

Energy and environmental assessment of hydrogen from biomass sources: Challenges and perspectives

Original

Energy and environmental assessment of hydrogen from biomass sources: Challenges and perspectives / Buffi, M.; Prussi, M.; Scarlat, N.. - In: BIOMASS & BIOENERGY. - ISSN 0961-9534. - 165:(2022), p. 106556. [10.1016/j.biombioe.2022.106556]

Availability:

This version is available at: 11583/2971045 since: 2022-09-07T12:02:51Z

Publisher:

Elsevier Ltd

Published

DOI:10.1016/j.biombioe.2022.106556

Terms of use:

This article is made available under terms and conditions as specified in the corresponding bibliographic description in the repository

Publisher copyright

(Article begins on next page)



Energy and environmental assessment of hydrogen from biomass sources: Challenges and perspectives

Marco Buffi^{*}, Matteo Prussi, Nicolae Scarlat

European Commission, Joint Research Centre (JRC), Ispra, Italy

ABSTRACT

Hydrogen is considered as one of the pillars of the European decarbonisation strategy, boosting a novel concept of the energy system in line with the EU's commitment to achieve clean energy transition and reach the European Green Deal carbon neutrality goals by 2050. Hydrogen from biomass sources can significantly contribute to integrate the renewable hydrogen supply through electrolysis at large-scale production. Specifically, it can cover the non-continuous production of green hydrogen coming from solar and wind energy, to offer an alternative solution to such industrial sectors necessitating of stable supply. Biomass-derived hydrogen can be produced either from thermochemical pathways (i.e., pyrolysis, liquefaction, and gasification) or from biological routes (i.e., direct or indirect-biophotolysis, biological water-gas shift reaction, photo- and dark-fermentation). The paper reviews several production pathways to produce hydrogen from biomass or biomass-derived sources (biogas, liquid bio-intermediates, sugars) and provides an exhaustive review of the most promising technologies towards commercialisation. While some pathways are still at low technology readiness level, others such as the steam bio-methane reforming and biomass gasification are ready for an immediate market uptake. The various production pathways are evaluated in terms of energy and environmental performances, highlighting the limits and barriers of the available LCA studies. The paper shows that hydrogen production technologies from biomass appears today to be an interesting option, almost ready to constitute a complementing option to electrolysis.

1. Introduction

1.1. Hydrogen as new energy vector

Hydrogen might be the most abundant element on Earth, but it is rarely found in its pure form. Pure hydrogen can be produced from thermochemical processing of fossil- or bio-derived resources, biological processes, or from water electrolysis. Hydrogen is one of the main pillars of the Europe's decarbonisation strategy for the next years, aiming at providing a clean solution for mobility, power generation and industrial applications. According to the European Green Deal (EGD) [1], issued by the European Commission in December 2019, hydrogen is today considered one of the main energy vectors towards the EU carbon neutrality by 2050. In line also with the Clean Energy for All Europeans' package [2], the hydrogen is rapidly getting momentum, but several technical and non-technical barriers regarding its production and sustainability are still present. In order to boost the sector, the European Commission adopted a new hydrogen strategy on July 8, 2020 with "A hydrogen strategy for a climate-neutral Europe" [3]. The strategy aims to promote renewable hydrogen production, with the expected targets being the installation of at least 6 GW of renewable-powered electrolyzers in the EU by 2024, and 40 GW by 2030. In addition, the "Next

Generation EU" recovery fund [4] is expected to stimulate clean hydrogen production, boosting the market uptake. Important steps towards the promotion of clean hydrogen are contained in a new initiative derived from the manifesto for the development of a European "Hydrogen Technologies and Systems" value chain, signed by 22 EU Member States and Norway. This new initiative is committed to promoting Important Projects of Common European Interest (IPCEIs) in the hydrogen sector. The Strategic Forum on IPCEIs identified in its report six strategic value chains that include hydrogen technologies and systems entitled to be supported.

At the current status of the art, there are several available options to produce hydrogen, potentially meeting in the long-term scenario the renewable and sustainable criteria set by the recast Renewable Energy Directive (RED II) [5], but uncertainty still exists on which will be the most effective pathway for a large-scale diffusion. Most of the hydrogen produced today is from fossil feedstocks via steam reforming of natural gas, partial oxidation of methane, and coal gasification [6–8]. However, due to the high environmental impact of the use of these non-renewable feedstocks, the use of renewable sources is of primary importance. Among the alternative conversion pathways, the process of electrolysis supplied by electricity and water offers multiple options, both considering low-temperature (Alkaline Electrolysis – AEL, and Polymer

^{*} Corresponding author.

E-mail address: marco.buffi@ec.europa.eu (M. Buffi).

Electrolyte Membrane Electrolysis – PEM) and high-temperature processes (Solid Oxide Electrolysis – SOEC) [9–11]. It is worth noticing that electrolyzers should be powered by low carbon electricity that requires large, efficient, and clean infrastructures, and hence major investments, with particular attention to greenhouse gases (GHG) emissions associated with its production and distribution [12]. In addition, a stable hydrogen supply cannot be only dependent by a variable production of electricity as solar and wind, so it should be integrated with stable production pathways that today are still powered by fossil fuels. For this scope, biomass energy could potentially assume a central role to cover this fraction using well-established technologies producing energy vectors (e.g. biomethane, syngas) ready to be converted in hydrogen depending on the required demand. In the current scenario of transition, the available technologies based on fossil feedstock to hydrogen production could potentially be re-converted on short term to new systems, using wastes and biomass feedstocks. This approach would preserve the existing infrastructures, and allow introducing renewable feedstocks in the industry to boost the bioeconomy [13,14].

1.2. Definitions and classification

Today, the larger part of the current hydrogen production is mainly divided into three categories, which are commonly referred to as grey, blue and green hydrogen. While the first two classifications are related to natural gas-derived hydrogen (varying from the presence or the absence of carbon capture and storage strategies), the third one considers “low carbon intensity” hydrogen production from renewable electricity, mainly derived from wind and solar energy. A fourth type of hydrogen can be produced from the gasification of coal and is referred to as brown or black hydrogen, depending on the grade of coal being used. This widely used colour-coding, associated with the primary feedstock used, is not sufficient to define the sustainability of the production, and each route should instead be assessed according to the materials and energy requirements, environmental impact and current Technology Readiness Level (TRL). Hydrogen from biomass, also called “bio-hydrogen” refers today only to the hydrogen produced from steam biomethane reforming, leaving out numerous interesting biomass to hydrogen pathways, such as gasification, biological processes and others.

From a legislative point of view, when renewable hydrogen is used as an energy vector in the European context, the producers have to comply with the existing provisions as defined in RED II [5] and its associated delegated acts. Therefore, renewable electricity-derived hydrogen (defined as Renewable Fuel of Non-Biological Origin) and biomass-derived hydrogen can contribute to the 13% GHG intensity reduction target for 2030, as set in the recent Fit-for-55 package [15], which replaces the former energy-based RED II targets for the transport sector. In the case hydrogen is produced with an initial feedstock listed in Part A of Annex IX, it can contribute to the 2.2% production target of advanced biofuel, with the minimum requirement to meet the 65% of GHG savings compared to the fossil counterpart. It is worth to mention also that hydrogen from renewable electricity has a major contribution within the supply chain of RFNBO, which have a 2.6% target on energy basis for the transport sector (according to the RED II revision). Apart from the direct use of renewable hydrogen and renewable electric-derived fuels in the transport sector, renewable hydrogen has a key role to play in industry as renewable raw material for oil refineries, but also for other industries, such as steel works. Differently than advanced biofuels, RFNBO must meet a 70% threshold for minimum GHG emission savings by means of a specific methodology that will be published in specific Delegated Act (as reported in the RED II recast [15]). Within this piece of legislation, a low-carbon hydrogen definition, tracking and tracing mechanism are required to demonstrate compliance with the above-mentioned targets to meet the GHG emissions savings from renewable liquid and gaseous transport fuels of non-biological origin and recycled carbon fuels. Moreover, it is worth

mentioning that the additionality concept will play an important role, as hydrogen production should guarantee that the incremental GHG emissions savings are additional to the current baseline. This implies that the production of hydrogen should derive from new projects, or rather additional renewable electricity supplies. Therefore, this intricate procedure to claim the sustainability of hydrogen derived from renewable electricity, makes of the biomass derived-hydrogen a ready opportunity to contribute to the short-/mid-term hydrogen provisions. For instance, adding a last processing step of bio-hydrogen conversion in a value chain (e.g. biomethane from manure or organic wastes, according to Annex V, RED II), the process carbon intensity will not be significantly altered, so the sustainability criteria of GHG emissions reduction can be easily met.

1.3. Goal and scope

This paper investigates hydrogen production from biomass sources that could be a ready alternative to complement the production of renewable hydrogen in the coming years. Differently from green hydrogen through water electrolysis, this pathway does not fully depend on electricity since the hydrogen is contained into the biomass itself (including water). Biomass feedstocks can be converted into bio-intermediates and then into pure hydrogen by means of a series of biological or thermochemical processes [16]. The paper reviews several pathways based on biomass feedstock and provides an exhaustive review of the most investigated technologies. From a literature review of most recent, peer-reviewed, scientific papers, several production pathways have been identified and assessed to address their actual TRL, energy consumptions and environmental performances. The aim of this paper is to define the state of the art of biomass-to-hydrogen technologies and compare the resulting findings against more traditional conversion pathways from fossil sources and electrolysis.

2. Hydrogen from biomass: setting the scene

2.1. Conversion pathways classification

Despite being widely spread in nature, hydrogen is not directly available in its pure form but bound into the chemical structures, and its separation from the raw material cannot necessarily be done in a single conversion step as for methane or water. This is particularly true for biomass feedstock, where hydrogen needs to be detached from the other elements constituting the biomass [16], in the first place. Biomass approximately contains 6% mass fraction hydrogen versus the 25% of methane, and is made of an intricate, mostly polymeric, structure [17]. A measure of the challenge in extracting hydrogen is in fact the Gibbs Free Energy (GFE) of the formation of its compounds (e.g. water, hydrocarbons and sugars), which ranges in negative values. This means that all processes to split water require external energy inputs. Water can be split into its constituting elements by electrolysis, or by high temperature reactions. Hydrocarbons and biomass can be used in a steam reforming reaction with water e.g. SMR (steam methane reforming). For steam glucose reforming, half of the hydrogen comes from the water and the other half from the carbon bound hydrogen. Since hydrogen bound to carbon atom requires less energy to be obtained in comparison with water separation, this results in a relevant advantage in terms of value chain primary energy conversion efficiency. Heat can be generated by the combustion of part of the biomass itself, providing energy to run several conversion steps up to pure H₂ and CO/CO₂. Differently, there are also biological mechanisms that do not require heat but only oxygen, light and/or nutrient to perform identical reactions with longer reaction times [18–20]. Hence, the environmental and energy performances of biomass to hydrogen systems strongly depend on the hydrogen origin, and the energy sources needed by the conversion process. Exergy analyses are an effective method using conservation of both mass and energy with the second law of thermodynamics for design and analyse

biomass conversion processes, in particular for biomass gasification process, which is strongly dependent on temperature, gasification medium and the addition of steam [21–23].

The biomass-to-hydrogen processes can be divided into two different categories [24–26]:

1. Thermochemical pathways including pyrolysis, hydro- and solvo-thermal liquefaction, and gasification followed by bio-oil upgrading and reforming, or syngas upgrading and biomethane reforming;
2. The biological pathways including water–gas shift reactions promoted by micro-organisms, photo-fermentation and dark-fermentation, anaerobic digestion and biomethane reforming, and bio-photolysis with photosynthetic organisms (microalgae and cyanobacteria) such as microbial electrolysis cell.

2.2. Processes description

Thermochemical pathways include all the previously mentioned processes, which aim to promote cracking reactions to break down biomass molecules into lower molecular weight polymers and hydrogen-rich gases. Among the thermochemical technologies, biomass pyrolysis, liquefaction and gasification are all suitable to generate pure hydrogen plus other solid, liquid and gaseous co-products. The produced bio-intermediates such as pyrolysis oil and hydrogen-rich gases can be further processed, either to obtain more hydrogen through steam reforming and water gas shift reaction [24], and valorised in other markets. Several reviews available in the scientific literature address these conversion pathways [8,25–31], describing the processes features, upgrading techniques and future developments.

Biological routes provide alternative methods of hydrogen production since they can be operated at ambient temperatures and pressures, and are resulting less energy intensive compared to thermochemical processes [32]. This conversion is based on the capacity of microorganisms to convert organic substrates and water into hydrogen by the catalytic activity of two key enzymes: hydrogenase and nitrogenase [33]. This approach opens new paths for the exploitation of new feedstocks since they can also use various waste materials, which contribute to waste recycling [34]. Hydrogen production by means of microorganisms can be divided into two additional sub-categories: one involving photo-fermentation; the other one exploiting the anaerobic fermentation [35–37] in a dark environment. The last category, today at the early stages of development, includes the use of Microbial Electrolysis Cells (MEC) that integrates microbial fuel cells (MFC) and electrochemical processes to generate energy by oxidising the organic matter [38–41].

2.3. Current limits and barriers

Among all of these pathways, only a few of them can be potentially integrated into existing, commercially ready, value chains [42]. For instance, the photo-biological processes are at a very early stage of development and display low conversion efficiencies, requiring large reactor areas. Parts of these technologies already exist for biofuels production, but the last stage of hydrogen upgrading is currently adopted only in the fossil refining sector. The only market-ready dark-fermentation process is the anaerobic digestion process, used to produce bio-methane, which is then upgraded to hydrogen. Anaerobic digestion is a full commercial process, which can be already performed with a large variety of organic wastes and biomasses [43]. Thermochemical reforming of biomass and bio-intermediates are more complex than natural gas reforming since they require additional processing steps (i.e. pyrolysis or gasification) to split the first split the biomass constituent in lighter compounds and water, then converted to hydrogen. However, these processes are more tolerant to trace contaminants such as metals and other impurities than SMR since generally they do not require catalysts. Moreover, the process energy demand is significantly

high, mostly due to the presence of oxygen, and therefore it is convenient to generate the required heat from the combustion of the carbon contained into the biomass itself (as done in the biomass autothermal gasification) [44,45], with an overall reduction of the process yield. Summarizing, most of the conversion pathways are intricate and consist in various processing steps, which lead to complex technologies and high costs. However, the potential development of some technologies producing multiple products as biofuels and biochemicals, may facilitate the promotion of hydrogen production too (see Fig. 1).

3. Material and methods of analysis

3.1. System analysis

A classification based on three different conversion steps is proposed to structure the information gathered about the state-of-the-art of each technology. As shown in Fig. 2, this sub-division allows for defining the conversion chain based on the specific TRL of each conversion step.

Starting from pure biomass sources or residues/wastes, a potential 1st level of conversion encompasses those processes aimed to pre-treat or upgrade the feedstock before being processed at the main conversion step (i.e., 2nd level of conversion). By means of these processes, biomass can be converted into bio-intermediates, such as fast pyrolysis oil, Hydrothermal Liquefaction (HTL) oils, lignin and/or sugars, which can be more easily converted to obtain hydrogen gaseous precursors. This initial conversion also densifies the biomass enabling its use in processes developed for coal/oil processing (e.g., entrained flow gasification of coal, FCC, hydrocracking, ...). At the 2nd level of our hierarchy, there are the conversion processes that can be fed by both pure biomass and bio-intermediates. Conversely to the conventional value chains for bioenergy and biofuel production, they here require an additional conversion step for the hydrogen production. Finally, the 3rd level conversion step, which is the gas upgrading section, includes methane reforming, water gas-shift and synthesis for hydrogen separation and purification. The next section reports some useful elements to select the most adequate conversion technologies, based on TRL assessment, mostly derived from literature [24,35,37,41,46–48].

3.2. Literature review

Data collection of energy and the environmental performance of the selected conversion routes has been derived from available data in peer-reviewed papers. The research tool used for this scope has been the Scopus' website, with the following keywords: "hydrogen", "biomass", "life cycle assessment". First results have been complemented exploiting the references of the papers, or from previous works of the same authors. A qualitative assessment has been performed to include only well-documented hydrogen from biomass pathways, reporting detailed LCA assessments (including not only those referring to ISO-based methodology [49], but also other methods) with exhaustive descriptions of system boundaries, input data and allocation criteria. From this process, over 30 studies were made available. The main conversion pathways considered for the analysis resulted:

- wood gasification and gas upgrading sourced from Refs. [50–64];
- biogas production and steam biomethane reforming sourced from Refs. [60,65–68];
- steam reforming of gasified bio-intermediates such as bio-oil, ethanol or glycerol, sourced from Refs. [55,58,69–74];
- biological processes such as dark- or photo-fermentation sourced from Refs. [58,64,75–80] and microbial electrolysis cells sourced from Refs. [40,60,79,81].

Detailed descriptions of specific processes can also be found from other papers [8,24–29,31,35,40,82].

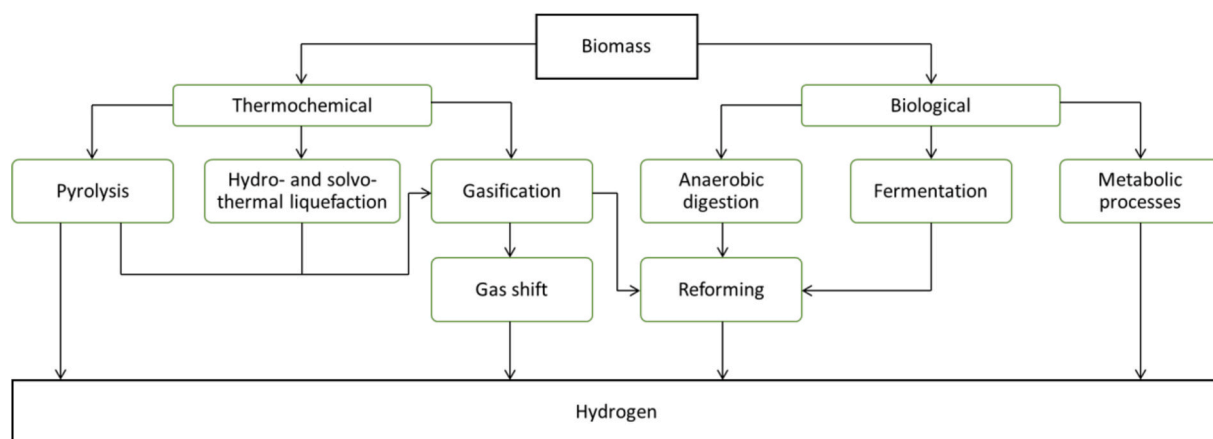


Fig. 1. Main conversion processes to produce hydrogen from biomass sources (elaborated from Ref. [25]).

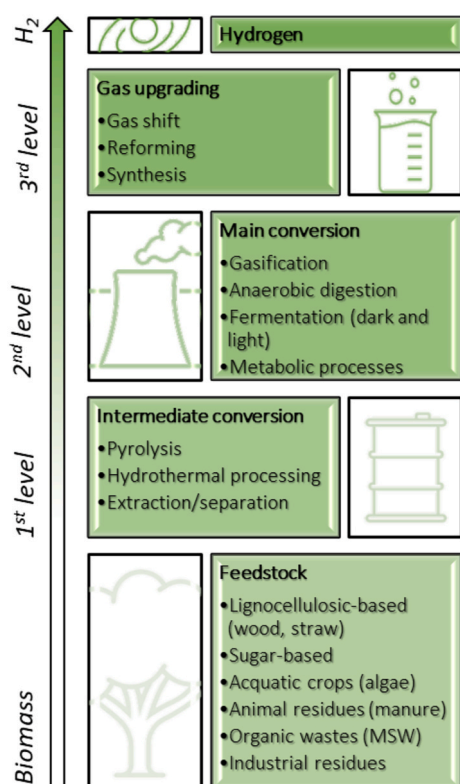


Fig. 2. Biomass to hydrogen production pathways at different conversion levels.

3.3. Method of work

The present study focuses on the elaboration of the figures of energy demand and carbon intensity, analysing data from selected studies, which allowed to produce a matrix including the whole set of data per conversion process and their boundary conditions. The other parameters calculated within the LCAs, such as acidification, ozone depletion and eutrophication potentials, have been only marginally considered, as this work focuses on GHG reduction of producing H₂ from biomass sources.

According to LCA methodology, the energy consumptions were determined as the Cumulative Energy Demand (CED), or simply considering the sum of all energy contributions used to produce a functional unit of product. Generally, biomass energy input is not necessarily considered into the cumulative energy demand in most LCA

studies reviewed. Therefore, this work is based on the analysis of two different figures as regards the energy required for the selected processes: (1) the energy efficiency as the ratio between the energy output and the sum of all energy contributions at the inlet, including biomass energy content; (2) a CED including only all non-renewable inputs, as depicted in the ISO LCA. As several studies propose different approaches, a double energy assessment has been proposed in order to be able to derive a general conclusion from this review work.

Additionally, another relevant methodological issue regards the way to determine the energy content of the final H₂ production. The authors would like to point out that Gibbs' free energy of hydrogen would be more appropriate to determine the overall output of a certain process, as hydrogen could be used as a reagent in other processes. For those works which investigated well-to-wheel performances, it consists of the maximum theoretical limit to the electrical energy obtainable by a fuel cell, while the Higher and the Lower Heating Values (HHV and LHV) are more appropriate to compare the fuel performances of internal combustion engines and gas turbines. As reported by Harrison et al. [83], in the United States, the efficiencies of appliances and heat engines usually are rated based on the HHV, whereas in European communities, the LHV is used. It is worth noticing that this difference can have an impact of about 18% of the estimations.

In order to compare the cumulative energy demands with non-standard system boundaries, the present work used the harmonised data proposed by Valente et al. [84,85]. According to the findings of these authors, the main difference consists in the last stage of hydrogen delivery, which generally considers a standard pressure set at 20 MPa, which is produced by the method three-stage intercooled compression at 25 °C according to Zhang et al. [86], at 75% efficiency.

As regards the environmental performances, the calculated carbon intensities are reported in kilograms of CO_{2eq} emissions to produce 1 kg of H₂ (in some cases, they have been converted to mass units from functional energy units). CO₂ equivalent is used to consider not only direct CO₂ emissions, but all the other GHG emissions involved in the investigated value chain (i.e., CH₄, N₂O).

4. Results

4.1. Outcomes from LCA studies comparison

Key-information from section 3.2 has been used for the generic review and elaborated in the next sections for the technological, energetic and environmental analysis proposed within this study.

As regards the initial feedstock, the large majority of the studies considers agro-residues or wood wastes (and just in a few cases, even farmed wood), and in smaller part also microalgae, energy crops, organic wastes (municipal solid waste or derived from the food industry)

and industrial co-products (as glycerol). The GHG emissions associated with biomass are the first issue that needs to be clarified to determine the performance of the proposed value chain. In some works, the initial feedstock is set at zero emissions associated (due to the biogenic CO₂ emissions), or even generates credits due to the recovery of waste material otherwise disposed of [55,66,67], while in others, the emissions for biomass production are calculated from the sum of all inputs (fertiliser, water resources) and energy consumptions (tillage, harvesting operations, logistics). The conversion technologies have been generally simulated by means of specific software and tools required to model and assess mass and energy balances. In performing a comparison based on different studies, it is of utmost importance to check the input data quality by considering the sources and libraries used by each study.

A specific focus on the actual energy demand required by the investigated processes has been carried out. As introduced in section 3.3, for thermochemical conversion processes the Gibbs' free energy should be considered to determine the process energy output, while for the useful energy used, the exergy should be considered. This is what has been considered by Kalinci et al. [23] for the production of hydrogen from gasification of biomass. Other authors [18] also reported that the exergetic efficiency of hydrogen production by gasification of biomass feedstocks with low water content, such as vegetable oil, wood and straw, is comparable with the value calculated for Steam Methane Reforming (SMR) based on fossil fuels, while wet feedstocks, such as biomass wastes (sludge, manure, or organic waste), present an exergetic efficiency lower both for gasification and biochemical processes. On the other hand, for biological processes, there is a negligible heat demand, thus the energy absorbed by the microorganisms comes from nutrients, gases and sun (except the anaerobic processes).

In addition, feedstock appeared as a significant influential factor in processes energy requirements: each biomass has its specific hydrogen content, which is bonded with different chemical compounds, hence requiring different energy levels to be separated. Moreover, the presence of moisture introduces an additional energy demand to recover additional hydrogen. Biomass particle size also plays a fundamental role in the heat exchange process, as the "contact surface" of biomass particles strongly influence the conversion yields. Summarizing, energy requirements should be compared with each other under the same conditions of feedstock, production rates and environmental conditions.

As regards the calculation methodologies, the model for the holistic evaluation of potential environmental impacts of hydrogen energy systems is Life Cycle Assessment, ISO 14040 guidelines [49]. ISO methodology sets an international procedure for the definition of the goal and scope of the analysis, the function unit (FU), the system boundaries, the collection of the overall input and output flows of the system, the data analysis, the quantification of the resulting environmental impacts, and the interpretation of the results. Although LCA is a standardised methodology, and despite the availability of EU guidelines of the Renewable Energy Directive (RED) and its recast [5,87], there are enormous differences as regards the methodological choices that can be used in LCA studies of hydrogen energy systems (e.g., input data, system boundaries, functional unit, allocation approach, etc.). For instance, most works use specific tools for LCA studies, such as commercially available software, which made use of their own libraries for the inventory phase. In the present review, the authors found that the following works used ISO methodology [51,54–56,59,64–67,72,75], while others proposed alternative methodological choices. System boundaries as "cradle-to-grave" or "cradle-to-gate", respectively assume either the whole life cycle assessment from initial resources extraction ("cradle" to the use phase "grave", i.e., fuel compression and distribution), or a partial product life cycle from resource extraction ("cradle" to the final production "gate", i.e., at the plant outlet). Together with assumptions of different scales of production, such as large industrial plants [58,59,69,75,77,79,80] compared with small units, and in some cases, even different assumptions as regards the allocation criteria [65,81], the final screening of the environmental and energy performances needed the use of

harmonisation protocols as reported in Section 3.3.

Finally, a short overview of different Life Cycle Impact Assessments (LCIA) [88] have been reported. There are many impact assessment methods like TRACI, commonly used in the United States; Ecoindicator, ReCiPe, and ILCD, employed in Europe; and others as CML and IPCC [89, 90]. Since the output of LCIA can be expressed by the midpoint and/or the endpoint impact categories, both modelling approaches were found among the reviewed studies, with a prevalence for midpoint assessment. Regarding the different environmental categories, the most discussed ones were the global warming potential (GWP), acidification potential (AP), and ozone layer depletion (ODP). Considering that the present review ranged between biological and thermochemical processes, most of them at the early stage of development, as well as the different assumptions that were made in the calculation methodologies, the results were not comparable among each other.

4.2. Technological readiness assessment

Five selected processes for biomass-to-hydrogen production have been evaluated on the basis of their current TRL. Despite there are no established value chains today producing hydrogen from biomass sources in large volumes, the paper proposes an analysis per conversion step, as reported in section 3.1. Table 1 reports the current TRLs for each conversion step of the selected processes summarised in section 3.2. As regards the first conversion level, both biomass gasification and biogas steam reforming pathways include all biomass pre-treatments from the raw biomass production to the pre-treated biomass for the main conversion step (i.e., size reduction and drying).

Just two production pathways (i.e., biomass gasification including gas upgrading and steam biomethane reforming from anaerobic digestion) are currently ready at commercial level, while the others need further assessment and development before being scaled up. For these specific two cases, these conversion levels include all biomass pre-treatments from the raw biomass production to the pre-treated biomass for the main conversion step (i.e., size reduction and drying).

In general, biogas plants and gasification units are commercially available technologies, mostly at small scale, resulting in a small-scale production of biomethane and syngas, respectively, which does not match up with the large scale of existing fossil upgrading facilities. For this reason, even if they are at a high TRL, they appear not ready to match the available technologies for hydrogen upgrading at oil refineries scale, such as the natural gas SMR. However, these conversion pathways can be scaled up to larger production if an established value chain collecting biomass feedstock would be further developed, such as the case of commercial bioethanol production (both from 1st and 2nd generation, that are full commercial at large-scale).

For the pathway of steam reforming of bio-intermediates, the first conversion step (i.e., bio-intermediate production) is almost at commercial level (e.g., production of fast pyrolysis bio-oil and glycerol), while the 2nd level of conversion this is not completely developed at larger scale. For this specific case, there are several demonstration activities operating biomass pyrolysis oil gasification in entrained flow gasifiers [91–95], but these solutions are still at pilot-scale resulting in a TRL of about 6.

Regarding dark- and photo-fermentation and Microbial Electrolysis

Table 1
Technology readiness level of biomass to hydrogen production technologies.

Conversion pathways	Current Technology Readiness Level (TRL)		
	1st level	2nd level	3rd level
Biomass Gasification	9	9	9
Biogas Steam Reforming	9	9	9
Bio-int. Steam Reforming	8	6	9
Fermentation	9	3	8
Microbial Electrolysis Cells	9	3	8

Cells (MEC) applications, although there are several studies providing full LCA assessments [75,77,79] of these processes, the conversion technologies are still at lab scale. However, differently than thermochemical processes, the biological processes are simpler to scale up since they work at standard thermodynamic conditions [96], therefore promising for the near term. The main challenge is to study how to scale up these systems to produce high rates of hydrogen [97], despite their 1st level of conversion, which is still at high TRL due to the available processes to convert the initial biomass or wastes to fermentable sugars or other feedstock suitable for the conversion by means of the organic substrate.

In conclusion, for all processes, the 3rd conversion level has high TRLs because both SMR and Gas-Shift technologies are already at the commercial level, mostly for the hydrogen production from fossil sources: Therefore, they could be supplied by biomass-derived hydrogen production. Our evaluation also resulted aligns with the published studies reporting the current TRLs of each single technology [42,98].

Summarizing, although some processes have higher TRLs for some of their steps, it is the step with the lowest TRL that defines the TRL of the process. This barrier still limits some conversion pathways that would have the potential to be easily scaled up thanks to well-established technologies for their upstream or downstream processes.

4.3. Energy assessment

According to the proposed methodology to investigate the biomass-to-hydrogen energy requirements (as reported in 3.3), the full energy conversion yield (including biomass) has been investigated first. Therefore, conversion process efficiency (as reported in Table 2) has been defined as the sum of all the energy content of hydrogen produced over the sum of all energy inputs. Among the processes investigated, the only output is hydrogen, while the input is biomass, in different forms (as presented in 4.1) and heat or/and electricity.

As shown, comparing the biomass-derived process efficiencies with the one of SMR supplied by NG, the latter results in the most efficient pathway. In particular, biological processes have the lowest conversion efficiencies, which are mainly due to the micro-organisms' ability to convert only part of the initial feedstock into pure hydrogen or hydrogen precursors. Conversely, thermochemical processes have higher conversion yields due to the intense thermodynamic conditions that are going to fractionate the whole biomass in hydrogen precursors. It is worth mentioning that electrolysis exhibits similar conversion efficiency, but the energy input is electrical power; hence, it would need a different

Table 2
Conversion efficiencies for several hydrogen production pathways, including both bio- and fossil-derived feedstock.

Biomass to Hydrogen conversion pathways	Conversion Process Efficiency	Sources
Wood Gasification ^a	0.43–0.7	[27,53,79,99]
Biogas Steam Reforming ^b	0.65–0.77	[65,66,68]
Bio-int. Steam Reforming ^b	0.35–0.5	[24,25,67]
Photo-fermentation	0.01–0.1	[24,79]
Dark-fermentation	0.1–0.25	[27,79,99]
Microbial Electrolysis Cells	0.06–0.26	[24,79,81]
Fossil benchmark conversion pathways	Conversion Process Efficiency	Sources
Natural Gas Steam Methane Reforming	0.74–0.85	[50,60,79,100]
Water electrolysis	0.6–0.8	[17,24,79,101]

^a Some studies considered the energy conversion of wood to syngas, and incorporate also the energy content of other gases than H₂.

^b An additional conversion yield of about 70% should be considered as the initial biomass is firstly converted into energy carriers as biogas and bio-intermediates such as pyrolysis oil.

comparison. The high range for each figure can be significantly reduced when LCA studies are investigated.

Specifically, the picture change dramatically if the energy investigation switches to the analysis of the Cumulative Energy Demand (CED) where inputs exclude the contributions of renewables, as it is the where the input energy is provided by the biomass itself. Although this approach is used to compare the energy intensity of processes (according to LCA ISO methodology), it misses in total energy contributions.

However, in order to compare the investigated processes among each other with a common methodology, the selected CEDs from the investigated LCA studies have been gathered and structured. They have been harmonised according to system boundaries, functional units and conversion rates in order to provide a fair comparison. The data have been then classified per production pathway, and then summarised in the distribution chart presented in Fig. 3.

In order to compare the results with a reference baseline, the chart includes the ranges and mean values of the calculated CEDs per pathway, with the addition of steam methane reforming (NG SMR) and electrolysis (calculated for an average electricity mix), used as benchmark values [50,55,58,60,72,79,84,100,101]. For consistency, the data has been gathered from the same studies of the biomass-to-hydrogen pathways.

When pathways are compared based on the CED, it is immediately evident that all values lie below the SMR/electrolysis benchmark, and this highlights the benefits of using biomass sources as feedstock for hydrogen production. This observation is widely recognised in literature when the LCA approach is used for this type of evaluation. This assumption also highlights that all mean values of CEDs lie below the dotted line representing the energy content of 1 kg of hydrogen (expressed as LHV and reported as the black dashed line), generating favourable net energy ratios in all cases.

In general, anaerobic digestion and the other fermentation processes require lower energy inputs but need longer conversion times; on the contrary, producing hydrogen from biomass through thermochemical conversions such as gasification and pyrolysis requires higher heat supply but lower conversion times. However, as regards the mean values, the higher figures are attributed to fermentation processes, which require higher energy costs due to the numerous procedures to manage the production plant. As regards the anaerobic digestion for biogas production, there are lower energy costs than the other fermentation processes due to the maturity of the technology and the lower amount of water that is needed by the microorganisms. Comparing the thermochemical processes among each other, as expected, wood gasification requires fewer energy inputs than bio-intermediate steam reforming, and this is mainly explainable with the absence of an additional conversion step. However, the use of bio-intermediates generates other advantages as the availability of higher energy-density carriers compared to the raw lignocellulosic biomass; this results in better storage options and the extension of the range of value chain outputs (e. g., fast pyrolysis oil can be used for many purposes [102,103]).

Focusing on the bandwidths of each conversion pathways (representing the range of the results), a larger band has been depicted for gasification and fermentation; this is mainly due to the variability of the process conditions and production scales that has been assumed for the hydrogen production, which leads to lower energy costs per unit of product. However, significant bandwidths exist for the other pathways; variability of processes conditions and parameters, assumptions of different biomass pre-treatments (size reduction and drying), use of different libraries for input data, overestimated or underestimated data due to the low TRL of some technologies (in particular for MECs) may be the main reasons.

4.4. Environmental assessment

Fig. 4 summarises the distribution of the calculated carbon intensity as carbon dioxide equivalence to produce 1 kg of H₂. The carbon

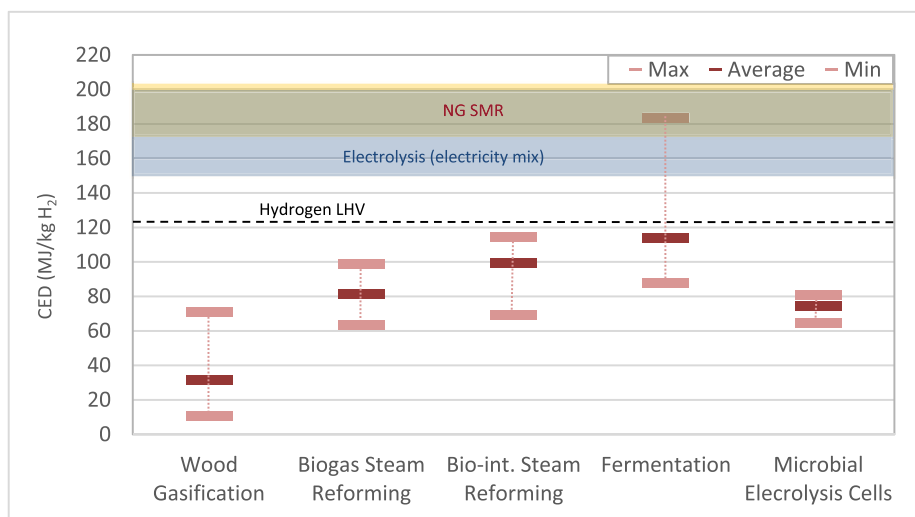


Fig. 3. Comparison of CEDs for five different biomass-to-hydrogen production pathways. The dark red bars represent the mean values, while the light red bars are the upper and lower limits for the selected values. It is also reported the benchmark range for the NG SMR (the yellow area) and for electrolysis (the blue area). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

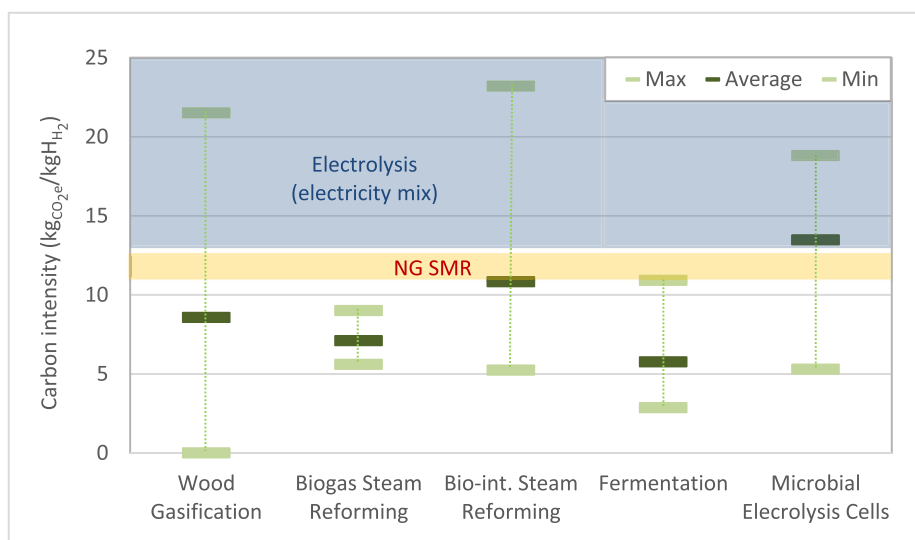


Fig. 4. Comparison of carbon intensities for five different biomass-to-hydrogen production pathways. The dark green bars represent the mean values, while the light green bars are the upper and lower limits in the range of the selected values. It also shows the benchmark range for the NG SMR (the yellow area) and for electrolysis (the blue area). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

intensity (in yellow) of Steam Methane Reforming (SMR) of natural gas and the electrolysis from a generic electricity mix (in blue) are highlighted as a benchmark. The former results in the range of 10.4–12.9 kgCO_{2e}/kgH₂ according to figures extrapolated within the selected LCA studies [50,55,58,60,72,79,84,100,101].

It is worth highlighting that the mean value (dark green bars) is within or below the benchmark areas, showing the potential environmental benefit of using biomass as feedstock/input for hydrogen production. Among the five selected conversion technologies, the larger bandwidths are attributed to the thermochemical processes. One of the reasons for such range is related to the emissions associated to biomass cultivation, which can vary significantly, reaching figures above 20 kgCO_{2e}/kgH₂ [54,64,70]. Differently, biological pathways have generally zero emissions associated with biomass cultivation since feedstock is mainly based on agro-residues or waste organic material. For gasification, there are also some studies that considered biomass biogenic emissions and CCS, that lead the calculations up to zero emissions [53,

80], or the adoption of different conversion technologies that resulted in different processing-derived emissions [57,61]. As regards the higher carbon intensities, for bio-intermediates steam reforming, the upper limit of the band is due to the high carbon footprint associated to glycerol as feedstock [55]. In general, this category assumes an additional conversion step (from biomass to bio-intermediate) that result in slightly higher processing-derived emissions than the other pathways. As for the energy assessment, wood gasification shows the larger bandwidth mostly due to a larger number of available studies, referring to significantly different plant sizes. On the other hand, for biological processes, the bandwidths are less with the lower mean values due to the lower emissions of the conversion processes. Fermentative processes also have the potential to generate a lower environmental impact due to the potential CO₂ captured by algal biomass or yeasts from exhaust industrial emissions, as reported in some studies [76,77]. A separate analysis should be done for MECs: due to the early stages of the technology compared to the other processes, there is a higher uncertainty of results as confirmed by other authors [60,79]. Another factor that can

lead to different results, given a specific technology, is the contribution of either renewable or fossil electricity, as for the study of Reano et al. [64].

In conclusion, most of the analysed works presented biomass-to-H₂ carbon intensities in the range of 6–11 kg_{CO_{2e}}/kg_{H₂}, on a mean lower than the NG SMR area. The bottom ends of the figures presented represent the most optimistic studies, which show how GHG emissions reach a very low levels, generally considering renewable energy input for biomass processing, carbon credits and optimistic conversion yields. However, process improvements may be necessary for reducing some relevant impacts, or estimations at larger scale production may be necessary to provide a more balanced comparison with current fossil-based hydrogen productions.

5. Discussion

5.1. Comparison with other studies

The calculated figures of CEDs and carbon intensities are compared with the results of the JEC (JRC-EUCAR-CONCAWE) study, version 5 [104]. JEC is a long-standing collaboration between the European Commission Joint Research Centre, EUCAR and CONCAWE, which scope is to evaluate the energy use and GHG emissions related to engine and vehicle technologies, fuel qualities, and the interaction between them.

The study considers several H₂ pathways, including a large category of different initial feedstocks, from fossil to biomass sources (a WtT, Well-to-Tank system modelling). For the natural gas derived H₂ (GMCH) converted through SMR process, the EU-mix natural gas supply is considered. Production of H₂ from coal is also modelled (KOCH), so to show the different GHG performance of the various fossil fuel options. Among the biomass supplied pathways, wood to H₂ through gasification (WFLH) and biomethane upgrade (OWCH) are the most representative. Finally, H₂ production via electrolysis is shown, both for renewable (WDEL) and EU-mix supplies (EMEL). Together with GHG emissions, the expanded energy, defined as the total primary energy needed, regardless of its origin, to produce one MJ of the finished fuel under study (LHV basis) is also reported in Table 3.

WtT carbon intensities have been converted on mass basis of hydrogen, assuming the 120 MJ/kg low heat value (as indicated in the

Table 3

GHG intensity and expanded energy for various JEC Well-to-Tank modelled H₂ pathways.

Pathway description	Pathway code	WtT value	Expanded Energy
	-	(kg _{CO_{2e}} /kg _{H₂})	(MJ/MJ _{fuel})
EU-mix natural gas supply, transport to EU by pipeline, transport inside EU, distribution through high-pressure trunk lines and low-pressure grid, small scale reformer at retail site, hydrogen compressed.	GMCH1	13.3	0.94
EU-mix hard coal without CCS, hydrogen pipeline transport, hydrogen compression at retail site.	KOCH1	28.2	1.44
Farmed wood, large-scale gasifier and hydrogen liquefaction, hydrogen cryo-compression into vehicle tank (35 MPa).	WFLH1	2.14	1.89
Upgraded biogas from municipal organic waste sent to onsite SMR closed digestate storage.	OWCH1	2.74	2.01
Compressed hydrogen from EU-mix electricity via electrolysis, distributed by pipeline.	EMEL1/ CH2	20.98	3.7
Liquified hydrogen from wind electricity via electrolysis.	WDEL1/ LH1	0.43	0.96

JEC study) as conversion factor. Regarding the expanded energy analysis, the values have been left as they are reported in the report, considering that one unit coincides with a value lying on the dotted line shown in Fig. 3.

Expanded energy analysis in JEC is similar to the comparison of CEDs carried out in Table 2. Comparing these results with the data elaborated from sections 4.3 and 4.4, biomass-to-H₂ conversion pathways present values that fall within the band of their respective pathways presented in Figs. 3 and 4. In particular, the calculated carbon intensity of wood gasification, converted in mass units, results in 2.14 kg_{CO_{2e}}/kg_{H₂}, a significant lower figure than the 8.5 kg_{CO_{2e}}/kg_{H₂} average value estimated in this work. The same for biomethane upgrading, that results in 2.74 against the 7.1 kg_{CO_{2e}}/kg_{H₂} as reported in the present study. The gaps are mainly attributable to the use of more recent input data, especially for the higher share of renewables electricity mix (EU27 mix in 2018), and the large scale assumed for the production (commercial level).

Regarding the energy assessment, in the JEC study, the energy demand results are in general much higher than the ones reported in Fig. 3, as in this study only the fossil inputs are considered, while in JEC, all the energy inputs are accounted for.

On the other hand, both SMR and electrolysis pathways remain in the boundaries provided by the areas shown in Figs. 3 and 4 for the fossil-pathways counterparts. In conclusion, comparing biomass-to-H₂ conversion pathways with the hydrogen produced from electrolysis powered by wind energy, there is a significant difference, mostly due to the emissions of renewable electricity that are set to zero within JEC. This assumption has also been made in several other LCA studies mentioned in the previous sections. It is worth remarking that emissions from equipment and plant construction and decommissioning (not considered within JEC) should be considered in the calculation of the GHG intensity; their inclusion in the calculations would result in not-zero GHG emissions from renewables and nuclear power.

5.2. Limits and barriers of LCA studies

The present analysis confirms the high data variability from the selected LCA studies, especially for those pathways which are not yet at commercial/large scale [85]. Despite the guidance of the international ISO methodology (i.e., ISO 14040 [49]) and of specific LCA methodological studies (i.e., EC JRC [105]), each analysed study proposes its own methodological choices, leading to a wide range of results. It is worth remarking that different assumptions in input data, system boundaries, allocation criteria, processes yields and plants sizes, are allowed by LCA methodology but generate significantly different outputs, often subjected to various interpretations [58,60,64]. Even if this study proposed some mitigation protocols from harmonisation process proposed by Valente et al. [84,106], some differences cannot be filled. Some measures to harmonise different models (e.g., GHGenius - Canada, GREET - USA, REDII methodology - EU, and VSB - Brazil) have been recently proposed by some IEA researchers [107,108] with promising results. However, differences among the evaluated models consider different agricultural processes, substitution procedures, allocation methods, renewable energy sharing, energy demand of processes at different scales, modes and distances for feedstock transportation (which are specific for each country).

The data extraction, elaboration and harmonisation followed within the present work allowed the creation of a dataset, mitigating the potential gaps in the results for the carbon intensity and energy assessment of the hydrogen production. According to this study, differences of about ±1.5 kg_{CO_{2e}}/kg_{H₂} for biomass gasification- and fermentation-derived hydrogen were mainly associated with the inclusion of emissions for capital goods, and non-uniform system boundaries. In particular, the energy demand of hydrogen compression or liquefaction by means of cryogenic conditions could have a significant contribution to the final result. Today, several international initiatives have been working for

proposing harmonisation method to perform calculation about carbon intensity and energy yields, so to promote the hydrogen market uptake across the world. These efforts will also help the LCA practitioners to standardise input data, operating conditions and storage parameters of the hydrogen traded, in view of the upcoming energy transition.

6. Conclusions

The recently issued EU targets for economy decarbonisation promote the deployment of a hydrogen market, foreseeing a very rapid uptake in various sectors, in particular for sustainable, low carbon technologies that comply with the requirements imposed by the carbon emissions reduction targets. That is expected to open possibilities and opportunities for new and existing value chains based on bio-based feedstock deriving from biofuels and bioenergy production. Besides hydrogen produced via electrolysis, currently available technologies for hydrogen production from biomass can be further developed, promoting integration in existing biorefineries for large scale production. The hydrogen supply chain based either on biomethane steam reforming or biomass gasification already have the potential to be integrated in commercial applications, but even being at high TRL, their economic viability is not doable yet. The specific analysis of TRLs at different stages of the supply chains showed where the current constraints exist for emerging technologies. In this context, other novel promising technologies may contribute to covering H₂ demand, such as direct fermentation to H₂ and MEC. However, these are at very low TRL today, so they require investment to further assess and validate the performance at a larger scale. The main challenge is to prove how the scale-up of these systems may allow higher production rates of hydrogen and larger feedstock flexibility.

For the five most promising identified biomass-to-hydrogen conversion pathways, the literature-based the review showed favourable environmental performances compared to steam methane reforming and electrolysis powered by a grid mix. On an energy basis, the comparison between biomass and fossil-based hydrogen is strongly dependent on the assumptions made for energy input. When only the fossil inputs are considered, the SMR represents the upper end, while gasification process shows the lowest range. This change significantly when all inputs are considered, regardless of their origin. Clearly, in a medium-term perspective, the comparison will have to be done against renewable hydrogen produced from electrolysis, which is expected to represent the new benchmark. Thanks to a harmonisation protocol based on data extraction and re-interpretation on a consistent basis between the selected studies, results have been made comparable among each other, but current LCA findings require a significant effort toward further reconciliation to allow for scientifically sound comparisons. Moreover, the calculated carbon intensity has the potential to be further reduced by considering the use of renewable energy for the electricity inputs, carbon credits due to waste feedstock, the potential integration of BECCS (BioEnergy Carbon Capture and Storage) technologies and higher conversion yields due to future technology improvement.

Disclaimer

The views expressed here are purely those of the authors and may not, under any circumstances, be regarded as an official position of the European Commission.

Data availability

The authors do not have permission to share data.

References

[1] European Commission (EC), Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee

and the Committee of the Regions - the European Green Deal, 2019. COM/2019/640.

[2] European Commission (EC), Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions - Clean Energy for All Europeans, 2016. COM/2016/860.

[3] European Commission (EC). Communication COM/2020/301: A Hydrogen Strategy for a Climate-Neutral Europe. EUR-Lex - 52020DC0301. Brussels, BE: n. d.

[4] European Commission (EC). Communication COM/2020/456: Europe's Moment: Repair and Prepare for the Next Generation EUR-Lex - 52020DC0456. Brussels, BE: n. d.

[5] The European Parliament, DIRECTIVE (EU) 2018/2001 on the promotion of the use of energy from renewable sources (recast), *Orkesterjournalen L 328* (2018) 82–209, 21122018 2018.

[6] M.V. Twigg, V. Dupont, Hydrogen production from fossil fuel and biomass feedstocks, *Adv. Hydrog. Prod. Storage Distrib.* 43–84 (2014), <https://doi.org/10.1533/9780857097736.1.43>.

[7] B. Gaudernack, Hydrogen production from fossil fuels, *Hydrog. Power Theor. Eng. Solut.* 75–89 (1998), https://doi.org/10.1007/978-94-015-9054-9_10.

[8] M. Kayfeci, A. Kecebas, M. Bayat, Hydrogen production, <https://doi.org/10.1016/B978-0-12-814853-2.00003-5>, 2019.

[9] A. Buttler, H. Spliethoff, Current status of water electrolysis for energy storage, grid balancing and sector coupling via power-to-gas and power-to-liquids: a review, *Renew. Sustain. Energy Rev.* 82 (2018) 2440–2454, <https://doi.org/10.1016/J.RSER.2017.09.003>.

[10] P. Millet, S. Grigoriev, Water electrolysis technologies, *Renew. Hydrog. Technol. Prod. Purification, Storage, Appl. Saf.* 19–41 (2013), <https://doi.org/10.1016/B978-0-444-56352-1.00002-7>.

[11] S. Shiva Kumar, V. Himabindu, Hydrogen production by PEM water electrolysis – a review, *Mater. Sci. Energy Technol.* 2 (2019) 442–454, <https://doi.org/10.1016/J.MSET.2019.03.002>.

[12] O. Schmidt, A. Gambhir, I. Staffell, A. Hawkes, J. Nelson, S. Few, Future cost and performance of water electrolysis: an expert elicitation study, *Int. J. Hydrogen Energy* 42 (2017) 30470–30492, <https://doi.org/10.1016/J.IJHYDENE.2017.10.045>.

[13] Z. Jun, W. Shuzhong, W. Zhiqiang, M. Haiyu, C. Lin, Hydrogen-rich syngas produced from the co-pyrolysis of municipal solid waste and wheat straw, *Int. J. Hydrogen Energy* 42 (2017), 19701, <https://doi.org/10.1016/J.IJHYDENE.2017.06.166>. –8.

[14] Z. Hameed, M. Aslam, Z. Khan, K. Maqsood, A.E. Atabani, M. Ghauri, et al., Gasification of municipal solid waste blends with biomass for energy production and resources recovery: current status, hybrid technologies and innovative prospects, *Renew. Sustain. Energy Rev.* 136 (2021), 110375, <https://doi.org/10.1016/J.RSER.2020.110375>.

[15] The European Commission (EC), Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions – ‘Fit for 55’: Moving towards Climate Neutrality – Delivering the EU’s 2030 Climate Target COM, vol. 55, 2021, 2021.

[16] T.J. Schildhauer, S.M.A. Biollaz, Synthetic Natural Gas from Coal and Dry Biomass, and Power-To-Gas Applications, John Wiley & Sons, Inc., Hoboken, New Jersey, 2016, <https://doi.org/10.1002/9781119191339>. John Wiley & Sons, Inc.

[17] T.A. Milne, C.C. Elam, R.J. Evans, Hydrogen from Biomass: State of the Art and Research Challenges, Golden, CO, 2002.

[18] Krzysztof J. Ptasinski, Efficiency analysis of hydrogen production methods from biomass, *Int. J. Alternative Propul.* 2 (2008) 1601–1608.

[19] P.C. Hallenbeck, J.R. Benemann, Biological hydrogen production; Fundamentals and limiting processes, *Int. J. Hydrogen Energy* 27 (2002) 1185–1193, [https://doi.org/10.1016/S0360-3199\(02\)00131-3](https://doi.org/10.1016/S0360-3199(02)00131-3).

[20] Y. Kalinci, A. Hepbasli, I. Dincer, Biomass-based hydrogen production: a review and analysis, *Int. J. Hydrogen Energy* 34 (2009) 8799–8817, <https://doi.org/10.1016/j.ijhydene.2009.08.078>.

[21] A. Boyano, A.M. Blanco-Marigorta, T. Morosuk, G. Tsatsaronis, Exergoenvironmental analysis of a steam methane reforming process for hydrogen production, *Energy* 36 (2011) 2202–2214, <https://doi.org/10.1016/j.energy.2010.05.020>.

[22] L. Cao, I.K.M. Yu, X. Xiong, D.C.W. Tsang, S. Zhang, J.H. Clark, et al., Biorenewable hydrogen production through biomass gasification: a review and future prospects, *Environ. Res.* 186 (2020), 109547, <https://doi.org/10.1016/j.envres.2020.109547>.

[23] Y. Kalinci, A. Hepbasli, I. Dincer, Exergoeconomic analysis of hydrogen production from biomass gasification, *Int. J. Hydrogen Energy* 37 (2012) 16402–16411, <https://doi.org/10.1016/j.ijhydene.2012.02.173>.

[24] P. Nikolaidis, A. Poullikkas, A comparative overview of hydrogen production processes, *Renew. Sustain. Energy Rev.* 67 (2017) 597–611, <https://doi.org/10.1016/j.rser.2016.09.044>.

[25] A. Blasi, G. Fiorenza, A. Verardi, Current Trends and Future Developments on (Bio-) Membranes, Elsevier Inc., Rende, CS, Italy, 2020, <https://doi.org/10.1016/B978-0-12-817384-8.00003-0>. Chapter 3 - Hydrogen from biomass.

[26] S.E. Hosseini, M.A. Wahid, Hydrogen production from renewable and sustainable energy resources: promising green energy carrier for clean development, *Renew. Sustain. Energy Rev.* 57 (2016) 850–866, <https://doi.org/10.1016/j.rser.2015.12.112>.

[27] C. Acar, I. Dincer, Comparative assessment of hydrogen production methods from renewable and non-renewable sources, *Int. J. Hydrogen Energy* 39 (2014) 1–12, <https://doi.org/10.1016/j.ijhydene.2013.10.060>.

- [28] H. Balat, E. Kirtay, Hydrogen from biomass - present scenario and future prospects, *Int. J. Hydrogen Energy* 35 (2010) 7416–7426, <https://doi.org/10.1016/j.ijhydene.2010.04.137>.
- [29] J.D. Holladay, J. Hu, D.L. King, Y. Wang, An overview of hydrogen production technologies, *Catal. Today* 139 (2009) 244–260, <https://doi.org/10.1016/j.cattod.2008.08.039>.
- [30] M. Ni, D.Y.C. Leung, M.K.H. Leung, K. Sumathy, An overview of hydrogen production from biomass, *Fuel Process. Technol.* 87 (2006) 461–472, <https://doi.org/10.1016/j.fuproc.2005.11.003>.
- [31] R. Schmersahl, M. Klemm, R. Brunsternmann, R. Widmann, Hydrogen from biomass, in: R.A. Meyers (Ed.), *Encycl. Sustain. Sci. Technol.*, Springer New York, New York, NY, 2012, pp. 5116–5133, https://doi.org/10.1007/978-1-4419-0851-3_318.
- [32] L. Singh, Z.A. Wahid, Methods for enhancing bio-hydrogen production from biological process: a review, *J. Ind. Eng. Chem.* 21 (2015) 70–80, <https://doi.org/10.1016/j.jiec.2014.05.035>.
- [33] N. Akhlaghi, G. Najafpour-Darzi, A comprehensive review on biological hydrogen production, *Int. J. Hydrogen Energy* 45 (2020) 22492–22512, <https://doi.org/10.1016/j.ijhydene.2020.06.182>.
- [34] J. Lui, W.H. Chen, D.C.W. Tsang, S. You, A critical review on the principles, applications, and challenges of waste-to-hydrogen technologies, *Renew. Sustain. Energy Rev.* 134 (2020), 110365, <https://doi.org/10.1016/j.rser.2020.110365>.
- [35] C.N.C. Hitam, A.A. Jalil, A review on biohydrogen production through photo-fermentation of lignocellulosic biomass, *Biomass Convers Biorefinery* (2020) 1–19, <https://doi.org/10.1007/s13399-020-01140-y>.
- [36] S. Rittmann, C. Herwig, A comprehensive and quantitative review of dark fermentative biohydrogen production, *Microb. Cell Factories* 11 (2012) 20–25, <https://doi.org/10.1186/1475-2859-11-115>.
- [37] R. Łukajtis, I. Hołowacz, K. Kucharska, M. Glinka, P. Rybarczyk, A. Przyjazny, et al., Hydrogen production from biomass using dark fermentation, *Renew. Sustain. Energy Rev.* 91 (2018) 665–694, <https://doi.org/10.1016/j.rser.2018.04.043>.
- [38] A. Kadier, Y. Simayi, M.S. Kalil, P. Abdesshahian, A.A. Hamid, A review of the substrates used in microbial electrolysis cells (MECs) for producing sustainable and clean hydrogen gas, *Renew. Energy* 71 (2014) 466–472, <https://doi.org/10.1016/j.renene.2014.05.052>.
- [39] F. Dalena, A. Senatore, A. Tursi, A. Basile, Bioenergy production from second- and third-generation feedstocks, in: *Bioenergy Syst. Futur. Prospect. Biofuels Biohydrogen*, Elsevier Inc., 2017, pp. 559–599, <https://doi.org/10.1016/B978-0-08-101031-0.00017-X>.
- [40] J. Chen, W. Xu, X. Wu, J. E. N. Lu, T. Wang, et al., System development and environmental performance analysis of a pilot scale microbial electrolysis cell for hydrogen production using urban wastewater, *Energy Convers. Manag.* 193 (2019) 52–63, <https://doi.org/10.1016/j.enconman.2019.04.060>.
- [41] Q. Wu, S. Jiao, M. Ma, S. Peng, Microbial fuel cell system: a promising technology for pollutant removal and environmental remediation, *Environ. Sci. Pollut. Res.* 27 (2020) 6749–6764, <https://doi.org/10.1007/s11356-020-07745-0>.
- [42] T. Lepage, M. Kammoun, Q. Schmetz, A. Richel, Biomass-to-hydrogen: a review of main routes production, processes evaluation and techno-economical assessment, *Biomass Bioenergy* 144 (2021), 105920, <https://doi.org/10.1016/j.biombioe.2020.105920>.
- [43] G. Nahar, D. Mote, V. Dupont, Hydrogen production from reforming of biogas: review of technological advances and an Indian perspective, *Renew. Sustain. Energy Rev.* 76 (2017) 1032–1052, <https://doi.org/10.1016/j.rser.2017.02.031>.
- [44] F. Samimi, T. Marzoughi, M.R. Rahimpour, Energy and exergy analysis and optimization of biomass gasification process for hydrogen production (based on air, steam and air/steam gasifying agents), *Int. J. Hydrogen Energy* 45 (2020) 33185–33197, <https://doi.org/10.1016/j.ijhydene.2020.09.131>.
- [45] L. Cao, I.K.M. Yu, X. Xiong, D.C.W. Tsang, S. Zhang, J.H. Clark, et al., Renewable hydrogen production through biomass gasification: a review and future prospects, *Environ. Res.* 186 (2020), 109547, <https://doi.org/10.1016/j.envres.2020.109547>.
- [46] M. Binder, M. Kraussler, M. Kuba, M. Luisser, IEA Bioenergy Task 33 Report. *Hydrogen from Biomass Gasification*, 2018. Paris (France).
- [47] Ludwig-Bölkow-Systemtechnik (LBST), Hincio. *Study on Hydrogen from Renewable Resources in the EU - Final Report*, 2015. Ottobrunn (Munich), Germany.
- [48] H. Tian, J. Li, M. Yan, Y.W. Tong, C.H. Wang, X. Wang, Organic waste to biohydrogen: a critical review from technological development and environmental impact analysis perspective, *Appl. Energy* 256 (2019), 113961, <https://doi.org/10.1016/j.apenergy.2019.113961>.
- [49] International Organization for Standardization, ISO 14040:2006 *Environmental Management - Life Cycle Assessment - Principles and Framework*, 2006. Geneva, Switzerland.
- [50] A. Susmozas, D. Iribarren, J. Dufour, Life-cycle performance of indirect biomass gasification as a green alternative to steam methane reforming for hydrogen production, *Int. J. Hydrogen Energy* 38 (2013) 9961–9972, <https://doi.org/10.1016/j.ijhydene.2013.06.012>.
- [51] M. Muresan, C.C. Cormos, P.S. Agachi, Comparative life cycle analysis for gasification-based hydrogen production systems, *J. Renew. Sustain. Energy* 6 (2014), <https://doi.org/10.1063/1.4864658>.
- [52] M. Martín-Gamboa, D. Iribarren, A. Susmozas, J. Dufour, Delving into sensible measures to enhance the environmental performance of biohydrogen: a quantitative approach based on process simulation, life cycle assessment and data envelopment analysis, *Bioresour. Technol.* 214 (2016) 376–385, <https://doi.org/10.1016/j.biortech.2016.04.133>.
- [53] Y.K. Salkuyeh, B.A. Saville, H.L. MacLean, Techno-economic analysis and life cycle assessment of hydrogen production from different biomass gasification processes, *Int. J. Hydrogen Energy* 43 (2018) 9514–9528, <https://doi.org/10.1016/j.ijhydene.2018.04.024>.
- [54] I. Bartolozzi, F. Rizzi, M. Frey, Comparison between hydrogen and electric vehicles by life cycle assessment: a case study in Tuscany, Italy, *Appl. Energy* 101 (2013) 103–111, <https://doi.org/10.1016/j.apenergy.2012.03.021>.
- [55] C. Wulf, M. Kaltschmitt, Life cycle assessment of hydrogen supply chain with special attention on hydrogen refuelling stations, *Int. J. Hydrogen Energy* 37 (2012) 16711–16721, <https://doi.org/10.1016/j.ijhydene.2012.03.028>.
- [56] C. Wulf, M. Kaltschmitt, Life cycle assessment of biohydrogen production as a transportation fuel in Germany, *Bioresour. Technol.* 150 (2013) 466–475, <https://doi.org/10.1016/j.biortech.2013.08.127>.
- [57] C. Koroneos, A. Domprios, G. Roumbas, Hydrogen production via biomass gasification-A life cycle assessment approach, *Chem. Eng. Process Process Intensif.* 47 (2008) 1261–1268, <https://doi.org/10.1016/j.ccep.2007.04.003>.
- [58] A. Mehmeti, A. Angelis-Dimakis, G. Arampatzis, S.J. McPhail, S. Ulgiati, Life cycle assessment and water footprint of hydrogen production methods: from conventional to emerging technologies, *Environ. Monit. Assess.* 192 (2018) 1–19, <https://doi.org/10.1007/s10661-018-02002-4>.
- [59] Y. Kalinci, A. Hepbasli, I. Dincer, Life cycle assessment of hydrogen production from biomass gasification systems, *Int. J. Hydrogen Energy* 37 (2012) 14026–14039, <https://doi.org/10.1016/j.ijhydene.2012.06.015>.
- [60] A.P. Borole, A.L. Greig, Life-Cycle Assessment and Systems Analysis of Hydrogen Production, *Biohydrogen*, 2019, pp. 485–512, <https://doi.org/10.1016/b978-0-444-64203-5.00020-4>.
- [61] M.R. Kabir, A. Kumar, Development of net energy ratio and emission factor for biohydrogen production pathways, *Bioresour. Technol.* 102 (2011) 8972–8985, <https://doi.org/10.1016/j.biortech.2011.06.093>.
- [62] A. Simons, C. Bauer, *Life Cycle Assessment of Hydrogen Production. Transit. To Hydrog. Pathways Toward Clean Transp.*, Cambridge University Press, 2011, pp. 13–57, <https://doi.org/10.1017/CBO9781139018036.006>.
- [63] J. Moreno, J. Dufour, Life cycle assessment of hydrogen production from biomass gasification. Evaluation of different Spanish feedstocks, *Int. J. Hydrogen Energy* 38 (2013) 7616–7622, <https://doi.org/10.1016/j.ijhydene.2012.11.076>.
- [64] R.L. Reaño, Assessment of environmental impact and energy performance of rice husk utilization in various biohydrogen production pathways, *Bioresour. Technol.* 299 (2020), 122590, <https://doi.org/10.1016/j.biortech.2019.122590>.
- [65] C. Antonini, K. Treyer, A. Streb, M. van der Spek, C. Bauer, M. Mazzotti, Hydrogen production from natural gas and biomethane with carbon capture and storage - a techno-environmental analysis, *Sustain. Energy Fuels* 4 (2020) 2967–2986, <https://doi.org/10.1039/d0se00222d>.
- [66] N. Hajjaji, S. Martinez, E. Trabaly, J.P. Steyer, A. Helias, Life cycle assessment of hydrogen production from biogas reforming, *Int. J. Hydrogen Energy* 41 (2016) 6064–6075, <https://doi.org/10.1016/j.ijhydene.2016.03.006>.
- [67] N. Hajjaji, M.N. Pons, V. Renaudin, A. Houas, Comparative life cycle assessment of eight alternatives for hydrogen production from renewable and fossil feedstock, *J. Clean. Prod.* 44 (2013) 177–189, <https://doi.org/10.1016/j.jclepro.2012.11.043>.
- [68] F. Battista, Y.S. Montenegro Camacho, S. Hernández, S. Bensaïd, A. Herrmann, H. Krause, et al., LCA evaluation for the hydrogen production from biogas through the innovative BioRobur project concept, *Int. J. Hydrogen Energy* 42 (2017) 14030–14043, <https://doi.org/10.1016/j.ijhydene.2016.12.065>.
- [69] A. Susmozas, D. Iribarren, J. Dufour, Assessing the life-cycle performance of hydrogen production via biofuel reforming in Europe, *Resources* 4 (2015) 398–411, <https://doi.org/10.3390/resources4020398>.
- [70] A. Susmozas, D. Iribarren, P. Zapp, J. Linßen, J. Dufour, Life-cycle performance of hydrogen production via indirect biomass gasification with CO₂ capture, *Int. J. Hydrogen Energy* 41 (2016), 19484, <https://doi.org/10.1016/j.ijhydene.2016.02.053>.
- [71] O. Siddiqui, I. Dincer, A well to pump life cycle environmental impact assessment of some hydrogen production routes, *Int. J. Hydrogen Energy* 44 (2019) 5773–5786, <https://doi.org/10.1016/j.ijhydene.2019.01.118>.
- [72] E. Heracleous, Well-to-Wheels analysis of hydrogen production from bio-oil reforming for use in internal combustion engines, *Int. J. Hydrogen Energy* 36 (2011) 11501–11511, <https://doi.org/10.1016/j.ijhydene.2011.06.052>.
- [73] M. Marquievich, G.W. Sonnemann, F. Castells, D. Montané, Life cycle inventory analysis of hydrogen production by the steam-reforming process: comparison between vegetable oils and fossil fuels as feedstock, *Green Chem.* 4 (2002) 414–423, <https://doi.org/10.1039/b203742b>.
- [74] S. Authayanun, U. Suwanmanee, A. Arpornwichean, Enhancement of dilute bio-ethanol steam reforming for a proton exchange membrane fuel cell system by using methane as co-reactant: performance and life cycle assessment, *Int. J. Hydrogen Energy* 40 (2015) 12144–12153, <https://doi.org/10.1016/j.ijhydene.2015.07.042>.
- [75] S.N. Djomo, D. Blumberga, Comparative life cycle assessment of three biohydrogen pathways, *Bioresour. Technol.* 102 (2011) 2684–2694, <https://doi.org/10.1016/j.biortech.2010.10.139>.
- [76] R. Pacheco, A.F. Ferreira, T. Pinto, B.P. Nobre, D. Loureiro, P. Moura, et al., The production of pigments & hydrogen through a *Spirogyra* sp. biorefinery, *Energy Convers. Manag.* 89 (2015) 789–797, <https://doi.org/10.1016/j.enconman.2014.10.040>.
- [77] A.F. Ferreira, J. Ortigueira, L. Alves, L. Gouveia, P. Moura, C.M. Silva, Energy requirement and CO₂ emissions of bioH₂ production from microalgal biomass, *Biomass Bioenergy* 49 (2013) 249–259, <https://doi.org/10.1016/j.biombioe.2012.12.033>.

- [78] A.F. Ferreira, J.P. Ribau, C.M. Silva, Energy consumption and CO₂ emissions of potato peel and sugarcane biohydrogen production pathways, applied to Portuguese road transportation, *Int. J. Hydrogen Energy* 36 (2011) 13547–13558, <https://doi.org/10.1016/j.ijhydene.2011.08.008>.
- [79] S. Manish, R. Banerjee, Comparison of biohydrogen production processes, *Int. J. Hydrogen Energy* 33 (2008) 279–286, <https://doi.org/10.1016/j.ijhydene.2007.07.026>.
- [80] A.F. Ferreira, J. Ortigueira, L. Alves, L. Gouveia, P. Moura, C. Silva, Biohydrogen production from microalgal biomass: energy requirement, CO₂ emissions and scale-up scenarios, *Bioresour. Technol.* 144 (2013) 156–164, <https://doi.org/10.1016/j.biortech.2013.06.079>.
- [81] Q. Dai, A. Elgowainy, J. Kelly, J. Han, M. Wang, Life Cycle Analysis of Hydrogen Production from Non-Fossil Sources, 2016, <https://doi.org/10.3303/CET1021194>. Argonne, IL, USA.
- [82] K.Y. Show, D.J. Lee, Z.P. Zhang, Production of Biohydrogen: Current Perspectives and Future Prospects, Elsevier Inc., Biofuels, 2011, pp. 467–479, <https://doi.org/10.1016/B978-0-12-385099-7.00021-8>.
- [83] K.W. Harrison, R. Remick, G.D. Martin, A. Hoskin, *Hydrogen Production: Fundamentals and Case Study Summaries*, 2010. Golden, CO (USA).
- [84] A. Valente, D. Iribarren, J. Dufour, Harmonising the cumulative energy demand of renewable hydrogen for robust comparative life-cycle studies, *J. Clean. Prod.* 175 (2018) 384–393, <https://doi.org/10.1016/j.jclepro.2017.12.069>.
- [85] A. Valente, D. Iribarren, J. Dufour, Life cycle assessment of hydrogen energy systems: a review of methodological choices, *Int. J. Life Cycle Assess.* 22 (2017) 346–363, <https://doi.org/10.1007/s11367-016-1156-z>.
- [86] J.Z. Zhang, J. Li, Y. Li, Y. Zhao, Util, Established Methods Based on Compression and Cryogenics. *Hydrog. Gener. Storage*, John Wiley & Sons Inc, Hoboken, USA, 2014, pp. 75–90, <https://doi.org/10.1002/9781118875193.ch5>.
- [87] The European Parliament, DIRECTIVE 2009/28/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 23 April 2009 on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC, *Orkesterjournalen L 140* (2008) 16–62, 5/6/2009 2009.
- [88] E. Nieuwlaar, Life cycle assessment and energy systems, *Encycl Energy* (2004) 647, <https://doi.org/10.1016/B0-12-176480-X/00233-3>. –54.
- [89] E. Bargiacchi, D. Candelaresi, A. Valente, G. Spazzafumo, S. Frigo, Life cycle assessment of substitute natural gas production from biomass and electrolytic hydrogen, *Int. J. Hydrogen Energy* 46 (2021) 35974–35984, <https://doi.org/10.1016/j.ijhydene.2021.01.033>.
- [90] M. Mohan, Perovskite photovoltaics: life cycle assessment. *Perovskite photovoltaics basic to, Adv. Concepts Implement.* (2018) 447, <https://doi.org/10.1016/B978-0-12-812915-9.00014-9>. –80.
- [91] G.V. Brigagão, O. de Queiroz Fernandes Araújo, J.L. de Medeiros, H. Mikulcic, N. Duic, A techno-economic analysis of thermochemical pathways for corn-cob-to-energy: fast pyrolysis to bio-oil, gasification to methanol and combustion to electricity, *Fuel Process. Technol.* 193 (2019) 102–113, <https://doi.org/10.1016/j.fuproc.2019.05.011>.
- [92] J.L. Zheng, Y.H. Zhu, M.Q. Zhu, K. Kang, R.C. Sun, A review of gasification of bio-oil for gas production, *Sustain. Energy Fuels* 3 (2019) 1600–1622, <https://doi.org/10.1039/c8se00553b>.
- [93] E. Boymans, B. Vreugdenhil, P. Abelha, M. Buffi, D. Chiaramonti, A value chain for large scale ft production: the case of pyrolysis oil-char slurry gasification, *Eur. Biomass Conf. Exhib. Proc.* (2019).
- [94] P. Feng, W. Lin, P.A. Jensen, W. Song, L. Hao, K. Raffelt, et al., Entrained flow gasification of coal/bio-oil slurries, *Energy* 111 (2016) 793–802, <https://doi.org/10.1016/j.energy.2016.05.115>.
- [95] E.J. Leijenhorst, D. Assink, L. van de Beld, F. Weiland, H. Wiinikka, P. Carlsson, et al., Entrained flow gasification of straw- and wood-derived pyrolysis oil in a pressurized oxygen blown gasifier, *Biomass Bioenergy* 79 (2015) 166–176, <https://doi.org/10.1016/j.biombioe.2014.11.020>.
- [96] J.S. Crater, J.C. Lieveuse, Scale-up of industrial microbial processes, *FEMS Microbiol. Lett.* 365 (2018) 138, <https://doi.org/10.1093/femsle/fny138>.
- [97] A. Xia, X. Zhu, Q. Liao, Hydrogen production from biological sources, in: *Fuel Cells Hydrog. Prod.*, Springer, New York, 2019, pp. 833–863, https://doi.org/10.1007/978-1-4939-7789-5_955.
- [98] A. Al-Qahtani, B. Parkinson, K. Hellgardt, N. Shah, G. Guillen-Gosalbez, Uncovering the true cost of hydrogen production routes using life cycle monetisation, *Appl. Energy* 281 (2021), 115958, <https://doi.org/10.1016/j.apenergy.2020.115958>.
- [99] C. Acar, I. Dincer, Hydrogen Production, vols. 3–5, 2018, <https://doi.org/10.1016/B978-0-12-809597-3.00304-7>.
- [100] P.L. Spath, M.K. Mann, Life Cycle Assessment of Hydrogen Production via Natural Gas Steam Reforming NREL/TP-570-27637, 2000, <https://doi.org/10.2172/764485>. Golden, CO (USA).
- [101] International Energy Agency (IEA), The Future of Hydrogen Report - Prepared by the IEA for the G20, Japan - Seizing Today's Opportunities, 2019, <https://doi.org/10.1787/1e0514c4-en>. Paris (France).
- [102] S. Czernik, A.V. Bridgwater, Overview of applications of biomass fast pyrolysis oil, *Energy Fuel.* 18 (2004) 590–598, <https://doi.org/10.1021/ef034067u>.
- [103] A. Oasmaa, J. Lehto, Y. Solantausta, S. Kallio, Historical Review on VTT Fast Pyrolysis Bio-Oil Production and Upgrading, vol. 35, *Energy & Fuels*, 2021, <https://doi.org/10.1021/ACS.ENERGYFUELS.1C00177>.
- [104] M. Prussi, M. Yugo, L. De Prada, M. Padella, R. Edwards, L. Lonza, JEC Well-To-Tank Report V5 | EUR 30269 EN | JRC119036, 2020, <https://doi.org/10.2760/959137>. Luxembourg.
- [105] European Commission, Joint Research Centre, Institute for Environment and Sustainability, International Reference Life Cycle Data System (ILCD) Handbook - General Guide for Life Cycle Assessment - Detailed Guidance, 2010, <https://doi.org/10.2788/38479>. Luxembourg.
- [106] A. Valente, D. Iribarren, J. Dufour, Harmonised life-cycle global warming impact of renewable hydrogen, *J. Clean. Prod.* 149 (2017) 762–772, <https://doi.org/10.1016/j.jclepro.2017.02.163>.
- [107] A. Bonomi, B.C. Klein, M.F. Chagas, N.R.D. Souza, IEA Bioenergy Task 39 Report. Comparison of Biofuel Life Cycle Analysis Tools - Phase 2, Part 1: FAME and HVO/HEFA, 2018. Paris (France).
- [108] A. Bonomi, B.C. Klein, M.F. Chagas, N.R.D. Souza, IEA Bioenergy Task 39 Report. Comparison of Biofuel Life Cycle Analysis Tools - Phase 2, Part 2: Biochemical 2G Ethanol, 2019. Paris (France).