

# RENEWABLE HYDROGEN PRODUCTION FROM BIOMASS



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## ABSTRACT

Hydrogen is highlighted as a key energy carrier in a future net zero green-house gas (GHG) emission society. It is a suitable energy carrier for many applications, e.g., heavy transportation and for industrial use. Furthermore, combusting hydrogen or using it in a fuel cell does not cause GHG emissions at site. This implies that, if produced without emitting GHG emissions, hydrogen can be a completely renewable energy carrier. However, currently over 90% of the world's hydrogen supply is produced from fossil natural gas and coal. If hydrogen is to be used as a sustainable alternative to fossil fuels, it needs to be produced without net emissions of GHG; one such alternative is to use forest biomass. This work presents a literature review of technologies for hydrogen production from sustainably harvested forest biomass. An overview of available technologies is included, but thermochemical production methods are emphasized. Results show that biomass gasification coupled with steam methane reforming and water gas shift reactors reaches the highest biomass to hydrogen conversion yields. Compared to other biomass based, technological pathways, gasification and pyrolysis also have the highest technological readiness levels. The literature review suggests hydrogen production costs from gasification or pyrolysis reaching from 0.078 to 0.21 EUR/kWh. This compares to a production cost of 0.019 EUR/kWh for natural gas SMR and 0.023 EUR/kWh for coal gasification and production costs of 0.045-0.12 EUR/MWh for water electrolysis.

## ABBREVIATIONS

ATR – Auto Thermal Reforming  
BECCS – Bio Energy Carbon Capture and Storage  
CCS – Carbon Capture and Storage  
Daf – Dry, ash-free  
DFB – Dual Fluidized Bed  
EF – Entrained Flow  
GHG – Greenhouse Gas  
LCA – Life Cycle Assessment  
MEC - Microbial Electrolysis Cell  
NG – Natural Gas  
PEM – Proton Exchange Membrane  
PEMEC - Proton Exchange Membrane Electrolysis Cell  
PSA – Pressure Swing Adsorption  
R&D – Research and Development  
SCWG – Super Critical Water Gasification  
SMR – Steam Methane Reforming  
TRL – Technological Readiness Level  
w.b. – wet basis  
WC – Wood Chips  
WGS – Water Gas Shift

## INTRODUCTION

Hydrogen has a heating value (LHV, mass basis), 2.4, 2.8 and 4 times higher than that of methane, gasoline and coal, respectively and an energy density more than 100 times higher than that of a conventional Lithium-ion battery. Furthermore, combustion of hydrogen, or using it in fuel cells, does not create any greenhouse gas (GHG) emissions at site. This implies that, if produced without emitting GHG emissions, hydrogen can be an almost CO<sub>2</sub> neutral energy carrier. Due to these desirable characteristics, hydrogen can be applied as a renewable energy carrier and is particularly interesting for applications that are hard to electrify, e.g., heavy transportation and for industrial applications. Owing to the fact that hydrogen is easier to store than electricity, it is also likely to be used for electricity storage in electricity systems reliant on intermittent electricity generation [1]. For these reasons hydrogen is viewed as a key energy carrier in reaching the climate goals stated in the Paris Agreement and several countries have developed hydrogen strategies as a means to reach their individual climate goals [2], [3], [4], [5]. The current (2017) world production of hydrogen exceeds 7.7 EJ where the majority is used for ammonia production (51%), followed by oil refining (31%) and methanol production (10%) [6]. As hydrogen is projected to be used increasingly as a supplement to fossil energy carriers that number is expected to increase to levels of approximately 50 EJ by 2050 [7], [8].

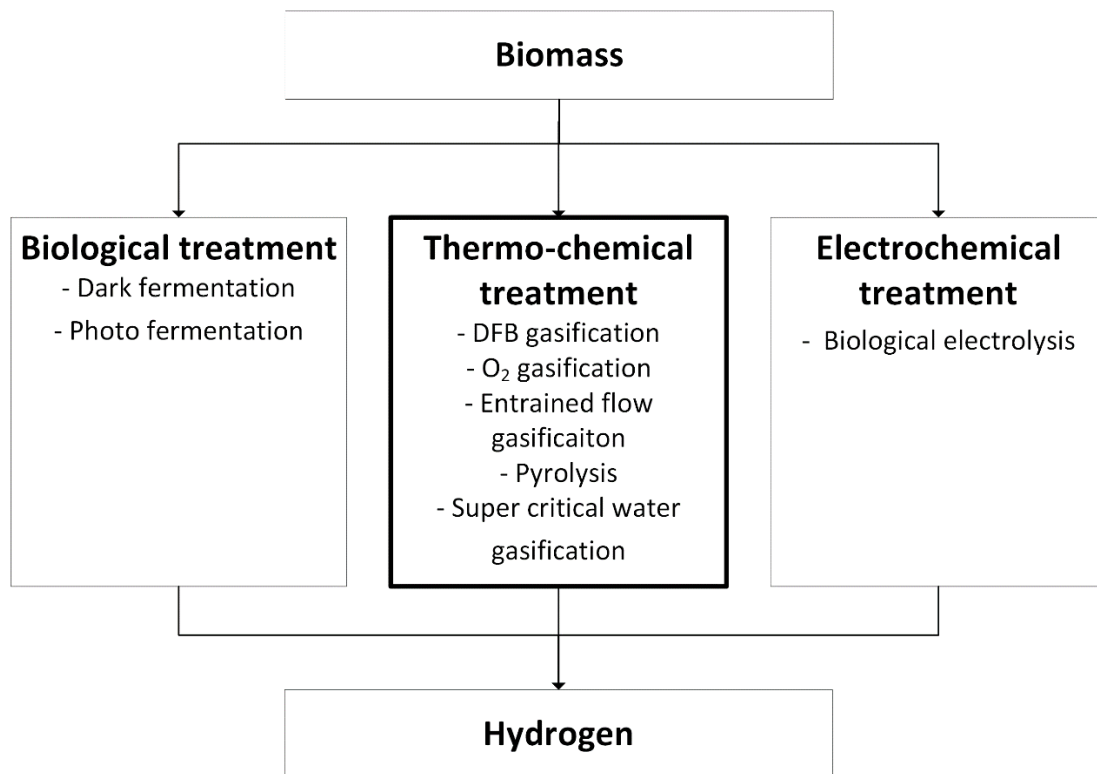
For hydrogen to become a sustainable alternative to fossil fuels, it is essential that it is produced using renewable energy. Currently, around 98% of the world's hydrogen production is based on fossil energy sources, with the majority (76%) coming from steam methane reforming (SMR) of natural gas (NG) and the remainder from liquid hydrocarbons and coal [9], [7]. The most discussed alternative for sustainable hydrogen production is water electrolysis using renewable electricity [10]. Water electrolysis is a technology with a TRL of 9 and is already responsible for around 2% of the world's hydrogen production. However, the technology remains relatively cost intensive and has issues competing with fossil-based alternatives. Nonetheless, as R&D progresses and the technology is scaled up, the costs are expected to decrease [11].

In a future where demand for electricity increases, while large branches of industry want to make use of hydrogen (see e.g. HYBRIT [12]) and the transport sector increases its hydrogen demand, there might be a need for alternative pathways for renewable hydrogen production. Furthermore, electrification of society and industry will put high demands on the electricity transmission infrastructure which might limit electricity use for hydrogen production, especially during a transition period [13]. For that purpose, the clearest option is hydrogen production from biomass [14]. Hydrogen production from biomass might also be beneficial in cases with specific local conditions in terms of resource availability, heat integration opportunities and limitations in electricity transmission.

The purpose of this work is to map and briefly describe potential technologies for conversion of forest biomass to hydrogen. The focus is on techno-economic evaluations and the work strives at mapping biomass-to-hydrogen yield, system aspects and production costs intervals for a variety of conversion technology options with an emphasis on thermochemical pathways. The work is not all encompassing and should not be viewed as a complete overview of all possible biomass-to hydrogen production technologies, rather as an overview and discussion of the promising options that are most heavily featured in the research literature.

## TECHNOLOGIES

The combined research literature suggests several different pathways for hydrogen production from forest biomass. The pathways are typically categorized into biological, thermochemical and electrochemical pathways. Figure 1 provides an overview of all the processes included in this work. For the biological and electrochemical pathway only a brief process description and state of the art performance is included, whereas a more in-depth description and literature review is provided for the thermochemical pathways.



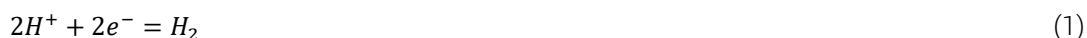
*Figure 1. Technologies considered for hydrogen production from forest biomass feedstock.*

All data gathered and used in the analysis is presented in tables in the appendix. A conversion factor of 0.84 EUR/\$ was used for economic calculations. Biomass LHV was assumed to 18.5 MJ/kg<sub>daf</sub> when left unspecified in the considered studies. The LHV of hydrogen is 120 MJ/kg.

### Biotechnical methods

Hydrogen can be produced from biomass by biotechnological methods by making use of the natural capabilities of microorganisms to generate hydrogen as one of the metabolic products. For this purpose, there are two main pathways: applying photosynthetic microorganisms, often referred to as photo fermentation, or applying anaerobic microorganisms often referred to as dark fermentation. Photosynthetic microorganisms use carbon dioxide and water for hydrogen gas production and phototrophic microorganism use carbohydrates or organic acids to produce hydrogen and carbon dioxide. The principal difference between the two pathways is the source of energy for the biomass decomposing bacteria. In photo fermentation, the bacteria take up energy from sunlight, where as in dark fermentation, the bacteria take up energy from the biomass itself [15].

Essentially both these processes build on the presence of hydrogen producing enzymes that catalyze the chemical reaction described in equation (1) [16].



## Dark fermentation

Dark fermentation is the decomposition of biomass by anaerobic bacteria that grow in the dark. According to Łukajtis et al. [17], dark fermentation is the most promising and most well-known of all biotechnical methods for hydrogen production from biomass. It consists of a series of complex reactions where the main enzymes regulating the hydrogen metabolism are hydrogenases.

Dark fermentation is particularly suitable for conversion of carbohydrates, which poses certain challenges when using lignocellulosic biomass, particularly concerning lignin, which is highly resistant to biodegradation [17]. There are, however, several studies concerning dark fermentation for production of hydrogen from lignocellulosic biomass, where different pretreatment methods are used to eliminate the issues caused by the lignin part of the biomass (see e.g. [16][18][19]). Pretreatment methods can be either biological, chemical, mechanical or a combination of two or more and include e.g. size reduction, acid treatment and enzyme treatment [19]. Furthermore, lignocellulosic biomass feedstock needs to be treated with hydrogenation with water when used for hydrogen production, in order to generate enough high-quality sugars. This can be done either in a separate step prior to the fermentation or in the same reactor [20].

According to Lepage et al. [14], hydrogen yield for dark fermentation is in the range of 0.004-0.044 kg H<sub>2</sub>/kg biomass, which for instance can be compared to steam gasification with a range of 0.040-0.0190 kg H<sub>2</sub>/kg biomass. Production costs are at best approximately 0.065 EUR/kWh H<sub>2</sub> and the technology has a TRL of around 5. These numbers are indicative, especially concerning production costs, as there are few full plant cost estimations. Several pilot facilities are in operation, but currently no commercial scaled plants have been constructed [21].

Although highlighted as more cost efficient than photo fermentation, dark fermentation suffers from low energy efficiency, poor durability of catalysts and product impurities [15]. The technology is not financially competitive and need to be further developed [22]. The need for expensive pre-treatment to make the feedstock enzymatically fermentable adds additional complexity to the process, making it more expensive, thus limiting its development at industrial scale [14].

## Photo fermentation

Photo fermentation utilizes light energy to convert biomass into hydrogen. The process is catalyzed by nitrogenases in purple non-sulfur bacteria [23]. This is a relatively novel process and currently the least financially competitive, biological, method for hydrogen production [24]. Two process configurations have been suggested for the technology, a single step and a two-step approach [25]. The single photo fermentation reactor has a low specific investment cost, but also suffers from low efficiencies. In the two-step approach, a dark fermentation is added before the light fermentation, where the organic acids formed in the dark fermentation step are further degraded in the second step, thereby increasing the overall process hydrogen yield. This process is however complex to operate. The hydrogen yields for photo fermentation are in the same range as for dark fermentation (0.004-0.049 kg H<sub>2</sub>/kg biomass), but the production costs are higher (approximately 0.071 EUR/kWh) [14]. As for dark fermentation, these numbers are indicative as there are few full plant techno-economic studies published. The technology is still under development and has an estimated TRL of 4. Although still under development, it is deemed to be less financially competitive than dark fermentation [24].



## Thermochemical conversion

Thermochemical conversion of biomass is often categorized into pyrolysis and gasification. There are other, more novel, technologies such as super-critical water gasification (SCWG). Here, emphasis is on gasification and pyrolysis, SCWG is briefly described. There is also the possibility of chemical looping gasification of biomass, where an oxygen carrier is used to separate the CO<sub>2</sub> already in the combustion stage [26]. This process is, however, not described further in this work.

## Gasification

Gasification is the thermochemical decomposition of biomass at elevated temperatures in an environment with limited oxygen [27]. Depending on operating conditions such as temperature, catalysts and gasification medium, a gas consisting to varying shares of H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>x</sub>H<sub>x</sub> and tars is produced. Gasification can in general be divided into three different categories, depending on how the process is designed: dual fluidized bed (DFB) steam blown gasification [28], also known as indirect gasification, direct blown, steam/oxygen or air, fluidized bed gasification [29] and entrained flow gasification [30]. Using steam as gasification medium shifts the equilibrium to an increased share of hydrogen in the product gas and it is therefore preferred when hydrogen is the intended end-product [31].

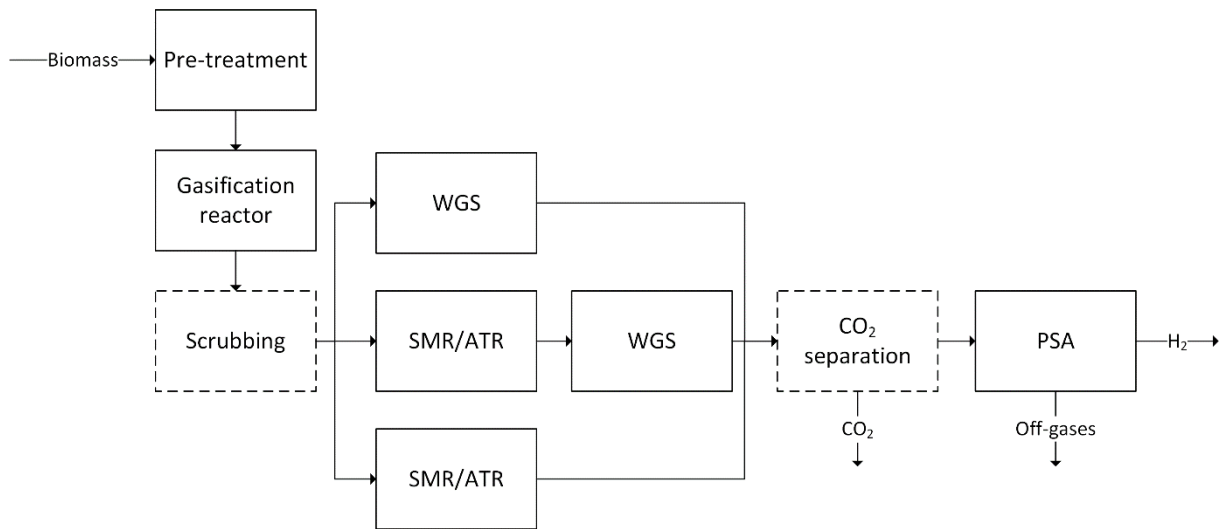
Prior to entering the gasification reactor, the feedstock is typically pre-treated. This often includes drying the biomass, to achieve higher conversion efficiencies in the gasification reactor, but can also include e.g. milling, to reach a homogeneous feedstock in terms of size [32]. A variety of product gas up-grading and conditioning sequences can be included in the process design, depending on the considered end-product of the gasification process. A generic flow chart of a biomass gasification process for hydrogen production is presented in Figure 2. When producing hydrogen, the gas is often upgraded through steam-methane reforming (SMR) (eq. 2), autothermal reforming (ATR) (eq. 3) and/or water-gas shift reaction (WGS) (eq. 4) [33], [34].



In that way CH<sub>4</sub> and CO is utilized to increase the hydrogen yield in the product gas.

When cleaning the gas, some processes opt for a separate CO<sub>2</sub> separation step, typically done through amine scrubbing. This makes the final hydrogen separation sequence cheaper. In addition, it makes it possible to store the CO<sub>2</sub>, thereby providing a potential additional revenue stream to the process, while contributing to negative CO<sub>2</sub> emissions. It is also possible to utilize the generated CO<sub>2</sub> for additional fuel production (CCU). The drawback is naturally the cost associated with separating the CO<sub>2</sub>. The hydrogen is finally separated from other species present in the gas to a satisfactory level of pureness. This can be done through a variety of techniques, where the far most common is pressure-swing adsorption (PSA) [35].

There are other options to the SMR, ATR and WGS reactions coupled with CO<sub>2</sub> separation. For instance, chemical looping reforming is an option where the CO<sub>2</sub> separation and ATR occurs in the same process step [36]. Another option is to use a calcium looping reactor system where the WGS reaction and CO<sub>2</sub> separation occurs simultaneously. In the primary reactor, the WGS-reaction is enhanced by removing CO<sub>2</sub> from through the carbonization reactor with CaO. In the second reactor, the CaCO<sub>3</sub> is regenerated to CO<sub>2</sub> which is released and CaO that is circulated to the WGS reactor [37]. However, the number of techno-economic studies relating these technologies to hydrogen production from forest biomass are limited.



*Figure 2. Simplified generic flow chart of a biomass gasification process for hydrogen production*

Potential benefits of thermochemically based hydrogen production from biomass, in relation to other biomass-to-hydrogen processes and water electrolysis, includes the potential for process integration and to have systems that have additional end-products besides hydrogen. Thermochemical process occurs at high temperatures and typically generate large quantities of excess heat. Integrating the plant with other industries implies that the combined heat requirements of the plant can be decreased, leading to an overall more energy efficient process. Excess heat could also be used for heat export through district heating or for electricity generation through steam turbines (see e.g. [38], [39]). Furthermore, decomposing thermochemical treatment of biomass generates other products than hydrogen, e.g. methane, biochar or off-gases, which can be exported and contribute to additional income in an multigeneration concept (see e.g. [40]).

## DFB gasification

DFB gasification builds on separating the gasification process from the combustion process required to sustain the heat to the process. This is done with two separate reactors with a circulating bed material stream between the two processes [28]. The benefit of this process is that it is possible to use air for combustion of the biomass, rather than pure oxygen, which is normally the case using other technologies if the gas is to be used for fuel synthesis. Thereby there is no need for an energy intensive air separation unit (ASU). DFB gasification typically occurs at lower temperatures than their counter parts (700-900°C), which results in a gas with higher concentrations of hydrocarbons, but also tars that needs to be handled down-stream in the process [41].

There have been several studies on hydrogen production and hydrogen hybrid production systems based on DFB gasification. Brau & Morandin [42] considered a process based on DFB gasification followed by SMR and a 2-step sequence of water gas shift integrated with an oil refinery. The raw gas is scrubbed of tar species using water, then the methane present in the gas is reacted to hydrogen at high temperature (800°C) in the SMR reactor, followed by a sequence of two WGS shift reactors, first a high temperature reactor (350°C), followed by a low temperature reactor (260°C). Hydrogen is then separated using PSA. Part of the syngas leaving the scrubber, as well as the off gas from the PSA units are combusted to generate the heat required by the SMR reactor. The overall hydrogen yield of the process is 0.1 kg H<sub>2</sub>/kg biomass, which corresponds to a biomass to hydrogen efficiency of 0.67 on a HHV<sub>daf</sub> basis. By means of heat integrating the gasification plant with an oil refinery, while producing high pressure steam or electricity as a by-product, the energy and exergy efficiency can be increased with 8 respectively 4



percentage points. Furthermore, the process contributes to lowering GHG emissions with up to 700 ktone/year if replacing H<sub>2</sub> produced from NG in the refinery, depending on assumed marginal electricity production technology.

Tock & Maréchal [43] considered a similar process with the addition of a torrefaction step before the gasification reactor. The process is integrated with a CHP plant where part of the off gases from the torrefaction step and excess heat from the process is used to generate electricity. Furthermore, parts of the hydrogen can be combusted for additional electricity generation. Heat from the CHP plant is used to run the SMR reactor, which means that there is no need to combust off gases. The process also differs compared to the process described by Brau & Morandin, in the final gas cleaning step, where a CO<sub>2</sub> amine scrubbing step is included before the PSA unit. This means that there is a clean CO<sub>2</sub> stream present in the process, which potentially can be stored. Tock & Maréchal report a hydrogen yield of 0.107 kg H<sub>2</sub>/kg biomass and a biomass to hydrogen efficiency of 0.696 on a LHV<sub>daf</sub> basis. The process is optimized for cost and GHG emission reduction using a multi-objective optimization approach. The resulting overall energy efficiency for hydrogen production and electricity generation with CO<sub>2</sub> capture was 0.6 and 0.39 respectively. This in turn corresponds to a hydrogen production cost of 0.05-0.176 EUR/kWh H<sub>2</sub>, depending on the price of biomass feedstock.

A DFB gasification concept was also studied in a techno-economic and LCA study by Salkuyeh et al. [44]. Their process is similar to the two previously described but differs in that no SMR reactor is included. Without the SMR reactor, there is a lower high-temperature heating demand in the process, which implies that a smaller part of the produced gas needs to be used internally in the process for heat generation. However, this process incorporates a tar reforming step, to increase the biomass to gas conversion, which in turn has a heat demand that is saturated by burning product gas. The process includes an amine-scrubbing step before the final PSA hydrogen separation, which means that a stream of pure CO<sub>2</sub> is produced. Off gases from the PSA unit are combusted to generate electricity and supply the process with heat. The process includes the option of liquefying the separated CO<sub>2</sub> stream for CCS, however, when running the liquefaction unit, additional NG needs to be co-combusted with the off gases to sustain the process with electricity and steam. Thereby, the overall energy efficiency is decreased from 0.45 to 0.41 if operating the CO<sub>2</sub> liquefaction step, while also making use of a fossil resource (NG) in the plant. The hydrogen yield is 0.061 kg H<sub>2</sub>/kg biomass corresponding to an approximate efficiency of 0.4 (biomass LHV<sub>daf</sub> assumed to be 18.5 MJ/kg). An overall hydrogen production cost of 0.061 EUR/MWh was reported.

Hydrogen production from biomass through DFB gasification has been studied in the pilot plant in Güssing, Austria [45]–[47]. A poly-generation concept generating hydrogen and electricity was studied in a study from 2018 [46]. This concept builds on a three step WGS reaction sequence, followed by RME scrubbing of tars and PSA for separating hydrogen. Here a substantial part of the hydrogen in the gas is used for electricity and district heating generation meaning that the hydrogen yield is sacrificed for electricity generation and a cheaper PSA unit. The overall yield is 0.03 kg H<sub>2</sub>/kg biomass which corresponds to an approximate efficiency of 0.2 (biomass LHV<sub>daf</sub> assumed to be 18.5 MJ/kg) while generating 0.6 and 1.7 MW of electricity and district heating per MW of produced hydrogen. In 2017, the same research group studied a similar process, consisting of a DFB gasifier, followed by WGS, RME scrubbing and PSA for the sole purpose of producing hydrogen [45]. Here an overall hydrogen yield of 0.058 kg H<sub>2</sub>/kg biomass and an efficiency of 0.4 was reached. It should be mentioned that also here, a relatively large part of the available hydrogen is recirculated from the PSA unit to be incinerated in the combustion reactor of the gasifier. An overall production cost of 0.148 EUR/kWh hydrogen was reported.

Overall, the processes combining SMR and WGS reactors reaches the highest conversion efficiencies, which is also theoretically supported. Turn et al. [48] experimentally studied steam gasification of biomass for hydrogen production. They concluded that it is theoretically possible to produce up to 0.165 kg H<sub>2</sub>/kg biomass when applying WGS and SMR. In their experiments an actual maximum of 0.128 kg

H<sub>2</sub>/kg biomass owing to conversion losses of biomass was reached. This corresponds to an hydrogen production rate of a factor approximately 2.1 times higher than the hydrogen available in biomass (assuming a hydrogen content of 6% on mass basis daf) [48].

#### *Direct blown, O<sub>2</sub> gasification*

Direct blown gasification of biomass can be performed with air as gasification medium, but as air consists mainly of nitrogen, this creates a diluted product gas unsuitable for synthesis. Therefore, direct blown gasification is often performed with pure oxygen and steam as gasification medium. The benefits of this process are the simpler process design compared to the DFB gasification process and that the gasification reactor potentially can be pressurized, which eliminates the need for compression later in the process and potentially allows for a smaller, and thereby cheaper, gasification reactor. The draw-back is the cost and energy penalty associated with the air-separation unit (ASU) required to sustain the process with oxygen [42].

Brau & Morandin studied a pressurized, direct oxygen and steam blown, gasification plant in combination with a WGS reactor for hydrogen production heat integrated with an oil refining plant [42]. The process includes an autothermal reforming (ATR) reactor and makes use of a membrane reactor where the WGS reaction and hydrogen separation occurs simultaneously, allowing for process intensification as compared to the DFB process studied in the same paper (see previous sub-heading). The ATR reactor removes the need for tar scrubbing while converting methane present in the gas to hydrogen, similarly to SMR, with the difference that oxygen is added to the process. This process reaches an overall hydrogen yield of 0.087 kg H<sub>2</sub>/kg biomass corresponding to an efficiency of 0.59, which implies that this process has a lower yield than the DFB gasification concept evaluated in the same study. As in the case of DFB gasification, the overall energy and exergy efficiency is improved through heat integration with the oil refinery, increasing with up to 11 and 6 percentage points respectively.

Bhattacharya et al. [49] studied an oxygen blown gasification process for production of hydrogen, also based on WGS and PSA. This process reaches a hydrogen yield of 0.102 kg H<sub>2</sub>/kg biomass meaning an efficiency of 0.654. However, the study also highlights that the duty of the ASU will lower the overall process energy efficiency with around 3.5 percentage points.

Economic data for direct blown biomass gasification for hydrogen production is limited. There are however several studies for production of other types of fuels, e.g. bio methane [50]. The conclusions of those studies differ, and it is difficult to make a clear distinction in terms of which process reaches the lowest production costs. However, In general the economic performance of direct blown gasification is in the same range as that of DFB gasification [51], [52].

## **Entrained flow gasification**

Entrained flow gasification differs to the previous two gasification processes in how the gasification reactor is designed and operated. As the name suggests, the feedstock is entrained with the gasification medium when injected in the top of the reactor. This puts high demands on the feedstock preparation and the feedstock needs to be grinded into a fine powder that can be sprayed into the reactor. Entrained flow gasification occurs at high temperatures compared to the previously mentioned options (around 1300°C), which results in high conversion rates and a clean gas with low levels of hydrocarbons and tar [53]. Hence, the process design can be simplified and thereby intensified. The drawback of this process is the high feedstock preparation cost and, similarly to oxygen blown gasification, the costs associated with the ASU. These facts imply that the benefits of entrained flow gasification are limited when it comes to certain feedstocks, e.g. forest residues, where there is a high cost associated with grinding the feedstock. On the other hand, it is suitable for feedstocks already in a fitting form, e.g. pyrolysis liquids, black liquor (BL) and saw dust [30], [54], [55].

Entrained flow gasification of biomass milled to powder, for production of hydrogen was studied by Salkuyeh et al. [44]. In this design, the gasification reactor is followed by gas cleaning sequences and COS hydrolysis. After gas cleaning, the gas is treated in a high temperature WGS reactor, followed by a low temperature WGS reactor. The synthesized gas is cleaned of CO<sub>2</sub> using an amine scrubber and the final hydrogen stream is cleaned using PSA. The hydrogen production cost was reported to be 0.085 EUR/kWh hydrogen. Like the DFB gasification process evaluated in the same study, the off gases from the PSA unit are combusted for heat and electricity production. If the CO<sub>2</sub> is to be liquefied, additional NG is burned, which in this case lowers the overall energy efficiency of the process from 0.56 to 0.49. This process has an overall yield of 0.078 kg H<sub>2</sub>/kg biomass which corresponds to a biomass to hydrogen efficiency of 0.5 (biomass LHV<sub>daf</sub> assumed to be 18.5 MJ/kg).

Andersson & Harvey [56] studied entrained flow black liquor (BL) gasification for hydrogen production integrated with a generic pulp mill. The process is similar to the one studied by Salkuyeh et al. but differs in the gas cleaning sequence as it does not include an amine scrubber, which implies that this process does not have the possibility for CCS. The off gases from the PSA unit are instead burned for heat generation in the biomass boiler present at the pulp mill. This process reaches a hydrogen yield of 0.055 kg H<sub>2</sub>/kg BL, which corresponds to a biomass to hydrogen efficiency of 0.54. The study assumes that all BL available at a generic pulp mill producing 630,000 air dried tonnes (ADt) pulp/year is used for hydrogen production and that the excess heat from the gasification process is used to generate steam used in the pulp mill. However, steam generation is not sufficient, and the plant must import biomass. Furthermore, when removing the recovery boiler, the electricity import of the pulp mill increases severely. Nonetheless, if all Swedish pulp mills were to adopt this concept, it has the potential to lower national CO<sub>2</sub> emissions with up to 8%.

Wang et al. [57] studied oxygen and steam blown entrained flow gasification of straw for production of hydrogen. The process includes WGS reaction and a PSA unit to separate the hydrogen. In this process, the off gases are combusted for heat and electricity generation. The process reaches a biomass to hydrogen yield of 0.091 kg H<sub>2</sub>/kg biomass and a production cost of 0.03 EUR/kWh H<sub>2</sub>, while generating 0.34 MW of electricity per MW of hydrogen.

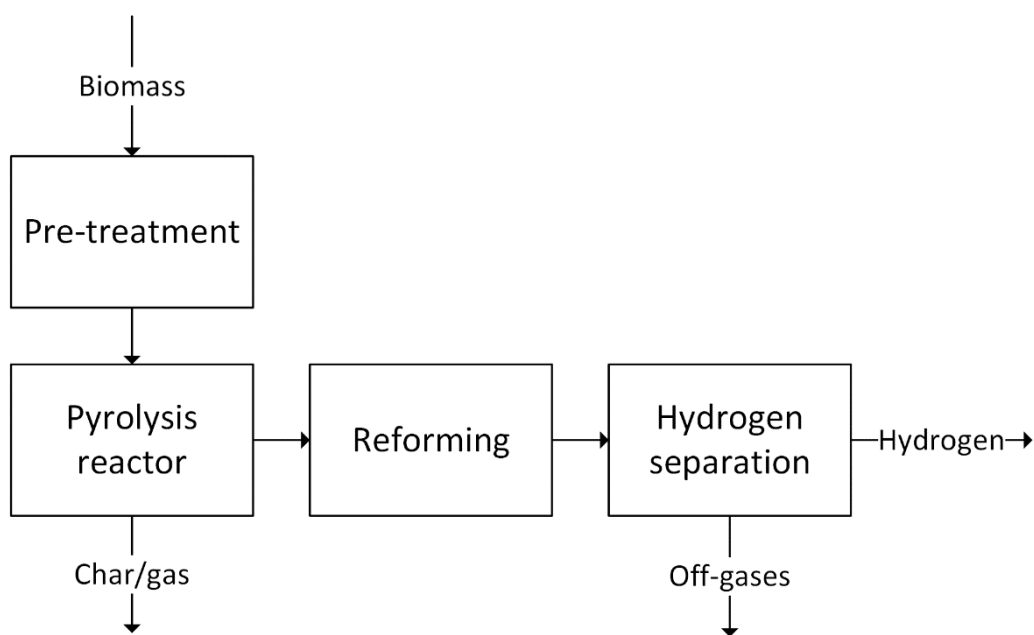
Johansson et al. [58] also studied biomass gasification for hydrogen production, integrated with an hydroskimming refinery. In a system analysis, they compared bubbling bed O<sub>2</sub> gasification to DFB gasification and entrained flow gasification. The entrained flow gasification-based process is similar to the previously described ones, with high and low temperature WGS reactors and PSA. However, in this case, the wood product is torrefied or pyrolyzed in a pre-treatment step. The DFB process includes SMR and two-stage WGS and the O<sub>2</sub>-gasification process includes reforming and two-step WGS reactors. Hydrogen separation is based on PSA in both cases. In all processes, excess heat from the refinery is utilized in the gasification processes, while off gases from the PSA step is used to replace NG for heating in the refinery. The results show a hydrogen yield of 0.08 kg H<sub>2</sub>/kg biomass which corresponds to a biomass to hydrogen efficiency of 0.53 for the entrained flow-based process, compared to a yield of 0.092 kg H<sub>2</sub>/kg biomass and efficiency of 0.65 for the O<sub>2</sub> gasification case and a yield of 0.083 and efficiency 0.6 for the DFB gasification case. The study conclude that the EF gasification process is favorable in cases where biomass availability is unlimited, as it generates the largest quantities of excess heat to be used in the refinery. In a scenario where biomass is limited, the O<sub>2</sub>-blown, gasification process is favored, owing to having the highest hydrogen yield. All three considered processes lower CO<sub>2</sub> emissions compared to NG SMR.

## Pyrolysis

Pyrolysis is in many aspects similar to gasification, but it occurs at lower temperatures (400-800°C) with the complete lack of an oxidizing agent. According to rising reaction temperature, pyrolysis is categorized

into three classes: slow pyrolysis, fast pyrolysis and flash pyrolysis [59]. Pyrolysis generates a gas fraction consisting of  $H_2$ ,  $CO$ ,  $CO_2$  and  $CH_4$ , a pyrolysis liquid fraction and a charcoal fraction. The pyrolysis liquid fraction, sometimes referred to as “bio-oil”, contains a water-soluble fraction and a non-soluble fraction. The share of the different fractions depends on the type of pyrolysis reactor, with the highest gas shares reached for flash pyrolysis reactors. However, the gas fraction is lower than for gasification [14].

A generic flowchart for the production of hydrogen through biomass-based pyrolysis is presented in Figure 3. The different fractions generated from biomass pyrolysis can be utilized in different ways when the intended end-product is hydrogen. The most common approach is to react the water-soluble fraction of the pyrolysis liquids in reforming reactors for hydrogen production [60]. This can be done e.g. through catalytic steam reforming [61] or steam reforming [62]. The non-soluble fraction can potentially be cracked into other smaller hydrocarbons, e.g. BTX, whereas the gas fraction can be separated for hydrogen production or used for heat recovery. Nonetheless, fast-pyrolysis typically yields a small gas fraction and it might not be economically feasible to separate out hydrogen from the gas fraction [63]. The charcoal fraction is typically used to provide the process with heat, although it is possible to use it for other applications as well.



*Figure 3. Generic flowchart for hydrogen production from biomass-based pyrolysis.*

The research literature on techno-economic assessments of biomass pyrolysis for hydrogen production is scarcer compared to gasification and there are few results for biomass-to-hydrogen yields and production costs. Czernik et al. [64] studied a pyrolysis process generating “bio-oil” which subsequently is reacted with catalytic steam reforming to generate hydrogen. A bio-oil to hydrogen yield of 0.12 kg of hydrogen per kg of bio oil was reached (biomass-to-bio-oil yield was left unspecified in the study). However, this study was solely experimental and did not include a full process design for hydrogen separation and energy recovery.

Zhao et al. [65] evaluated a hydrogen production process based on pyrolysis of rice husk followed by catalytic steam reforming of the gas and liquid fractions. This process generates a gas with hydrogen molar concentrations over 60%, with an overall yield of 0.065 kg  $H_2$ /kg biomass. However, also this study was experimental, with external heating and the gas mixture was not separated. No economic data was published.

Arregi et al. [66] studied pyrolysis of pine sawdust and HDPE (plastic) for production of biomass. The experimental process includes a fluidized bed, Ni catalyzed, steam reforming reactor. The results show a hydrogen yield of 0.1 kg H<sub>2</sub>/kg biomass & HDPE which corresponds to an approximate biomass to hydrogen efficiency of 0.65, when using only biomass as feedstock. If the same process is operated with 100% HDPE, the hydrogen yield can be increased to 0.373 kg H<sub>2</sub>/kg HDPE. This study was also solely experimental and only focused on the pyrolysis reactor and following reforming reactor.

Czernik & French [67] studied a process using an autothermal reforming reactor to produce hydrogen from pyrolysis liquids. This process reaches a pyrolysis liquid to hydrogen yield of 0.11 H<sub>2</sub>/kg pyrolysis liquid (full biomass to hydrogen yield was not specified in the study). According to the economic estimates this would correspond to a hydrogen production cost of 0.11 EUR/kg for a plant producing 1,500 kg H<sub>2</sub> a day, of which 53% are related to the feedstock cost.

In a recent literature review of hydrogen production pathways from biomass performed by Lepage et al. [14], the production cost for hydrogen from pyrolysis was estimated to be in the range of 0.031-0.064 EUR/kWh hydrogen which is in the same range as what they estimate for gasification (0.031-0.088 EUR/kWh). These results were contradicted by Balat [68] who concluded that gasification of biomass followed by reforming results in higher hydrogen yields than fast pyrolysis followed by reforming of the soluble fraction of the bio oil, thereby implying lower production costs. In the same study, the TRL of different biomass-to-hydrogen processes were estimated. Both gasification and pyrolysis were estimated to be at a TRL of 7, the highest of any, non-commercial, technologies considered.

Super critical water gasification

SCWG of biomass is the decomposing of biomass using water in a super critical condition (373.9°C, 22.06 kPa) [69]. An ideal reaction for complete conversion of biomass to hydrogen is displayed in equation (5), with glucose as a generic representative for biomass.



However, in the reaction carbon monoxide is also formed, which reacts with water to form carbon dioxide and hydrogen according to equation (6).



A clear benefit of SCWG is that water is a reactant. This means that using wet biomass does not contribute to lower efficiencies, which is the case in gasification and pyrolysis processes.

SCWG yields a clean product gas, mainly consisting of hydrogen and carbon dioxide. Dos Santos et al. showed how, given a specific scenario, concentrations of H<sub>2</sub> at around 68, 67 and 66 % can be reached with a feedstock consisting of guaiacol, phenol and glucose, respectively [70]. This process yields a clean gas consisting of H<sub>2</sub>, CO<sub>2</sub> and small amounts of CH<sub>4</sub> and other hydrocarbons. However, SCWG is sensitive to type of biomass, catalysts and operating conditions. For these reasons it is often considered expensive.

SCWG has been successfully demonstrated in the VERENA plant at Karlsruhe Institute of Technology [71], where a gas mixture of hydrogen, CO<sub>2</sub> and methane was produced from biomass feedstock. After CO<sub>2</sub> separation the gas reached H<sub>2</sub> concentration of up to 77% for operating temperatures of 540-600°C.

Fiori et al. [72] constructed a process flowsheet model in Aspen plus for a SCWG plant for production of hydrogen to a fuel cell. A biomass/water mixture is pre-heated in two steps before the gasification reactor, where the first heat exchanger is heated with the gas/water mixture leaving the reactor. The generated gas mix is cooled in two steps. Water is separated out and reused in the process. The syngas is then sent to a hydrogen separation step based on the HYSEP technology, where a palladium filter is used at elevated temperature and pressure (300°C, 60 bar). Hydrogen is then pure enough to be used in fuel cells (or exported), and the remaining gas, consisting mainly of CH<sub>4</sub>, CO and CO<sub>2</sub>, is combusted to



produce heat to the gasification reactor. Their results indicate that, using glycerol feedstock with a concentration of 25%<sub>w.b.</sub>, it is possible to reach a hydrogen yield of 0.085 kg H<sub>2</sub>/kg biomass.

Gutiérrez Ortiz et al. [73] also studied SCWG of glycerol for production of hydrogen using process modeling in software Aspen plus. Glycerol and water are mixed and heated before the reactor and the product stream is cooled, similarly to the process design by Fiori et al. [72]. However, in this process, a water-gas-shift reactor is included to further increase the hydrogen share of the syngas. A flash-reactor is used to separate the liquid phase from the gas, but a H<sub>2</sub> separation sequence is not included in their model, which would be required to get a pure stream of H<sub>2</sub>. The report shows a final syngas stream with a mole fraction of maximally around 70% H<sub>2</sub>, around 28% CO<sub>2</sub> and traces of CO and no remaining CH<sub>4</sub>. Their results also show how the molar fraction of hydrogen in the syngas decreases with an increase of biomass concentration in the feed. This highlights potential issues with scaling up the process; large reactors and high water-consumption are required for an efficient generation of H<sub>2</sub>.

There are few techno-economic assessments of SCWG for hydrogen production. However, Özdenkçi et al. [74] performed a techno-economic assessment of SCWG of black liquor for hydrogen production. The process uses PSA to separate out hydrogen from the product gas exiting the SCWG reactor. A production cost between 0.03-0.1 EUR/kWh H<sub>2</sub> was reported.

According to Correa et al. [69], SCWG is still facing issues related to production costs and lack of knowledge of operation with different biomass feedstocks. Most new experiments are conducted using glucose as feedstock. The technology has only been investigated at experimental scale and although there have been promising results, the TRL is at 4, which is low, especially in comparison to more developed technologies such as gasification [14].

## Discussion and potential improvement of thermochemical conversion

The yields for biomass-based hydrogen production through thermochemical pathways reaches from 0.057-0.107 kg H<sub>2</sub>/kg biomass feedstock depending on process design and eventual by-products. This corresponds to a production cost of 0.078 to 0.21 EUR/kWh H<sub>2</sub>. Lepage et al. [14] claim production cost for both pyrolysis and gasification reaching down to 0.03 kg/kWh H<sub>2</sub>. However, the specific technology used was left unspecified and the author has not been able to verify the numbers. It should be highlighted that the presented cost estimations are indicative. The different studies assume different time horizons, are performed at different years, some assume n<sup>th</sup> plant construction costs (meaning that several similar plants have been constructed before, which contributes to lower investment costs), whereas others estimate cost for a new plant. Furthermore, feedstock cost, electricity price and other costs vary between the studies, as do assumptions for interest rate and economic lifetime. Thereby these numbers should be compared with caution.

There are two clear technical pathways to improve the performance of thermochemical methods for hydrogen production: CCS or using electricity to increase the carbon efficiency of the process. In all thermochemical processes for hydrogen production, there is CO<sub>2</sub> present in the gas, which needs to be separated out to reach a clean enough product [75]. Storing CO<sub>2</sub> emissions from processes utilizing biomass contributes to lowering the GHG concentration in the atmosphere; the emissions are negative. This concept is often referred to as bioenergy carbon capture and storage (BECCS). Negative emissions of GHG might be required to reach stringent climate targets and for that purpose BECCS is highlighted as a key technology [76]. Thus, in a future with high charges on GHG emissions, separating out and storing the CO<sub>2</sub> can provide additional income to a biofuel plant while increasing the climate benefit. There have been several studies of BECCS in relation to thermochemical biofuel production (see e.g. [77], [78], [79]), however there are currently no studies relating BECCS to hydrogen production from biomass gasification. Such a process would need to include a separate CO<sub>2</sub> separation sequence, through e.g.



amine scrubbing, as is done in some of publications included in this review (e.g. [43]). Nonetheless, in hydrogen production from biomass, or production other biofuels via thermochemically based processes, there is a need to remove CO<sub>2</sub> to produce a pure product stream. Thereby the additional cost of CCS is smaller in comparison to e.g. applying the concept to a flue gas stream or using direct air capture of CO<sub>2</sub>. Nonetheless, there are additional costs associated with compressing or liquefying, transporting and storing CO<sub>2</sub>.

The option of making use of electricity in the hydrogen plant intends to increase the biomass to hydrogen yield. All thermochemical processes are endothermic, which means that they need to be supplied with heat. Furthermore, both SMR and ATR reactors are endothermic, which increases the heat needs of the process. These heat needs are generally sustained by combusting part of the feedstock and/or the product gas. By instead using electricity for heating, it is possible to increase the share of biomass that ends up in the product stream. There are two clear options to achieve this in a thermochemical-based hydrogen production process. The first option is to use electricity for direct heating in the gasification or pyrolysis reactor. The effects of electric heating in a DFB gasification process was studied by Alamia et al. [80]. Their results show that by adding electricity to the reactor, corresponding to 3%<sub>LHV,daf</sub> of the energy in the feedstock, it is possible to reach a higher char gasification rate and increase the cold gas efficiency of the plant. Another option is to use electricity to heat the SMR reactor. The concept of electricity SMR (eSMR) was studied by Wismann et al [81]. Their result show that it is possible to use electricity instead of combustion to heat SMR reactors, and by doing so, it might be possible to decrease the reactor size with up to a factor of 100. Naturally, for these concepts to be interesting from a sustainability perspective, the electricity used in the process should be renewable.

Besides utilizing technical innovations such as eSMR and BECCS, there are also clear cost and efficiency benefits to be made from process integration and multi product systems, as highlighted through this work. Generating steam from high temperature excess heat from the gasification for direct use in other processes or electricity production contributes to increased energy and exergy efficiency. Process integration is essential in creating overall efficient value chains for thermochemical bio fuel processes [82]. As shown by e.g. Tock et al. and by Brau & Morandin, proper process integration with a host industry or power plant, can contribute to increased energy efficiency, also in the case of hydrogen production from biomass gasification [42], [43].

## Electrochemical pathway

Biological electrolysis is similar to electrolysis of water with the difference being that the reaction occurs at the anode rather than the cathode and the fact that biomass is the main feedstock. There are currently two different technologies for this purpose: Proton Exchange Membrane Electrolysis Cell (PEMEC) and Microbial Electrolysis Cell (MEC) [24]. The benefit of biological electrolysis is that it is more energy efficient than water electrolysis. The main drawback is naturally that the feedstock comes at a severely higher cost (water/biomass). Furthermore, it is not possible to use the technology on cellulosic biomass without pre-treatment. The feedstock needs to be fermented and converted into organic acids or alcohols before it can be treated. Thereby the capital cost and complexity of the process is increased, which makes commercialization of the technology more difficult [83]. An alternative pre-treatment is to first produce bioethanol from biomass and use it as feedstock for biological electrolysis. Chen et al. [84] showed how electricity consumption can be decreased with up to 26.5 kWh/kg H<sub>2</sub> compared to an PEM electrolyzer. However, the efficiency loss from the methanol process is too high to make the process economically viable. The biological electrolysis process is also penalized by low production rates. Kadier et al. [85] reports hydrogen production costs from biological electrolysis of biomass reaching from 0.11-0.42 EUR/kWh H<sub>2</sub>.

Out of all the technologies considered in this work, biological electrolysis has the lowest TRL at 3 [14]. Therefore, although interesting, more development is required before biological electrolysis for hydrogen production can be comparable to thermochemical options for hydrogen production.

## Discussion and conclusions

This work gives an overall presentation of potential technologies for hydrogen production from biomass. The collected literature suggests multiple pathways, including biological, thermochemical and electrochemical conversion technologies. Overall, the pyrolysis and gasification pathways have the highest technology readiness levels and among the highest production yields and lowest production costs. Furthermore, thermochemical processes for production of hydrogen are suitable for process integration and has the possibility to be part of multi-product system. This study has shown that by efficient process integration and by considering by-products such as HP-steam and/or electricity, the overall process energy efficiency is increased. This conclusion is also supported by previous studies on production of other types of biofuels via thermochemically based processes. Ultimately, this implies that if implemented carefully, thermochemical processes for hydrogen production contributes to more efficient use of biomass.

There are several technologies such as SCWG and biological electrolysis, which theoretically also can reach low production costs. However, the literature is scarce on these technologies and most studies are only experimental; there are few techno-economic assessments. A lot of the data that can be found is also based on other types of biomass, e.g. sugar beets, and those processes are likely less suitable for conversion of forest biomass. This makes it hard to estimate realistic yields and production costs. Furthermore, these technologies have low TRL and a lot of R&D remains before they can be considered interesting from a commercial perspective.

Between the different gasification pathways and pyrolysis, it is hard to differentiate as there is more techno-economic data published on different gasification processes compared to pyrolysis-based production. Some studies suggest that the production costs are equal for pyrolysis and gasification (see e.g. [14]), however, the literature included in this work suggests slightly higher hydrogen yields and lower production costs for gasification-based production. Of the three considered gasification processes, the results are relatively difficult to compare as they are sensitive to assumptions on e.g. by-products and raw materials. However, the overall interpretation is that DFB gasification of biomass in combination with SMR and WGS general reaches the highest biomass-to-hydrogen conversion efficiencies, although entrained flow gasification also has a high potential, especially as reported in some studies. Concerning economic performance, the research literature is even scarcer. However, DFB gasification seems to reach the lowest production costs although it should be highlighted that the differences are small.

This literature review shows how it is possible to produce hydrogen from biomass using gasification or pyrolysis to a cost from 0.078 to 0.21 EUR/kWh. This compares to a production cost of 0.019 EUR/kWh for natural gas SMR and 0.023 EUR/kWh for coal gasification, meaning that hydrogen production from biomass cannot compete with fossil hydrogen production without economic policy support. However, water electrolysis reaches production costs of 0.045-0.12 EUR/MWh, highly dependent on the electricity price [3][14]. Thereby, hydrogen production from biomass can potentially be competitive with water electrolysis, depending on development of capital costs as both technology types matures and depending on electricity price development in relation to the development of biomass prices.

This literature review also shows how it might be possible to make gasification-based hydrogen production more economically attractive by combining BECCS with the plant. Another potential option is to increasingly electrify the plant, this could e.g. be achieved through direct economic heating in the biomass conversion reactor, or by means eSMR.

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## Appendix

Table 1. Conceptual and techno-economic studies on biomass gasification-based hydrogen production.

Reference	Technology	Feedstock	Biomass-to-H <sub>2</sub> Efficiency [LHV]	Yield [kg H <sub>2</sub> /kg of dry biomass]	Cost [EUR/kWh]
[45]	DFB+WGS+PSA (tar removed)	WC	40	0.058	0.148
[45]	Anaerobic digestion + Steam reforming	maize silage	47	0	0.152
[45]	Electrolysis	water	66.4	0	0.191
[44]	DFB	pine wood	0.38	0.061	0.078
[44]	EF+WGS	pine wood	0.50	0.078	0.086
[42]	DFB +SMR	pine (nordic)	67% HHV	0.1	N.a.
[42]	O <sub>2</sub> gasification with WGS and PSA	pine (nordic)	59% HHV	0.087	N.a.
[43]	Torrefaction +DFB+SMR+WGS (2-step)	pine	69.6	0.107	0.05-0.176
[46]	DFB+WGS (3-step)+PSA (tar removed)	pine	0.19	0.03	0.21
[48]	O <sub>2</sub> +SMR+WGS	wood fuel	0.82	0.126	N.a.
[49]	O <sub>2</sub> +WGS+PSA	wood	0.65	0.102	N.a.
[56]	EF +WGS	wood fuel	0.54	0.055	N.a.
[58]	EF +WGS	wood fuel	0.53	0.081	N.a.
[58]	O <sub>2</sub> +WGS	wood fuel	0.6	0.085	N.a.

*Table 2. Conceptual and techno-economic studies on pyrolysis-based hydrogen production.*

Reference	Technology	Feedstock	Efficiency [LHV]	Yield [kgH <sub>2</sub> /kg of dry biomass]	Cost [EUR/kWh]
[64]	Fast Pyrolysis + steam reforming	hard wood	n.a	0.12	n.a
[65]	Fast pyrolysis + unknown high temperature upgrading	rice husk	n.a	0.065	n.a
[66]	Continuous pyrolysis +reforming	biomass (pine)	0.65	0.10	n.a
[67]	Pyrolysis oil and auto thermal reforming	pyrolysis oil	n.a	0.11	0.11
[14]	Pyrolysis oil and auto thermal reforming	wood	n.a	0.03	n.a
[14]	Pyrolysis oil and auto thermal reforming	wood	n.a	0.065	n.a

*Table 3. Indicative biomass to hydrogen efficiency and yield for all considered processes.*

Fossil	Reference	Efficiency [LHV]	Yield [kgH <sub>2</sub> /kg feedstock]	Technology Readiness Level (TRL)
SMR (NG)	[14]	N.a	0.019	9
Coal gasification	[14]	N.a	0.023	9
<b>Biological pathways</b>				
Dark fermentation	[63]	0.044	0.066	5
Photo fermentation	[63]	0.049	0.071	4
<b>Electrochemical pathways</b>				
Bio electrolysis	[85]	0.015-0.1	0.059	3
Water Electrolysis (nuclear)	[14]	N.a	0.059	9
<b>Thermochemical pathways</b>				
DFB gasification	[44]	0,061	0.078	7
O <sub>2</sub> gasification	[49]	0.065	0.1	7
Entrained flow gasification	[44]	0.078	0.086	7
Pyrolysis	[67]	n.a	0,12	7
SCWG	[74]	0.02	0.043	4