



Original article

Analysis of photon-driven solar-to-hydrogen production methods in the Netherlands

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ABSTRACT

Hydrogen is deemed necessary for the realization of a sustainable society, especially when renewable energy is used to generate hydrogen. As most of the photon-driven hydrogen production methods are not commercially available yet, this study has investigated the techno-economic and overall performance of four different solar-to-hydrogen methods and photovoltaics-based electrolysis methods in the Netherlands. It was found that the photovoltaics-based electrolysis is the cheapest option with production cost of 9.31 \$/kgH₂. Production cost based on photo-catalytic water splitting, direct bio-photolysis, and photoelectrochemical water splitting are found to be 18.32 \$/kgH₂, 18.45 \$/kgH₂, and 18.98 \$/kgH₂, respectively. These costs are expected to drop significantly in the future. Direct bio-photolysis (potential cost of 3.10 \$/kgH₂) and photo-catalytic water splitting (3.12 \$/kgH₂) may become cheaper than photovoltaics-based electrolysis. Based on preferences of three fictional technology investors, i.e. a short-term, a green and a visionary investor, the overall performance of these methods are determined. Photovoltaics-based electrolysis is the most ideal option, with photoelectrochemical water splitting a complementary option. While photovoltaics-based electrolysis has an advantage on the short-term because it is a non-integrated energy system, on the long-term this might lead to relatively higher cost and performance limitations. Photochemical water splitting are integrated energy systems and have an advantage on the long-term because they need a relatively low theoretical overpotential and benefit from increasing temperatures. Both methods show performance improvements by the use of quantum dots. Bio-photolysis can be self-sustaining and can use wastewater to produce hydrogen but sudden temperature changes could lead to performance decrease.

Introduction

The emerging renewable energy transition to combat climate change leads to many positive changes. Still, there are obstacles to overcome before the transition can be fully completed. Mainly two major obstacles make that renewables have a long way to go before they can play a significant role in the global economy. The first is that on a large scale fossil fuels are still heavily subsidized which makes it difficult for renewable energy to penetrate the energy markets [1]. Another problem is that renewable energy sources such as wind and solar energy, which are two of the most adopted sources of renewable energy production, are not consistently available due to the intermittent nature of these sources [2]. This leads to potential imbalance problems in the electricity grid. To overcome this problem energy storage can be a viable solution [3].

Hydrogen is an energy carrier which can be used to store energy. At

the moment the Netherlands is one of the biggest producers of hydrogen in Europe with an energy content of about 110 PJ/yr [4]. It is produced mostly from non-renewable energy sources and is therefore not sustainable. In the Netherlands, hydrogen plays already a large role in the industrial sector, and this is expected to continue in the future. Therefore, looking into renewable produced hydrogen is necessary for a more sustainable future [4]. An example of a renewable hydrogen production method is photovoltaic (PV) electricity used in electrolysis, an indirect method, which is a commercial option already. Utilizing energy from other photon-driven solar-to-hydrogen (STH) methods have promising prospects because of the relatively high theoretical efficiency potential and potentially lower cost than the indirect hydrogen production methods [5]. Although a lot of research has been done on the theoretical aspects of these direct renewable hydrogen production methods, the actual technologies are not yet adopted commercially, nor are they

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experimentally researched in non-laboratory environments on a large scale [6]. Hence, a knowledge gap exists related to the performance, potential, and cost of these renewable hydrogen production options. Therefore, in this study, the techno-economic performance and overall performance of several photon-driven STH methods is assessed in comparison to the mature STH method PV-Electrolysis. The scope is limited to the photon-driven STH methods by the use of water splitting (WS). Thus, two main photon-driven hydrogen production methods (photochemical water splitting and bio-photolysis) are compared to the reference method (PV-Electrolysis). The photochemical water splitting method can be subdivided into photoelectrochemical water splitting (PEC-WS) and photocatalytic WS (PC-WS). The bio-photolysis (BP) method can be subdivided into direct and indirect bio-photolysis (DBP, IBP). A description of the basic principles underlying these methods is provided below.

Hydrogen can be produced in many ways, which leads to different ‘types’ of hydrogen: Grey Hydrogen (produced used fossil-fuel based technology), Blue Hydrogen (climate-neutral using carbon capture and storage technologies), and Green Hydrogen (using renewables) [7]. In this study, only Green Hydrogen is investigated. An overview of the researched technologies is presented in Fig. 1.

Photochemical water splitting

There are two types of photochemical water splitting methods, termed photoelectrochemical (PEC-WS) and photocatalytic WS (PC-WS). We note that in literature, there is no consensus on this distinction: PC and PEC are frequently used interchangeably. There are many similarities between these two methods. In essence, the same steps occur for both methods, but for PC-WS all processes take place in single particles,

whereas for PEC-WS the different components are separated [8].

PC-WS is in some literature referred to as particulate photo-catalytic water splitting [9] or as Type 1 or Type 2 reactors of the PC-WS methods. While processes are similar, the main difference in reactor types is that O₂ and H₂ are produced separately in Type 2 reactors, which makes for a more flexible and safer energy system [10,11], whereas in Type 1 reactors this is not the case. Our study focuses on Type 2 reactors, as most of the literature refers to this type. A schematic representation of hydrogen production via PC-WS is shown in Fig. 2.

Photoelectrochemical water splitting is also referred to as a Type 3 or Type 4 reactor. A Type 3 reactor is a fixed panel, while a Type 4 reactor makes use of a solar concentrator to optimize the energy uptake [10,11]. As in most of the previous research on PEC-WS one refers to Type 3 reactors, also in this study the focus is on the Type 3 reactor. The most common catalysts that are utilized for a PEC-WS system have a metal oxide included, due to the fact that they have a high level of electrochemical stability, are relatively cheap, and come in a wide range of band gaps [12]. Especially a combination of Platinum (Pt) and Iridium Oxide (IrO₂), or a combination of Pt and Titanium Oxide (TiO₂), is often utilized [13], although also much research is done on implementing Iron Oxide (Fe₂O₃) because of its high STH efficiency potential [14]. A schematic representation of hydrogen production via PEC-WS is shown in Fig. 2.

Bio-Photolysis

Direct bio-photolysis is an aerobic process, while indirect bio-photolysis is an anaerobic process [15]. For the latter, CO₂ is temporarily sequestered and fermentation takes place due to this anaerobic process [15]. The schematic of both methods can be found at Fig. 3.

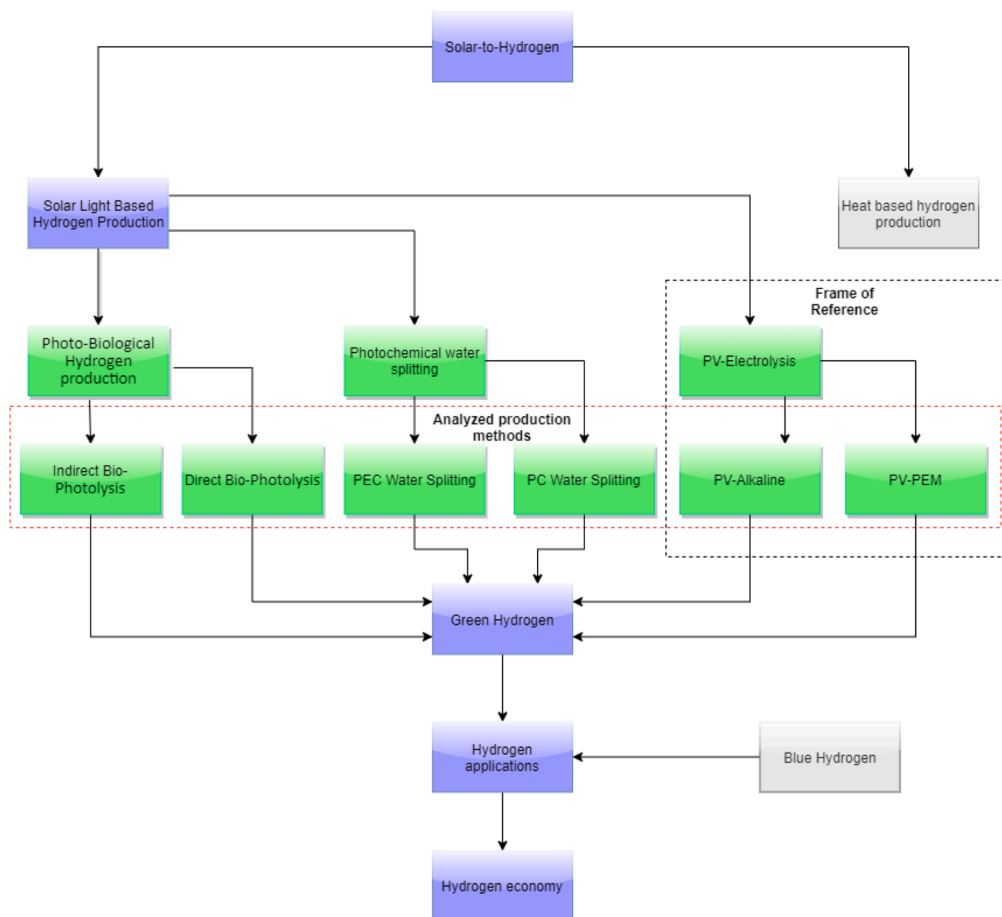


Fig. 1. Overview of technologies researched based on the scientific knowledge of the photon-driven hydrogen production Methods. The green squares refer to the technologies that are investigated in this study, while the blue squares refer to the independent variables that are related to these technologies and which are referred to in this research. The light grey squares are independent variables that are not addressed in this study. The black dotted line refers to the Frame of Reference, which indicates the reference STH Methods. The red dotted line frames the STH methods that are researched in this study.

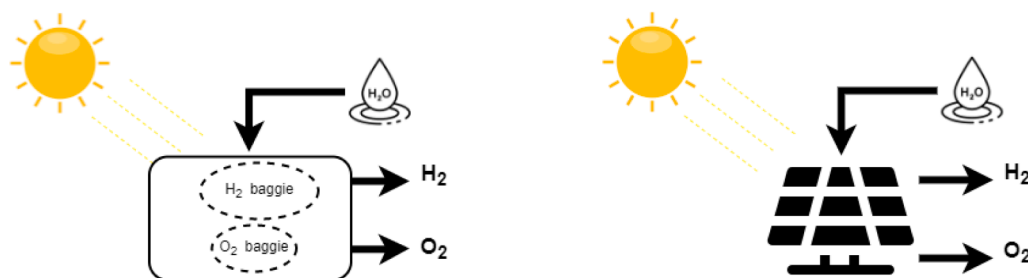


Fig. 2. Schematic of PC-WS for hydrogen production (left) and PEC-WS for hydrogen production (right). For PC-WS the production of H₂ and O₂ takes place in so-called ‘baggies’ [10]. This is a plastic casing in which all the particles are contained, while light can penetrate [11]. PEC-WS is different to PV-Electrolysis since it is a production method in which via an integrated solar panel hydrogen is produced directly.

Analysis of Photon-Driven H₂ production

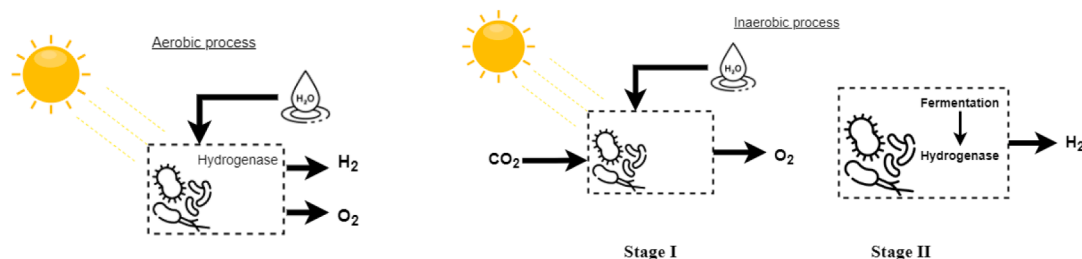


Fig. 3. Schematic for DBP (left) and IBP (right). Bio-photolysis is a light-dependent process. Photosynthesis makes it possible to split water molecules and produce hydrogen. Using the incoming solar light for the production is done by bio-photolysis. Both methods commonly utilizes microalgae like green algae, more specifically the single-cell *Chlamydomonas reinhardtii* algae [16,17], as hydrogenase is present in the microalgae. This is important since it enables the catalysis for CO₂ reduction and hydrogen formation [18]. Generally, cyanobacteria or green algae are considered for this process and hydrogenase and nitrogenase enzymes are utilized as catalysts [19]. The cyanobacteria are commonly mutants of *Anabaena* and the green algae are *Chlamydomonas reinhardtii* algae [20].

PV-Electrolysis

With PV-electrolysis hydrogen is produced via an indirect method utilizing PV electricity that powers an electrolyser. A schematic is given in Fig. 4. Both PV and electrolysers are mature technologies, but currently only a few percent of global hydrogen is produced in this way [21]. The most common water electrolyser methods are the alkaline electrolyser and the polymer electrolyte membrane or proton exchange membrane (PEM) electrolyser [22]. Both generate hydrogen and oxygen by using a cathode and anode.

Research objective

The assessment in this paper is performed using literature review combined with techno-economic modelling, and a model to investigate

the overall performance of each STH method. As a result, the current development status of these STH methods is highlighted. While the focus of the study is on the situation in the Netherlands, results can be used on a wider geographical scale.

In the overall performance analysis, next to the techno-economic analysis, several other factors that influence the implementation potential on the energy market in the Netherlands are taken into account. In this way, this research adds knowledge on a very specific segment of renewable hydrogen production methods and makes a clear and elaborate overview of the performance from a broad perspective of different photon-driven STH methods. Since the Netherlands, like in other countries, has different kinds of stakeholders with motives to invest in the specific technologies, three fictional stakeholders are selected to represent variety in potential investors. These stakeholders are termed: Short-Term Investor, Green Investor, and Visionary Investor, and are

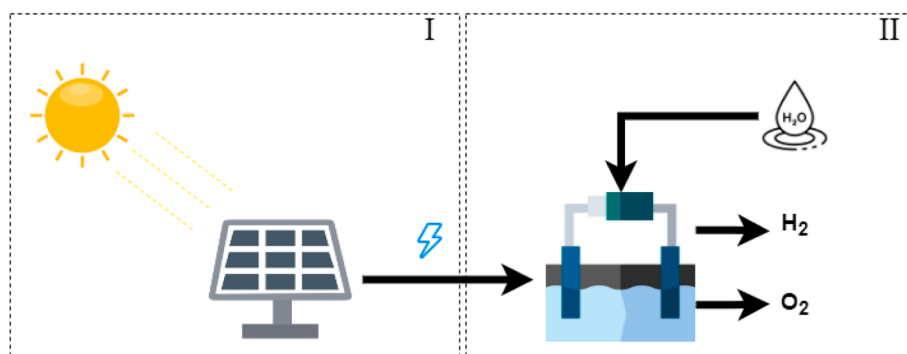


Fig. 4. Schematic of PV-electrolysis: An indirect hydrogen production method in which first electricity is generated via the PV cell and that electricity is utilized in the electrolyzer to produce hydrogen.

used in a novel multicriteria analysis approach as outlined in the Methodology section.

The rest of this paper is organized as follows. In Section 2 the used methodology is described, followed by results in Section 3. A discussion is presented in Section 4 and the paper is concluded in Section 5.

Methodology

The research consists of a literature review concerning the Technology Readiness Level (TRL), the Levelised Cost of Hydrogen (LCOH), other general parameters, and specific key parameters. The input found related to the STH efficiencies, the LCOH, and the other general parameters are used as input for a Multicriteria Analysis (MCA) to model the outcomes by taking into account the preferences of the different stakeholders.

LCOH

For the techno-economic analysis, the LCOH is calculated for all methods and it is assumed that they are operated off-grid. The results are expressed in \$ per kgH₂ (we use kgH₂ as proxy for energy) and are obtained via the following equation:

$$LCOH = \frac{\sum_t^n \frac{I_0 + OM_t + F_t}{(1+r)^t}}{\sum_t^n \frac{E_t}{(1+r)^t}} \tag{1}$$

where I_0 is Initial Investment Costs (CAPEX), OM_t yearly Operation and Maintenance Costs, F_t annual Fuel Costs, r inflation rate corrected Discount Rate, E_t annual Energy Production, and n is the total economic lifetime of the energy system [23]. Data from literature is, when necessary, converted to and expressed as \$/m² and corrected for the Consumer Price Index of 2020 to find the corresponding cost for the photoactive area, and sometimes land area, needed for each STH method. The price in 2020 (p_{2020}) is calculated as follows:

$$p_{2020} = p_Y * \frac{CPI_{2020}}{CPI_Y} \tag{2}$$

where p_Y is the price in year Y (in \$), CPI_{2020} the dimensionless Consumer Price Index of 2020, and CPI_Y the Consumer Price Index of year Y .

For the LCOH calculations, the most common materials/semiconductors and photocatalysts are taken for the techno-economic analysis. Table 1 gives an overview of the researched STH methods for the techno-economic analysis in this study, including the methods used as the frame of reference (Fig. 1). Specific materials and catalysts are selected for the LCOH calculation.

The system's energy efficiency refers to the STH efficiency, which can be calculated by determining several variables like the incoming solar irradiance and the operating current density. In the Netherlands, long-term average annual global horizontal solar irradiance (GHI) is 1030 kWh/m² per year, or 3.72 GJ/m². Direct normal irradiance (DNI) is 885 kWh/m² per year or 3.19 GJ/m² [24]. The annual energy yield E_t , i.e., the amount of hydrogen production in kg, of each STH method is

calculated by multiplying the GHI (in GJ/m²) by the STH efficiency (η_{STH}), area A (in m²) and performance ratio PR [25], and dividing it by the lower heating value (LHV_{H_2}) of hydrogen (GJ/kg), as follows:

$$E_t = \frac{GHI \times A \times STH_{efficiency} \times PR}{LHV_{H_2}} \tag{3}$$

The unitless PR is taken as 0.84, in case of PV-Electrolysis and PEC-WS, and equals unity for the other methods. Literature values of STH are assumed to be realizable in the Netherlands as well. To compare the different photon-driven STH methods several fixed and assumed parameters are considered for the calculation of the LCOH. The parameters are presented in Table 2.

Sensitivity analyses are executed to find the effects of specific parameters on the LCOH of each STH method. One of the most important parameters is the investment cost or CAPEX. This depends on many variables, namely reactors/module(s), semiconductor(s), membrane(s), (photo) catalyst(s), Balance of System (BoS) cost, installation cost, engineering cost, and/or labour cost. The range of initial investment cost is set to 20%, unless a specific range was found in the literature. This is chosen since in many previous studies there is no consensus on the range for this parameter and 20% is a significant range. In Table 3, the parameters of the sensitivity analyses are indicated and the range of the values or an interval is given. One of the main parameters is solar irradiance. The variation interval for this parameter is taken from 3.00 GJ/m² (about 20% lower than in the Netherlands, and about the GHI of south-west Norway, to 6.50 GJ/m², which is about the GHI of southern parts of Spain [24]). This range is selected to see the effects if the hydrogen would be produced in different areas of Europe. The range for the operation and maintenance cost and the discount range is based on previous research by Detz et al. [27]. For the contingency cost parameter the range is based on the findings in the literature for all the STH

Table 2

Overview of the fixed parameters for the calculation of the LCOH of the different STH methods. Also, several values are presented that are assumed for this research based on multiple sources.

Parameter	Value	Unit	Source
GHI	3.72 (De Bilt, the Netherlands)	GJ/m ² /year	[24]
hydrogen production	10,000	kg/day	[10,11,13,26]
construction period	1	year	[13,26]
O&M Cost	0.5% of CAPEX plus potential replacement cost	\$	[27]
inflation rate	1.9	%	[13,26,27]
discount rate	12	%	[13,26,27]
land cost	0.15	\$/m ² _{land}	[26]
economic life	20	year	[10,11,13,26]
land area	1.3 × photoactive area	m ²	[10,11]
water consumption	89,678	t/day	[10,11,28]

Table 1

Overview of the different STH methods that are investigated in this study. They are divided into overarching methods and also subdivided into sub-methods. c-Si is crystalline silicon.

Overarching STH method	Sub-method	Photoactive material(s)	Photocatalyst(s)	Extra/other
PV-Electrolysis	PV-PEM electrolysis	c-Si	electrocatalyst not specified	non-integrated system, external components: PV cell and electrolyser (PEM)
Photochemical	PC-WS PEC-WS	TiO ₂ & Fe ₂ O ₃ c-Si	TiO ₂ & Fe ₂ O ₃ combination of Pt & IrO ₂	integrated system on particle level, Type 2 reactor. integrated system, Type 3 reactor.
Bio-Photolysis	DBP IBP	green algae (Chlamydomonas reinhardtii) cyanobacteria (mutants of Anabaena)	hydrogenase enzymes hydrogenase and nitrogenase enzymes	integrated system integrated system

Table 3

Overview of the parameters of the sensitivity analysis for the LCOH with the range/interval.

Parameter	Initial value	Range/interval
Solar irradiance (GHI)	3.72 (De Bilt, the Netherlands)	3.00–6.50 GJ/ $m^2/year$
STH efficiency	STH dependent	range from literature (STH dependent)
initial investment cost	STH dependent	–20% - +20%
operation and maintenance costs (excluding the replacement cost)	0.5% of CAPEX	0.3–1.0%
contingency cost PV-electrolysis	10% of CAPEX	5–15%
contingency cost other STH methods	20% of CAPEX	10–30%
discount rate	12%	5–20%
electrolyser & PEC cell lifetime	5 years	3–10 years
baggie lifetime	7 years	5–10 years

methods, except for the reference STH method [10,11,26]. For the PV-Electrolysis method the same range of 50% higher and lower is assumed as range for the sensitivity analysis. The ranges of the baggies lifetime are based on and inspired by previous research for baggies [10,11] and for the electrolyser and PEC cell [26].

Overall performance analysis

Other aspects and parameters, which are not directly included in the LCOH, are of importance for a technology to be implemented in energy markets. Since this also largely depends on the preferences of stakeholders a multicriteria analysis (MCA) is performed to account for that. Lastly, the specific key parameters give insight on more abstract, qualitative, and/or incomparable parameters.

The other general parameters which are considered are potential (future) STH efficiency, theoretical STH efficiency, safety risks, relative carbon footprint (RCF), minimum (tested) stable operation time (MTSOT), and upscaling potential. These are selected since they are an important influence on the performance of the STH methods or because they are of importance for the current or future situation in the Netherlands.

Record-high efficiencies of STH methods tend to achieve these efficiencies for a short time (sometimes only for seconds) and under standard test conditions (STC) only. Therefore, the potential energy efficiency is rather an indication of what the STH efficiency might be in the nearby future, while the theoretical STH efficiency reflects a theoretical limit.

Safety risks refer here to the probability that the splitting of water might lead to (large scale) explosions or other hazards. Implementing this parameter in the MCA could be interpreted as straightforward since no technology can be utilized on a larger scale without considering safety.

The carbon footprint of the STH methods is mainly the result of the materials used for the process of producing these STH methods. Still, since most of the STH methods are not implemented yet the actual carbon emissions are not known for all STH methods and therefore a relative carbon footprint estimate is taken as data input.

Since the Netherlands is already producing a large amount of hydrogen, making the transition towards more sustainable hydrogen production should also be possible in terms of upscaling. Therefore upscale potential is taken as parameter to find which STH methods are, at this stage, able to produce high quantities of hydrogen without too many obstacles.

The minimum (tested) stable operation time relates to the stability of the STH methods during a specific operation time. It was assumed that the operation time of a specific technology should be sufficient and stable for 500–1000 h at minimum, without too many losses in efficiencies or other important performance aspects.

Finally, the overall performance may also be enhanced and/or

limited by method-specific key performance parameters. These parameters are specific to one or several STH methods, are mostly qualitatively based, or incomparable between the other STH methods and are not implemented in the MCA.

Multicriteria analysis

After all the relevant data was obtained and analysed it was used as input for the MCA with a weighted summation method. Here, all the chosen parameters are assigned a specific weight corresponding to the level of importance related to the preferences of a specific stakeholder. Based on the preferences of various stakeholders the different parameters have different effects on the relative implementation potential. The MCA was performed by the use of the software Definite/BOSDA [29].

The different components are given a weight corresponding to the selected level of importance for each stakeholder. Three fictional investors are looked at as stakeholders. These are: the Short-Term Investor, the Green Investor, and the Visionary Investor. These three types of stakeholders are chosen since they represent different real-life preferences.

The Short-Term Investor

For this stakeholder, the LCOH parameter is taken to be the most important parameter. Least important is the theoretical STH efficiency and the RCF since the theoretical STH efficiency is something that might never be realized in practice and concerning the carbon footprint a lot is still unknown. At this time, no carbon tax is introduced and there is a lot of uncertainty about how and when it might be introduced. However, when this would change this would be of great importance as well to reduce the cost.

The Green Investor

The motive of this investor is to be part of a green hydrogen economy and this investor thus values environmental benefits as much as economic ones. The stakeholder wants to reduce carbon footprint as much as possible, but at the same time wants to reduce LCOH as well. Safety is also of great importance. The upscaling potential and MTSOT are of importance too since they highlight the stability and scaling potential, which are of importance for such a nation-wide focused stakeholder. Less important is the theoretical STH efficiency since, although a high theoretical efficiency might indicate a better performance of an STH method in the (distant) future, currently it is not certain to what extent this could be reached.

The Visionary Investor

This type of stakeholder is created to show the relative implementation potential based on theoretical future demand and supply. It was chosen that this investor is not interested in short-term benefits but wants to contribute to a sustainable future by striving for the highest possible performances of the STH methods. Low current cost is important to make the vision a reality, but only to reach future goals. Because of this, the LCOH is important, but the potential STH efficiency and the RCF are far more important. The theoretical STH efficiency is of high importance, as it shows the performance limits of a potential efficiency in the future. The least important parameter is the current STH efficiency.

To test the robustness of the comparative outcomes for the MCA an uncertainty analysis was performed. For the eight input parameters three levels of uncertainty were chosen (low, medium, and high). Based on the findings in the literature a low uncertainty value range, 10%, was given to the theoretical STH efficiency, RCF, and upscaling potential because the corresponding values were relatively certain. Slightly more uncertain was the parameter safety risks since not much large scale research has been done on the safety risks of most STH methods. This was given a uncertainty of 20%. Current STH efficiency, LCOH, potential STH efficiency, and MTSOT were found to be most uncertain and were

given an uncertainty value range of 30%. Next to this, uncertainty ranges were given per stakeholder for the weight of each parameter depending on the assumed preferences. For weight distribution values that are expected not to have a high level of certainty a 10% uncertainty level is chosen, for medium 20%, and for relatively uncertain weight 30% (see Supplementary Information).

Research reflection and relevance

The choice for a techno-economic analysis to compare these STH methods is not uncommon. Since most of the STH methods are still strongly developing the aim was to look at studies that were published recently or that can be considered as highly influential and/or fundamental for the discipline. Two of the most influential and fundamental studies are performed by James et al. [10] and Shaner et al. [13]. Although these studies are not published recently, their assumptions and corresponding outcomes are still relevant. This is the case since for the LCOH not many studies have been performed on these STH methods in the past couple of years. Most of the studies related to these STH methods are based on energy performances, like STH efficiencies. Also, for this study the LCOH highlights only production of hydrogen and excludes transportation, storage, and other components of the hydrogen supply chain. For future studies we recommend looking into these aspects.

The research method, which we named the overall performance analysis, is the combination of the MCA and literature reviews of which the latter highlighted the qualitative and/or incomparable parameters. This has not yet been done in previous studies. There were some similar literature review studies on several of the STH methods or the specific STH methods, but to our knowledge there was no MCA performed that compared the STH methods on the LCOH and the other general parameters based on the preferences of different stakeholders. One of the biggest benefits of adding such a research method is that it considered more aspects when comparing technologies. Techno-economic analysis can lead to a simplified representation of the current state of a technology and adding the overall performance analysis takes into account aspects that are not highlighted by the techno-economic analysis, like carbon footprint, safety risks and several more. At the same time, there is a beneficial aspect to the techno-economic analysis that is not present when performing solely such an overall performance analysis. Overall performance analysis only looks at specifically chosen technologies, in this case, the five STH methods, and the outcomes cannot directly be compared to other technologies outside of the scope.

Results

Technology readiness level

We estimated the TRL levels of the three considered STH technologies, based on literature analysis. The TRL of PV-Electrolysis is 9 at it is used on a global scale in industry [19,30–34]. This holds for both the PV-alkaline and the PV-PEM electrolysis systems, which is also recognized by Parkinson et al. [35]. Combining the two technologies to either the PV-alkaline electrolysis or PV-PEM electrolysis does not lead to a lower TRL since that only occurs when the 'upgrade' of a technology implements new technologies [36].

Both the PEC-WS as the PC-WS methods are not implemented commercially. Most research on these STH methods is still performed in the laboratory and usually not in outside environments. Currently, most of the state-of-the-art research is no longer in the conceptual phase [37–39], but the methods are still only laboratory prototypes [40]. Therefore, a TRL of 5 is considered for PEC-WS and PC-WS.

DBP and IBP are also not developed to a commercial level yet. Dincer and Joshi [17] have shown that both methods have mainly been researched in the laboratory and on a small scale outside environment. Mahidhara et al. [41] confirm this. Hassan et al. [42] have found that

these two photon-driven hydrogen production methods still need a lot of research and it can be interpreted that these methods are only just past the 'concept' levels in the TRL scale. Experiments on these methods are performed but only in the laboratory environment. This is also confirmed in many other recent studies [19,43–45]. Therefore, the TRL of both DBP and IBP is interpreted to be 4.

Current STH efficiency

The current STH efficiencies are presented in Table 4, Table 5, and Table 6. The tables contain the different STH efficiencies of each overarching STH method. Also, the corresponding materials, the testing environment, and the corresponding sources are presented. Based on these tables average STH efficiencies are used in the rest of this paper, as follows: $11.4 \pm 1.9\%$ (PV-electrolysis), $10.6 \pm 1.2\%$ (PEC-WS), $0.7 \pm 0.4\%$ (PC-WS), $2.00 \pm 0.02\%$ (DBP), and $1.0 \pm 0.7\%$ (IBP).

LCOH

In this section, LCOH values for the different STH technologies are presented, including cost breakdowns. Fig. 5 presents the overall results.

The calculated LCOH for PV-electrolysis is 9.31 \$/kgH₂. For PEC-WS, PC-WS and DBP LCOH is about double, while the largest LCOH is found for IBP at a value of about four times that of PV-electrolysis. The cost breakdowns are shown in Figs. 6–8.

The LCOH breakdown for PV-electrolysis shows that mainly the hard balance-of-system (BoS) cost of the electrolysers have a large impact, with 30% of the total LCOH (Fig. 6). Of the other two influential components, soft BoS Cost (25%) and O&M Cost (22%), the component of the soft BoS Cost with the largest impact is the contingency cost with 7% of the LCOH. replacement cost (part of O&M cost) of the electrolysers is 14% of the LCOH.

The calculated LCOH for PEC-WS is 19.98 \$/kgH₂. Fig. 7 shows that the largest component is the O&M Cost. Of this component the replacement cost has the largest influence with 44% of the LCOH. The other influential component is the module cost, of which the membrane is the most expensive part with 8.6% of the LCOH. The contingency cost is the third most expensive component with 8.5% of the LCOH. For PC-WS, the calculated LCOH is 18.32 \$/kgH₂. The biggest component is the O&M Cost, mainly replacement cost with 45% of the LCOH. The second-largest component of the LCOH is the cost of the baggies (12%), which is part of the reactor cost. Two other components that have a large impact are contingency cost (8%), and installation cost (10%). Both are part of the soft BoS cost. The main differences between both methods is larger module cost for PEC-WS and a somewhat larger soft BoS cost for PC-WS.

For DBP, the LCOH was calculated to be 18.45 \$/kgH₂. The cost breakdown is presented in Fig. 8. The reactor cost is taken as an average from the previous studies since there was no consensus in the literature on the exact cost [15,67,19,68,69]. Almost 75% of the LCOH consist of bioreactor cost of which the bioreactor materials and nutrients cost are the largest part, totalling 63% of the LCOH. Another larger component of the LCOH is the contingency cost with 15%, as part of the soft BoS cost. The LCOH of IBP is twice as large compared to DBP at 36.39 \$/kgH₂, while cost breakdown is similar to that for DBP.

Other general parameters

Potential and theoretical STH efficiency

In Fig. 9, an overview of potential and theoretical STH efficiencies is given. These efficiencies are based on experimental research from reported studies and based on the theoretical limitations per STH method. The efficiencies for PV-electrolysis range from 16.9% [70] to 30% [9,71]. Both efficiencies were demonstrated for about 50 h. The other found efficiencies 18.00% [30], 18.10% [72], 22.40% [73], and 24.40% [74], were taken as input for the average potential STH efficiency (which is 22.83%) for use in the MCA. The theoretical efficiency is

Table 4

Overview of the STH efficiencies of PV-alkaline electrolysis and PV-PEM electrolysis. Per STH efficiency the specific testing environment and source are presented. AM1.5 is the incident solar light spectrum corresponding to Air Mass 1.5.

STH method	STH efficiency	Materials	Environment	Source
PV-Alkaline Electrolysis	11.9%	Perovskite + Alkaline (a multilayer anode nickel-iron hydroxide (NiFe) electrocatalyst layer coated on a nickel sulfide (NiS _x) layer formed on porous Ni foam (NiFe/NiS _x -Ni).	Laboratory AM1.5	[31]
	12.3%	Perovskite + Alkaline (Complemented by Earth-Abundant Electrocatalysts).	Laboratory AM1.5	[46]
	10.5%	III-V + Alkaline (Complemented by Stable Earth-Abundant Electrocatalysts).	Laboratory AM1.5	[47]
	12.3%	Perovskite + Alkaline (NiMoFe and NiMoFeP as Complementary Electrocatalysts).	Laboratory AM1.5	[48]
PV-PEM Electrolysis	9.8%	c-Si + PEM (Electrocatalyst not specified)	Laboratory AM1.5	[13]
	12.0%	c-Si + PEM (Electrocatalyst not specified)	Laboratory AM1.5	[49]
	8.1%	Solarex polycrystalline + PEM (Electrocatalyst not specified)	Laboratory AM1.5	[50]
	14.2%	c-Si + PEM (Earth-Abundant Electrocatalysts Nickel (Ni))	Laboratory AM1.5	[51]

Table 5

Overview of the STH efficiencies of the photochemical WS methods. Per STH efficiency the specific testing environment and source are presented.

STH method	Rounded STH Efficiency	Materials	Environment	Source	
PC-WS	0.4%	SrTiO ₃	Outside environment (Japan)	[52]	
	0.1%	TiO ₂	Laboratory AM1.5	[53]	
	0.4%	SrTiO ₃ :Al	Laboratory AM1.5	[9]	
	0.1%	Si and TiO ₂	Laboratory (simulated sunlight)	[54]	
	1.0%	Not specified	Not specified	[55]	
	1.1%	SrTiO ₃ :La, Rh/Au/BiVO ₄	Laboratory AM1.5	[56]	
	1.0%	Not specified	Laboratory AM1.5	[57]	
	1.0%	SrTiO ₃ :La,Rh/Au/BiVO ₄ :Mo	Laboratory AM1.5	[58]	
	1.1%	SrTiO ₃ :La,Rh/Au/BiVO ₄ :Mo photocatalyst sheet loaded with Ru and Cr ₂ O ₃	Laboratory (simulated sunlight)	[52]	
	1.1%	SrTiO ₃ :La,Rh/Au/BiVO ₄ :Mo	Laboratorium (simulated visible sunlight)	[59]	
	PEC-WS	10.0%	c-Si + Electrocatalyst: Pt, IrO _x	Laboratory (simulated sunlight)	[27]
		9.8%	c-Si + Electrocatalyst: Pt, IrO _x	Laboratory (simulated sunlight)	[13]
12.7%		Perovskite photovoltaic + Earth-Abundant Electrocatalysts	Laboratory AM1.5	[60]	
10.0–16.0%		Not specified, but based on multiple studies	Laboratory AM1.5	[57]	

35.00% as demonstrated by Dincer and Joshi [17].

For PC-WS potential STH efficiencies were found of 1.80% [75], 2.00% [54], and 5.00% [11,76]. The higher efficiencies are commonly obtained for a few minutes. The average potential STH efficiency is 3.45%. The theoretical STH efficiency is much higher with a value of

Table 6

Overview of the STH efficiencies of the BP methods. Per STH efficiency the specific testing environment and source are presented.

STH method	Rounded STH efficiency	Materials	Environment	Source
DBP	2.0%	Green Algae: Chlamydomonas reinhardtii D1 protein mutant	Laboratory	[61]
	2.0%	Green Algae: Sulfur-deprived Chlamydomonas reinhardtii	Laboratory AM1.5	[62]
	2.0%	Green Algae: Chlamydomonas reinhardtii	Laboratory AM1.5	[63]
	0.5%	Green Algae: Chlamydomonas reinhardtii	Laboratory AM1.5	[43]
IBP	0.5–2.5%	Cyanobacteria: mutant of Anabaena	Laboratory AM1.5	[43]
	1.5–2.0%	Cyanobacteria: Anabaena variabilis mutant PK84	Laboratory AM1.5	[64]
	1.5–2.0%	Cyanobacteria: Anabaena variabilis ATCC 29413	Outdoor conditions	[65]
	0.1%	Green Algae: Chlamydomonas reinhardtii	Laboratory AM1.5	[66]
	<1.0%	Green Algae: Chlamydomonas reinhardtii	Laboratory AM1.5	[45]

11.20% [11]. Potential STH efficiencies of PEC-WS are found to be 18.00% [58], 20.00% [13], 21.80% [77], 25.00% [10], and 31.00% [10]. The average STH efficiency is 23.16%. For PEC-WS the theoretical STH efficiency can be up to 40.00% [10].

The BP STH methods have similar potential STH efficiencies. DBP has a higher range from 10.00% [19] to 12.00% [43,78]. This results in an average potential STH efficiency of 11.33%. IDP has a range from 6.00% [43,44] to 12.00% [79,43]. The average potential STH efficiency is 9.50%. For both BP methods the theoretical STH efficiency is 13.40% [66]. The higher efficiencies are expected not to be achieved for DBP and IBP due to physiological and biochemical limitations [43].

Safety risks

The safety risks when producing hydrogen from electrolysis are generally quite small, as for most of the methods (i.e., PV-electrolysis, PEC-WS, and DBP and IBP) the oxygen evolution reaction (OER) stage

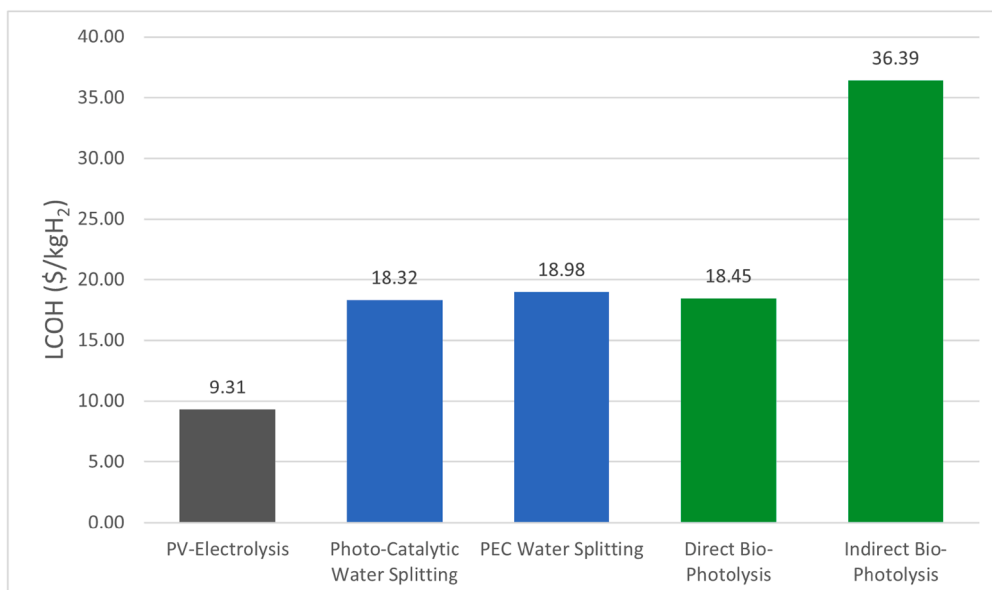


Fig. 5. Overview of the LCOH per STH method.

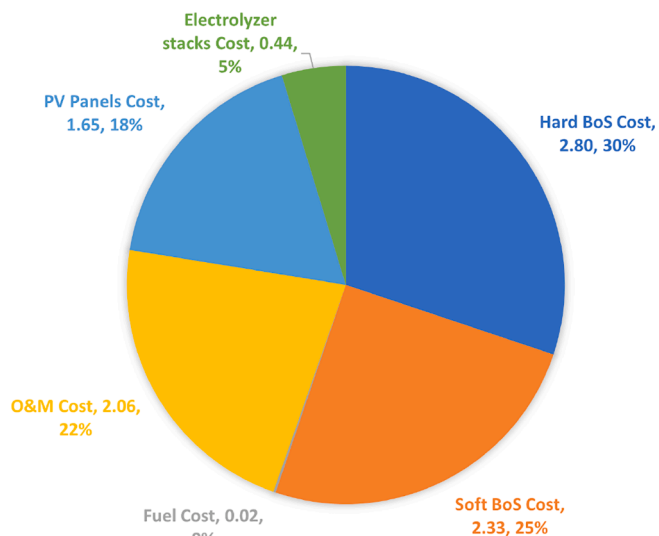


Fig. 6. LCOH breakdown of the PV-electrolysis STH method. Values are given in \$/kgH₂ and in rounded percentages as part of the total LCOH.

and the hydrogen evolution reaction (HER) stage are separated. Thus, these STH methods have relatively low safety risks when producing hydrogen in a controlled system. Nevertheless, safety measures have to be taken, such as fast leakage detection and the availability of fire protection equipment [80]. Leakage risks also are present for the BP methods [81]. Only for the PC-WS, specifically reactor Type 1, a higher risk level is apparent. Since for this type of STH method, the hydrogen production takes place in one baggie [10,11], and thus if the OER and HER are not actively separated this could lead to significantly higher explosion risks than the other STH methods. In Type 2 reactors, this is separated and therefore, when taking both types into account, the ‘average’ risk level for PC-WS could be interpreted as medium. For the other STH methods, in practice a low risk level is present. Safety risk levels are summarized in Table 7.

Upscaling potential

Ottone et al. [82] found that upscaling of PV-electrolysis is manageable. Although some extra costs can be expected for the separated components of the energy systems, a relatively large area would be needed, and some efficiency decrease would occur due to the losses at the conductor, collection grids, and electrical wires. The increase of production would not lead to significant problems. PV cells and electrolyzers can be optimized independently and the energy system’s efficiency is not affected much because of its stable energy system. Large scale hydrogen production based on PV-electrolysis is thus possible

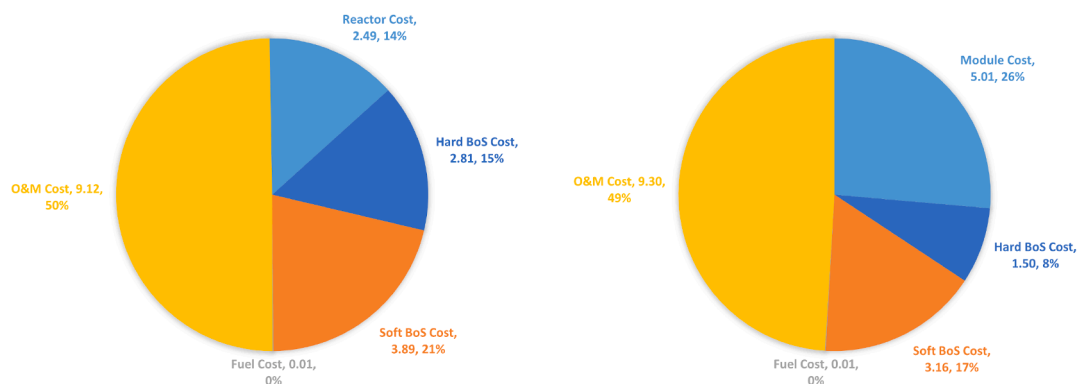


Fig. 7. LCOH breakdown of the PEC-WS (left) and PC-WS methods (right).

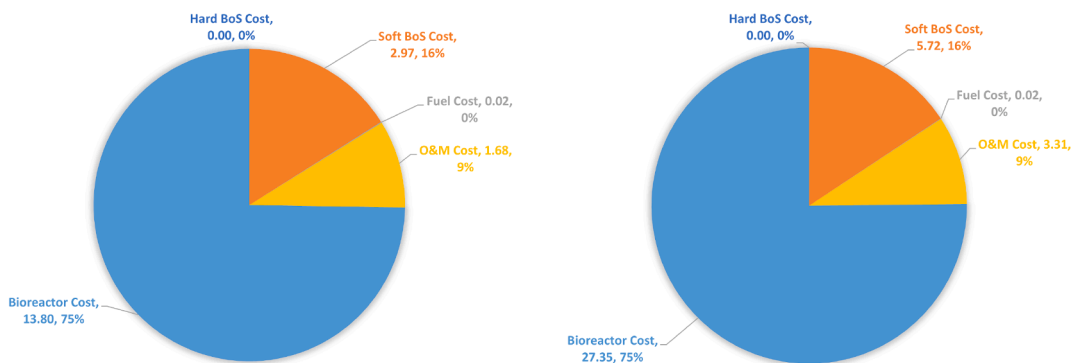


Fig. 8. LCOH breakdown of DBP in (left) and IBP STH (right) methods.

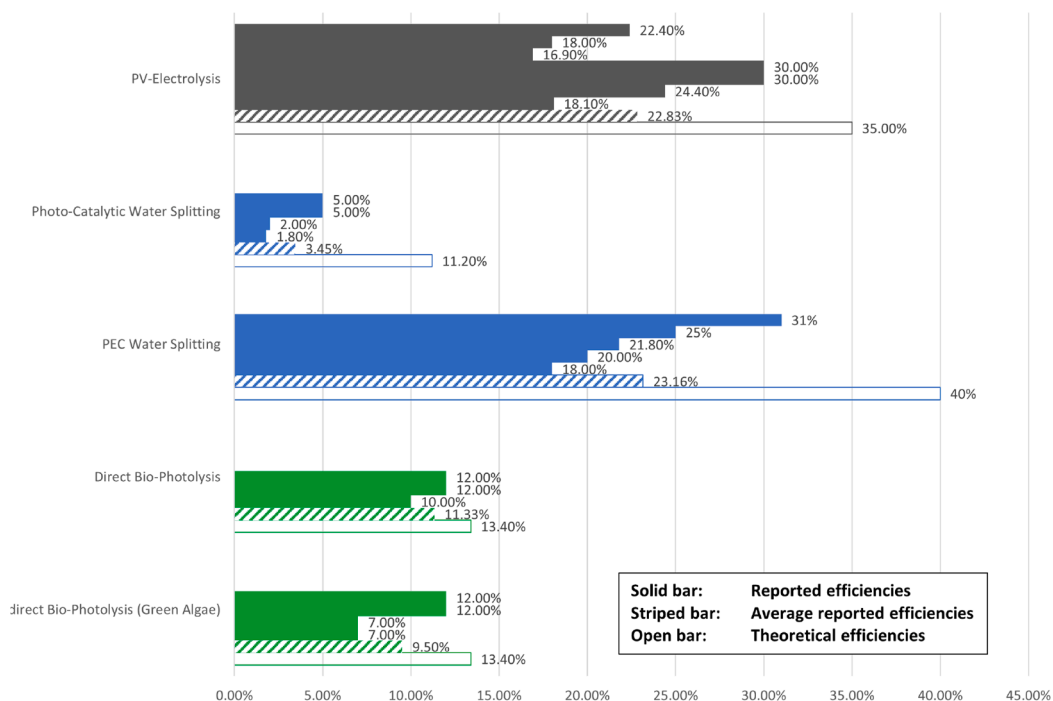


Fig. 9. Overview of the potential and theoretical efficiencies for each STH method. Each value of the found potential STH efficiency is presented as a solid bar, the diagonal striped bars are the average of the potential STH efficiency per STH method, and the open bars are the theoretical STH efficiencies per STH method.

Table 7
Overview of safety risk levels, upscaling potential and relative carbon footprint per STH method.

Overarching STH method	Sub STH method	Safety risk	Upscaling potential	Relative carbon footprint
PV-electrolysis	PV-alkaline	low	high	emissions
	PV-PEM	low	high	emissions
Photochemical water splitting	PC-WS	medium	very high	zero emissions
	PEC-WS	low	high	emissions
Bio-Photolysis	DBP	low	low	uptake
	IBP	low	low	uptake

[17,83,84], while some issues need to be addressed such as pH gradients and solution resistance as reduction and oxidation sites may be at substantial distance from each other [52]. Overall the upscaling potential is interpreted to be high.

In a study by Takata and Domen [52], it is stated that it is relatively easy to expand the production of hydrogen with the photo-catalytic WS method. They expect it even to be easier to scale-up than the production of the PV-electrolysis method, as reduction and oxidation steps take place on individual semiconductor particles. This high scale-up potential is also confirmed by others using particulate photo-catalytic WS [9,56]. Therefore the upscaling potential is assessed to be very high.

PEC-WS upscaling of production was found to be relatively easy [82], as this STH method makes use of an integrated system, which needs fewer components and less space. This makes that the process can be intensified well. Like PV-electrolysis, PEC-WS has some limitation due to the pH gradients and the high levels of solution resistance [52]. When comparing PEC-WS to PV-electrolysis one major advantage is the relatively low spatial demand since the integrated system only has one

component instead of two for the PV-electrolysis method. A disadvantage of this integrated system is that there is a larger instability risk, due to issues with direct contact between photo absorbers and electrolyte [82]. The upscaling potential can thus be interpreted as high.

Many problems occur when the production would be scaled up for bio-photolysis. Especially in outdoor environments, it is expected that the STH efficiency would drop significantly [81]. Oncel and Farloni [81] state that "meaningful amounts of H₂ can only be attained by a two-stage, sulphur deprivation protocol, where the aerobic, biomass phase is separated temporally from the anaerobic, H₂-production phase". Also, it is believed that the cost increase would be disproportional to the hydrogen production increase [81]. Also other studies confirm upscaling problems [85,67]. Because of this, the upscaling potential of both BP methods is interpreted to be low.

In Table 7, an overview of the upscaling potential of each STH method is shown.

Relative carbon footprint

Although there is some vapour generation and sometimes low amounts of NO_x are emitted, all STH methods emit negligible to none CO₂-eq/kg during their operation time [86]. Therefore, all of the methods can be considered as a sustainable option in the operation phase based on their greenhouse gas emissions. However, constructing these STH methods leads to CO₂-eq emissions in some situations; this is the case for PV-electrolysis. Yadav and Banerjee [87] found that the total carbon footprint would be 178 kgCO₂-eq/m², or 1.03–1.87 kgCO₂-eq/kgH₂. Parkinson et al. [35] and Dincer and Joshi [17] found a higher value of 1.32–2.50 kgCO₂-eq/kgH₂ and 2.50 kgCO₂-eq/kgH₂ for this STH method. This is indicated qualitatively in Table 7 denoting 'emissions' for relative carbon footprint.

There are little to no life cycle assessments (LCA) performed on PC-WS. Nevertheless, it is assumed that emissions are negligible: greenhouse gas emission rate is zero kgCO₂-eq/kgH₂. Studies describe this method as 'clean' and/or 'environmentally friendly' [9,52,88], as it does not need a solar panel, unlike PV-electrolysis or PEC-WS, which is responsible for a large part of the CO₂-eq emissions for those STH methods [80,87].

Not many studies were performed on the carbon footprint of PEC-WS. Maljusch and Wullenkord [80] researched the CO₂-eq emissions of this STH method. The carbon footprint of a Type 3 reactor PEC-WS was found to be 1.64 kgCO₂-eq/kgH₂. This value was based on a silicon PEC cell with an assumed STH efficiency of 6.80% with an annual production of 1900 kWh/m² (in Seville, Spain) [80].

Both BP methods are considered to have no emissions of greenhouse gasses. To produce hydrogen by this method, no net CO₂-eq is emitted and the necessary materials also have zero greenhouse gas emissions [89]. In another research by Oncel [81], it is reported that photobiological production uses water and light while taking up CO₂. This could lead to negative CO₂ emissions [19]. It is unclear how much CO₂ is consumed in the process of BP [19,81], hence a qualitative indication of 'uptake' is shown in Table 7.

Minimum tested stable operation time

When looking at the PV-electrolysis methods some experiments have been done with tandem III-V light absorbers protected by amorphous TiO₂ films, which led to a MTSOT of at least 40 h [47]. Generally, these methods can operate much longer: at least 500 to 1000 h [31,50]. Because of these high measured MTSOT, the TRL level, and the many assumptions concerning operating time in previous studies [13,27] it can be interpreted that MTSOT of PV-electrolysis is 500 h or more.

Studies of PC-WS and PEC-WS often have not specified the MTSOT. The studies that did include it report large variations. Takata and Domen [52] showed that the photocatalyst sheet, SrTiO₃:La,Rh/Au/BiVO₄:Mo loaded with Ru and Cr₂O₃, could operate for sixteen hours under simulated light and a similar study by Wang et al. [56], who used SrTiO₃:La, Rh/Au/BiVO₄, found a minimum stable operation time of at

least ten hours. But the study by Huang et al. [90] measured a minimum stable operation time of over 100 h. Since most of the studies [53,55,90] show an operation time for PC-WS much larger than Takata and Domen [52] and Wang et al. [56], the minimum stable operation time is interpreted to be at least 50 h. For PEC-WS it is interpreted that the MTSOT would be at least 50 h as well.

An extensive literature research was performed by Oncel [89] to find, among others, the stable operation time of BP. For DBP, it was found that the minimum operation time varied highly per research performed, but most of the studies had an operation time of at least 100 h. Since several other studies [61–63] showed production times of at least 100 h as well, it is assumed that the MTSOT would be at least 100 h. The MTSOT of IBP is more difficult to interpret since it varies highly per study. Several studies found an operation time of between 50 and 150 h [89], but also 260 h was reported when using Cyanobacteria [43] or even 4000 h using green algae [91]. As a result, it is interpreted that the MTSOT would be at the higher end of the range from 50 to 150 h, and thus 150 h is taken as input for the MCA. In Fig. 10, an overview of the interpreted MTSOT level of each STH method is shown.

Multicriteria analysis

In Fig. 11 the MCA scores per parameter are presented for each STH method for the three different stakeholders, viz. the Short-Term Investor, the Green Investor, and the Visionary Investor. The resulting MCA scores are between zero and one, with one being the highest possible score. MCA scoring are dependent on the type of stakeholder, and ranking of STH methods is different for the different investors. Also, the MCA scores are much more leveled for the Green Investor and the Visionary Investor than for the Short-Term Investor. Finally, the contribution of the eight categories in the MCA clearly differs per STH method and stakeholder.

For the Short-Term Investor PV-electrolysis has the highest score of 0.81, with PEC-WS ranked second with a much lower score of 0.59. Third place is DBP with 0.41, fourth place is PC-WS with 0.40, and at the last place is IBP with 0.29.

The highest MCA score for The Green Investor also is the PV-Electrolysis, with a score of 0.68, PEC-WS is ranked second with a score of 0.52, but the score for DBP is very close with 0.50, fourth place is IBP with 0.42, and at the last place is PC-WS with 0.41.

For The Visionary Investor, PV-electrolysis is also the best performing STH method, with a score of 0.62, second place is PEC-WS with a score of 0.53, third place is DBP with 0.50, fourth place is IBP with 0.44, and at the last place is PC-WS with 0.40.

Specific key parameters

One of the biggest advantages of PV-electrolysis is the high development level of both the components individually: the PV cell and the electrolyser. These have relatively high efficiencies and relatively low production cost. However, the downside of an indirect system on the long-term is that it consists of two components for which, theoretically, a higher initial overpotential of 1.90 eV is required [92] in comparison to the 1.60 eV for PC-WS and PEC-WS [93]. Also, due to having separated components, LCOH could be negatively affected since theoretically more material, for packaging for example, is needed than for the direct STH methods [5]. Also, an increase in temperature could lead to a loss of efficiency of the PV. Soliman et al. [94] refer to extreme temperature rises which would occur more often in some areas in the world due to climate change [95]. For crystalline PV cells the efficiency could decrease easily by 20% [96].

Quantum dots (QDs) are seen as having a very large potential use for PV-electrolysis, PC-WS and PEC-WS. QDs are zero dimensional semiconductors that can be made to be highly efficient photocatalysts [97,98]. Their band gap can be tuned to cover a wider spectral range, and this tunability distinguishes them from bulk materials and organic

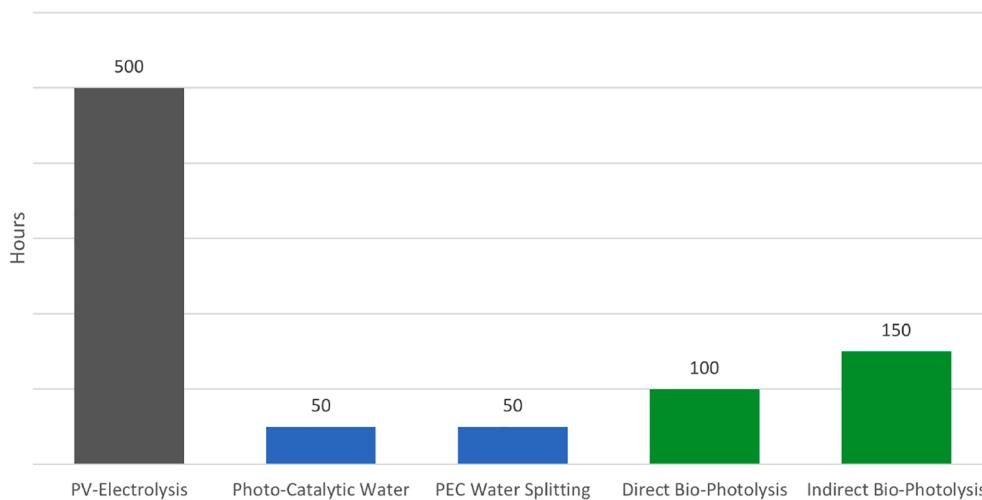


Fig. 10. Overview of the MTSOT per STH method in hours.

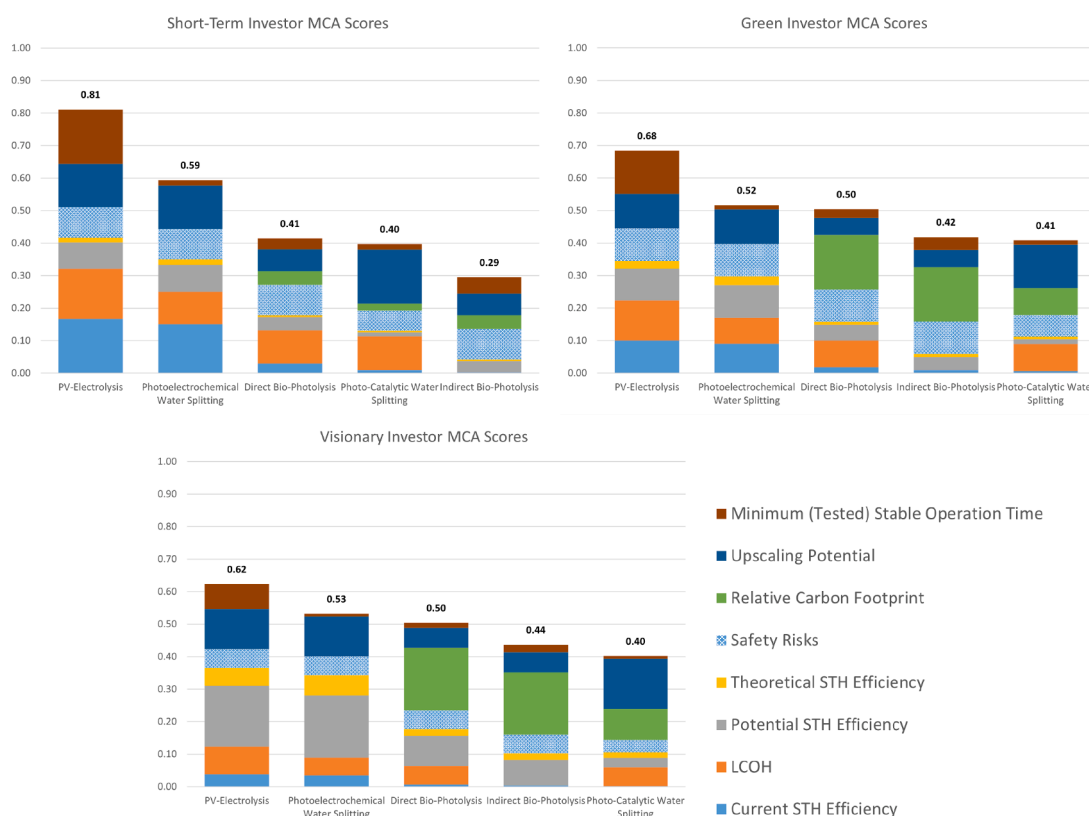


Fig. 11. Diagrams of the MCA Scores per STH method for the Short-Term Investor, Green Investor, and Visionary Investor. The scores per parameter are shown using different colours.

dye molecules [97]. Furthermore, QD enhanced STH methods have a greater exciton generation and charge separation than normal photon-based WS methods [99]. Thus, QDs can lead to cost reduction for STH methods also because they can be coupled to many different cheap and widely abundant materials.

Both PC methods would theoretically need an overpotential of only 1.6 eV for hydrogen production [93]. Since PC methods are integrated systems, fewer materials are needed than with a system with several components. Lastly, the STH efficiency increases with a rise in temperatures [37], which could be beneficial with global temperature increase.

PC-WS is a relatively simple method [100]. As a result, at a larger scale, this system is not highly affected by issues such as solution resistances [9]. One of the biggest benefits for PEC-WS is that it can utilize, to a large extent, the materials that are also utilized for PV cells, which is a highly developed technology already [60].

One of the biggest problems for algae-based hydrogen production is its sensitivity to oxygen, which leads, in extreme cases, to a total activity loss in less than ten minutes [101]. This is especially problematic for green algae but less for cyanobacteria since these have a different strategy to produce hydrogen. It makes that oxygen is consumed easily

and thus it is protected more against the negative effects of the oxygen [89]. Another disadvantage of BP is that it is based on photosynthesis, which has theoretical limitations due to the process in which 48 photons are needed to fix six carbon dioxide molecules to form glucose [89]. Next to that, BP is greatly influenced by environmental changes, such as sudden temperatures differences, which could lead to loss of productivity. Therefore, it is important to control the culture environment as much as possible [89]. There are also specific key parameters that positively affect the implementation potential of BP. For example, BP methods do not need to utilize clean water, in contrast to the other photon-driven WS methods, but can utilize salty brackish water and even waste water. In this way, this method can also be used in a water treatment system [89]. Next to that, BP methods are mostly self-sustaining STH methods since under the right conditions (pressure and temperature) no replacement is needed during the lifetime of the STH method [102]. As a result this could drastically reduce the cost of the STH methods.

Discussion

Notable results

Many assumptions in our assessment have been based on reported research results. Two of these highly influential assumptions used here are the lifetime of the modules and reactors, and the discount rate. Since the STH methods, except for the reference STH method, are not commercially available it is difficult to know what the actual lifetime is of each STH method. Moreover, most STH methods are tested in laboratories and not yet in outside environments. The discount rate was assumed to be 12%, but the economic situation differs per region and over time and therefore this value might be different in reality.

We found that the reference STH method is far cheaper than the other STH methods. In comparison to PC-WS, PEC-WS, and DBP it would be about two times more expensive to have a hydrogen production rate of 10,000 kg per day in the Netherlands. In comparison to IBP, PV-electrolysis is almost four times less expensive. We found that PEC-WS in the Netherlands is expected to have a LCOH of 18.98 $\$/\text{kgH}_2$. This can be compared to other hydrogen production methods, like fossil fuel-based hydrogen production of which cost is between 1.50–2.50 $\$/\text{kgH}_2$ or wind energy based electrolysis which cost is about 5.89–6.03 $\$/\text{kgH}_2$ [103]. With this knowledge, it can be stated that from a cost perspective PEC-WS would not be an interesting option today. However, the overall performance assessment has highlighted other aspects that are of influence for the implementation of the STH methods. From the Short-Term Investor perspective it followed that the most cost competitive option, PV-electrolysis, should only be considered since it had a much higher MCA score than the other STH methods. For the Green Investor, this is slightly different. Still, PV-electrolysis has the highest MCA score but PEC-WS shows to be more competitive and could thus be considered as an complementary option. Lastly, we have found that for the Visionary Investor the MCA scores were relatively close between the STH methods. Still, PV-electrolysis has the highest MCA score, but PEC-WS and DBP have scores that are also competitive. From this perspective, these STH methods may be considered as a complementary option next to PV-electrolysis. Thus the overall performance analysis is an additional research method to get more insight in application of technologies with a multitude of influential parameters.

LCOH sensitivity analysis

The results presented above on LCOH are for today's situation using several assumptions. In this subsection the effect of varying these assumptions. Fig. 12 illustrates that the LCOH of PV-Electrolysis is mainly influenced by variations in STH Efficiency, solar irradiance, initial investment cost, and discount rate. Ranges of these parameters are detailed in Table 3. A larger discount rate can lead to a LCOH of 14.10 $\$/\text{kgH}_2$, while a larger solar irradiance can lead to a strong decrease of

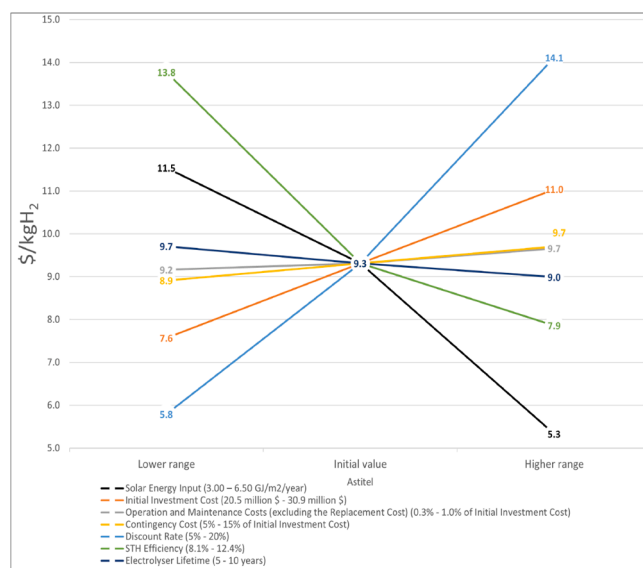


Fig. 12. Sensitivity analysis of the LCOH of PV-Electrolysis. In total seven parameters are highlighted.

the LCOH to 5.30 $\$/\text{kgH}_2$. The effects of O&M cost, contingency cost, and electrolyser lifetime have a much smaller effect on the LCOH.

Fig. 13 shows the sensitivity analysis for PEC-WS and PC-WS. LCOH of PEC-WS is mainly affected by variations in solar irradiance, PEC cell lifetime, initial investment cost, STH efficiency, and discount rate. Lower solar irradiance can increase the LCOH to 23.50 $\$/\text{kgH}_2$. A larger discount rate can increase the LCOH to 26.40 $\$/\text{kgH}_2$. The effects of ranges of O&M cost, contingency cost, and initial investment cost have a much smaller effect on the LCOH. LCOH of PC-WS is mainly influenced by variations in STH efficiency. Solar irradiance, baggie lifetime, and discount rate have great influence as well. Lower STH efficiency can increase the LCOH dramatically to 155.70 $\$/\text{kgH}_2$. The largest decrease of the LCOH can be obtained for the higher solar irradiance. With this value, the LCOH can become 5.30 $\$/\text{kgH}_2$. The effects of ranges of O&M Cost, contingency cost, and initial investment Cost have a much smaller effect on the LCOH.

Fig. 14 shows the sensitivity analyses for DBP and IDP. LCOH of DBP is mainly influenced by alterations of the STH Efficiency, solar irradiance, initial investment cost, and discount rate. Lower STH efficiency can increase the LCOH to 23.20 $\$/\text{kgH}_2$. Higher value of discount rate can increase LCOH to 28.90 $\$/\text{kgH}_2$. The lowest LCOH, of 10.60 $\$/\text{kgH}_2$, is obtained with the higher range value of solar irradiance. The effects of ranges of O&M cost and contingency cost have a much smaller effect on the LCOH. LCOH of IDP is strongly influenced by variations in the STH Efficiency. For the lower range value, the LCOH can increase to 121.50 $\$/\text{kgH}_2$. Solar irradiance and discount rate have also a great influence on the LCOH. A higher range value of solar irradiance can decrease the LCOH to 20.80 $\$/\text{kgH}_2$. The effects of ranges of the O&M cost, contingency cost, and initial investment cost have a much smaller effect on the LCOH.

Future potential cost

Based on the potential STH efficiency, a potential LCOH can be obtained for each STH method. This gives an indication of what the future LCOH might be. In Fig. 15, the potential LCOH of each STH method is presented. Fig. 15 represents two scenarios compared to the reference scenario, which is the current situation as shown in Fig. 5. Scenario 1 is a moderately optimistic scenario and uses the lowest value of the potential STH Efficiency of each STH method, while Scenario 2 is the most optimistic scenario with the highest value of the Potential STH Efficiency of each STH method. The findings shown in Fig. 15 are only an indication

Analysis of Photon-Driven H₂ production

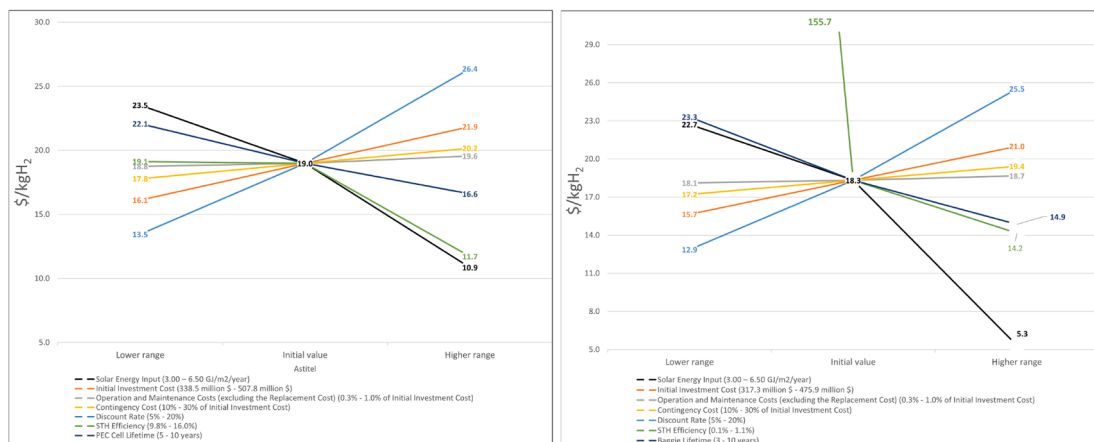


Fig. 13. Sensitivity analysis of the LCOH of PEC-WS and PC-WS. In total seven parameters are highlighted.

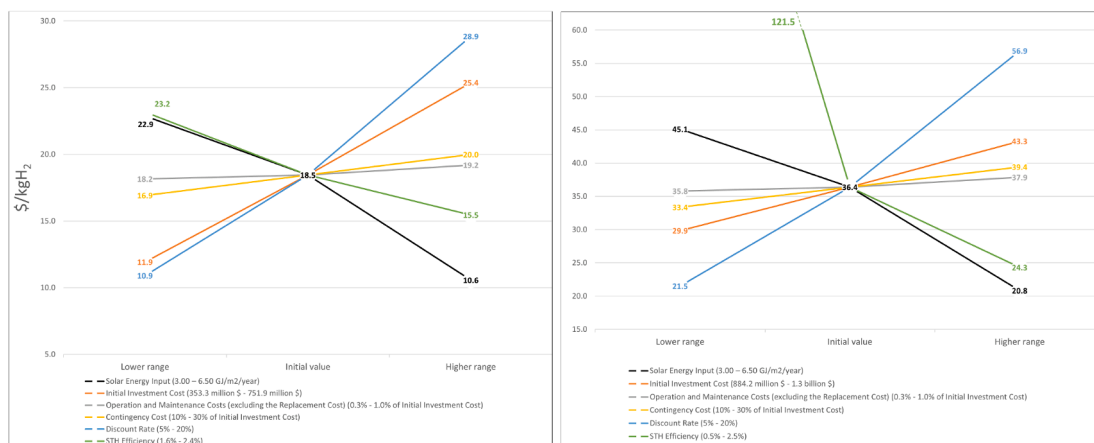


Fig. 14. Sensitivity analysis of the LCOH of DBP and IBP. In total six parameters are highlighted. Note different y-axis scales.

of what the potential LCOH could be since these potential STH Efficiencies might not be obtained at a large scale, region, or other reason. Interestingly, for both scenarios, PV-electrolysis would no longer be the least cost option and mainly the LCOH of IBP is in both scenarios drastically decreased. The range in LCOH values is smaller in both scenarios, but still are large than today’s cost for fossil fuel based hydrogen production technologies.

Comparison to literature

In Table 8, LCOH per STH method as found in literature is presented, in comparison to LCOH resulting from this study. The reasons for the found differences in results are the different assumptions made and input parameters chosen. One of the most influential differences is that this study focuses on the Netherlands and thus is based on the solar energy irradiation in the Netherlands while other studies are all based on areas with more solar energy input. In our sensitivity analysis it was clearly shown that this could lead to a factor of two difference in LCOH between different locations. This is also the main reason for the difference between the LCOH of the PEC-WS that was in this study and the value that was found by Grimm et al. [26].

All studies that estimated LCOH for the PC-WS, DBP or IBP methods assumed a much higher STH efficiency. James et al. [10] and Pinaud et al. [11] assumed STH efficiencies of 5 to 10% for Photo-Catalytic WS, whereas for this research, based previous, mostly experimental, studies, a much lower value was used. In the studies by Hallenbeck and

Benemann [67], Nikolaidis and Poullikkas [19], and Show et al. [15], efficiencies up to 10% were assumed where for this study 2.01% and 1.67% were found for BP methods. For example, when changing solar irradiance input to the higher range and using an STH Efficiency of 10%, the LCOH would become only 3.49 \$/kgH₂. Not in all studies the discount rate was specifically mentioned which could thus have been different to this study.

Another notable difference is that in some studies [19,67] the LCOH of the IBP method was lower than that of the DBP method. It is difficult to find the exact reason for this, but one reason is that in those studies it was chosen to look at green algae instead of the cyanobacteria for the IBP method which alters the input variables. Next to that, it was stated that there was a high uncertainty for the calculation of the IBP LCOH [67] which could explain why in this study IBP was found to be much more expensive than DBP.

Robustness of MCA scores

For the Short-Term Investor, the uncertainty analysis showed that the outcomes are robust. In Fig. 16, the probabilities of each STH method to obtain a specific position is presented. It is visible that PV-electrolysis is the most optimal option for this stakeholder, with a probability of 92% that this STH method is the best option even when including the uncertainties as input for the parameters and weights. Other STH methods have quite robust positions as well. Only some

Analysis of Photon-Driven H₂ production

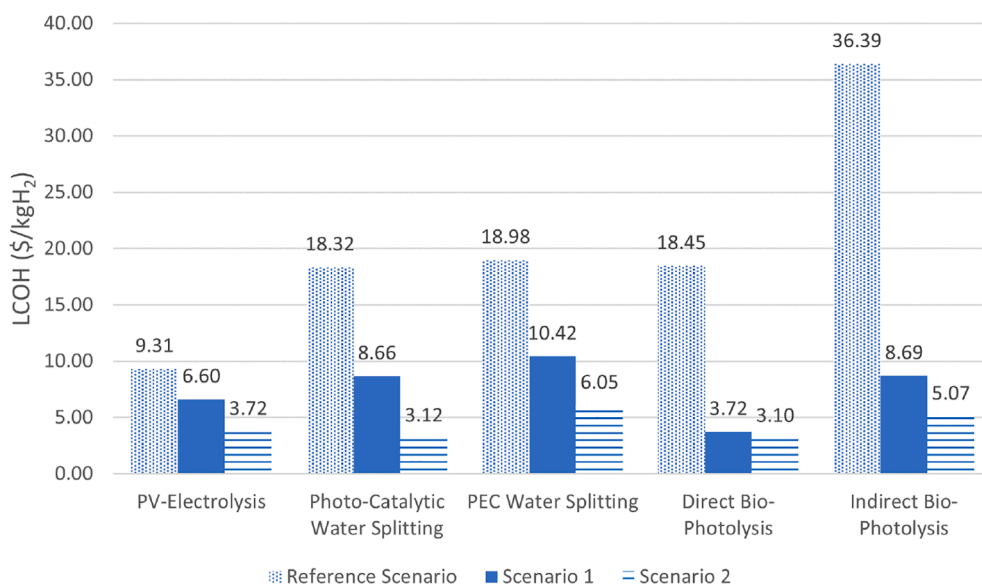


Fig. 15. Potential LCOH of the different STH methods comparing the reference scenario with scenarios 1 and 2.

Table 8

Overview of LCOH values (in \$/kgH₂) per STH method as found in other studies in comparison to LCOH values from this study (in bold).

PV-electrolysis	PC-WS	PEC-WS	DBP	IBP	Source
9.31	18.32	18.98	18.45	36.39	this study
–	3.00	10.20	–	–	[10]
–	3.20	10.40	–	–	[11]
12.1	–	11.4	–	–	[13]
–	1.60–3.20	4.10–10.40	–	–	[104]
5.60–7.10	–	10.8	–	–	[27]
6.22	–	8.43	–	–	[26]
–	–	–	1.80	1.20	[67]
–	–	–	1.38	1.38	[89]
–	–	–	2.13	1.42	[19]
–	–	–	1.20–2.40	1.20–2.40	[15]

dynamics is seen regarding the third and fourth position since both DBP and PEC-WS have a probability of over 30% to obtain these positions.

In the uncertainty analysis for the Green Investor we have found that the outcomes are less robust than for the Short Term Investor as can be found in Fig. 16. Notably, PV-electrolysis has a robust MCA score, but the second-best option is less certain since although PEC-WS has a higher probability to become the second-best option DBP performs

better overall and might thus be, based on these uncertainties, a more suitable option for implementation. This is also the case for PC-WS and IBP. Since there are more scenario’s where PC-WS performs better than IBP, when considering uncertainties, PC-WS might be more interesting for implementation than IBP for this stakeholder.

Like for the other stakeholders, also for the Visionary Investor PV-Electrolysis is in first position with a robust MCA score. Also, the other scores are quite robust even though the total scores of PEC-WS and DBP are quite similar. The outcomes of the uncertainty analysis of the Visionary Investor show that the findings of the MCA are quite robust.

Conclusions

In this study, we have investigated the techno-economic performance and overall performance for two overarching STH methods (photochemical water splitting and biophotolysis), and have compared them to the reference STH method PV-electrolysis. It was found that PV-electrolysis was the most economic competitive option with a LCOH of 9.31 \$/kgH₂. PC-WS had a LCOH of 18.32 \$/kgH₂, PEC-WS of 18.98 \$/kgH₂, DBP of 18.45 \$/kgH₂, and IBP of 36.39 \$/kgH₂.

As evidenced in our sensitivity analyses, LCOH of the STH methods was mostly influenced by changes in solar irradiance, discount rate, and STH Efficiency. With higher solar irradiance the LCOH of PV-electrolysis and PC-WS could drop to 5.30 \$/kgH₂ but this would mean moving the production to another (southern) region in Europe. Using potential STH

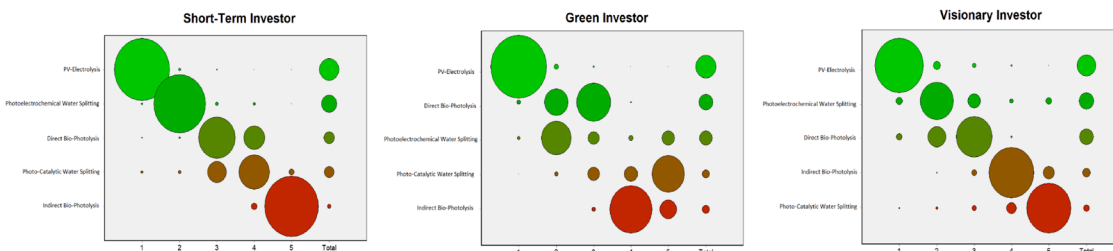


Fig. 16. Diagram of the relative positions of the STH methods based on the preferences of the Short-Term Investor, the Green Investor, and the Visionary Investor when considering the uncertainty range of each parameter and corresponding weight. The circles range in colour from red (lowest position) to green (highest position). The larger the circle the larger the probability that specific position is obtained.

efficiencies, the LCOH would drop significantly for most of the STH methods. Based on two future scenarios an indication of the potential LCOH was found. For both scenarios it was found that DBP might become the least costly option with only 3.10 and 3.72 \$/kgH₂.

An MCA approach using three different stakeholders (Short Term, Green, Visionary) showed that for all the stakeholders PV-electrolysis was the most optimal STH method for implementation when looking at the overall performance. Since this STH method is the reference STH method, this was not unexpected. PEC-WS performed quite well for all stakeholders as well and might be an interesting option to complement the PV-electrolysis option. For the Green Investor and the Visionary Investor, DBP could also be considered as a complementary option for implementation. The MCA scores for each technology were quite different for the Short-Term Investor meaning that for the Short-Term Investor the relative differences in the implementation potential of the STH methods scores were the largest.

Based on the findings in this study, recommendations can be made for actors in the Netherlands who resemble the stakeholders from this research. Actors that have similar preferences as the Short-Term Investor might, next to PV-electrolysis, consider PEC-WS as a (complementary) option since it has a relatively high MCA score. Based on the findings of the specific key parameters the techno-economic performance might be increased greatly when this STH method is further developed. For actors like the Green Investor, PV-electrolysis would be most suitable but it would also be recommended to invest in the development of PEC-WS and DBP based on the MCA scores and the specific key parameters. PEC-WS has a good techno-economic performance potential when this STH method is developed more and DBP has a low potential LCOH and might become self-sustaining which could lower the LCOH even further. Lastly, based on the preferences of the Visionary Investor PV-electrolysis had the highest MCA score. Still, it can be recommended not to invest in this STH method but rather in PEC-WS and DBP which also had a relatively high MCA score. Not only were the MCA scores more levelled than for the other stakeholders but taking into account the specific key parameters PV-electrolysis might not be the most optimal option for this stakeholder. PV-electrolysis has mainly benefits on the short-term while PEC-WS and DBP have a large potential for the long-term as was already stated in the recommendation for the Green Investor.

IBP performed quite poorly for all the stakeholders in this research and it would be recommended not to invest in this STH method for any stakeholder. For PC-WS, which performed quite poorly in the MCAs, it is more complicated since it has, like PEC-WS, a high performance increase potential and the cost might also drop significantly in the future. Since there is still a lot uncertain about these STH methods it would be strongly recommended to research the specific performance potential further.

Supplementary documentation

Supplementary documentation can be found with the following link: (to be added).

CRedit authorship contribution statement

Laurens S.F. Frowijn: Conceptualization, Methodology, Software. Wilfried G.J.H.M. van Sark: Supervision.

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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References

- [1] Skovgaard J, van Asselt H. The politics of fossil fuel subsidies and their reform: Implications for climate change mitigation. *Wiley Interdiscip Rev Clim Change* 2019;10(4):1–12.
- [2] Abujarad SY, Mustafa M, Jamian J. Recent approaches of unit commitment in the presence of intermittent renewable energy resources: A review. *Renew Sustain Energy Rev* 2017;70:215–23.
- [3] Ambec S, Crampes C. Decarbonizing electricity generation with intermittent sources of energy. *J Assoc Environ Resour Econ* 2019;6(6):1105–34.
- [4] Detz R, Lenzmann F, Sijm J, Weeda M. Future role of hydrogen in the Netherlands. a meta-analysis based on a review of recent scenario studies. *Tech. rep.* 2019.
- [5] Minggu LJ, Daud WRW, Kassim MB. An overview of photocells and photoreactors for photoelectrochemical water splitting. *Int J Hydrogen Energy* 2010;35(11): 5233–44.
- [6] Yang W, Prabhakar RR, Tan J, Tilley SD, Moon J. Strategies for enhancing the photocurrent, photovoltage, and stability of photoelectrodes for photoelectrochemical water splitting. *Chem Soc Rev* 2019;48(19):4979–5015.
- [7] Gigler J, Weeda M. Contouren van een Routekaart Waterstof. *TKI Energie & Industrie*; 2018.
- [8] Marepally BC, Ampelli C, Genovese C, Quadrelli EA, Perathoner S, Centi G. Production of solar fuels using CO₂. In: *Studies in surface science and catalysis*, vol. 178. Elsevier; 2019. p. 7–30.
- [9] Goto Y, Hisatomi T, Wang Q, Higashi T, Ishikiriyama K, Maeda T, Sakata Y, Okunaka S, Tokudome H, Katayama M, et al. A particulate photocatalyst water-splitting panel for large-scale solar hydrogen generation. *Joule* 2018;2(3): 509–20.
- [10] James BD, Baum GN, Perez J, Baum KN. Technoeconomic analysis of photoelectrochemical (PEC) hydrogen production, DOE report.
- [11] Pinaud BA, Benck JD, Seitz LC, Forman AJ, Chen Z, Deutsch TG, James BD, Baum KN, Baum GN, Ardo S, et al. Technical and economic feasibility of centralized facilities for solar hydrogen production via photocatalysis and photoelectrochemistry. *Energy Environ Sci* 2013;6(7):1983–2002.
- [12] Yang Y, Niu S, Han D, Liu T, Wang G, Li Y. Progress in developing metal oxide nanomaterials for photoelectrochemical water splitting. *Adv Energy Mater* 2017; 7(19):1–26.
- [13] Shaner MR, Atwater HA, Lewis NS, McFarland EW. A comparative technoeconomic analysis of renewable hydrogen production using solar energy. *Energy Environ Sci* 2016;9(7):2354–71.
- [14] Sivula K. Nanostructured a-Fe₂O₃ Photoanodes. In: *Photoelectrochemical hydrogen production*. New York: Springer; 2012. p. 121–56.
- [15] Show K-Y, Yan Y, Ling M, Ye G, Li T, Lee D-J. Hydrogen production from algal biomass—advances, challenges and prospects. *Bioresour Technol* 2018;257: 290–300.
- [16] Artz JH, Mulder DW, Poudel S, Colman D, Schut GJ, Williams SG, et al. Structure-function of [fefe]- and [nife]-hydrogenases: an overview of diversity, mechanism, maturation, and bifurcation. In: *Microalgal hydrogen production*; 2018. p. 31–66.
- [17] Dincer I, Joshi AS. Solar based hydrogen production systems. Springer; 2013.
- [18] Abdalla AM, Hossain S, Nisfindy OB, Azad AT, Dawood M, Azad AK. Hydrogen production, storage, transportation and key challenges with applications: A review. *Energy Conv Manage* 2018;165:602–27.
- [19] Nikolaidis P, Poullikkas A. A comparative overview of hydrogen production processes. *Renew Sustain Energy Rev* 2017;67:597–611.
- [20] Gutekunst K, Schulz R. The physiology of the bidirectional nife-hydrogenase in cyanobacteria and the role of hydrogen throughout the evolution of life. In: *Microalgal hydrogen production*; 2018. p. 107–38.
- [21] International Energy Agency. Hydrogen a key part of a clean and secure energy future, Tech. rep., IEA; 2021. URL: <https://www.iea.org/topics/hydrogen/production/>.
- [22] Stojić DL, Grozdić TD, Umićević N, Maksić AD. A comparison of alkaline and proton exchange membrane electrolyzers. *Russ J Phys Chem A* 2008;81(11): 1958–60.
- [23] Blok K, Nieuwlaar E. *Introduction to energy analysis*. Routledge; 2020.
- [24] Solargis. Global solar atlas. URL: <https://globalsolaratlas.info/map?c=51.486856,5.663462,7&s=52.145625,5.316369&m=site> (Dec 2020). url: <https://globalsolaratlas.info/map?c=51.486856,5.663462,7&s=52.145625,5.316369&m=site>.
- [25] Reich NH, Mueller B, Armbruster A, Van Sark WGJHM, Kiefer K, Reise C. Performance ratio revisited: is PR > 90 % realistic?. *Progr Photovolt Res Appl* 2012;20(6):717–26. doi:10.1002/ppv.1219.
- [26] Grimm A, de Jong WA, Kramer GJ. Renewable hydrogen production: A techno-economic comparison of photoelectrochemical cells and photovoltaic-electrolysis. *Int J Hydrogen Energy* 2020;45(43):22545–55. <https://doi.org/10.1016/j.ijhydene.2020.06.092>. URL: <http://www.sciencedirect.com/science/article/pii/S0360319920322291>.
- [27] Detz R, Reek J, Van Der Zwaan B. The future of solar fuels: when could they become competitive? *Energy Environ Sci* 2018;11(7):1653–69.
- [28] Waternet. Kosten drinkwater voor 2020. URL: <https://www.waternet.nl/service-en-contact/drinkwater/kosten/>; 2020.
- [29] SPINLAB, VU University Amsterdam. Definite/BOSDA. URL: <https://spinlab.vu.nl/support/tools/definite-bosda/>; 2021).

- [30] Burhan M, Chua KJE, Ng KC. Long term hydrogen production potential of concentrated photovoltaic (cpv) system in tropical weather of singapore. *Int J Hydrogen Energy* 2016;41(38):16729–42.
- [31] Kuang Y, Kenney MJ, Meng Y, Hung W-H, Liu Y, Huang JE, Prasanna R, Li P, Li Y, Wang L, et al. Solar-driven, highly sustained splitting of seawater into hydrogen and oxygen fuels. *Proc Natl Acad Sci* 2019;116(14):6624–9.
- [32] Nicodemus JH. Technological learning and the future of solar h2: A component learning comparison of solar thermochemical cycles and electrolysis with solar PV. *Energy Policy* 2018;120:100–9.
- [33] Bessarabov D, Wang H, Li H, Zhao N. PEM electrolysis for hydrogen production: principles and applications. CRC Press; 2016.
- [34] Kováč A, Marciuš D, Budin L. Solar hydrogen production via alkaline water electrolysis. *Int J Hydrogen Energy* 2019;44(20):9841–8.
- [35] Parkinson B, Balcombe P, Speirs J, Hawkes A, Hellgardt K. Levelized cost of CO₂ mitigation from hydrogen production routes. *Energy & Environmental Science* 2019;12(1):19–40.
- [36] Mankins JC. Technology readiness levels, White Paper, April 6 (1995) 1–5. URL: http://www.artemisinnovation.com/images/TRL_White_Paper_2004-Edited.pdf.
- [37] Joy J, Mathew J, George SC. Nanomaterials for photoelectrochemical water splitting—review. *Int J Hydrogen Energy* 2018;43(10):4804–17.
- [38] Zhang D, Shi J, Zi W, Wang P, Liu S. Recent advances in photoelectrochemical applications of silicon materials for solar-to-chemicals conversion. *ChemSusChem* 2017;10(22):4324–41.
- [39] Pan L, Vlachopoulos N, Hagfeldt A. Directly photoexcited oxides for photoelectrochemical water splitting. *ChemSusChem* 2019;12(19):4337–52.
- [40] Wang S, Liu G, Wang L. Crystal facet engineering of photoelectrodes for photoelectrochemical water splitting. *Chem Rev* 2019;119(8):5192–247.
- [41] Mahidhara G, Burrow H, Sasikala C, Ramana CV. Biological hydrogen production: molecular and electrolytic perspectives. *World J Microbiol Biotechnol* 2019;35(8):1–13.
- [42] Hassan AH, Mietzel T, Brunstermann R, Schmuck S, Schoth J, Küppers M, Widmann R. Fermentative hydrogen production from low-value substrates. *World J Microbiol Biotechnol* 2018;34(12):1–11.
- [43] Kosourov S, Murukesan G, Seibert M, Allahverdiyeva Y. Evaluation of light energy to H₂ energy conversion efficiency in thin films of cyanobacteria and green algae under photoautotrophic conditions. *Algal Res* 2017;28:253–63.
- [44] Sakurai H, Masukawa H, Kitashima M, Inoue K. How close we are to achieving commercially viable large-scale photobiological hydrogen production by cyanobacteria: A review of the biological aspects. *Life* 2015;5(1):997–1018.
- [45] Hallenbeck P, Peters J, Bruschi M, Schulz R, Armstrong F, Kruse O, Posewitz M, Peltier G, Ghirardi M, Antal T, et al. Microalgal hydrogen production: achievements and perspectives. *Royal Society of Chemistry*; 2018.
- [46] Luo J, Im J-H, Mayer MT, Schreier M, Nazeeruddin MK, Park N-G, Tilley SD, Fan HJ, Grätzel M. Water photolysis at 12.3% efficiency via perovskite photovoltaics and earth-abundant catalysts. *Science* 2014;345(6204):1593–6.
- [47] Verlage E, Hu S, Liu R, Jones RJ, Sun K, Xiang C, Lewis NS, Atwater HA. A monolithically integrated, intrinsically safe, 10% efficient, solar-driven water-splitting system based on active, stable earth-abundant electrocatalysts in conjunction with tandem III–V light absorbers protected by amorphous TiO₂ films. *Energy Environ Sci* 2015;8(11):3166–72.
- [48] Baek M, Kim G-W, Park T, Yong K. NiMoFe and NiMoFeP as Complementary Electrocatalysts for Efficient Overall Water Splitting and Their Application in PV-Electrolysis with STH 12.3%. *Small* 2019;15(49):1–11.
- [49] Gibson TL, Kelly NA. Optimization of solar powered hydrogen production using photovoltaic electrolysis devices. *Int J Hydrogen Energy* 2008;33(21):5931–40.
- [50] Clarke R, Giddey S, Ciacchi F, Badwal S, Paul B, Andrews J. Direct coupling of an electrolyser to a solar pv system for generating hydrogen. *Int J Hydrogen Energy* 2009;34(6):2531–42.
- [51] Schüttauf J-W, Modestino MA, Chinello E, Lambelet D, Delfino A, Dominé D, Faes A, Despeisse M, Bailat J, Psaltis D, et al. Solar-to-hydrogen production at 14.2% efficiency with silicon photovoltaics and earth-abundant electrocatalysts. *J Electrochem Soc* 2016;163(10):F1177–81.
- [52] Takata T, Domen K. Particulate photocatalysts for water splitting: recent advances and future prospects. *ACS Energy Lett* 2019;4(2):542–9.
- [53] Mubeen S, Lee J, Singh N, Krämer S, Stucky GD, Moskovits M. An autonomous photosynthetic device in which all charge carriers derive from surface plasmons. *Nat Nanotechnol* 2013;8(4):247–51.
- [54] Liu J, Liu Y, Liu N, Han Y, Zhang X, Huang H, Lifshitz Y, Lee S-T, Zhong J, Kang Z. Metal-free efficient photocatalyst for stable visible water splitting via a two-electron pathway. *Science* 2015;347(6225):970–4.
- [55] Li R, Li C. Photocatalytic water splitting on semiconductor-based photocatalysts. In: *Advances in catalysis*, vol. 60, Elsevier; 2017. p. 1–57.
- [56] Wang Q, Hisatomi T, Jia Q, Tokudome H, Zhong M, Wang C, Pan Z, Takata T, Nakabayashi M, Shibata N, et al. Scalable water splitting on particulate photocatalyst sheets with a solar-to-hydrogen energy conversion efficiency exceeding 1%. *Nat Mater* 2016;15(6):611–5.
- [57] Chowdhury FA, Trudeau ML, Guo H, Mi Z. A photochemical diode artificial photosynthesis system for unassisted high efficiency overall pure water splitting. *Nat Commun* 2018;9(1):1–9.
- [58] Li R. Latest progress in hydrogen production from solar water splitting via photocatalysis, photoelectrochemical, and photovoltaic-photoelectrochemical solutions. *Chin J Catal* 2017;38(1):5–12.
- [59] Chen X, Shi R, Chen Q, Zhang Z, Jiang W, Zhu Y, Zhang T. Three-dimensional porous g-C₃N₄ for highly efficient photocatalytic overall water splitting. *Nano Energy* 2019;59:644–50.
- [60] Luo J, Vermaas DA, Bi D, Hagfeldt A, Smith WA, Grätzel M. Bipolar membrane-assisted solar water splitting in optimal pH. *Adv Energy Mater* 2016;6(13):1–7.
- [61] Scoma A, Krawietz D, Faraloni C, Giannelli L, Happe T, Torzillo G. Sustained H₂ production in a Chlamydomonas reinhardtii D1 protein mutant. *J Biotechnol* 2012;157(4):613–9.
- [62] Volgusheva A, Styring S, Mamedov F. Increased photosystem II stability promotes H₂ production in sulfur-deprived Chlamydomonas reinhardtii. *Proc Natl Acad Sci* 2013;110(18):7223–8.
- [63] Oey M, Sawyer AL, Ross IL, Hankamer B. Challenges and opportunities for hydrogen production from microalgae. *Plant Biotechnol J* 2016;14(7):1487–99.
- [64] Liu J, Bukatin VE, Tsygankov AA. Light energy conversion into H₂ by Anabaena variabilis mutant PK84 dense cultures exposed to nitrogen limitations. *Int J Hydrogen Energy* 2006;31(11):1591–6.
- [65] Berberoglu H, Jay J, Pilon L. Effect of nutrient media on photobiological hydrogen production by Anabaena variabilis ATCC 29413. *Int J Hydrogen Energy* 2008;33(4):1172–84.
- [66] Torzillo G, Seibert M. Hydrogen Production by Chlamydomonas reinhardtii. In: *Handbook of microalgal culture*, John Wiley & Sons Ltd. p. 417–32.
- [67] Hallenbeck PC, Benemann JR. Biological hydrogen production; fundamentals and limiting processes. *Int J Hydrogen Energy* 2002;27(11–12):1185–93.
- [68] Benemann J. Feasibility analysis of photobiological hydrogen production. *Int J Hydrogen Energy* 1997;22(10–11):979–87.
- [69] Akkerman I, Janssen M, Rocha J, Wijffels RH. Photobiological hydrogen production: photochemical efficiency and bioreactor design. *Int J Hydrogen Energy* 2002;27(11–12):1195–208.
- [70] Chen H, Song L, Ouyang S, Wang J, Lv J, Ye J. Co and Fe Codoped WO_{2.72} as Alkaline-Solution-Available Oxygen Evolution Reaction Catalyst to Construct Photovoltaic Water Splitting System with Solar-To-Hydrogen Efficiency of 16.9%. *Adv Sci* 2019;6(16):1–9.
- [71] Jia J, Seitz LC, Benck JD, Huo Y, Chen Y, Ng JWD, Bilir T, Harris JS, Jaramillo TF. Solar water splitting by photovoltaic-electrolysis with a solar-to-hydrogen efficiency over 30%. *Nat Commun* 2016;7(1):1–6.
- [72] Nordmann S, Berghoff B, Hessel A, Zielinsk B, John J, Starschich S, Knoch J. Record-high solar-to-hydrogen conversion efficiency based on a monolithic all-silicon triple-junction IBC solar cell. *Sol Energy Mater Sol Cells* 2019;191:422–6.
- [73] Bonke SA, Wiechen M, MacFarlane DR, Spiccia L. Renewable fuels from concentrated solar power: towards practical artificial photosynthesis. *Energy Environ Sci* 2015;8(9):2791–6.
- [74] Nakamura A, Ota Y, Koike K, Hidaka Y, Nishioka K, Sugiyama M, Fujii K. A 24.4% solar to hydrogen energy conversion efficiency by combining concentrator photovoltaic modules and electrochemical cells. *Appl Phys Expr* 2015;8(10):1–4.
- [75] Kibria M, Chowdhury F, Zhao S, Alotaibi B, Trudeau M, Guo H, Mi Z. Visible light-driven efficient overall water splitting using p-type metal-nitride nanowire arrays. *Nat Commun* 2015;6(1):1–8.
- [76] Liao L, Zhang Q, Su Z, Zhao Z, Wang Y, Li Y, Lu X, Wei D, Feng G, Yu Q, et al. Efficient solar water-splitting using a nanocrystalline coo photocatalyst. *Nat Nanotechnol* 2014;9(1):69–73.
- [77] Döschner H, Young JL, Geisz JF, Turner JA, Deutsch TG. Solar-to-hydrogen efficiency: shining light on photoelectrochemical device performance. *Energy Environ Sci* 2016;9(1):74–80.
- [78] Ghirardi ML, Dubini A, Yu J, Maness P-C. Photobiological hydrogen-producing systems. *Chem Soc Rev* 2009;38(1):52–61.
- [79] Bolton JR, Hall DO. The maximum efficiency of photosynthesis. *Photochem Photobiol* 1991;53(4):545–8.
- [80] Maljusch A, Wullenkord M. Technoeconomic analysis of PEC water splitting at various scales. In: *Advances in Photoelectrochemical Water Splitting*. Royal Society of Chemistry; 2018. p. 266–84.
- [81] Oncel SS, Faraloni C. Environmental factors affecting hydrogen production from Chlamydomonas reinhardtii. In: *Microalgal hydrogen production*; 2018. p. 265–98.
- [82] Ottone C, Hernández S, Armandi M, Bonelli B. Scaling up the process of photoelectrochemical water splitting. In: *Testing novel water oxidation catalysts for solar fuels production*. Springer; 2019. p. 93–114.
- [83] Parkinson B, Turner J. The potential contribution of photoelectrochemistry in the global energy future. In: *Photoelectrochemical water splitting: materials, processes and architectures*. The Royal Society of Chemistry; Cambridge, UK; 2013. p. 1–18.
- [84] Liu G, Sheng Y, Ager JW, Kraft M, Xu R. Research advances towards large-scale solar hydrogen production from water. *EnergyChem* 2019;1(2):1–51.
- [85] Razu MH, Hossain F, Khan M. Advancement of bio-hydrogen production from microalgae. In: *Microalgae biotechnology for development of biofuel and wastewater treatment*. Springer; 2019. p. 423–62.
- [86] Baykara SZ. Hydrogen: a brief overview on its sources, production and environmental impact. *Int J Hydrogen Energy* 2018;43(23):10605–14.
- [87] Yadav D, Banerjee R. Net energy and carbon footprint analysis of solar hydrogen production from the high-temperature electrolysis process. *Appl Energy* 2020; 262:1–15.
- [88] Ni M, Leung MK, Leung DY, Sumathy K. A review and recent developments in photocatalytic water-splitting using TiO₂ for hydrogen production. *Renew Sustain Energy Rev* 2007;11(3):401–25.
- [89] Oncel SS. Biohydrogen from microalgae, uniting energy, life, and green future. In: *Handbook of marine microalgae*. Elsevier; 2015. p. 159–96.
- [90] Huang L, Meng Q, Shang C, Jin M, Shui L, Zhang Y, Zhang Z, Chen Z, Yuan M, Wang X, et al. Modified nanopillar arrays for highly stable and efficient photoelectrochemical water splitting. *Global Challenges* 2019;3(3):1–5.

- [91] Fedorov AS, Kosourov S, Ghirardi ML, Seibert M. Continuous hydrogen photoproduction by *Chlamydomonas reinhardtii*. *Appl Biochem Biotechnol* 2005; 121(1–3):403–12.
- [92] Keene S, Chandran RB, Ardo S. Calculations of theoretical efficiencies for electrochemically-mediated tandem solar water splitting as a function of band gap energies and redox shuttle potential. *Energy Environ Sci* 2019;12(1):261–72.
- [93] Gaudy YK, Gačević Ž, Haussener S. Theoretical maximum photogeneration efficiency and performance characterization of InxGa1-xN/Si tandem water-splitting photoelectrodes. *APL Mater* 2020;8(7):1–11.
- [94] Soliman AM, Hassan H, Ahmed M, Ookawara S. A 3d model of the effect of using heat spreader on the performance of photovoltaic panel [PV]. *Math Comput Simul* 2020;167:78–91.
- [95] Nkemelang T, New M, Zaroug M. Temperature and precipitation extremes under current, 1.5 °C and 2.0 °C global warming above pre-industrial levels over botswana, and implications for climate change vulnerability. *Environ Res Lett* 2018;13(6):1–11.
- [96] Hussin NSM, Amin NAM, Safar MJA, Zulkafli RS, Majid MSA, Rojan MA, Zaman I. Performance factors of the photovoltaic system: A review. In: *MATEC Web of Conferences*, vol. 225, EDP Sciences; 2018. p. 1–8.
- [97] Li X-B, Tung C-H, Wu L-Z. Semiconducting quantum dots for artificial photosynthesis. *Nat Rev Chem* 2018;2(8):160–73.
- [98] Kandi D, Martha S, Parida K. Quantum dots as enhancer in photocatalytic hydrogen evolution: a review. *Int J Hydrogen Energy* 2017;42(15):9467–81.
- [99] Zrazhevskiy P, Sena M, Gao X. Designing multifunctional quantum dots for bioimaging, detection, and drug delivery. *Chem Soc Rev* 2010;39(11):4326–54.
- [100] Fabian DM, Hu S, Singh N, Houle FA, Hisatomi T, Domen K, Osterloh FE, Ardo S. Particle suspension reactors and materials for solar-driven water splitting. *Energy Environ Sci* 2015;8(10):2825–50.
- [101] Rogers E, Megarity CF, Esselborn J, Winkler M, Happe T, Armstrong FA. Assessment of electrochemically-based strategies to protect [FeFe]-hydrogenases from oxygen. In: *Microalgal Hydrogen Production*; 2018. p. 139–54.
- [102] Dincer I, Acar C. Review and evaluation of hydrogen production methods for better sustainability. *Int J Hydrogen Energy* 2015;40(34):11094–111.
- [103] Kayfeci M, Keçebaş A, Bayat M. Hydrogen production. In: *Solar hydrogen production*. Elsevier; 2019, p. 45–83.
- [104] Chen S, Takata T, Domen K. Particulate photocatalysts for overall water splitting. *Nat Rev Mater* 2017;2(10):1–17.