Biohydrogen production from agro-industrial waste: toward clean energy and a circular economy

Britel *Ilyass*[1], Moummou *Hanane*[2], Fariss *Meriem*[3], Elyadin *Meryem.*[1], Abdelmoume *Hanaa*[1]

[1] Mohammed V University, Faculty of Sciences, Rabat
[2] Private University of Marrakech (UPM)
[3]Mohammed V University, Faculty of Legal, Economic and social sciences, souissi

Abstract. The growing world need of clean and renewable energy requires formulation of sustainable strategies that are capable of effectively converting organic waste into substitutes. Agro-industrial residues which include beet pulp, used coffee grounds and whey, in this case form an enormous unused biomass with high bioenergetic potential. This paper presents a combined discussion of the main biological routes to biohydrogen generation based on agro-industrial wastes and dark fermentation, photofermentation, and coupled H_2-CH 4. Dark fermentation is based on the capability of anaerobic microorganisms to quickly transform organic material to hydrogen, whereas the ratio of photofermentation improves the product by recovering organic acids of the first step with the aid of photosynthetic bacteria. Moreover, the biohydrogen generation in combination with anaerobic digestion would allow the complete valorization of organic waste to biomethane, hence, maximizing the total energy balance and reducing environmental costs. The effect of important operating parameters such as pH, temperature, substrate composition, and fermentation time are also talked about in order to streamline the process performance. All in all, combined biological methods of agro-industrial waste include the integrated valorization of waste, which is a promising concept in terms of sustainable energy generation, greenhouse gas emissions, and the concept of a circular economy.

Keywords: Biohydrogen, Agro-industrial waste, Dark fermentation, Photofermentation, Coupled H2-CH4 system, Circular economy.

1. Introduction

Biohydrogen as a clean energy carrier is thus an excellent solution to the energy switch and global environmental issues especially the problem of increasing agro-industrial waste management [1-7]. Hydrogen has a bright side as it is highly energetic with zero-emission combustion generating nothing but water as the byproduct [4,7,8]. Compared to thermochemical and electrochemical schemes, biohydrogen production of biomass is a green technology, non-pollutant and not demanding as it reacts under mild conditions with low-energy consumption [4,8,9].

Agro industrial wastes present a huge feedstock that has a large bioenergetic capacity in production of biohydrogen [5, 10-15]. About 1.3 billion tonnes of food are wasted or lost per year in the whole world which is a third of the food production [16]. The build up of this waste has some serious consequences in the environment [13, 17]. The process of valorizing these residues is fully consistent with the concept of a circular economy since it aims at turning low-value byproducts into an energy source and at the same time, minimizes pollution [18, 19].

Among the agro-industrial wastes that could be used to produce biohydrogen, it is worth noting that we have this beet pulp, used coffee ground, and whey [10]. These are materials that contain high organic compounds and have high fermentable potential [13,16,20]. As an example, the lignocellulosic biomass residues can serve as a source of abundant and inexpensive sources of hydrogen production [21, 22]. Other byproducts high in soluble sugars (79.8% +- 0.8% salvageable) and fiber (12.3% +- 0.4% salvageable) are also produced in date production [23]. Likewise, Palm Oil Mill Effluent [POME] although a significant environmental problem, has potentials of being used to produce biohydrogen [24].

2. Biological pathways for biohydrogen production:

The biological pathways used to produce biohydrogen also largely include dark fermentation and photofermentation, which is largely used in a sequential mode with an aim of maximizing the overall hydrogen production [1, 3, 25–31].

Ethics of biohydrogen production through dark fermentation.

Dark fermentation is an anaerobic mechanism, where microorganisms convert organic matter into hydrogen gas [3, 11, 15, 32]. This technique is specifically appropriate when valorizing agro-industrial waste since it operates under mild working conditions which are ambient temperature and pressure [11].

An aerobic bacterium, especially a genus of bacteria called Clostridium, are commonly used in dark fermentation [32]. The organisms break down the complex carbohydrates to volatile fatty acids [VFAs] and hydrogen [33].

There are metabolic pathways that are important in the process of breaking down sugars into pyruvate, which is further changed into acetyl-COA. Hydrogen is synthesized with the help of the essential enzyme hydrogenase that helps in deprotonating reduced NADH and/or ferredoxin [34].

Parameters that affect Yield:

PH: The optimal pH is also a very important determinant. Ideally, a range of 5.5 to 6.5 is considered a range that will encourage hydrogen-producing processes whilst trading-off methanogenesis [1, 34].

Temperature: The dark fermentation may be performed in mesophilic (30-40°C)] or thermophilic (50-60°C) temperature [1, 35]. The thermophilic cultures have been proven to be better in producing high yield of hydrogen, especially food waste [35].

Type of Substrate and Concentration: The best feedstock is carbohydrate-rich feedstocks [food waste and lignocellulosic biomass] [10, 20, 21, 32, 36]. It is important to establish the optimal concentration of substrates since a high concentration will result in inhibition of the process [35].

Fermentation Time: To allow the microorganisms to get minimal degradation of the substrate in order to produce hydrogen, a proper hydraulic retention time [HRT] is necessary [1].

Advantages and limitations:

At the first place, one can mention such bonus as the possibility of utilizing a wide range of organic waste, non-aggressive operating conditions, and the possibility to work in incomplete light [11, 32]. Hydrogen yields and production with byproducts that accumulate to inhibit production are among the limitations, though [34, 37]. To scale back these limitations, integration with other processes that complement them [e.g. photofermentation] is often suggested [29, 30]. Also, ensuring the stability of the systems is a long-standing issue [38].

Biohydrogen production through photofermentation principle:

Photofermentation refers to a biological reaction and involves the use of photosynthetic microorganisms to generate hydrogen with the presence of light [3, 26, 37]. It can sporadically be considered complementary to dark fermentation since it can valorize the VFA-rich effluents produced in the dark stage [29, 30, 39, 40].

Photosynthetic microorganisms, especially purple non-sulfur bacteria [PNSB] use the light energy to break down organic acids and generate hydrogen [26, 37, 41, 42]. Nitrogenase enzyme catalyzes this reaction [41].

Interactive photosynthetic microorganisms:

An example of bacteria which have been studied extensively with regard to their effectiveness in the production of hydrogen through the process of photofermentation include: Rhodobacter capsulatus [29, 3, 39, 43].

The operating conditions and light role:

Light is an important requirement in photofermentation [26,37]. Irradiance and spectral composition have significant effects on hydrogen yields. In this connection, PBRs are now commonly used to optimise the high light exposure settings [31, 43]. Such parameters as pH, concentrations of different nutrients (especially nitrogen since nitrogenase is highly sensitive to ammonia), and temperature are all essential in optimisation of production efficiency [39, 41].

Dark fermentation effluents need to be valorised:

One of the major benefits of photofermentation is the ability to use the volatile fatty acids (VFAs) present in the effluents of dark fermentation as a feedstock [29, 30, 39, 40]. It enables a more thorough transfer of the chemical energy of the original substrate to hydrogen and will improve the results in waste management [29, 31]. The production of biohydrogen using the dark fermentation effluents of molasses and thick juice has been reported to be successful in terms of result in empirical studies [31, 43].

Opportunities, limitations, and supplementarity:

Photofermentation has a high substrate conversion efficiency [42] and the ability to react with residual VFAs of dark fermentation and engage in the establishment of more efficient integrated system [40]. However, it is plagued with inefficient light conversion efficiency, and low biohydrogen generation, which altogether limit large-scale applications [26, 37, 41]. The dark fermentation in combination with photofermentation has a promising, synergizing, approach to proletiate the drawbacks of the two methods to enable maximum

biomass-to-hydrogen transformation [29, 30]. Enhanced strategies, such as media optimisation and biotechnological interventions, are already being evaluated to supplement the performance of photofermentative treatments [37, 41].

3. The coupled hydrogen (H 2) and methane (CH 4) system:

The paired system of H 2 -CH 4 is a novel practice of agro-industrial waste to realize dual energisation and enhance the waste management behavior [44]. This idea is completely corroborated with the values of the circular economy, and bioeconomy, where the targets of creating a sustainable energy transition and minimizing greenhouse gas (GHG) emissions can be achieved [44].

Idea and principle of biohydrogen biomethane coupling:

This coupled hybrid system to produce biohydrogen and biomethane uses the integration of dark fermentation and anaerobic digestion (AD), also known as biohythane [45]. This two-phase approach has been considered more effective than the traditional one-stage anaerobic procedures as the allowance of the optimisation of conditions to each microbial consortium maximises energy recoveries [45].

It is traditionally initiated with the dark fermentation where anaerobic bacteria are used to metabolise the carbohydrates obtained through an organic waste into biohydrogen and VFAs [46]. The organic constituents in substrates, e.g. food waste and agro-industrial wastewater, especially suit this stage. An example is the production of hydrogen using the cassava processing, dairy, and citrus wastewaters, which gave 31.41, 37.25, and 28.95 ml of H 2 per gram Chemical Oxygen Demand (COD), respectively [47]. The best pH of the hydrogenic stage is usually 5.5-6.

The resulting VFA-enriched effluents are then moved to a methanogenic anaerobic reactor in which the methanogenic archaea transform them into biomethane [48]. The ideal pH of methane production is found under the range of 6.8 to 7.2 [48]. Getting these two processes connected leads to the more complete degradation of organic matter and an increased recovery of energy as compared to isolated processes [48].

Other novel systems also include Microbial Electrolysis Cells (MECs) with dark fermentation in order to increase biohydrogen production [49]. This blend allows the occupational conversion of non-hydrogenic fermentation outputs into further hydrogen and therefore the maximum transformation of energy [49]. Furthermore, some designs integrate the process of methanogenesis with MECs, to produce both biomethane and biohydrogen, bypassing the difficulties engaged with traditional membrane frameworks, including high expenses and contamination [49].

4. Global energy recovery and reducing residual organic load optimisation:

One of the main goals of coupled H 2 -CH 4 system is the agreement of maximum total energy recovery [44]. The separation of hydrogen and methane production steps will allow the use of the best conditions of the process that will maximize the performance of the particular microbial population. Production of biohythane using agro- industrial waste is recognized as an effective cleaner energy source [44].

In addition, anaerobic digestion which follows dark fermentation produces a significant decrease in residual organic load [48]. The digester transforms VFAs and other by-products of the fermentation process into methane hence reducing COD in the effluent and the potential to pollute the atmosphere. The resulting digestate can even be used as a bio-fertiliser so the nutrient cycle is complete and therefore waste is reduced to a minimal [48].

Endocrine contribution to circular economy and bioeconomy :
The coupled H 2 -CH 4 system of valorisation of agro-industrial waste fits perfectly well with the model of the circular economy and bioeconomy. The given economic models are aimed at reducing the use of fossil resources, reducing the production of waste, and creating value out of the second stream. The food waste, such as that of food, is a perfect feedstock to such processes since it is very moist and rich in organic matter [44].
A system like this reduces the environmental impact of the conventional disposal systems (e.g., landfilling and incineration) by converting them into biofuels (H - and CH 4) and value-added products (e.g., digestate). It develops a circular economy through continued utilization of resources over long periods of time as well as acquiring the highest value out of waste streams [44].

5. Impacts on the environment and energy:

Production of biohydrogen and bio-methane as a result of agro industrial waste produces huge positive environmental and energy procedures.
The greenhouse gas (GHG) emission reduction:
The use of renewable biofuels like biohydrogen and biomethane significantly reduces the emissions of CO 2, CH 4 and N2O, which are the main GHGs resulting in the disintegration of organic waste and burning of fossil fuels. Specifically, the honouring of agricultural organic refuse prevents the significant GHG gaseous emissions that would otherwise become a reality during the landfilling or by burning in the open air. Research has revealed that by integrating biomethanation system with a wastewater treatment plant, the organic constituents can be used to produce 13420kg of biomethane, which is equivalent to about 133826kWh electricity [50].
Comparison to conventional energy pathways:
In comparison with traditional sources of fuel, biohydrogen and biomethane synthesis are based on renewable sources, which provide a cleaner alternative. Hydrogen, especially, is a better clean-energy vector due to its large calorific value and the fact that its combustion produces no toxic by-products. Hydrogen-based energy systems are, therefore, seen to be central towards achieving low-carbon industrialisation and high-quality development goals [51].
International eco-energetic and green advantages.
The integrated system encourages the saving of resources, improved air and water quality, reduction in the amount of waste and conservation of biodiversity. It provides a twofold usage waste-management device and produces energy, a key foundation of sustainable development.
Donation to sustainability and carbon neutrality targets:
The coupled system is the direct next step to the United Nations Sustainable Development Goals (SDGs), in particular, to such areas as "Affordable and Clean Energy" and "Responsible Consumption and Production." It also supports national and international policies to shut the carbon-neutrality grid through lessening the use of fossil fuels and through the appraisal of renewable energy sources [50].

6. Future and technology issues and prospects:

Well meaning as it is, the coupled system faces a number of technological and biological challenges.
Existing Biological and Technical constraints.

There is a great variation in the hydrogen yield and production rate, as shown by studies that clearly indicates the importance of optimising the process conditions. Furthermore, enzymatic stability necessary to perform biocatalytic GHG conversion is often low, and enzymatic activity is very vulnerable to the environmental factors. Selectivity in reactions can be problematic too and undesirable by-products will appear.

Industrial upscaling constraints:

The process of leaving laboratory scale production to an industrial application is complicated, due to the enormous volumes of waste that need treatment and the necessity to maintain both stable and cost effective performance. Infrastructure capital and risk investments to optimise integrated systems are the salient risks. As an example, pre-treatment of lignocellulosic feedstock may be expensive and energy-demanding [52].

Process optimisation needs:

Strategies used to optimise its operation, such as the selection of substrates, co-digestion, enhanced pretreatment methods, enrichment of inoculum and a precise control of all operational parameters (temperature, pH, hydraulic retention time and substrate concentration) are critical in improving the hydrogen yields and stability of the process. Optimising the allocation of energy and the efficiency of a process by regulating redox potentials and materials Direct Interspecies Electron Transfer (DIET) Direct Interspecies Electron Transfer (DIET) using thermodynamic analyses can be used to optimise the distribution of energy and efficiency of a process in the context of syntrophic methanogenesis of hydrogen (this example).

7. Future innovations and perspectives of research:

The study in future should focus on the creation of hybrid and integrated technologies to overcome presently existing limitations in biohydrogen production procedures [54]. Process optimisation can also be enhanced with the help of the use of kinetic modelling and computational simulations and the use of artificial intelligence. The stabilization of enzymes and catalysts, as well as the process of enhancing the conversion process, is a promising body of research. Lastly, the effects on the environment will have to be further enriched with extensive Life cycle Assessments (LCA) to stringently compare divergent biofuel production methods [54].

8. Conclusion:

An example of a green solution to the dual requirements of energy transition and a sustainable use of organic waste demonstrated through the valorisation of agro-industrial waste to produce biohydrogen is a green and environmental benign solution with the capacity to satisfy long-term challenges in energy production. The results provided in this work highlight the potential of such biological methods as dark fermentation and photofermentation as the effective pathway of converting organic residues into clean hydrogen. Dark fermentation allows the fast generation of biohydrogen, compared to photofermentation which holds the possibility of increasing the amount of hydrogen retrieved across the by-products of fermentation, thus increasing the total production.

The adoption of these processes into coupled systems where biohydrogen and methanogenesis processes are coupled together has a significant impact in enhancing the sustainability of the sector by rendering full valorisation of the residual organic matter into biomethane. The integrated approach enhances energy recovery leading to a reduction in

greenhouse-gas emissions besides reduction in the amount of pollutant load related to agro-industrial waste.

However, despite the bright future, the technologies continue to deal with a number of challenges connected with optimisation of the operating conditions, microbiological stability, and upscaling of industry. More research works are still needed to improve the performance, economic sustainability, and industrialization of these systems. Finally, the agro-industrial biomass and its interdependent biological valorisation is a key avenue of developing circular bioenergy systems, which actively can help to meet clean energy production and sustainable development over the long term.

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