
BIOHYDROGEN PATHWAYS – AN ENERGY COMPARATIVE REVIEW OF PRODUCTION PATHWAYS

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ABSTRACT

The environmental consequences of using fossil fuels based energy systems and the rapid growth of global energy demands are currently the major concerns on sustainable development in the world. Therefore, alternative, renewable and sustainable energy sources are in the need of extensive development and commercialisation. Hydrogen has been pointed out as a potential solution and energy carrier in the future global clean energy systems. Moreover, the biological hydrogen production is a promising technology that may bypass some of the disadvantages of conventional hydrogen production, such as fossil resources dependency or costly processes (e.g. natural gas reforming or electrolysis). Although being a promising solution, as every innovative technology, biohydrogen production is facing technological and economical challenges in terms of industrial scale application. The goal of this research is to identify and evaluate gaps fulfilment occurring in biohydrogen production technology pathway in order to present a clear, wide and bright perspective of biohydrogen as a green fuel of the future. Aspects such as biomass feedstock, different methods of obtaining biohydrogen as well as biohydrogen economy, energy consumption and CO₂ emission of the production processes were reviewed and assessed in a life cycle perspective. Although biohydrogen presents great improvements comparatively to conventional hydrogen sources (and conventional fuels), the production technology still needs further research and development in terms of cost-effectiveness and technological limitations mitigation for an industrial scale production, in a financially viable way and with profitable yields. Overall, biohydrogen appears as the ideal fuel of the future due to the highest energy content than any other known fuel, being less energy intensive due to ambient temperatures and pressures use in biohydrogen production processes, being environmentally friendly not only due to no contribution to greenhouse gas emissions and therefore, no impact on climate change but also to waste treatment contribution by using waste as a substrate.

Keywords biohydrogen; microalgae; energy; biophotolysis; fermentation; life-cycle

1 Introduction

1.1 Energy contex

Today we – as a global society – are facing severe energy crisis. The problem is extremely complex in its nature with many uncertainties and variables such as economic, environmental and political. In terms of environmental impacts, the modern world is facing climate change problems with global warming being the biggest concern. Unless the energy system changes in almost every aspect, the greenhouse gases emitted at the current rate will lead to average global temperature increase of around 4°C. Raising sea levels, climate zones shift as well as more and more frequently occurring extreme weather conditions and droughts would be consequences of such situation. It is projected that global climate will be affected by current global energy situation as close as in the coming 50 to 100 years [20]. In December 12, 2015 during United Nations climate change conference in Paris, 195 countries agreed and sign a legally binding agreement that aims at keeping global warming well below 2°C. The goals are ambitious and current efforts and plans agreed during COP21 are insufficient. At current CO₂ emissions of 34 Gt per year, the limit will be reached by 2050.

1.2 Biohydrogen

Interest in hydrogen as a potential fuel started in the early 90's. Hydrogen as a fuel has many social, economic and environmental benefits. Those benefits include:

- Reduction of fossil fuels use as an energy carrier.
- No contribution to climate change, if produced from renewable sources.
- Hydrogen can serve as long-term carbon-free seasonal storage medium.
- Increase in energy security at local and country levels.
- Lack of adverse combustion products (water as a final product of combustion).
- Hydrogen can be centralised or decentralised source of primary or backup energy.
- Energetic conversion of high efficiency hydrogen in fuel cells (on level of 45-60%).
- Organic waste recycles into more environmentally-friendly product.

However, transition to hydrogen energy-based economy is burden with many technical and technological challenges, for instance the fundamental challenge of obtaining hydrogen by biological routes is the urgent need to increase the efficiency of these transformations, from the cost-effective point of view this efficiency needs to be significantly increased [20]. Acquiring hydrogen by biological pathway in comparison with other methods seems to be the most economically justified method. Therefore, most studies focus on hydrogen production using microorganisms.

2 Resources for biohydrogen production

Many different potential resources have been investigated under the feasibility of biohydrogen production. Criteria like cost, availability, fermentability and carbohydrate content are said to be most important in terms of raw material selection for biohydrogen production. Another important criteria are related to pre-treatment, the simplest and less complex pre-treatment the more desired the biomass source. The main source of hydrogen are carbohydrates, therefore the feedstock rich in sugars, like food industry waste, sewage sludge from wastewater treatment, microalgae, wood and wood waste, is applicable. The best raw material for biohydrogen are simple sugars such as glucose, lactose and sucrose, but simple sugars are expensive raw materials on an industrial scale, more complex feedstock is economically more viable.

Wastewater from dairy industry, olive mill, baker's yeast and breweries can be used as raw material for biohydrogen production due to its rich carbohydrates content [17, 23]. In dairy industry, whey is a by-product of cheese production and it is considered a dangerous waste. Dry matter of whey consists of 70-80% lactose, 8-20% of minerals and trace components and 9% of proteins, which makes it suitable feedstock for biohydrogen [25, 36]. The biggest advantages of waste as biohydrogen production feedstock is its abundance and recycle-like approach, where waste is revalued into promising resource for conversion into valuable product. Waste also doesn't compete with food industry.

Microalgae advantage over first- and second-generation feedstock is algae capability of growing in aqueous media, which means that no arable land is needed for microalgae cultivation, therefore microalgae don't compete with food production which is the major limitation for 1st generation biofuels. Microalgae require less water than terrestrial crops. Microalgae are capable of CO₂ biofixation, this ability is extremely promising way of CO₂ sequestration and could potentially be a sufficient solution for significant reduction of this greenhouse gas in the atmosphere.

Biohydrogen production is possible through photobiological process [9]. Potential microorganisms capable of producing hydrogen are presented in Figure 1.

3 Biohydrogen technology

There are many technologies for obtaining biohydrogen production. In general, we can divide them into two groups thermochemical conversion of biomass-based biohydrogen and biological conversion. Diagram of biohydrogen production pathways is pictured in figure 3.

3.1 Fermentation

Biohydrogen can be produced by photoheterotrophic (light fermentation) and anaerobic (dark fermentation) microorganisms using biomass rich in carbohydrates as a renewable resource.

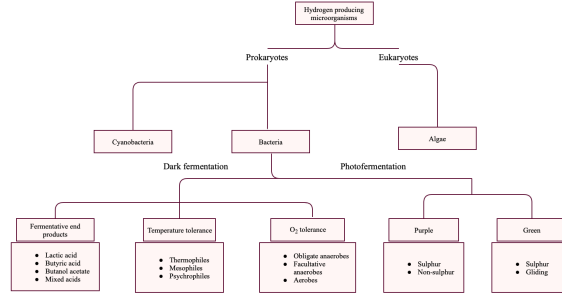


Figure 1: Scheme representing potential biohydrogen microorganisms [10].

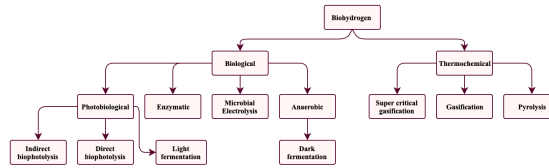


Figure 2: Biohydrogen production pathways [34].

3.1.1 Dark fermentation

Dark Fermentation (light independent) is recognized as one of the most promising biological pathways for biohydrogen production [43]. During dark fermentation process anaerobic bacteria grow on carbohydrates-rich biomass feedstock without access to light producing biohydrogen. Bacteria species like *Enterobacter*, *Bacillus* and *Clostridium* are known to produce biohydrogen [26]. Dark fermentation reactions can be operated in various of temperature conditions: mesophilic (25-40°C), thermophilic (40-65°C), extreme thermophilic (65-80°C) and hyper thermophilic (>80°C). The end product is a biogas mixture containing primarily H_2 and CO_2 but can also contain minor amounts of H_2S , CH_4 and CO , this composition brings problematic technical challenges such as separation and purification process application. Depending on fermentation pathway and end-products, different feedstock yields are obtained with different amounts of H_2 per mole of glucose. Therefore, when the end-product is acetic acid, according to stoichiometry we can obtain maximum of 4 mole H_2 per mole of glucose by facultative anaerobic bacteria:



On the other hand, when the end-product is butyrate we can obtain theoretical maximum of 2 moles H_2 by strict anaerobic bacteria:



From stoichiometry we can conclude that the highest theoretical yield of H_2 is connected with acetate being the end-product of fermentation. In practice, however it was concluded that the highest yields of H_2 are in fact connected not only to acetate end-product but the mixture of acetate and butyrate products, the lowest yields of H_2 are said to be associated with products like lactic acid and alcohols [26]. Fermentation end-products greatly depend on environmental conditions in which bacteria grow. Fermentation process should be directed away from alcohol products (ethanol, butanol) and reduced acids (lactate) towards volatile fatty acids (VFA) in order to maximise the H_2 yield. Dark fermentation potential mass production is promising due to relatively simple process, wide spectrum of potential feedstock, high rate of biohydrogen production and no light sources requirement. Moreover, fermentation process operation is easy as fermentation reactor technology and bioprocess control are all well known since other fermentation processes exist on the industrial scale [37]. There are many inhibitors of dark fermentation that can be classified as pre-process inhibitors which are already present in microflora or substrates before the process or in-process inhibitors which appear along the dark fermentation process. One of the solution for pre-process inhibition problem is use of mixed microflora which in general appears to be more practical and economically viable on a large scale than pure cultures with the main advantage of being capable of operating in non-sterile environment, unlike pure cultures, as well as the ability of using wider spectrum of feedstock, on the other hand the downside of mixed cultures is possibility of containing variety of microorganisms that compete for substrates with hydrogen-producing bacteria or it may contain hydrogen-consuming bacteria consequently lowering biohydrogen production yield [45, 48, 49].

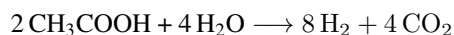
3.1.2 Photofermentation

Photofermentation (light fermentation) is a process of light energy to biomass conversion where photosynthetic bacteria degrade various of substrates in order to produce H₂ and CO₂. Theoretically, process of photofermentation is capable of complete conversion of organic matter into H₂, reaching relatively high yields of H₂. Another big advantage is the capability of wide variety of feedstock use by fermentation bacteria like industrial wastewater and agricultural waste such as dairy food, olive mill waste or molasses. Even with the high conversion to biohydrogen in the process there are several limitations for practical application, including low-light conversion efficiency that leads to need for extraordinary large surface areas for any bioreactors, low volumetric rates of production [34], low photosynthetic conversion efficiency. More and more photofermentation is discussed in terms of possibility of dark fermentation and photofermentation two-stage hybrid process, where photofermentation would be a second stage of the process to extract more biohydrogen from dark fermentation by-products [40]. Maximisation of utilisation of the substrates in this process synergy, without this hybrid process, is impossible to achieve due to thermodynamics barriers. First stage of this combination process is thermophilic dark fermentation where biomass is fermented to acetate, biohydrogen and carbon dioxide. In the second stage acetate from first stage is converted into biohydrogen and carbon dioxide in a separate photobioreactor [18, 31]. The hybrid system is expected to reach the theoretical maximum production of 12 mol of H₂ (mol glucose)⁻¹ equivalent in a following reactions [30]:

Stage I - dark fermentation (facultative anaerobes)



Stage II - photofermentation (photosynthetic bacteria)



3.2 Biophotolysis

Biophotolysis is a process of oxygenic photosynthesis where solar energy is captured and water splitting coupling to proton reduction occurs. Feedstock like green algae and photoautotrophic cyanobacteria break down water to biohydrogen and oxygen in the presence of light, converting therefore, solar energy to biochemical energy. Two types of biophotolysis can be recognised: direct and indirect.

3.2.1 Direct Biophotolysis

Direct biophotolysis is a process of simple water splitting producing biohydrogen by either green algae or cyanobacteria. Very high energy input from solar radiation is demanded in water splitting reaction. Direct biophotolysis is the same process that can be found in algal photosynthesis and plants but instead of adapting biomass containing carbon the process is manipulated for biohydrogen generation. Biohydrogen production in direct biophotolysis appears very attractive as it uses highly available sources, for this reason direct biophotolysis appears to allow for unlimited biohydrogen production from the most abundant resources on Earth which are sunlight and water. Unfortunately, major limitation for this process is simultaneous production of oxygen. In order to use green algae as a resource for biohydrogen production, crucial first step is needed for the synthesis as well as activation of enzymes mainly hydrogenase enzyme, this step is obtained by few minutes up to several hours of anaerobic incubation without access of light. As it was mentioned previously reversible hydrogenase, the key enzyme that catalyses the biohydrogen production in algae is very sensitive to presence of oxygen. Therefore, oxygen is an inhibitor in biohydrogen production process, which results in 1.5% of general conversion efficiency from solar energy to biohydrogen. If oxygen is removed immediately the conversion efficiency can increase to 3-10%. The oxygen level content needs to be kept below 0.1% in order to achieve successful biohydrogen production [8, 37].

3.2.2 Indirect Biophotolysis

Indirect biophotolysis was designed to address the oxygen inhibition of biohydrogen production problem in direct biophotolysis. This process involves two stages: biohydrogen production and oxygen separation in space or time. Oxygen separation in space method consists of two phases, where in first phase the photosynthesis into carbohydrates and oxygen from atmospheric CO₂ is taking place in an open pond. In the second phase anaerobic and dark conditions are applied in closed bioreactor where carbohydrates are degraded to acetic acid and biohydrogen.

3.3 Electrohydrogenesis

The most recent technology introduced in biohydrogen production pathways group is biocatalysed electrolysis which is used in microbial electrolysis cells (MECs) and bio-electrochemical systems (BESs). The principle of biocatalysed

electrolysis is biochemical conversion obtain with addition of low voltage from external power supply, therefore it's a variation of the microbial fuel cell (MFC). MEC and dark fermentation process integration emerged, since typical by-products of dark fermentation, mainly acetate, operates the best in MEC process. Integration of MEC with dark fermentation appears to be promising approach since both processes exhibit high biohydrogen yields and both are in similar technology development scale [29]. An overall H₂ recovery of 96% was obtained by treating molasses feedstock with MEC and dark fermentation integrated system [51]. It is a fresh concept and only few researches have been performed, therefore the integration concept needs more development and research.

3.4 Gasification

Gasification is a very well-known thermochemical process in which carbonaceous materials are converted to syngas by means of partial oxidation with air, oxygen, carbon dioxide and steam. Gasification converts any carbon-containing material like coal, petroleum coke and biomass into synthesis gas which is composed primarily of carbon monoxide and hydrogen. The chemistry of gasification is of a very complex nature where the series of physical transformations and chemical reactions occur in the gasifier. The biggest advantage of this process is ability to directly deal with high moisture content of biomass (>50%), which eliminates problematic and costly drying pre-treatment of biomass [22]. Steam gasification appears to be most suitable for biohydrogen production and it is one of the most promising thermochemical biohydrogen production pathways.

3.5 Pyrolysis

Pyrolysis of biomass is a conversion of biomass feedstock into gaseous, liquid and solid fractions in a direct heating of biomass in the oxygen absence at around 500-600°C. The conditions vary depending on biomass composition. Biomass pyrolysis is endothermic process that can obtain hydrogen-rich gas. This process is considered as one of the most economically profitable nowadays. In terms of thermochemical conversion processes for biohydrogen production, pyrolysis is said to be one of the most promising pathways [44]. Since the process is taking place in the absence of oxygen, by-products like dioxins are eliminated, moreover the formation of carbon oxides is minor, pyrolysis is noticeably decreased in problematic emissions, simplicity of the process as well as adaptability of the fuel are advantages of this technology [7].

4 Results and comparison of available data

The goal of this chapter is to present available data on biohydrogen production potential regarding different pathways, biohydrogen economy as well as energy consumption and CO₂ emissions.

4.1 Energy consumption and CO₂ emissions

There are few papers regarding energy consumption by biohydrogen production as well as CO₂ emissions. Ferreira A., Ribau J., Silva C. [14] analysed the biohydrogen production pathways from sugarcane and potato peels, their LCA Wheel-to-Tank (WTT) analysis showed that biohydrogen from potato peels LCA is 0.49-0.61 MJ/MJH₂ for energy consumption and 59.78-70.39g CO₂/MJH₂ for CO₂ emission. In sugarcane case the results were 0.30-0.34 MJ/MJH₂ for energy consumption and 23.74-31.06g CO₂/MJH₂ for CO₂ emission. All obtained results are shown in figure 3.

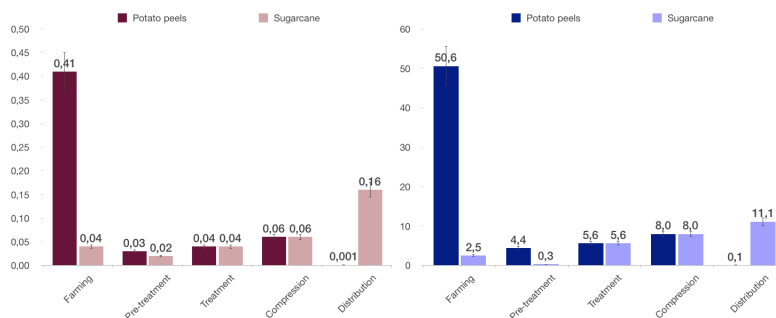


Figure 3: Energy consumption and CO₂ emissions regarding biohydrogen production from potato peels and sugarcane. Results obtained by Monte Carlo simulation [14].

This research showed, regarding WTT, that feedstock used have a potentially lower energy consumption and CO₂ emissions than hydrogen produced from natural gas reforming and electrolysis [14]. Sugarcane as feedstock exhibits lowest values for energy consumption and CO₂ emission. Farming in potato peels case stands for 75% of total energy consumption and CO₂ emissions, however if potato peel would be considered as by-product of potato production, farming should be excluded from LCA and consequently the WTT energy consumption and CO₂ emission values would drop to 0.13-0.28 MJ/MJH₂ and 14-25 gCO₂/MJH₂ respectively [14]. Energy costs and requirements of biohydrogen production were also considered by researches and they concluded a potato peels biohydrogen cost of 1.1-1.7 /kg H₂ and a sugarcane biohydrogen cost of 0.5-0.7 /kg H₂. This research show that availability as well as kind of feedstock are crucial factors, not only in optimisation and sustainability of biohydrogen production process but also in CO₂ emission and energy consumption of the process, which directly influence economic viability of bioH₂ technologies.

Aall Ø., Strømman A., Arvesen A. [1] conducted a Scenario for 2050 case for electricity mix and heat, where it was assumed that all the processes, which include use of steam and heat using fossil fuels as a source, use biomass instead. The assumption was a reduction of GHG emissions by 37% per kWh in European electricity mix in comparison to present emissions level. Similar conclusions were achieved in research conducted by Ferreira A., Ortigueira J., Alves L. et al. [15]. The results of using biomass as energy carrier for steam and heat are presented below in figure 4.

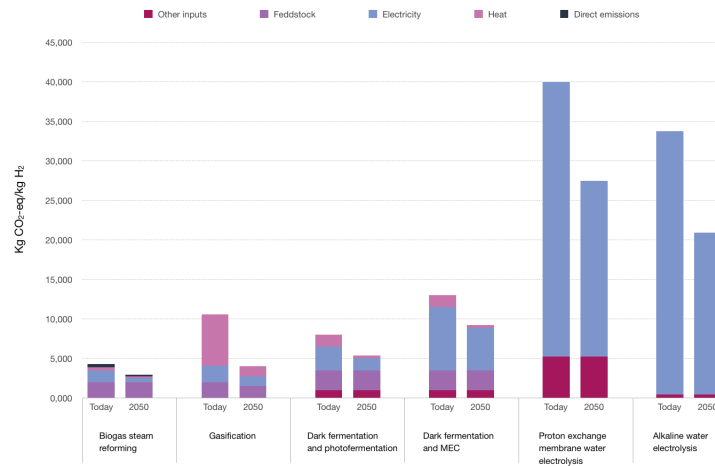


Figure 4: Scenario 2050 for GHG emissions per hydrogen unit for various methods [1].

4.2 Biohydrogen economy

In every technology development, economic viability of the process is crucial aspect in terms of industrial scale application. Highly interesting techno-economic analysis were conducted by Randolph K. And Studer S. from U.S. Department of Energy [38]. The aim of analysis was projection of cost of biohydrogen production via dark fermentation of biomass (corn stover). Two cases were considered, projected Current year case based on 2015 technology and projected Future case based on projected technological advancements by 2025 [38]. The cost analysis was performed using the Hydrogen Analysis version 3.101 model, the production capacity was assumed at 50.000 kg H₂/day. The capital cost was taken from a 2013 NREL report on hydrocarbons production from lignocellulosic compounds. Since there is no commercial biohydrogen production via dark fermentation plant which could be used as base system for the analysis, the techno-economic inputs were taken from hypothetical system. In table 1 cost projections are given in both case studies. One of the technological improvements in Future case study introduced was microbial consortium, which shows ability to enhance biohydrogen yields. The fermentation reactor was projected at 55°C for given batch time. The maximum fermentation period was limited to 74 hours as maximum conversion is achieved at that time according to NREL data. This fermentation time is also said to be corresponded to the minimum cost for both Current and Future case study. In Figure 5 optimisation curve for Future case is given. After fermentation, liquid waste are redirected to waste water treatment, which consist of anaerobic digestion process, where methane is produced as a by-product. Methane is later combusted along with lignin and, as a thermal energy, it is used to heat the system. In case of projected Current, the thermal energy excess is converted into electricity and is sold to the grid for by-product credit equivalent to \$11.93 per kg of hydrogen produced, whereas for projected Future it is \$8.19 per kg of hydrogen produced [38]. In case of no by-product scenario, hydrogen price is higher due to lack of revenue from electricity sales. However, in that case the capital cost of the system is decreased as gas turbine for electricity production is no longer needed [38].

Case Study	Optimistic Value [2007\$/kg H ₂]	Baseline [2007\$/kg H ₂]	Conservative Value [2007\$/kg H ₂]
Current Case (2015)	59.76\$	67.71\$	75.67\$
Current Case (2015) with by-product credit	40.88\$	51.02\$	61.16\$
Future Case (2025)	7.68\$	8.56\$	9.43\$
Future Case (2025) with by-product credit	3.40\$	5.65\$	7.91\$

Table 1: High volume cost projections for biohydrogen production [38].

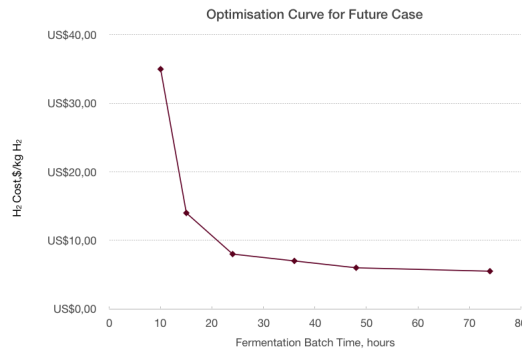


Figure 5: Optimisation curve for Future case study based on the modelled corn stover loadings and variables [38].

4.3 Biohydrogen production potential

Many studies have been conducted to investigate biohydrogen production potential. Biohydrogen production potential from various agricultural waste is presented in table 2. This results show that lignocellulose waste exhibits low yields, which is directly associated with low accessibility of carbohydrates as well as its resistance to biodegradation [44]. Hemicellulose and lignin protect the easily fermentable glucose that is ingrained into cellulose micro fibrils [39]. Therefore, pre-treatment of lignin solubilisation and removal leading to sugar rich feedstock is needed [12, 32]. In table 3, raw materials and methods of hydrogen production are given. The substrates for hydrogen production can be classified as direct and indirect sources (direct marked as D, indirect as ID), where direct stand for one-stage process and indirect consist of two or more stages in a process. In the last stage of indirect process there is a mixture of simple

Substrate	Type of inoculum/pre-treatment	Process conditions (g, 1-1/°C(pH))	Type of process	H ₂ production (ml H ₂ .g ⁻¹)
Beet pulp	Seed sludge	20/35/6.0	Batch	90.1 ml H ₂ .g ⁻¹
Leaf shape of mixed vegetable and potatoes	Indigenous microflora	-37/6.7	Batch	19 ml H ₂ .g ⁻¹
Lettuce	Heat-treated anaerobic sludge	20/37/5.5	Batch	48 ml H ₂ .g ⁻¹
Potatoes	Heat-treated anaerobic sludge	20/37/5.5	Batch	102 ml H ₂ .g ⁻¹
Rice straw	Anaerobic sludge	90/55/6.5	Batch	24.8 ml H ₂ .g ⁻¹
Soybean straw	Cracked cereal acclimated in continuous stirred tank reactor (CSTR)	-37/7.0	Batch	5.46 ml H ₂ .g ⁻¹
Sunflower stalks	Anaerobic digested sludge	5/35/5.5	Batch	2.3 ml H ₂ .g ⁻¹
Wheat bran	Activated sludge paper mill	100/36/7.0	Batch	50.6 ml H ₂ .g ⁻¹
Wheat bran	Digested sludge paper	100/36/7.0	Batch	28.6 ml H ₂ .g ⁻¹
Wheat bran	Mill cornstalk compost	100/36/7.0	Batch	22.6 ml H ₂ .g ⁻¹
Wheat bran	Wheat straw compost	100/36/7.0	Batch	17.7 ml H ₂ .g ⁻¹
Wheat stalks	Anaerobic digested activated sludge	60/35/6.5	Batch	23 ml H ₂ .g ⁻¹
Wheat straw	Seed sludge from H ₂ producing CSTR	6/35/-	Batch	5.69 ml H ₂ .g ⁻¹
Wheat straw	Mesophilic anaerobically digested sludge	4/37/5.5	Batch	10.52 ml H ₂ .g ⁻¹
Wheat straw	Clostridium butyricum	40/35/7.2	Batch	9 ml H ₂ .g ⁻¹ substrate
Wheat stalks	Anaerobic digested dairy manure	60/35/6.5	Batch	37 ml H ₂ .g ⁻¹
Wheat straw	Cow dung compost	25/36/7.0	Batch	0.5 ml H ₂ .g ⁻¹

Table 2: Biohydrogen production potential from various agriculture waste [44].

compounds that can be used in direct processes. It can be concluded while analysing data from table 3 that most of

Material	Chem. Form.	Method	Type	Remark
Citric Acid	$C_6H_8O_7$	Photofermentation	D	Hydrogen yield 36 ml of H_2 per g of citric acid (R. plaustris AT7)
Isocutane	C_8H_{18}	Plasmolysis	D	Process occurs in 5-15% solution in water
Sucrose	$C_{12}H_{22}O_{11}$	Dark fermentation	D	Hydrogen yield 109.40 ml of H_2 per g of sucrose (E. aerogenes strain HO-39)
Sucrose	$C_{12}H_{22}O_{11}$	Photofermentation	D	Hydrogen yield 33 of H_2 per g of sucrose (R. plaustris AT7)
Maltose	$C_{12}H_{22}O_{11}$	Dark fermentation	D	Hydrogen yield 140.65 ml of H_2 per g of maltose (E. aerogenes strain HO-39)
Lactose	$C_{12}H_{22}O_{11}$	Dark fermentation	D	Hydrogen yield 37.767 ml of H_2 per g of lactose (E. aerogenes strain HO-39)
Starch	$(C_6H_{10}O_5)_n$	Dark fermentation	ID	Common food waste component
Cellulose	$(C_6H_{10}O_5)_n$	Dark fermentation	ID	Promising material due to its abundance
		Pyrolysis	ID	Dehydration is quite expensive

Table 3: Substrates for various hydrogen production routes from carbohydrates, isocutane and citric acid [46].

biological methods for hydrogen production use substrates in water solution. More interestingly, more substrates have even number of hydrogen atoms than odd numbers. In short-chained organic compound (hydrogen sources especially for dark fermentation) the ratio of oxygen to carbon O/C is 1. The O/C ratio for starch and cellulose in molecule is 0.83 and for sucrose, maltose and lactose is 0.92 [46].

5 Discussion

The aim of this chapter is a critical summary of the biohydrogen pathways as well as an attempt to distinguish the best possible pathway at present by comparing biohydrogen production methods.

One of the major advantages of thermochemical processes is their scalability to industrial scale due to their similarity to well-known processes already implemented in oil refineries. Thermochemical processes exhibit high potential to be economically viable and competitive on a large scale in near future. Moreover, thermochemical routes, in comparison with biological pathways, exhibit lower costs as well as higher overall efficiencies (thermal to hydrogen) [6, 13]. Hydrogen production from biomass via thermochemical pathways is by far more developed and approachable in the near perspective than biological ways. Biomass as a feedstock is challenging to work with due to impurities as well as its variable nature, mainly variable moisture and chemical content. Therefore, hydrogen yields obtained are rather low since the hydrogen content in biomass is quite low to begin with [6]. Biomass transportation in a form of raw material or formed gaseous products is another issue in the overall cost of thermochemical processes, therefore in order to lower the cost of transportation, the gasification plant requires to be implemented in areas with biomass wide availability [6]. Nevertheless, thermochemical processes will play a major role in global energy system in the future of power and heat generation as well as fuels and chemicals production. Gasification and pyrolysis are considered the most promising among thermochemical processes for commercialization of biohydrogen production from biomass. The hydrogen costs are estimated to be in the range of 1.25-2.20\$/kg for both pyrolysis and gasification, in comparison hydrogen from steam methane reforming costs are 2.08\$/kg and 2.27\$/kg without CO_2 sequestration cost and with CO_2 sequestration, respectively [33]. Biomass can be transferred either to bio-oil or synthetic gas via pyrolysis and gasification, these products due to their complex composition and low hydrogen concentration are usually used as low-quality fuels. Therefore, in order to increase hydrogen yields, reforming technologies over catalysts are required.

Among many variations of gasification process, steam as gasifying agent exhibits enhancement in hydrogen formation and its purity. Steam gasification highly endothermic nature increases the energy costs compared to air gasification as well as produces maximum tar yield, in comparison with other gasification variations, but eliminates costs of oxygen separation process [41]. Tar formation is a serious limitation for the gasification process due to fouling, corrosion, blockage of pipes, particle filters and heat exchangers, consequently one of the most challenging constrains in gasifier design is the increase of tar cracking performance (most stable tertiary tars elimination requires residence time above 0.5s and temperature above $125^\circ C$) [4]. With the temperature increase, the yield of hydrogen also increases and the tar content decreases, nevertheless the economics will be a limiting agent in selection of the temperature of steam gasification process. The products obtained from biomass steam gasification is a mixture of H_2 , CO , CO_2 , CH_4 and tar [21]. The yields as well as qualities of the obtained gases varies and depends on many factors such as operating conditions of the process, reactor configurations, catalyst used and initial composition of biomass. The most problematic characteristics of biomass, in terms of gasification process optimization, are biomass moisture content, particle size and biomass type especially ash content. In general, high moisture content results in the loss of gasification efficiency, although gasifiers are designed to handle biomass moisture content around 10-15wt%, most gasifiers can handle feed with moisture content below 35%. High ash content directly results in high char yields, but also creates the need for downstream removal of the matter by means of gas cleaning process. The smaller the particle size of biomass the better

heat and mass transfer occurs in a process, however reduction of biomass particle size results in exponential increase in energy consumption of the process [4, 35].

Chemical looping appears to be a promising solution for tar minimalisation due to process operation temperatures above the condensation point of tar as well as the oxygen carrier ability to decompose tar content into small organic matter [47]. The principle of biomass chemical looping gasification (BCLG) system is integration of biomass gasification and water gas shift reaction in two solid loops. In the first loop, biomass is gasified and syngas is produced. The second loop is in water shift gas reactor where steam reacts with CO and converts it to H₂ and CO₂. The WGS reaction is shifted in favourable way due to CO₂ absorption by circulating solid. The oxygen carrier (OC) usually has chemical composition of M_xO_y⁻¹ and is solid, metal-based compound in the form of single metal oxide such as copper, nickel or iron oxide or a metal oxide supported on a high surface area substrate like alumina or silica [16]. Nonetheless metal oxides just like catalyst in catalytic reforming are prone to deactivation as a consequence of coke deposition, sintering as well as some contamination by sulphur, alkali metals and chlorine. One of the advantages of BCLG comparing to conventional gasification is better syngas quality since oxygen carrier provides the oxygen for gasification, therefore there is no direct contact between fuel and air. The use of oxygen carrier brings many improvements, consequently the key factor in successful chemical looping technology is the right selection of oxygen carrier [13]. Many technical issues need to be addressed, widely researched and optimised, for example deactivation of oxygen carriers during biomass conversion due to attrition in fluidised bed, agglomeration, carbon deposition, sulphur present in the fuels, ash [52]. Second major issue is fouling associated to complex biomass chemistry due to tar formation, biomass ash melting, fouling and corrosion.

Another noteworthy thermochemical pathway for biohydrogen production is biomass pyrolysis. The gaseous products of pyrolysis standalone process exhibit too low hydrogen concentration for industrial scale. Therefore, the need for methods maximising hydrogen yields arises. Increase in H₂ concentration can be achieved by applying catalyst, high temperature and long residence time in processes such as bio-oil reforming obtained via fast pyrolysis and pyrolysis and in-line catalytic reforming process. Under fast pyrolysis conditions (short residence time and high heating rates) high yields of bio-oil are obtained (around 60-75wt%) [4], that bio-oil is further manipulated by catalytic reformation steps to produce biohydrogen as the main product. The main advantage of bio-oil over biomass itself is up to ten times higher energy density, which naturally decreases the costs of transportation. Bio-oil properties such as low heating value, high corrosiveness, high viscosity, high oxygen and water content, bio-oil aging, due to thermal and chemical instability, therefore causing problematic storage, are main drawbacks and challenges for this process development [35]. Due to limitations mentioned, mainly in order to minimise the carbon deposition, there is a need for an upgrade. This can be done by changes in parameters of the process like temperature, steam to carbon ratio, O₂ or H₂ addition to feed or use of catalyst, which is most efficient and researched solution. Ni-based catalyst are most used in catalytic steam reforming of bio-oil. Many catalyst support materials such as MgAl₂O₄, CeO₂, CeZrO₂, Al₂O₃ were investigated. Catalyst promoters mostly Ce, La, Mg and Ca were studied in order to increase stability and activity of catalyst in bio-oil aqueous fraction and raw bio-oil reforming [4, 11]. Nevertheless, the coke deposition is inevitable. At the present state of knowledge, the fundamental understanding, the kinetics and mechanism of bio-oil steam reforming complex reactions is very limited. Most research are based on single compound models, therefore more work on real bio-oil steam reforming is needed. Carbon deposition leading to catalyst deactivation is major burden in bio-oil steam reforming development on a large scale, the other major issue on industrial scale application might be bio-oil polymerisation forming gum and carbon deposit causing clogging of pipes, due to bio-oil thermal and chemical instability, in traditional heat exchanger feed heating system. Over last couple of years, pyrolysis and in-line catalytic reforming of volatiles gained interest as an alternative for H₂ production in thermochemical biomass conversion processes. This is very interesting approach for H₂ production via biomass that eliminates some of the drawbacks of biomass steam gasification and fast pyrolysis and bio-oil reforming. This hydrogen production pathway is two-step continuous process, where the first step is biomass pyrolysis and the second one is catalytic steam reforming of the volatiles obtained from the pyrolysis step. Pyrolysis reactor (conical spouted bed reactor being the favourable one) and catalytic reforming reactor (fluidized bed reactor being the favourable one) are connected in series and operating in continuous regime with the separate control [3]. This separation of pyrolysis and catalytic reforming steps brings few practical advantages, both from an operational point of view as well as for the performance of the catalytic reforming. The main advantage of pyrolysis and in-line catalytic reforming process over gasification is rich H₂ gas production free of tars, which is considered main burden of gasification process [21]. In terms of hydrogen focus production, the pyrolysis and in-line reforming process appears to be more favourable comparing to gasification since hydrogen is the main product of pyrolysis-reforming process, whereas syngas (CO and H₂ mixture) is the main product of gasification, therefore as it was mentioned previously gasification is not a process focused mainly on hydrogen production itself [21]. The catalytic steam reforming step is crucial in this process as it improves the gas composition in comparison to gasification by increasing hydrogen and CO₂ concentrations and simultaneously decreases CH₄ and CO concentrations.

Biological hydrogen production as a natural by-product of microbial metabolism is alternative and very exciting pathway that potentially can become sustainable technology from renewable resources. Biological processes exhibit few major

advantages over thermochemical pathways, they are more environmentally friendly, they contribute to waste recycling as they utilize renewable energy resources and less energy input is required as most of those processes operate at ambient temperature and pressure [19, 27, 42]. Biological hydrogen production plants are capable of complete by-product CO₂ absorption through photosynthesis [28]. Biological pathways also fit perfectly into the global green ideology and environmentalism movement, that raised exponentially in recent years in all areas of modern society lifestyle on a global scale. Biohydrogen can be produced by three types of microorganisms: fermentative bacteria, anaerobic bacteria and cyanobacteria. Dark fermentation, light fermentation, direct and indirect biophotolysis are processes that most research are devoted to. Fermentative processes like dark fermentation and photofermentation appear to be most promising biological methods for biohydrogen production. Dark fermentation is a process that operates under anaerobic conditions, therefore the biohydrogen production can run continuously and independently from light without extensive land requirement as well as there is no O₂ limitation that other biological processes struggle with. Fermentation processes are more stable and efficient comparing to biophotolysis processes. They use simple control system therefore operational costs are minimised on industrial scale. Dark fermentation and photofermentation can use wide variety of organic wastes from various origins (manure, glycerol after FAME production, cheese whey, olive mill wastewater, sewage sludge, distillery wastewater, molasses, whey etc.) as substrate providing not only energy generation but also simultaneously waste treatment [5]. The main constrain of dark fermentation technology is relatively low H₂ yields for industrial application due to the principle that with the H₂ yield increase hydrogen fermentation becomes unfavourable thermodynamically. The need of fermentation products removal is also a burden in keeping constant production level on a large scale [20]. In order to develop dark fermentation into competitive technology on an industrial scale, comprehensive research is needed, especially finding new strains of bacteria, improving and isolating already existing ones that are able to convert lignocellulosic materials into biohydrogen [28]. Studies are focused on photofermentation process in an integrated two-steps system with dark fermentation rather than standalone technology. In an integrated system, first stage is dark fermentation process and the second stage uses acetate from the first step to produce more biohydrogen and therefore increases the biohydrogen yield [28]. This technology is fast and simple and can use variety of organic wastes as feedstock. It combines advantages of both photofermentation and dark fermentation therefore, it is currently the most promising biological pathway. According to studies, estimated cost of biohydrogen is 2.57\$/kg for dark fermentation and 2.83\$/kg for photofermentation, for integrated system the cost is not available but it is assumed to be lower than for individual processes [33]. Fermentative biohydrogen production and integrated processes fit well into biorefinery concept. Both direct and indirect biophotolysis are able to produce biohydrogen directly from water and sunlight. These technologies utilize water as renewable source and consume CO₂. The biggest drawback for photobiological processes is that the evolution of H₂ generation is inhibited by O₂. Moreover, in order to collect sufficient amount of light in algal H₂ production, significant surface area is required [2, 24]. Indirect biophotolysis was design to overcome this limitation through separation (into two stages) of H₂ and O₂ generation reactions. This system integrates biophotolysis with dark fermentation through CO₂ fixation. Major burden for this solution is the continuity of this process since it was observed that after 100h of the process the algae need to be rejuvenated [50] also the cost of photobioreactors is quite high and the overall rate of the process is low. In both direct and indirect biophotolysis the biohydrogen yields do not exceed 10% [28].

Thermochemical biomass conversion is the best approach for biohydrogen production on a big scale in the near future (2020-2030), where biological processes are pathways for a long-term biohydrogen production strategy for rather small-scales, more locally oriented production systems. Distinguishing whether biological or thermochemical pathway is optimal solution for biohydrogen generation is not the best approach, due to complexity of the matter, but rather establishing best possible option considering multiple variables for specific area to meet environmental and hydrogen production needs.

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