PHOTOBIOLOGICAL HYDROGEN AS A RENEWABLE FUEL

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ABSTRACT

The huge global energy consumption has raised concerns over the depletion in readily available conventional energy resources. Besides, there are harmful atmospheric effects of fossil fuels and the qualms of future energy resources. The world hence is in dire need of new renewable energy sources that are cheap, non-polluting, environmentally friendly, and clean. This is the only way we can stop using fossil. Hydrogen is considered as an ideal fuel for the future because of its high energy content and its clean combustion to water. However, extensive technologies are required to introduce hydrogen as an alternative clean and cost-effective future fuel, which brings about the relevance of the exploitation of the microorganisms for large-scale renewable energy production. Reports of photobiological hydrogen production by oxygenic photosynthetic microbes, such as green algae and cyanobacteria and by anaerobic photosynthesis, are summarized in this paper, with a focus on the major obstacles that must be overcome by scientific and technical breakthroughs to make way for commercially feasible energy. The principle, progress, and prognosis of photobiological hydrogen as a renewable energy source are reviewed.

Keywords: *photobiology, renewable fuel, hydrogen*

INTRODUCTION

Concerns about environmental pollution, looming climate change, and dwindling fossil fuels are compelling reasons to switch to renewable energy sources sufficiently large in scale to meet worldwide demand. A variety of renewable energy sources have been proposed and are presently under study, but hydrogen appears to have several advantages. First, its use in fuel cells is innately more efficient than the combustion that is currently required for the conversion of other potential fuels to mechanical energy. Secondly, its breakdown generates no pollutants unlike ethanol whose large scale use is predicted to release large amounts of carcinogenic acetaldehyde with the generation of large amounts of smog.

Thirdly, all presently studied alternative sources are largely carbon neutral since the carbon released by their combustion is derived, directly or indirectly, from recently fixed atmospheric CO_2 [1]. Since it is the lightest carbon-neutral fuel rich in energy per unit mass and easy to store, hydrogen has attracted worldwide attention as a secondary energy carrier. Biological hydrogen production could even be carbon negative.

Biological production of hydrogen is a method for its renewable production. It could be through direct capture of solar energy or utilization of energy-rich organic material for photosynthetic fixation of carbon. Each approach has advantages and disadvantages along with challenging technical barriers to practical application.

In photolytic biological systems, water is used as a substrate**.** Microorganisms, such as green microalgae or cyanobacteria, use sunlight to split water into oxygen and hydrogen ions [2]. Its effectiveness is limited by low rates of hydrogen production and the fact that splitting water also produces oxygen, which quickly inhibits the hydrogen production reaction. The highly explosive hydrogen-oxygen mixture could be a safety issue; this process is also a very oxygen-sensitive process.

In photofermentative biological systems, organic matter is used as a substrate. Its effectiveness is limited by a very low hydrogen production rate and low solar-to-hydrogen efficiency [3].

Photobiological production technologies may provide economical hydrogen production from sunlight with low to net-zero carbon emissions. The algae and bacteria could be grown in water that cannot be used for drinking or agriculture and could potentially even use wastewater [4].

PRINCIPLE AND PROGRESS

In the long run, the highest efficiencies of using hydrogen as a fuel can be achieved with technologies such as photoelectrochemistry or photochemistry, which can produce hydrogen directly from solar energy. Biological hydrogen production can be categorized into five different groups: (1) direct biophotolysis of water, (2) indirect biophotolysis of water, (3) biophotofermentation, (4) hydrogen production by water gas reaction, and (5) dark fermentation [5].

Direct hydrogen gas production can be done by the activity of hydrogenase without intermediate molecules, such as carbohydrates. Indirectly, hydrogen gas could be produced after the storage of carbohydrates or glycogen. Direct photobiological H_2 production from water uses solar energy for largescale production of hydrogen gas by photosynthesis, in which solar energy is used to split water into H_2 gas [6].

Different species of green algae (freshwater and marine) have been used for this. Examples include single-cell cyanobacteria (*Synechocystis*), multicellular cyanobacteria (*Nostoc* sp.), and green algae (*Chlamydomonas* sp.) [7]. H_2 production by algae is a desired option since it produces hydrogen from easily available water, with no accumulation of CO_2 and theoretical solar energy conversion efficiency of about 80 %. Though the process has many advantages, the hydrogenase enzyme involved in hydrogen production is inhibited by oxygen. Overall, the reaction of direct biophotolysis can be described as following [8]:

$$2H_2O + \text{light} \rightarrow 2H_2 + O_2$$

Indirect biophotolysis is composed of two stages: carbohydrates synthesis in the light and dark fermentation of carbohydrates for H_2 production. Cyanobacteria are ideal candidates for this process since they have the simplest nutrient requirements [9]. Examples of various species used include *Anabaena*, *Oscillatoria*, *Callithrix* and *Gloeocapsa*. Theoretical light conversion efficiency is 16.3 % while in actual practice is at 1 – 2 % [10]. Indirect biophotolysis can be described by the following reactions:

$$6H_2O + 6CO_2 + \text{light} \rightarrow C_6H_{12}O_6 + 6O_2$$
$$C_6H_{12}O_6 + 2H_2O \rightarrow 4H_2 + 2CH_3COOH + 2CO_2$$
$$2CH_3COOH + 4H_2O + \text{light} \rightarrow 8H_2 + 4CO_2$$

Hydrogen gas can also be produced by photofermentation. Organic compounds like acetic acids, lactic acids, and butyric acids are converted into H_2 and CO_2 by photosynthetic bacteria in the presence of sunlight in anaerobic conditions. During photofermentation both hydrogenase and nitrogenase enzymes are involved in H_2 production [11]. The overall pathway is:

$$(CH_2O)_2 + \text{NADPH (Nicotinamide adenine dinucleotide phosphate (reduced form))} \rightarrow \text{Ferredoxin} + \text{ATP (Adenosine triphosphate)} \rightarrow \text{Nitrogenase} \rightarrow H_2$$

In photosynthetic bacteria, light intensity, light wavelength, duration of light and temperature are important for photofermentative H_2 production. Factors that limit nitrogenase-mediated photofermentation in purple non-sulphur bacteria are: (1) the occurrence of an H_2 uptake enzyme, (2) low photofermentation efficiency for H_2 production, (3) the low turnover rate of nitrogenase, (4) a low rate of carbon conversion, and (5) the availability of organic acids [12].

Research has been conducted into optimizing feedstock for photobiological H_2 production; to produce H_2, photosynthetic bacteria *Rhodopseudomonas* used sewage and wastewater, *Rhodopseudomonas* and *Cyanobacterium anacystis* used dairy and sugarcane wastewater, *Rhodobacter sphaeroides* used feedstock, sugar refinery and brewery wastewater [13 - 15].

Photofermentation can be coupled with dark fermentation or used as a wastewater technique [16]. Dark fermentation is a carbon-neutral process for the production of H_2 and CO_2 from biomass by facultative and obligate anaerobic fermentative bacteria. It does not require light energy as input. The reaction is the following:

$$C_6H_{12}O_6 + 2H_2O \rightarrow 4H_2 + 2CH_3COOH + 4H_2 + 2CO_2$$

The main advantage of dark fermentation is that the hydrogen evolution rate is higher in contrast to other processes. The drawback is the low yield of H_2 per substrate consumed. Pre-treatment techniques can inhibit bacterial activity and due to this H_2 consumption decreases and yield increases.

Oxygenic photosynthesis of unicellular green algae generates biomass and, via the [Fe]-hydrogenase enzyme, quantities of H_2 gas. The algal biomass is used as feedstock for dark fermentation, producing hydrogen and organic acids [17]. The fermentative broth is used for photofermentation to produce H_2. While green algae absorb visible light, photosynthetic bacteria absorb the infrared portion of solar radiation. This combination can increase total light conversion efficiency as well [18].

Algal hydrogen production is naturally inhibited by the presence of oxygen, which is a major product of photosynthesis. This leads to the transient production of hydrogen. Overcoming that inhibition is a major focus of photobiological hydrogen production research. The inhibition depends on oxygen’s ability to physically diffuse into the enzyme’s catalytic centre and irreversibly bind to it, thus halting further catalytic activity. Strategies for extending the catalytic lifetime of such enzymes (hydrogenases) include: (1) molecular engineering of pathways for oxygen gas diffusion into the catalytic site of hydrogenases to block O_2 from reaching the catalytic site, (2) mutagenizing the hydrogenase gene and then screening for an oxygen-tolerant version of this enzyme, and (3) searching for more oxygen-tolerant hydrogenases from nature and then transferring such genes into green algae and cyanobacteria [19]. It is necessary to separate the hydrogen and oxygen being produced to avoid flammable mixtures. One could also resort to a two-stage method to temporally separate O_2 evolution and H_2 production activities, thereby allowing H_2 production for extended periods without resorting to the use of any mechanical or chemical manipulations. The method demonstrates the successful operation of a single organism, a two-stage photobiological H_2 evolution process in a green alga. It is based on the concept of substrate S as a reversible switch to metabolically regulate the activity of the O_2-evolving PSII (Photosystem II) complex. The method was also checked reversible [20].

Hydrogen production by anaerobic bacteria (e.g. *Clostridium pasteurianum*) through fermentations results in the generation of an abundance of small organic acids, such as malate, lactate, propionate, butyrate, and/or acetate besides of H_2. The further conversion of these small organic acids to H_2 is not an energetically favourable reaction. Hence, small organic acids accumulate in the growth medium. This inhibits the rate of growth and limits the yield of H_2 production by the anaerobes.

Sulphur-deprived *Chlamydomonas reinhardtii* was able to induce photobiological H_2 production under photoautotrophic, photoheterotrophic growth conditions. Hence, hydrogen production can be sustained artificially by inhibiting photosynthesis. Sulphate deprivation hampers the production of a key enzyme for photosynthesis. As the sulphate is used up, photosynthesis slows and less oxygen is produced than consumed for respiration, and the culture becomes anaerobic and switches from carbon fixation to a combination of hydrogen-production and starch degradation [21]. Starch degradation supports the consumption of the low amount of oxygen that is still derived from residual photosynthesis and contributes reductants to hydrogen production. So, the culture starts accumulating the hydrogen gas.

CONCLUSION

Biological systems offer a variety of ways to generate renewable energy. Biohydrogen is one such potentially useful way to fulfil energy consumption, which currently met by fossil fuels. That makes photobiological hydrogen production using photosynthetic microorganisms a useful as well as exciting topic for research. It also shows promise for generating carbon-free, clean fuel free of greenhouse gas emissions from abundant natural resources, such as water and sunlight. For a more feasible and a better yield of hydrogen, a few ideas need to be explored, improved, and incorporated. Integrating hydrogenase and nitrogenase into suitable microorganisms, enhancing culture conditions, sustainable use of feedstocks, analysing various techniques of photobiological H_2 production, integrating multiple mechanisms of photobiological hydrogen production in the photobioreactors are among those ideas. The use of bioreactors is a good way to minimize energy loss and harvest light energy more easily. After the identification of suitable strains of algae and cyanobacteria, various bioreactors can be used for photobiological H_2 production by microorganisms in which light energy is converted into biochemical energy [22]. Factors influencing the performance of bioreactors are area-volume ratio, temperature, agitation and gas exchange.

REFERENCES

[1] U. Sen, M. Shakdwipee, R. Banerjee, Status of Biological hydrogen production, Journal of Scientific and Industrial Research 67(2008), 980-993.

[2] Office of energy efficiency & renewable energy, Hydrogen Production: Photobiological https://www.energy.gov/eere/fuelcells/hydrogen-production-photobiological, Accessed: February 12, 2020.

[3] P.C. Hallenbeck, Fermentative hydrogen production: Principles, progress and prognosis, International Journal of Hydrogen Energy 34(2009), 7379-7389.

[4] K. Seifert, M. Waligorska, M. Laniecki, Brewery wastewaters in photobiological hydrogen generation in presence of Rhodobacter sphaeroides O.U. 001, International Journal of Hydrogen Energy 35(2010) 9, 4085-4091.

[5] R.S. Poudyal, I. Tiwari, A.R. Koirala, H. Masukawa, K. Inoue, T. Tomo, M.M. Najafpour, S.I. Allakhverdiev, T.N. Veziroğlu, Hydrogen production using photobiological methods, in:

Compendium of Hydrogen Energy, Volume 1: Hydrogen Production and Purification, ed.: V. Subramani, A. Basile, T.N. Veziroğlu, Elsevier, 2015, 289-317.

[6] C.N. Dasgupta, J.J. Gilbert, P. Lindblad, T. Heidorn, S.A. Borgvang, K. Skjanes, D. Das, Recent trends on the development of photobiological processes and photobioreactors for the improvement of hydrogen production, International Journal of Hydrogen Energy 35(2010) 19, 10218-10238.

[7] F.A.L. Pinto, O. Troshina, P. Lindblad, A brief look at three decades of research on cyanobacterial hydrogen evolution, International Journal of Hydrogen Energy 27(2002) 11-12, 1209-1215.

[8] D. Das, N. Khanna, T.N. Veziroğlu, Recent developments in biological hydrogen production processes, Chemical Industry & Chemical Engineering Quarterly 14(2008) 2, 57-67.

[9] V. Subramani, A. Basile, T.N. Veziroğlu, Compendium of Hydrogen Energy, Volume 1: Hydrogen Production and Purification, Woodland Publishing Series in Energy: Number 83, Great Britain, 2015.

[10] R.C. Prince, H.S. Kheshgi, The photobiological production of hydrogen: Potential efficiency and effectiveness as a renewable fuel, Critical Reviews in Microbiology 31(2005), 19-31.

[11] R.P. Gfeller, M. Gibbs, Fermentative metabolism of Chlamydomonas reinhardtii: I. Analysis of fermentative products from starch in dark and light, Plant Physiology 75(1984), 212-218.

[12] I. Akkerman, M. Jansen, J. Rocha, R.H. Wijffels, Photobiological hydrogen production: photochemical efficiency and bioreactor design, International Journal of Hydrogen Energy 27(2002) 11-12, 1195-1208.

[13] M. Yetis, U. Gündüz, I. Eroglu, M. Yücel, L. Türker, Photoproduction of hydrogen from sugar refinery wastewater by *Rhodobacter sphaeroides* O.U. 001, International Journal of Hydrogen Energy 25(2000) 11, 1035-1041.

[14] A. Thangaraj, G. Kulandaivelu, Biological hydrogen photoproduction using dairy and sugarcane waste waters, Bioresource Technology 48(1994) 1, 9-12.

[15] H. Zhu, T. Suzuki, A.A. Tsygankov, Y. Asada, J. Miyake, Hydrogen production from tofu wastewater by Rhodobacter sphaeroides immobilized in agar gels, International Journal of Hydrogen Energy 24(1999) 4, 305-310.

[16] M. Sunita, C.K. Mitra, Photoproduction of hydrogen by photosynthetic bacteria from sewage and waste water, Journal of Biosciences 18(1993) 1, 155-160.

[17] N.M. Saifuddin, P. Puvunathan, Developments in Bio-hydrogen Production from Algae: A Review, Research Journal of Applied Sciences, Engineering and Technology 12(2016) 9, 968-982.

[18] A. Melis, M.R. Melnicki, Integrated biological hydrogen production, International Journal of Hydrogen Energy 31(2006), 1563-1573.

[19] A. Melis, L. Zhang, M. Forestier, M.L. Ghirardi, M. Seibert, Sustained Photobiological Hydrogen Gas Production upon Reversible Inactivation of Oxygen Evolution in the Green Alga *Chlamydomonas reinhardtii*, Plant Physiology 122(2000) 1, 127-135.

[20] N. Quintana, F. Van der Kooy, M.D. Van de Rhee, G.P. Voshol, R. Verpoorte, Renewable energy from Cyanobacteria: energy production optimization by metabolic pathway engineering, Applied Microbiology and Biotechnology 91(2011) 3, 471-490.

[21] S. Kosourov, V. Makarova, A.S. Fedorov, A. Tsygankov, M. Seibert, M.L. Ghirardi, The effect of sulfur re-addition on Hydrogen photoproduction by sulfur-deprived green algae, Photosynthesis Research 85(2005) 3, 295-305.

[22] D. Das, N. Khanna, C.N. Dasgupta, Biohydrogen Production: Fundamentals and Technology Advances, Taylor & Francis Group LLC, USA, 2014.