic and environmental perspective [23]. The literature reveals that, from a purely economic standpoint, the production of H_2 from fossil fuels currently represents the most practical method. Depending on the price of natural gas, Lee et al. report an LCOH from SMR of 1.8–2.3 $\$/kgH_2$ [24], whereas Ali Khan et al. identify a range between 1.38 and 2.3 $\$/kgH_2$ for grey hydrogen and 2.0–3.42 $\$/kgH_2$ with the addition of CCS for blue hydrogen [25]. It should however be pointed out that these prices are highly dependent on the cost of the natural gas feedstock.

To the best of the authors' knowledge, there are no comprehensive studies that compare various hydrogen generation systems based on all the abovementioned indicators (EROEI, LCOH and LCA) for the specific use of hydrogen in the maritime industry. The majority of the papers currently available to do not approach the topic from a comprehensive and interdisciplinary perspective, focusing instead on the analysis of single aspects. Whereas the approach presented in this paper includes energetic, economic and environmental factors, based on accurate material and energy balances and costs data. Additionally, the comparison of different hydrogen colors is frequently approached from an absolute standpoint rather than being related to a specific and practical context, resulting in the attainment of frequently disputed conclusions [13,26–28].

Process Simulation (PS) provides all the data required to assess the desired indicators, with material and energy balances computed via trustworthy and tested models. PS is normally used with confidence for process design, optimization and feasibility studies for chemical [29] and biological [30] processes. Target values can be obtained for all the desired indicators and impact categories by combining PS with EROEI estimation, LCOH calculation and LCA, thus allowing to evaluate the sustainability of the proposed technical solution at an early stage of the process design [31].

This paper describes how to use PS for the estimation of the performance indicators reported above for hydrogen production processes. Specifically, in Fig. 1 different methods to obtain hydrogen are compared: (i) green hydrogen, produced by electrolysis of water using electricity from renewable sources; (ii) grid hydrogen, again by water electrolysis but using grid electricity; (iii) grey hydrogen, produced from natural gas using steam reforming; and (iv) blue hydrogen, which is obtained like the grey one, but coupled with carbon capture and storage (CCS). A block diagram of hydrogen production for maritime transportation considered in this paper is schematically shown in Fig. 2.

Floating photovoltaic (FPV) systems will be considered as power generators for the production of green hydrogen, as FPV greatly facilitates the applicability of hydrogen production in coastal areas. Recent estimations indicate that FPV will produce 10% of the solar energy by 2030 [32]. FPV shows several advantages compared to onshore PV: high power density, no fixed structures, simple decommissioning and low environmental impact: these advantages are counterbalanced by higher investment costs compared to onshore PV.

As far as blue hydrogen is concerned, an environmentally friendly, yet mature, carbon capture technology, based on chemical absorption with hot potassium carbonate, is considered in this work.

As a case study, this paper refers to the production of hydrogen required for a medium size ferryboat to navigate for 7 h, full electric, in the Adriatic Sea, with an energy requirement of about 275 MWh. Considering an energy content of hydrogen of 140 MJ/kg and an efficiency of fuel cells of 60%, the quantity of hydrogen to be produced for a one-way trip is 11,750 kg. The production of hydrogen will be set to consider 2 trips per day.

This article presents two main innovative aspects: on one hand, a mature electrolyser technology coupled with FPV energy generation is simulated, designed and compared with conventional SMR (with and without CCS) processes for hydrogen energy production, dedicated to fuel ferryboats in the Adriatic Sea. On the other hand, a quantitative comparison between alternatives is presented, demonstrating how the outcomes of process simulation in terms of mass balance, energy balance and equipment cost evaluation may be effectively used for the *a priori* estimation of relevant indicators, such as the EROEI, LCOH and LCA. These indicators are helpful in defining long-term strategies for the growth of domestic and global H_2 energy systems for port operations and maritime transportations.

The paper is organized as follows: section Hydrogen production processes describes in detail the different hydrogen production processes considered and the implementation in the corresponding process simulations; section Methods reports the methods used for the estimation of capital and operating costs, as well as the computation of the EROEI, LCOH, and LCA indicators; section Results And Discussion presents and examines the outcomes of the previously discussed evaluations; lastly, section Conclusions summarizes the main conclusions.

Hydrogen production processes

Aspen Plus v. 12.1™ was used to simulate all the processes considered. The software allowed to estimate physical property values, perform material and energy balances, design/rating calculations, sensitivity analyses and process optimization for any hydrogen generation process that was taken

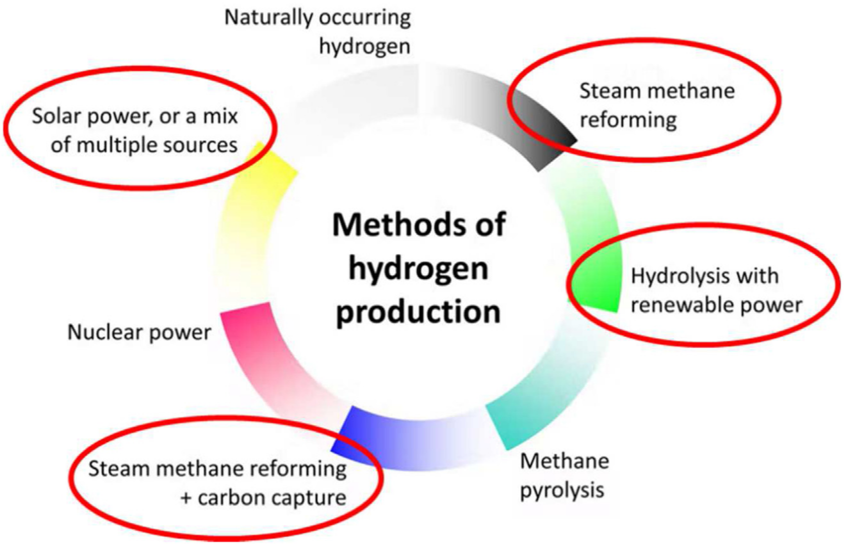

Fig. 1 – Hydrogen production methods considered in this work.

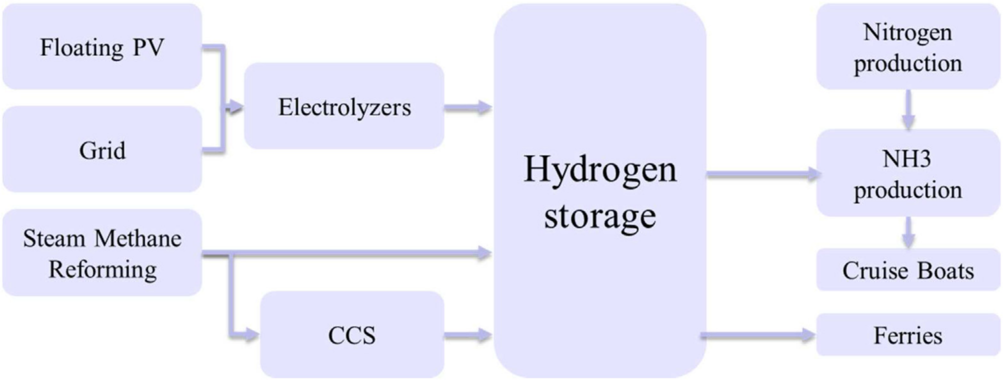

Fig. 2 – Block diagram of hydrogen production for maritime transportation including NH_3 production.

into consideration. Aspen Process Economics Analyzer™ (APEA) was used for economic analysis to retrieve the capital and operating expenses of each process, while Aspen Energy Analyzer™ (AEA) was used to perform heat integration by pinch analysis to decrease the overall energy duty.

In process simulators, constants and equations for the most common unit operations are already built-into the system, so that it is only necessary to develop the process flowsheet selecting the unit models, thermodynamic and reaction models and methods of solution. For non-conventional unit operations (such as the electrolysers), the material and energy balance equations were implemented by means of an Excel spreadsheet coupled with the Aspen Plus simulator. The equations are solved, the results are subsequently analyzed and the procedure is repeated until the whole process is finally optimized.

Grey hydrogen: steam methane reforming production process

Natural gas is converted to grey hydrogen using steam methane reforming (SMR). The SMR process flowsheet previously developed by Mio et al. [33] was appropriately upscaled to meet the daily hydrogen production of about 1000 kg/h. All the process unit operations employed the Redlich-Kwong-Soave equation of state with Boston Mathias modifications (RKS-BM) as thermodynamic model. In Fig. 3, the process flow diagram is displayed.

The processes is comprised of the following steps: (i) hydro-desulfurization treatment to remove sulphur (DESULF-R), (ii) natural gas reaction with steam in a primary reformer (PREF-T) at 30 bar and 500 °C–900 °C, (iii) natural gas reaction in a secondary reformer (SREF-R), where hot compressed air is added, (iv) water-gas shift (HT-WGS) in a high-temperature reactor (T = 380–460 °C), (v) water-gas shift (LT-WGS) in a low-temperature reactor (T = 210–270 °C) and finally (vi) hydrogen purification in the unit H-PUR, which recovers pure H_2 at a pressure of 26 bar.

The main reactions occurring in the reformers involve the catalytic conversion of methane into a mixture of CO, CO_2 and H_2, at high temperature and pressure (T = 500–900 °C, P = 30–34 bar) over Ni catalyst supported on alumina ceramics, according to the following stoichiometry:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad (\Delta H_R = 206\ \text{kJ / mol}) \tag{1}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (\Delta H_R = -41\ \text{kJ / mol}) \tag{2}$$

The reformers are modelled as plug-flow reactors (RPlug), where reaction kinetics, heat transfer rate (the net reaction is endothermic) and pressure drops are rigorously modelled by means of Fortran user subroutines [34].

In WGS reactors, the H_2 yield is increased by favoring reaction (2) over iron oxide and copper oxide catalysts in the HT and LT reactors, respectively. Both units are modelled as plug-flow reactors (RPlug), with user-defined reaction kinetics.

Heat integration was implemented to minimize the energy duties. In fact, heating duties are completely satisfied by means of process streams, except for the furnace, where the tail gases recovered after hydrogen purification are burnt together with natural gas to satisfy the heating duty of the primary reformer. Instead, the heat available from the hot products of the reformers and WGS reactors are used to preheat the reactants as well as to generate the steam required by the primary reformer. More details of the SMR process are reported in Ref. [33].

Blue hydrogen: steam methane reforming with CCS

Blue hydrogen is produced by capturing CO_2 from the flue gas output generated by the SMR process described above, using a suitable solvent. In previous papers [33,35] different amines have been used as solvent: in this paper a hot potassium carbonate (HPC) solution is used, since it represents a more environmentally friendly option, while still being a mature technology [36]. In fact, HPC is a non-volatile and non-toxic inorganic salt, which makes it not susceptible to oxidative degradation (which may be a problem with amines when working with flue gases), as well as fully recoverable within the process, while amines tend to be lost in the gaseous stream from the head of the absorption column. The only drawback of HPC is that it needs to be compressed to moderate pressures (6–8 bar) to enhance the reaction kinetics.

The HPC CCS process flowsheet is reported in Fig. 4. The FLUEGAS out stream (20 mol% of CO_2, 435 °C, 1 bar) from the SMR process is cooled down to 35 °C in a series of heat

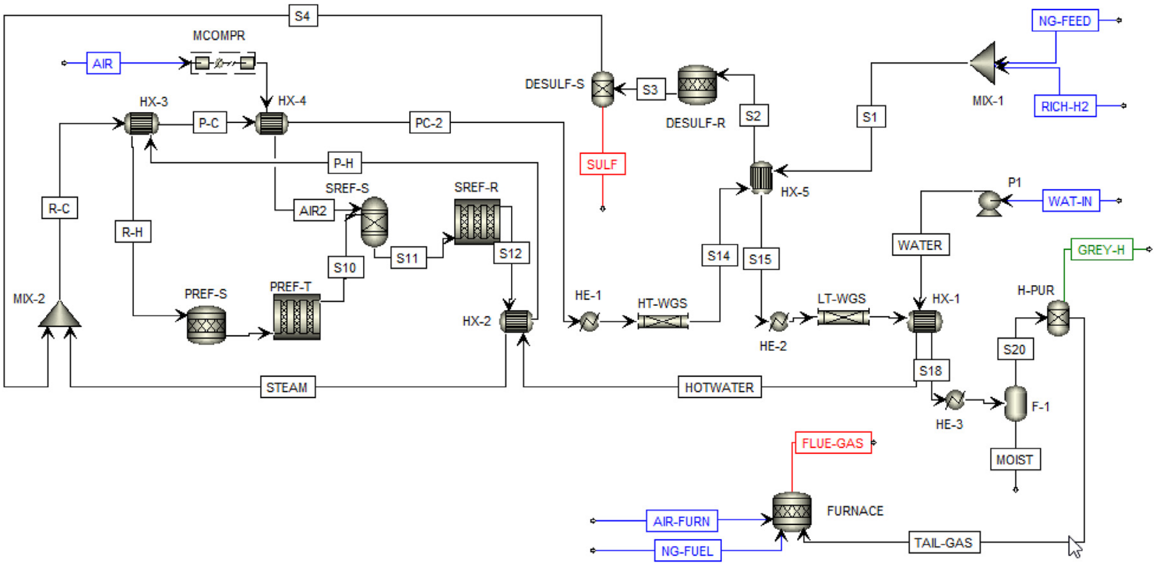

Fig. 3 – Aspen Plus process flowsheet of the SMR process as implemented in Aspen Plus.[34] Inlet streams are depicted in blue, hydrogen product in green, and by-products in red. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

exchangers, compressed to 6 bar by means of a two-stage compressor (K-101), and fed to the absorption column at 65 °C, counter-current to the lean potassium carbonate solution (LEANIN, 65 °C). The heat available from the flue gases is used to partially offset the reboiler duty of the following high-pressure stripper (HP-STRIP), which operates at 127 °C. The absorber (height H = 15 m and diameter D = 1.5 m) captures 91% of the CO_2 from the inlet gases. The high-pressure clean gas from the top of the column is sent to a turbo-expander (K-102) coupled with the compressor, to reduce the power demand by about 50%. The rich solution is then regenerated by means of a dual pressure system: 60% of the solution (RICHIN-H) is fed to a reboiled stripper operating at 2.1 bar (HP-STRIP), while the remaining 40% (RICHIN-L) is regenerated in a lower-pressure stripper (LP-STRIP) at 1.2 bar, exploiting the partial gasification of the lean solution from the HP unit upon pressure reduction. CO_2 is recovered from the top of both columns, after gas-liquid separation (T = 45 °C (HE-4+V-102)), at a purity of 99.9 mol% on dry basis. More information on the HPC CCS process is reported in Ref. [35].

Green hydrogen: water electrolysis from renewables

Green hydrogen, often referred to as renewable hydrogen, is H_2 produced by water electrolysis using renewable energy sources such as photovoltaics, wind, hydro, geothermal and biomass.

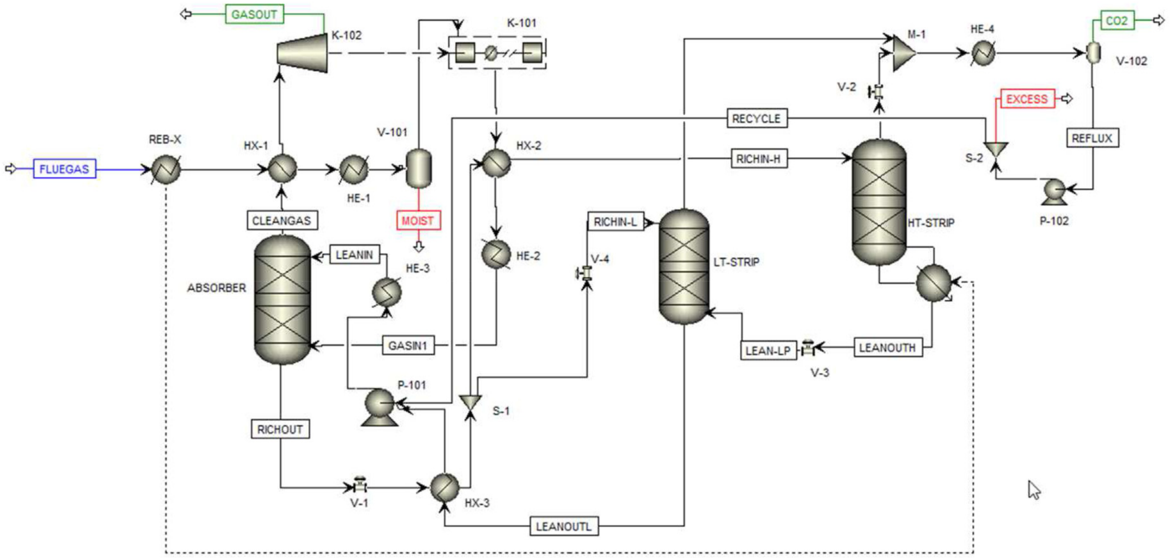

Fig. 4 – Aspen Plus flowsheet[34] of CCS process designed to capture CO_2 from the FLUEGAS stream of SMR, using a hot potassium carbonate (HPC) solution.

For the purpose of producing green hydrogen, it is assumed that the electrolysers run at a high capacity factor (cf = 0.97), utilising all of the electrical energy provided by a local floating photovoltaic system with a total installed capacity of 55 MWp and the remaining energy needed coming from an Italian green grid energy supplier. As a result, when evaluating the indicators, both the cost of installing the FPV plant and the provider's green energy prices must be considered (section Capital and operating costs).

Water electrolysis (WE) is the electrochemical separation of water into hydrogen and oxygen due to the application of an electrical voltage:

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2 \tag{3}$$

The voltage that must be applied to the electrolytic cell (V_{cell}) is determined by adding the reversible voltage (V_{rev}), which is the minimum voltage necessary for the reaction to occur and is determined by thermodynamics, to a number of overvoltages brought on by ohmic resistances (V_{ohm}), restrictions on electrode kinetics (i.e., activation overvoltage, V_{act}), and mass transfer (concentration overvoltage V_{conc}):

$$V_{cell} = V_{rev} + V_{ohm} + V_{act} + V_{conc} \tag{4}$$

The type of electrolyte used to separate the two half-reactions occurring at the anode (oxygen evolution reaction) and at the cathode (hydrogen evolution reaction) is what categorises different water electrolysis technologies. The core of an electrolysis process is the cell stack, which is made up of several electrolytic cells connected in series, as well as the balance of plant (BoP), which consists of all the additional units required for product purification, liquid recirculation and other operations.

In this paper we have considered the most mature electrolyser technology, namely the Alkaline Electrolysis Cell (AEC). The process flowsheet developed in Aspen Plus™ is shown in Fig. 5.

In order to produce the required daily hydrogen stock, the system is composed by 6 electrolyser modules operating in parallel. The design is based on the largest single stack alkaline electrolyser currently developed (Asahi Kasei), made of 170 cells and characterized by a maximum input power of 10 MW [37]. The BoP equipment is instead shared among the 6 modules.

Since Aspen Plus does not support electrolysis stack models, the relevant material and energy balance equations were added using a user-defined unit block with Microsoft Excel. In the stack, the electrodes are immersed in a liquid electrolyte separated by a diaphragm. The electrolyte solution (ST-IN, with 35 wt% KOH) is continuously recirculated within the stack. The semi-reactions occurring at the electrodes are the following:

$$\text{Cathode}: 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{5}$$

$$\text{Anode}: 2OH^- \rightarrow \frac{1}{2}O_2 + H_2O + 2e^- \tag{6}$$

Water is thus created at the anode and consumed at the cathode, requiring mixing of the two recirculated liquid streams before they enter the electrolyser. Material and energy balances were computed according to the model by Sánchez et al. [38] which includes calculating cell voltage, Faraday efficiency and gas product purity as a function of temperature, pressure, and current density. From this, the stack power (W_{stack}), hydrogen and oxygen production rates and heat release (Q_{stack}) are calculated. Based on the findings of the same authors, the stacks are operated at 80 °C, 5 bar, and 2500 A/m^2, with 170 series-connected cells having an active area of 11.5 m^2, with a resulting input power of 9.2 MW for each stack.

The liquid electrolyte and product gases produced at the cathode (H2-STACK) and anode (O2-STACK) are transferred through liquid-gas separation vessels (SEP-H2 and SEP-O2, respectively). The recovered liquid electrolyte is then circulated as the gases travel through water traps to remove humidity, feeding make-up deionized water (H2O-FEED) to the oxygen separation vessel. The Elec-NRTL thermodynamic model was used for all process units. For a fair comparison with the previous grey and blue hydrogen routes, the purified H_2 is compressed to 25 bar by means of a 2-stage compressor (C-1).

The main characteristics and performances of the AEC considered in this work are summarized in Table 1.

Grid hydrogen: water electrolysis from grid electricity

In this case, all electrical energy required to achieve the target hydrogen generation is drawn straight from the grid with the available energy mix, which comprises both renewable and fossil sources and no FPV system is considered. Furthermore, in this case the electrolysers are operating at high capacity factor (cf = 0.97). The composition of the energy mix considered (Italy's energy mix) is listed in Table 2, together with that of the mix acquired from a green electricity supplier, which produces electrical energy using a well specified energy mix for green hydrogen production. In this case, the share of the original mix attributed to fossil fuels has been distributed to renewable sources, keeping constant the ratio between each contributor to green electricity production mix.

Methods

Capital and operating costs

The capital costs (CAPEX) (€) of all the processes considered were calculated by means of Aspen Plus Economic Analysers. In particular, the value of the total installed cost (TIC) obtained by Aspen Plus is utilised to calculate the plant Fixed Capital Investment (FCI), according to the procedure proposed by Douglas [44]. The CAPEX is then estimated by adding the Start-up Cost (SC), which is estimated to be 10% of FCI, according to:

$$CAPEX = FCI + SC = 1.1 \cdot FCI = 1.1 \cdot \frac{TIC}{0.6} \tag{7}$$

Since electrolysers are non-conventional units in Aspen Plus, their investment cost is estimated according to market values [45] for green and grid hydrogen.

For green hydrogen, CAPEX includes the price of FPV system installation and acquisition, estimated to be 30% higher

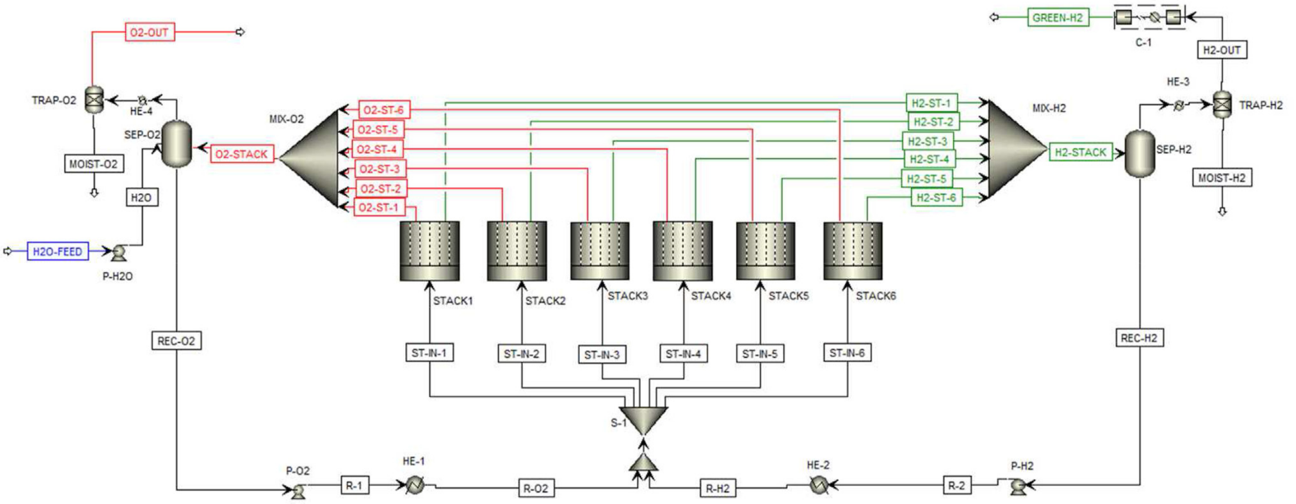

Fig. 5 – Aspen Plus flowsheet[34] of Alkaline Electrolysis Cells (AEC).

Table 1 – Summary of the main characteristics and performances of AEC.

Element	Value
Electrolyte	KOH (35 wt%)
Cathode	Ni
Anode	Ni
Cell area (m2)	11.5
Number of cells	170
Operating temperature (°C)	80
Current density (A/m2)	2500
Stack power single stack (MW)	9.18
Stack power total (MW)	55.11
System efficiency (HHV)	70.2
Specific electric energy consumption (kWh/kgH2)	56.13
Lifetime (years)	20
Stack duration (years) [39]	10
Capacity factor	0.97
Electrolyser cost (€/kW) [40]	938
Cost of stack replacement (% CAPEX) [39]	50%

Table 2 – Grid and green electrical energy mix [41] and EROEI [42,43] of the fuels used in the calculations (section Energy Return on Energy Invested (EROEI)).

Resource	EROEI	Grid energy mix	Green energy mix
Oil	19	3.16%	0.0%
Natural Gas	19	44.29%	0.0%
Coal	46	4.58%	0.0%
Nuclear	14	4.63%	0.0%
Hydro	84	19.48%	44.93%
PV	25	8.27%	19.09%
Waste	2	1.76%	4.06%
Biofuels	1.8	5.65%	13.05%
Wind	18	6.25%	14.41%
Geothermal	13	1.93%	4.44%
Tide	5	0.003%	0.007%

than the cost of an onshore PV plant of approximatively the same size. Assuming a cost of 800 k€/MW for the onshore PV, the cost of FPV is estimated to be 1040 k€/MW [46]. Higher structural costs related to the floats and anchoring system and complex design are the largest contributors to the higher CAPEX of FPV. Nonetheless, in cases where land use is constrained, not easily accessible, or land leasing is expensive, FPV could be an interesting alternative to on-shore PV systems. In addition to reducing land use competition, FPV can potentially provide advantages such as reducing evaporation from water bodies, enabling dual-use installation with aquaculture, and increasing energy yield [46]. FPV has experienced significant growth since 2016, but is still at an early stage of development, and additional experience, best practice and new configurations and technologies could help reduce the costs of FPV systems over time.

Concerning operating expenditures (OPEX), they can be distinguished into fixed and variable costs. For grey and blue hydrogen processes, water, chemicals, and catalysts are examples of necessary consumables, while fuel costs are accounted separately. Direct labour, administration/general overheads, insurance/local taxes, and maintenance are instead fixed OPEX. The total yearly OPEX are assumed to be a fixed proportion of the CAPEX, namely 8.7% for grey hydrogen via SMR and 9.5% for blue hydrogen via SMR + CCS [45].

For green and grid hydrogen production, variable OPEX refer to the cost of water feed as well as to the expected annuitized stack replacement costs as reported in Table 1 [47]. As for the other two processes, direct labour, administration/general overheads, insurance/local taxes and maintenance represent the fixed OPEX. Regardless of the electrolyser technology, fixed OPEX are most frequently modelled as a percentage of the initial CAPEX (generally estimated to be between 1 and 3% of the electrolyser CAPEX) [48]. According to what is described by Glenk et al. [47], a fixed OPEX cost of 2% of the total CAPEX is used in this case, while the total OPEX, after adding the variable costs, amounts to 3.06% of CAPEX.

Energy return on energy invested (EROEI)

The Net Energy Analysis (NEA) is a tool for comparing various energy production systems. The purpose of NEA is to determine whether any process under consideration produces more energy than is needed to construct, run and maintain the infrastructure. The most appropriate indicator for the processes of interest among those that can be obtained from NEA is the EROEI, which is defined as:

$$EROEI = E_{out}/E_{in} \tag{8}$$

where E_{out} is the available energy that the process provides (GWh). In the case of hydrogen production processes, E_{out} is defined as:

$$E_{out} = (HHV_{H2} \cdot Q_{H2} - P_{aux}) \cdot cf \cdot L \tag{9}$$

where HHV_{H2} is the higher heating value of hydrogen (kWh/kg), Q_{H2} is the flow rate of hydrogen produced (kg/h), cf is the capacity factor (namely the fraction of time the process is productive), P_{aux} is the power consumed by process auxiliaries (kW) and L is the estimated total time of operation of the production process (hours).

E_{in} is the total energy provided and consumed during the production and operations periods of the plant, and is made up of three contributions:

$$E_{in} = E_{cap} + E_{o\&m} + E_f \tag{10}$$

In equation (10), E_{cap} is the capital energy embodied in the materials and used for construction and decommissioning of the plant; $E_{o\$m}$ is the energy needed for operating and maintaining the plant; E_f is the energy needed for procuring and distributing the fuels, which also includes the energy used for extracting, refining and transporting the fuels from the production well to the plant. All terms are expressed in GWh for consistency: the EROEI is thus dimensionless.

The capital energy embodied in the materials and used for construction and decommissioning of the plant, E_{cap}, is defined as follows:

$$E_{cap} = CAPEX\ /\varepsilon_c \tag{11}$$

Where CAPEX (€) is defined in equation (7), and ε_c is the proportionality coefficient between the costs of energy and CAPEX. In this work ε_c is considered constant and is evaluated from real plant data [49].

The energy needed for operating and maintaining the plant, $E_{o\$m}$, is defined as:

$$E_{o\&m} = E_{cap} \cdot L \cdot OPEX_{year} \tag{12}$$

where $OPEX_{year}$ includes fixed and variable OPEX for each production technology considered. It is calculated as % of CAPEX per year (section Grid hydrogen: water electrolysis from grid electricity), according to:

$$OPEX_{year} = s_{o\&m} \cdot \left(1 + \frac{CSRE}{CAPEX}\right) \tag{13}$$

where $s_{o\$m}$ is the share of the investment costs dedicated to operation and maintenance. CSRE is the cost [€] for the substitution of the electrolyser's stacks, defined as:

$$CSRE = CAPEX \cdot CRE\% \left(\frac{L}{L_{el}}\right) \tag{14}$$

where L_{el} is the period after which the electrolysers stack should be replaced and CRE% is the cost, expressed in % of CAPEX, for its substitution (Table 1). Clearly, CSRE is equal to 0 for grey and blue hydrogen.

The energy needed for procuring and distributing the fuels, E_f, is defined as:

$$E_f = \frac{E_{out}}{\eta \cdot EROEI_{fuel}} \tag{15}$$

Where η is the efficiency of transformation for the process of interest, $EROEI_{fuel}$ refers to the particular technology that is used to transform the source of energy (natural gas or solar irradiation in our case) into useable energy for the process [14]. Literature values of $EROEI_{fuel}$ from different recent sources are reported in Table 2. They consider all the boundaries of various types of EROEI analyses and the energy losses associated with the processing of fuel as it is transformed from "fuel at the wellhead" to consumer-ready fuels. For electrolysers, the calculation of EROEI is done considering the entire process from the source of energy (the solar energy) to the hydrogen produced.

Levelized cost of hydrogen (LCOH)

The Levelized Cost Of Hydrogen (LCOH) is an indicator specifically developed for hydrogen as an energy carrier. It is calculated as follows:

$$LCOH = \frac{Net\ Present\ Value\ of\ Total\ \ Costs}{Net\ Present\ Value\ of\ Hydrogen\ Production} \tag{16}$$

Specifically, the LCOH (€/kg) is calculated according to Fan et al. [27] as:

$$LCOH = \frac{CAPEX + \sum_{t=1}^{N} \frac{OPEX_{year}}{(1+r)^t}}{\sum_{t=1}^{N} \frac{HP_t}{(1+r)^t}} \tag{17}$$

Where CAPEX [€] is the initial capital investment, $OPEX_{year}$ [€] is the OPEX at year t, r [%] is the discount rate, and HP_t [kg_{H2}/hr] the hydrogen production at year t. By assuming that $OPEX_{year}$ and HP_t are constant over the years, the equation simplifies as:

$$LCOH = \frac{CAPEX + \left(EC + OPEX_{year}\right) \sum_{t=1}^{N} \frac{1}{(1+r)^t}}{HP_t \sum_{t=1}^{N} \frac{1}{(1+r)^t}} \tag{18}$$

where EC is the cost of the source of energy per year (€/year).

For electrolysers, EC is the cost of the electricity drawn from the grid, which is the entire amount of energy required for electrolysis in the case of grid hydrogen production and only the amount of energy required to make up for that which the FPV plant does not provide for green hydrogen. For green electrolysers EC is thus defined as follows:

$$EC = P_{elec} \cdot EL_{cost} \cdot (cf \cdot 8760 - 1300) \tag{19}$$

Where P_{elec} [MW] is the power supplied to the electrolysers from the grid, EL_{cost} [€/MWh] is the cost of the electricity [50], 8760 is the number of hours in a year, and 1300 is the annual yield of a 1 kWp photovoltaic plant operating at the considered location [51]. For grid electrolysers, EC is defined as in equation (19), without subtracting the 1300 h corresponding to photovoltaics yield.

For grey and blue hydrogen, EC is the cost of natural gas, which is calculated as follows:

$$EC = Q_{NG} \cdot NG_{cost} \cdot (cf \cdot 8760) \quad (20)$$

where NG_{cost} is the cost of natural gas per cubic meter [50] and Q_{NG} is the input volumetric flow rate of natural gas (Nm^3/h).

Life cycle assessment

The Life Cycle Assessment (LCA) is a method for calculating a product's emissions over the course of its whole service life, from the extraction and refining of raw materials to the manufacturing processes, usage, transport and disposal. The four following processes make up the LCA framework, which is comprehensively defined by ISO Standards [52,53]. The first is goal and scope, or the description of the study's characteristics, the second is the Life Cycle Inventory (LCI), or the gathering of material and energy balances over the course of a product system's life cycle, the third is the Life Cycle Impact Assessment (LCIA), or the evaluation of environmental performance across various environmental compartments using scores from several impact categories, and the forth is the interpretation, or the process of coming to conclusions about the study's findings. The findings of such investigations are frequently published using well-established impact methodologies, such as ReCiPe, CML2001, Environmental Footprint (EF) or Tool for Reduction and Assessment of Chemicals and Other Environmental Impacts (TRACI). The environmental performances of the product systems investigated in this paper have been evaluated using Recipe 2016 Midpoint (H) [54], which adopts the following impact categories: Global Warming Potential (GWP), Fine Particulate Matter Formation (PMFP), Stratospheric Ozone Depletion (ODP), Ionizing Radiation (IRP), Photochemical Oxidant Formation including human Health contributions (HOFP) and Ecosystem quality ones (EOFP), Human Toxicity Potential with cancer (HTPc) and non-cancer (HTPnc)-related impacts, Ecotoxicity Potential related to Freshwater (FETP), Marine (METP) and Terrestrial (TETP) perspectives, Freshwater (FEP) and Marine (MEP) Eutrophication Potential, Terrestrial Acidification (TAP), Land use (LOP), Mineral Resource Scarcity (SOP), Fossil Resource Scarcity (FFP), and Water Consumption Potential (WCP).

In this work, a comparative LCA study has been carried out, dealing with the identification of the most sustainable technology for hydrogen production, using “1 kg of hydrogen” as the functional unit. According to a cradle-to-gate perspective, the system boundary includes the extraction, refinement, and transportation of raw materials, energy, and fuels, as well as the infrastructure, machinery and equipment required for producing 1000 kg/h of hydrogen for the 20-year operation of the plant. Using a cut-off allocation approach, secondary data was gathered using ecoinvent v3.8, while primary data on the key processes was retrieved by using process simulation. In fact, the weight of SMR and CCS equipment, the electricity and heat demand, the raw material consumption and the main process emissions of all the processes, may all be determined by process simulation.

The data source for the impacts of stacks and BoP of electrolysers was the study published by Zhao et al. [39]. The assumptions on photovoltaic modules and efficiencies made by Barbera et al. [35] were applied to the installation of the photovoltaic plant, with the exception that the plant was placed on a floating dock.

Results and discussion

The complete material and energy balances for the hydrogen production processes considered and required for the assessment of the EROEI, LCOE, and LCA indicators, were obtained by process simulations. Table 3 provides a summary of the information needed to calculate each indicator.

Table 4 reports the results from the simulations of the various hydrogen production processes investigated in this work. AEC process has been considered for both green and grid hydrogen. In the former, the installed FPV plant provides the necessary electrical energy when it is operating, while a fully green energy source from the grid is used when the FPV is

Table 3 – Summary of data needed for the estimation of EROEI, LCOH and LCA.

Data	Units	EROEI	LCOH	LCA
Hydrogen production (Q_{H2})	kg/h	X	X	X
Higher heating value of hydrogen (HHV_{H2})	kWh/kg	X		
Power for auxiliary equipment (P_{aux})	kW	X	X	X
Inlet natural gas flow rate	Nm^3/h	X	X	X
Total capital cost (CAPEX)	€	X	X	
Proportion between CAPEX and energy cost for construction (ε_c)	€/kWh	X		
Capacity factor (cf)	–	X	X	X
Plant life time (L)	years	X	X	X
Efficiency	–	X		X
Share of investment costs for operation and maintenance ($s_{o\&m}$) - OPEX	%	X	X	
EROEI fuels	–	X		
Cost of replacement of electrolytic stack (CAPEX %)	%	X	X	
Period after which the electrolytic stack should be replaced	years	X	X	X
Power supplied to electrolysers	MW		X	X
Cost of the source of energy per year (electricity/natural gas)	€		X	
Total amount of materials	kg			X
Discount rate (r)	%		X	

Table 4 – Summary of the numerical data used for the evaluation of the performance indicators.

Data	Units	Grey H_2	Blue H_2	Grid H_2	Green H_2
Hydrogen production flow rate	kg/h	951.44	951.44	1003.85	1003.85
HHV hydrogen	kWh/kg	39.4	39.4	39.4	39.4
Power for auxiliary equipment (P_{aux})	kW	524.8	4349	1242	1242
Net Power output, P	kW	36,962	33,138	38,310	38,310
Volumetric flow rate of natural gas in input	Nm^3/h	4288	4288	–	–
Electrical power for electrolysers	MW	–	–	55.11	55.11
CAPEX	k€	22,338	38,390	54,504	54,504
PV plant CAPEX	k€	–	–	–	57,315
Ratio of the cost of energy and CAPEX, εc	€/kWh	0.656	0.656	0.656	0.656
capacity factor		0.80	0.80	0.97	0.97
Plant life time	years	20	20	20	20
Duration of electrolysers stack	years	–	–	10	10
Cost of replacement of electrolysers stack (% of CAPEX)	%	–	–	50	50
Round trip efficiency		0.76	0.69	0.85	0.85
% total cost for o&m – OPEX (no stack substitution), $s_{o\&m}$	%	0.087	0.095	0.02	0.02
Energy return of energy invested for fuels only		8	8	25	46
Discount rate	%	0.073	0.073	0.073	0.073
CAPEX per KW (OC)	€/kW	596	1024	1115	2564

not operating. Instead, in the case of grid hydrogen all of the electrical energy required for electrolysis is obtained from the grid using the Italian energy mix (see Table 2).

Hydrogen production flow rate is kept constant at a value of about 1000 kg/h for the different technologies compared. Consequently, the net power output is also almost constant at a value of around 37 MW. This production capacity fulfills the need of almost 23.5 tH_2/day required by the ferry boat to perform a daily return trip.

CAPEX and OPEX reported in Table 4 are well in agreement with the literature [45], with CAPEX ranging between 700 and 1300 €/kW for SMR and SMR + CCS, and between 500 and 1100 €/kW for AEC. The CAPEX for green hydrogen is higher than the literature range due to the rather high capital cost of the FPV, but it is compensated in the long term by the lower cost of electricity. The size of the FPV plant compatible with 55 MWp of power is estimated to be 1000 m × 300 m. As far as grid hydrogen is concerned, the main difference is related to the absence of the FPV plant in the system, which lowers the CAPEX compared to green hydrogen, but is balanced by a higher cost of electricity from the grid.

Table 4 clearly shows that adding CCS treatment of the flue gas significantly raises CAPEX (by 72%), and consequently OPEX, of blue hydrogen compared to the grey route, and that the overall plant efficiency drops as a result of the increased energy expenditure required for carbon capture. However, the inclusion of CCS results in a significant decrease in the carbon emission factor.

The capacity factor of grey and blue hydrogen has been fixed at a reasonable value lower than that of the electrolysers, according to literature values. The plant life time considered for all the cases compared was 20 years, and the discount rate was fixed at 0.073 for all considered cases.

The indicators described in section Hydrogen Production Processes are used to compare the production technologies investigated in this work. Table 5 summarizes the results obtained in terms of EROEI (equation (8)) and LCOH (equation (18)). EROEI is defined as the energy return of invested energy and the higher the value, the higher the energetic efficiency of the production process. As expected, EROEI is relatively low for the grey hydrogen, and is even lower when CCS is added to reduce the CO_2 emissions. Literature values of EROEI for grey hydrogen range between 2 and 3 [55], perfectly in line with the values obtained in this work. On the other hand, EROEI values for electrolysers are much higher compared to the SMR-based processes. This can be ascribed to the higher value of $EROEI_{fuels}$ of the energy mix characterizing green and grid hydrogen, compared to that of natural gas (Table 4). The best value of EROEI is the one obtained for the grid hydrogen production process (14.28), but not so different from the green hydrogen one (13.39).

Regarding LCOH, the values reported in Table 5 show that the cost of hydrogen produced by SMR without CCS is lower than the one obtained by AEC, and, as expected, the cost raises if CCS is applied. This result is in line with the literature, where LCOH of grey and blue hydrogen ranges between 1.5

Table 5 – EROEI and LCOH values for the different hydrogen colors considered (LCOH-2021 is estimated considering the costs of energy and natural gas in 2021, while the LCOH-2022 refers to the costs in 2022).

Quantity	Units	Grey H_2	Blue H_2	Grid H_2	Green H_2
E_{out}	GWh	5180.57	4644.65	6510.52	6510.52
E_{in}	GWh	945.37	1011.14	455.93	486.37
EROEI	–	5.48	4.59	14.28	13.39
LCOH-2021 cost of NG and electricity	€/kg	2.87	3.35	6.80	6.81
LCOH-2022 cost of NG and electricity	€/kg	5.01	5.50	9.10	8.76

and 2.5 €/kg, while for green hydrogen it is between 3 and 9 €/kg [40,56]. A detailed analysis of LCOH for renewable energy (solar and wind) hydrogen refueling station is available in literature [57,58] reporting values of LCOH from solar energy ranging from 2.92 to 4.83 €/kg (5.5–7.38 if hydrogen storage is included). Values of LCOH [59] from wind energy and hydrogen storage are slightly higher (6.24–11.5 €/kg). Considering that in this paper the cost of the refueling station is not included, the literature values compare well with the LCOH values evaluated in this paper.

Table 5 also shows the effect of the price of natural gas and electricity according to the Italian Regulatory Authority for Energy Networks and Environment [50], comparing the situation in 2021 (0.5 €/Nm^3 and 108 €/MWh) to the one at the end of 2022 (0.976 €/Nm^3 and 150 €/MWh). As expected the market price of natural gas plays a relevant role in the evaluation of the LCOH for these processes, while for electricity-based production processes its effect is mitigated by the contribution of other electricity sources. Higher price of electricity influences less the LCOH of green hydrogen due to the local electrical energy production provided by the FPV system.

The LCA procedure is based on material and energy balances over the entire life cycle of the product system, taking into consideration the extraction of raw materials, manufacturing, use phase, end-of-life and the transportation between life cycle stages. The results of life cycle assessments are represented by means of several impact categories, which are able to represent the entire range of ecological burdens associated with the product system, avoiding shifting the impact among environmental compartments.

The normalized results of LCA are shown in Fig. 6, while the absolute scores for the different impact categories are reported in Table 6.

The analysis of hydrogen produced by SMR, either alone (grey hydrogen), or in combination with CCS (blue hydrogen) shows that, except for GWP, all the other impact categories are negatively affected by CCS. This is due to the carbon capture process, which certainly reduces direct carbon dioxide emissions, but requires increased material and energy expenses, which worsen blue hydrogen environmental performances overall. Therefore, from a sustainability standpoint, blue hydrogen does not seem so appealing, which makes grey hydrogen worth being considered for comparison with other technologies, even if its CO_2 emissions are not mitigated by any capture process. For these reasons we have used grey hydrogen for comparison with green and grid hydrogen.

When considering hydrogen production from electrolysis using alkaline electrolysers, the selection of the most sustainable option is mainly driven by the source of electricity used for the required energy supply. In fact, since the electricity consumption is quite significant for running the AEC electrolysis process, the electricity mix plays a crucial role to reduce the overall environmental burdens. As clearly shown in Fig. 6, the grid hydrogen exhibits poor results for the majority of impact categories, and this effect is due to the emissions from the mix used for electricity generation in Italy. Green hydrogen shows large impacts where the effect of renewable electricity production is more significant, such as toxicity potentials (FETP, METP, TETP, HTP) due to raw materials extraction, ODP due to electricity production, and SOP, LOP and WCP for raw materials, land and biofuels procurement, respectively. Since the development of alternative hydrogen synthesis pathways is primarily focused on reducing GHG emissions, AEC has been compared to traditional fossil-based production, thanks to its GWP outcomes, higher technology readiness level (TRL) in comparison with other electrolyser technologies, and AEC's overall general performance, also in terms of EROEI and LCOH.

From a GHG reduction viewpoint, green hydrogen is the best method, with a score lower than blue hydrogen, which is the second-best option, followed by grey hydrogen and grid

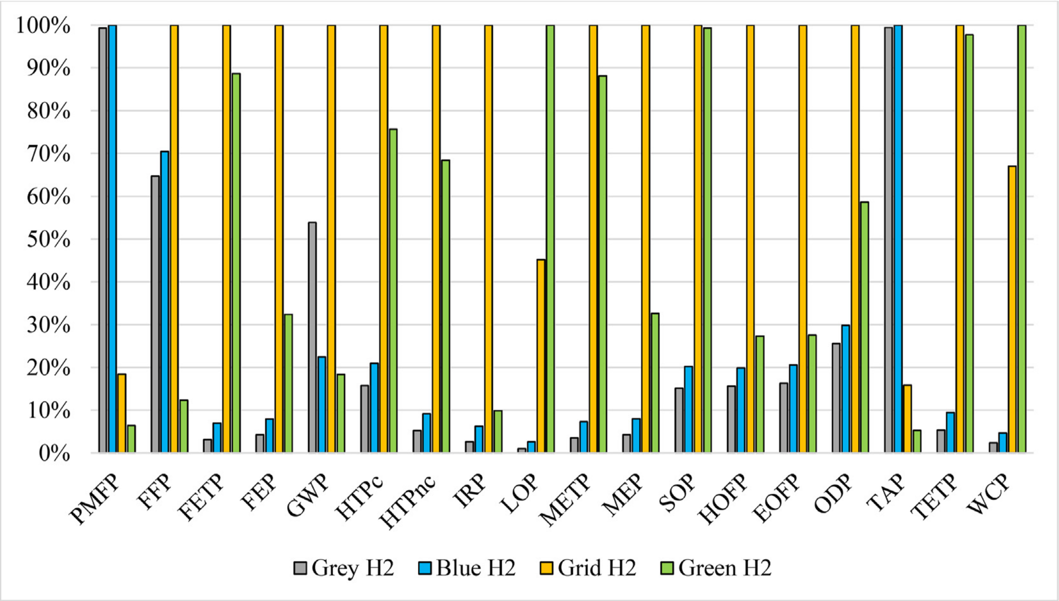

Fig. 6 – LCIA outcomes normalized for each hydrogen color. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 6 – Impact categories scores for the production of 1 kg of hydrogen using different production pathways.

Impact Category	Acronym	Unit	Grey H_2	Blue H_2	Grid H_2	Green H_2
Fine particulate matter formation	PMFP	kg PM2.5 eq	3.90E-03	4.91E-03	9.34E-03	2.68E-02
Fossil resource scarcity	FFP	kg oil eq	4.63E+00	5.04E+00	8.83E-01	7.15E+00
Freshwater ecotoxicity	FETP	kg 1,4-DCB	6.54E-02	1.43E-01	1.83E+00	2.06E+00
Freshwater eutrophication	FEP	kg P eq	2.40E-04	4.50E-04	1.84E-03	5.68E-03
Global warming	GWP	kg CO2 eq	1.26E+01	5.27E+00	4.32E+00	2.35E+01
Human carcinogenic toxicity	HTPc	kg 1,4-DCB	1.42E-01	1.88E-01	6.81E-01	9.00E-01
Human non-carcinogenic toxicity	HTPnc	kg 1,4-DCB	9.51E-01	1.66E+00	1.24E+01	1.82E+01
Ionizing radiation	IRP	kBq Co-60 eq	6.38E-02	1.53E-01	2.39E-01	2.43E+00
Land use	LOP	m2a crop eq	1.14E-02	2.87E-02	1.09E+00	4.94E-01
Marine ecotoxicity	METP	kg 1,4-DCB	9.07E-02	1.88E-01	2.26E+00	2.57E+00
Marine eutrophication	MEP	kg N eq	1.95E-05	3.67E-05	1.50E-04	4.60E-04
Mineral resource scarcity	SOP	kg Cu eq	7.76E-03	1.04E-02	5.10E-02	5.14E-02
Ozone formation, Human health	HOFP	kg NOx eq	6.29E-03	7.99E-03	1.10E-02	4.02E-02
Ozone formation, Terrestrial ecosystems	EOFP	kg NOx eq	6.69E-03	8.43E-03	1.13E-02	4.10E-02
Stratospheric ozone depletion	ODP	kg CFC11 eq	3.75E-06	4.36E-06	8.58E-06	1.46E-05
Terrestrial acidification	TAP	kg SO2 eq	1.20E-02	1.49E-02	2.66E-02	7.92E-02
Terrestrial ecotoxicity	TETP	kg 1,4-DCB	4.01E+00	7.07E+00	7.29E+01	7.46E+01
Water consumption	WCP	m3	1.22E-02	2.42E-02	5.21E-01	3.49E-01

hydrogen. Note that grid hydrogen, despite being based on a carbon-free feedstock, performs very poorly in terms of carbon emissions, due to the high specific energy consumption, which is derived for more than 50% by fossil sources.

As a result of LCA methodology, the use of alkaline electrolysers supplied with renewable energy produced by a dedicated floating photovoltaic plant (FPV) complemented by a green energy mix is the best option to reduce GHG emissions and, in general, most of the indicators related to air pollution (PMFP). However, care must be taken to minimize environmental impacts when different compartments are considered. There is still room for improvement regarding other impact categories, where the impacts of green hydrogen are larger than other hydrogen synthesis pathways. They are primarily related to the use of electricity, which accounts for the majority of each individual impact. The electricity emissions are mostly related to the construction and maintenance of the electricity grid, and the production of electricity using biofuels and other material-intensive technologies. Indeed, the extraction and processing of raw materials (especially metals) releases hazardous compounds into the aquatic environment, whereas the use of biofuels derived from dedicated plantations increases the need of fertilizers and land usage. This is aligned with other studies published in the scientific literature [60]. Therefore, it would be necessary to adopt less burdensome strategies for generating renewable electricity, such as minimizing the impact of the mining industry and avoiding the need of plantations dedicated to the production of biofuels. In this regard, there is a wide margin for improvement. Concerning land usage (LOP) green hydrogen appears to have a significantly larger impact compared to any other alternative, however the absolute score is equal to less than 6 m^2/kWp, which does not pose a concern, particularly when the PV plant is located offshore. Noteworthy, due to its large electricity consumption, grid hydrogen shows worst overall performances compared to green hydrogen, and for most of the impact categories even compared to grey hydrogen. Therefore, the choice of a renewable electricity mix is essential to provide a sustainable hydrogen.

Conclusions

This work aimed at establishing a rigorous method for the evaluation of the sustainability of hydrogen production and its use as a locally produced alternative fuel in logistical operations with focus on maritime transportation.

A major contribution of our paper is the extension of process simulation methodology to tackle a novel multidisciplinary approach, allowing a rigorous estimation of indicators such as the Energy Return on Energy Invested (EROEI), the Levelized Cost of Hydrogen (LCOH) and the Life Cycle Assessment (LCA). This methodology is entirely based on systematic process simulations to evaluate mass, energy balances, and capital and maintenance costs, to be done at design time during the development of a new process, without requiring real plant process data.

Although the suggested methodology is quite general, this paper focuses on the situation of a port with hydrogen-fueled ferryboats. Different technologies for producing hydrogen were considered: (i) water electrolysis powered by a floating PV plant coupled with renewable sources (green hydrogen), (ii) grid electricity (grid hydrogen) with electricity taken from the grid and (iii) hydrogen produced by steam methane reforming with and without carbon capture and storage (grey and blue hydrogen).

The indicators considered were the Energy Return on Energy Invested (EROEI), the Levelized Cost of Hydrogen (LCOH) and the Life Cycle Assessment (LCA). They allowed a quick and accurate comparison of various options while taking energy, economic and environmental factors into account. Comparing the indicators' values, it was concluded that green hydrogen is completely sustainable in terms of both energy use and greenhouse gas emissions. In addition, green hydrogen may be easier to deploy economically than blue one, when hydrogen is produced locally.

The integration of indicators' evaluation with process simulation ensures a double benefit: (i) the scope of process simulation is extended by considering up-to-date indicators of impact on energy, economy and environment and (ii) the evaluation of any new process may be performed at design time. The values of the key performance indicators showed that the best route for producing hydrogen in terms of global impact is the green hydrogen, based on electrolysis of water with electricity produced by a floating photovoltaic system, although further improvements should be employed to reduce the environmental impacts besides GHG emissions.

Credit author contributions statement

Andrea Mio: Investigation, Software, Data curation, Formal analysis, Writing - original draft.
Elena Barbera: Investigation, Software, Data curation, Formal analysis, Writing - original draft.
Alessandro Massi Pavan: Conceptualization, Writing - review & editing.
Alberto Bertucco: Conceptualization, Supervision, Writing - review & editing.
Maurizio Fermeglia: Conceptualization, Methodology, Data curation, Supervision, Writing - original draft, Writing - review & editing.

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.

Acknowledgements

This research did not receive any specific grants from funding agencies in the public, commercial, or not-for-profit sectors.

REFERENCES

[1] Syvitski J, Waters CN, Day J, Milliman JD, Summerhayes C, Steffen W, et al. Extraordinary human energy consumption and resultant geological impacts beginning around 1950 CE initiated the proposed Anthropocene Epoch. n.d Commun Earth Environ 2022. https://doi.org/10.1038/s43247-020-00029-y.

[2] IPCC. AR6 synthesis report: climate change. 2023. n.d, https://www.ipcc.ch/report/sixth-assessment-report-cycle/. [Accessed 20 December 2022].

[3] IEA. Net zero by 2050 – analysis. n.d, https://www.iea.org/reports/net-zero-by-2050. [Accessed 20 December 2022].

[4] Staffell I, Scamman D, Velazquez Abad A, Balcombe P, Dodds PE, Ekins P, et al. The role of hydrogen and fuel cells in the global energy system. Energy Environ Sci 2019;12:463–91. https://doi.org/10.1039/C8EE01157E.

[5] Noh H, Kang K, Seo Y. Environmental and energy efficiency assessments of offshore hydrogen supply chains utilizing compressed gaseous hydrogen, liquefied hydrogen, liquid organic hydrogen carriers and ammonia. Int J Hydrogen Energy 2023;48(20):7515–32.

[6] Ahmadi P, Khoshnevisan A. Dynamic simulation and lifecycle assessment of hydrogen fuel cell electric vehicles considering various hydrogen production methods. Int J Hydrogen Energy 2022;47(62):26758–69.

[7] Liu W, Wan Y, Xiong Y, Gao P. Green hydrogen standard in China: standard and evaluation of low-carbon hydrogen, clean hydrogen, and renewable hydrogen. Int J Hydrogen Energy 2022;47(58):24584–91.

[8] Dilshani A, Wijayananda A, Rathnayake M. Life cycle net energy and global warming impact assessment for hydrogen production via decomposition of ammonia recovered from source-separated human urine. Int J Hydrogen Energy 2022;47(57):24093–106.

[9] Zhang J, Ling B, He Y, Zhu Y, Wang Z. Life cycle assessment of three types of hydrogen production methods using solar energy. Int J Hydrogen Energy 2022;47(30):14158–68.

[10] Iannuzzi L, Hilbert JA, Silva Lora EE. Life Cycle Assessment (LCA) for use on renewable sourced hydrogen fuel cell buses vs diesel engines buses in the city of Rosario, Argentina, 2021. Int J Hydrogen Energy 2021;46(57):29694–705.

[11] Fuel Cells and Hydrogen 2 Joint Undertaking. Hydrogen roadmap Europe : a sustainable pathway for the European energy transition. 2019.

[12] Ministero delle Imprese e del Made in Italy. Pnrr - piano Nazionale di Ripresa e Resilienza. 2022.

[13] Howarth RW, Jacobson MZ. How green is blue hydrogen? Energy Sci Eng 2021;9:1676–87. https://doi.org/10.1002/ese3.956.

[14] Hall CAS, Lambert JG, Balogh SB. EROI of different fuels and the implications for society. Energy Pol 2014;64:141–52. https://doi.org/10.1016/j.enpol.2013.05.049.

[15] EIA - US Energy Information Administration. Annual energy outlook. 2013. 2013.

[16] Minutillo M, Perna A, Forcina A, Di Micco S, Jannelli E. Analyzing the levelized cost of hydrogen in refueling stations with on-site hydrogen production via water electrolysis in the Italian scenario. Int J Hydrogen Energy 2021;46:13667–77. https://doi.org/10.1016/J.IJHYDENE.2020.11.110.

[17] EC-JRC. ILCD handbook - general guide for life cycle assessment. 2010. https://doi.org/10.2788/38479.

[18] Mio A, Fermeglia M. Multiscale modelling techniques in life cycle assessment: application to product design. Procedia CIRP 2022;105:688–93. https://doi.org/10.1016/J.PROCIR.2022.02.115.

[19] Mio A, Bertagna S, Cozzarini L, Laurini E, Bucci V, Marinò A, et al. Multiscale modelling techniques in life cycle assessment: application to nanostructured polymer systems in the maritime industry. Sustain Mater Technol 2021;29. https://doi.org/10.1016/j.susmat.2021.e00327.

[20] Petrescu L, Burca S, Fermeglia M, Mio A, Cormos CC. Process simulation coupled with LCA for the evaluation of liquid - liquid extraction processes of phenol from aqueous streams. J Water Process Eng 2021;41. https://doi.org/10.1016/j.jwpe.2021.102077.

[21] Lindstad E, Lagemann B, Rialland A, Gamlem GM, Valland A. Reduction of maritime GHG emissions and the potential role of E-fuels. Transp Res Part D Transp Environ 2021;101:103075. https://doi.org/10.1016/J.TRD.2021.103075.

[22] Gray N, McDonagh S, O'Shea R, Smyth B, Murphy JD. Decarbonising ships, planes and trucks: an analysis of suitable low-carbon fuels for the maritime, aviation and haulage sectors. Adv Appl Energy 2021;1. https://doi.org/10.1016/J.ADAPEN.2021.100008.

[23] Ji M, Wang J. Review and comparison of various hydrogen production methods based on costs and life cycle impact assessment indicators. Int J Hydrogen Energy 2021;46:38612–35. https://doi.org/10.1016/J.IJHYDENE.2021.09.142.

[24] Lee S, Kim HS, Park J, Kang BM, Cho CH, Lim H, et al. Scenario-based techno-economic analysis of steam methane reforming process for hydrogen production. Appl Sci 2021;11. https://doi.org/10.3390/app11136021.

[25] Ali Khan MH, Daiyan R, Neal P, Haque N, MacGill I, Amal R. A framework for assessing economics of blue hydrogen production from steam methane reforming using carbon capture storage & utilisation. Int J Hydrogen Energy 2021;46:22685–706. https://doi.org/10.1016/J.IJHYDENE.2021.04.104.

[26] Romano MC, Antonini C, Bardow A, Bertsch V, Brandon NP, Brouwer J, et al. Comment on "How green is blue hydrogen?". Energy Sci Eng 2022;10:1944–54. https://doi.org/10.1002/ESE3.1126.

[27] Fan JL, Yu P, Li K, Xu M, Zhang X. A levelized cost of hydrogen (LCOH) comparison of coal-to-hydrogen with CCS and water electrolysis powered by renewable energy in China. Energy 2022;242:123003. https://doi.org/10.1016/j.energy.2021.123003.

[28] Bauer C, Treyer K, Antonini C, Bergerson J, Gazzani M, Gencer E, et al. On the climate impacts of blue hydrogen production. Sustain Energy Fuels 2021;6:66–75. https://doi.org/10.1039/D1SE01508G.

[29] Barbera E, Mantoan F, Bertucco A, Bezzo F. Hydrogenation to convert CO2 to C1 chemicals: technical comparison of different alternatives by process simulation. Can J Chem Eng 2020;98:1893–906. https://doi.org/10.1002/cjce.23755.

[30] Barbera E, Sforza E, Musolino V, Kumar S, Bertucco A. Nutrient recycling in large-scale microalgal production: mass and energy analysis of two recovery strategies by process simulation. Chem Eng Res Des 2018;132:785–94. https://doi.org/10.1016/j.cherd.2018.02.028.

[31] Turton R, Bailie RC, Whiting WB, Shaeiwitz JA. Analysis, design and synthesis of chemical processes. 2008.

[32] International Renewable Energy Agency. Renewable energy statistics 2022. 2022.

[33] Mio A, Barbera E, Massi Pavan A, Danielis R, Bertucco A, Fermeglia M. Analysis of the energetic, economic, and environmental performance of hydrogen utilization for port logistic activities. Appl Energy 2022;347:121431. https://doi.org/10.1016/j.apenergy.2023.121431.

[34] Aspen Technology Inc. Aspen Plus ammonia model. 2008.

[35] Barbera E, Mio A, Pavan AM, Bertucco A, Fermeglia M. Fuelling power plants by natural gas: an analysis of energy efficiency, economical aspects and environmental footprint based on detailed process simulation of the whole carbon capture and storage system. Energy Convers Manag 2022;252. https://doi.org/10.1016/j.enconman.2021.115072.

[36] Giammarco-Vetrococke Engineering s.r.l. Personal communication. 2019.

[37] Fujita Y. Asahi kasei's activities for green hydrogen production. 2022.

[38] Sánchez M, Amores E, Abad D, Rodríguez L, Clemente-Jul C. Aspen Plus model of an alkaline electrolysis system for hydrogen production. Int J Hydrogen Energy 2020;45:3916–29. https://doi.org/10.1016/J.IJHYDENE.2019.12.027.

[39] Zhao G, Kraglund MR, Frandsen HL, Wulff AC, Jensen SH, Chen M, et al. Life cycle assessment of H2O electrolysis technologies. Int J Hydrogen Energy 2020;45:23765–81. https://doi.org/10.1016/J.IJHYDENE.2020.05.282.

[40] Christensen A. Assessment of hydrogen production costs from electrolysis: United States and Europe. 2020.

[41] IEA. Key energy statistics. 2020 [Italy n.d].

[42] King LC, Van Den Bergh JCJM. Implications of net energy-return-on-investment for a low-carbon energy transition. Nat Energy 2018;3:334–40. https://doi.org/10.1038/s41560-018-0116-1.

[43] Capellán-Pérez I, de Castro C, Miguel González LJ. Dynamic Energy Return on Energy Investment (EROI) and material requirements in scenarios of global transition to renewable energies. Energy Strategy Rev 2019;26:100399. https://doi.org/10.1016/J.ESR.2019.100399.

[44] Douglas JM. Conceptual design of chemical processes. McGraw-Hill; 1988.

[45] UK Government - BEIS. Hydrogen production costs by production 2021. 2021.

[46] Ramasamy V, Margolis R. Floating photovoltaic system cost benchmark: Q1 2021 installations on artificial water bodies. Natl Renew Energy Lab 2021;1:1–15.

[47] Glenk G, Reichelstein S. Economics of converting renewable power to hydrogen. Nat Energy 2019;4:216–22. https://doi.org/10.1038/s41560-019-0326-1.

[48] Brynolf S, Taljegard M, Grahn M, Hansson J. Electrofuels for the transport sector: a review of production costs. Renew Sustain Energy Rev 2018;81:1887–905. https://doi.org/10.1016/j.rser.2017.05.288.

[49] Sgouridis S, Carbajales-Dale M, Csala D, Chiesa M, Bardi U. Comparative net energy analysis of renewable electricity and carbon capture and storage. Nat Energy 2019;4:456–65. https://doi.org/10.1038/s41560-019-0365-7.

[50] Italian Regulatory Authority for Energy Networks and Environment (ARERA). Dati e statistiche [n.d].

[51] European Commission. Photovoltaic geographical information system [n.d].

[52] International Standard Organization. ISO 14040 series -environmental management – life cycle assessment – principles and framework. 2006. Geneva, Switzerland.

[53] The International Standards Organisation. ISO 14044 Environmental management — life cycle assessment — requirements and guidelines, vol. 2006; 2006.

[54] Huijbregts MAJ, Steinmann ZJN, Elshout PMF, Stam G, Verones F, Vieira M, et al. ReCiPe 2016: a harmonised life cycle impact assessment method at midpoint and endpoint level. Int J Life Cycle Assess 2017;22:138–47. https://doi.org/10.1007/s11367-016-1246-y.

[55] Palmer G, Roberts A, Hoadley A, Dargaville R, Honnery D. Life-cycle greenhouse gas emissions and net energy assessment of large-scale hydrogen production via electrolysis and solar PV. Energy Environ Sci 2021;14:5113–31. https://doi.org/10.1039/d1ee01288f.

[56] IEA - International Energy Agency. Global hydrogen review. 2021 [n.d].

[57] Barhoumi EM, Okonkwo PC, Farhani S, Ben Belgacem I, Zghaibeh M, Mansir IB, Bacha F. Techno-economic analysis of photovoltaic-hydrogen refueling station case study: a transport company Tunis-Tunisia. Int J Hydrogen Energy 2022;47(58):24523–32.

[58] Barhoumi EM, Okonkwo PC, Ben Belgacem I, Zghaibeh M, Tlili I. Optimal sizing of photovoltaic systems based green hydrogen refueling stations case study Oman. Int J Hydrogen Energy 2022;47(75):31964–73.

[59] Barhoumi EM, Salhi MS, Okonkwo PC, Ben Belgacem I, Farhani S, Zghaibeh M, Bacha F. Techno-economic optimization of wind energy based hydrogen refueling station case study Salalah city Oman. Int J Hydrogen Energy 2023;48(26):9529–39.

[60] Mehmeti A, Angelis-Dimakis A, Arampatzis G, McPhail SJ, Ulgiati S. Life cycle assessment and water footprint of hydrogen production methods: from conventional to emerging technologies. Environ 2018;5:24. https://doi.org/10.3390/ENVIRONMENTS5020024. 2018;5:24.