Assessment of biological Hydrogen production processes: A review

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Abstract. Energy crisis created a special attention on renewable energy sources. Among these sources; hydrogen through biological processes is well-known as the most suitable and renewable energy sources. In terms of process yield, hydrogen production from various sources was evaluated. A summary of microorganisms as potential hydrogen producers discussed along with advantages and disadvantages of several bioprocesses. The pathway of photo-synthetic and dark fermentative organisms was discussed. In fact, the active enzymes involved in performance of biological processes for hydrogen generation were identified and their special functionalities were discussed. The influential factors affecting on hydrogen production were known as enzymes assisting liberation specific enzymes such as nitrogenase, hydrogenase and uptake hydrogenase. These enzymes were quite effective in reduction of proton and form active molecular hydrogen. Several types of photosynthetic systems were evaluated with intention of maximum hydrogen productivities. In addition dark fermentative and light intensities on hydrogen productions were evaluated. The hydrogen productivities of efficient hydrogen producing strains were evaluated.

1. Introduction
Global warming and accumulation of air pollutions cause by combustion of fossil fuel is one of serious environmental issue of new millennium. Such concern demanded to conduct and search for a new renewable energy source that has no pollution for environment. One of the alternatives for fossil fuels is biohydrogen which can be produced by microorganisms via their photosynthetic systems. The biohydrogen has no pollution and no harm or undesirable by-products produces during formation of hydrogen. Production of hydrogen by combination of water and sunlight in a microbial or green algae cell made this process very attractive[1].

The available processes for production of energy from biomass are divided into two main categories such as thermochemical and biological processes. Thermochemical processes include gasification, liquefaction [2, 3], pyrolysis [4] and biomass combustion. Biological processes are involved living organisms include direct and indirect biophotolysis, photo fermentation, dark fermentation and biological water-gas shift reaction. There are known enzymes; hydrogenase and

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nitrogenase mostly related to proton reductions which are evolved in all biological hydrogen production processes[5]. A summary of hydrogen production processes can be shown in Figure 1.

![Figure 1. General view of Hydrogen production processes.](image)

2. Biological hydrogen production processes

2.1. Biological water-gas shift reaction

Reaction of carbon monoxide and water resulted in hydrogen and carbon dioxide. For production of pure hydrogen, carbon dioxide should be removed by the means of any carbon dioxide absorbent or any microorganisms can utilize carbon dioxide as substrate.[6] The following reactions are provided the energy for conduction of biological water-gas shift reaction by transferring electron from CO to H₂O:

\[
\begin{align*}
\text{CO} + \text{H}_2\text{O} & \rightarrow \text{CO}_2 + 2\text{e}^- + 2\text{H}^+ \\
\text{H}^+ + 2\text{e}^- & \rightarrow \text{H}_2
\end{align*}
\]

Carbon monoxide dehydrogenase and hydrogenase are two enzymes which are responsible for the supply of electron and proton while electron transport and energy supply devoted to cell growth.[7, 8] The overall reaction which is the sum of reactions (1) and (2) is stated as follows:

\[
\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \quad \Delta G = -20.1 \text{ kJ/mol}
\] (3)

Oxidation of carbon monoxide can take place in both aerobic and anaerobic conditions; while aerobic oxidation of carbon monoxide is exothermic process; it may generates -283 kJ/mol CO while in anaerobic microbial oxidation process just liberate very limited chemical energy in form of methane and other by-products (-19 kJ/mol CO) [9].

\[
\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2
\] (4)

Biological water-gas shift reaction basically is oxidation of the carbon monoxide under anaerobic conditions by hydrogenetic microorganisms. There are bacteria can produce hydrogen from carbon monoxide while catalyze the water-gas shift reaction. For instance *Rhodospirillum rubrum*, *Rubrivivax gelatinosus* and *Carboxythermus hydrogenoformans* are gram negative and gram positive actively involved in the above reaction[10]. Pakpour et al.[11] conducted studies on an isolated *Rhodopseudomonas* strain which was locally isolated and they have reported that the isolated strain
can generate significant amount of hydrogen (33.5 mmol/l $H_2$) and the isolated strain was able to utilize 86% of CO uptake and produce hydrogen through water-gas shift reaction.

Najafpour et al.[11] investigated on the effect of various carbon sources for hydrogen production using anaerobic bacteria known as *Rhodospirillum rubrum* which was capable of producing hydrogen via water-gas shift reaction. They used carbohydrate sources such as glucose, fructose and sucrose and organic acids like formate, acetate and malate as carbon sources. They reported that the maximum cell dry weight was obtained from malate and fructose. They also reported that maximum yield of CO conversion and cell growth from acetate and the highest yield of biomass production obtained while the specified organism utilized fructose as carbon source.

Ismail et al.[12] investigated the effect of configuration or type of bioreactor on hydrogen production of *Rhodospirillum rubrum*. Maximum rate of hydrogen production did not lead to the reactor condition; due to instability of process operation obtained at high agitation rate (500 rpm). In contrary, application of micro sparger had positive impact on high hydrogen production yield.

2.2. Direct biophotolysis

Direct biophotolysis is a suitable hydrogen production process which is utilizing microalgae to convert solar energy to hydrogen as chemical energy. Equation (5) shows the reaction of direct biophotolysis.

$$H_2O + \text{Solar energy} \rightarrow H_2 + O_2$$ \hspace{1cm} (5)

Two types of photosystem are involved in production of hydrogen in direct biophotolysis process. One of them is responsible for reducing CO$_2$ and the second one dividing the water and evolves oxygen. The hydrogenase enzyme in microalgae is responsible to demonstrate the ability of hydrogen production. Due to lack of hydrogenase enzyme in green plants they cannot produce hydrogen even photosynthetic systems are active. The second photosystem generates electron after absorbing the light, and rule of first photosystem is to absorb electrons to ferredoxin by absorbing solar energy, then the electrons which absorbed by ferredoxin transfers to hydrogenase. After transferring the electrons from ferredoxin to hydrogenase, then production of hydrogen is completed[5]. A schematic diagram of direct biophotolysis is shown in Figure 2. Hydrogenase enzyme is very sensitive to presence of oxygen, hydrogen production only can occur under anaerobic conditions (under 0.1% O$_2$)[13].

![Figure 2. Schematic flow diagram of hydrogen production in direct biophotolysis process.](image-url)

2.3. Dark fermentation

Dark fermentation is known as active processes operate biologically in absence of light sources. Hydrogen production is conducted in low temperatures (30-80 °C) and in dark condition by anaerobic bacteria and microalgae. These microorganisms consume rich carbohydrate substrates and produce
hydrogen under mentioned conditions[14]. A schematic of dark fermentative hydrogen production process showed in Figure 3[15].

![Diagram](image)

**Figure 3.** Dark fermentation hydrogen production process.

Products of dark fermentation process are combination of hydrogen, carbon dioxide, methane or hydrogen sulfide. The fraction of methane and hydrogen sulfide depends on the substrate used for hydrogen production. Hawkes et al.[16] conducted studies on optimum hydrogen production in dark fermentation and proposed reactions (6) and (7) for hydrogen production,

\[ \text{C}_6\text{H}_{12}\text{O}_6 + 2\text{H}_2\text{O} \rightarrow 2\text{CH}_3\text{COOH} + 4\text{H}_2 + 2\text{CO}_2 \]  
(6)

\[ \text{C}_6\text{H}_{12}\text{O}_6 + 2\text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OOH} + 2\text{H}_2 + 2\text{CO}_2 \]  
(7)

The mole of hydrogen produced depends on byproduct, in first reaction (6) acetic acid and 4 moles of hydrogen is the product of process while in second one (7) butyrate is the unwanted byproduct of reaction. In practice no one claimed that achieved to yield of 100%. For the low hydrogen production; it can be explained by the presence of organic acids such as acetate and butyrate in products[16]. An important parameter in amount of hydrogen in product is pH value. According to literature, pH value should be maintained in the range of 5-6[17-19]. Hydrogen partial pressure and HRT are the other important factors in producing hydrogen from the above process.

In a study which was conducted by Van Niel et al.[20] inhibitors of hydrogen production in dark fermentation studied and they reported that after accumulation of hydrogen the pathway of microorganism changed and more reduced substrates produced; lactate, ethanol, acetone and butanol or alanine are some of reduced substrates were reported.

2.4. *Indirect biophotolysis*

Indirect biophotolysis consists of four stages[21] that sum of them leads a microorganism to produce hydrogen by absorbing light. The four stages are stated as follow:

1. producing biomass by photosynthesis
2. concentrating the produced biomass from first stage
3. aerobic dark fermentation of biomass
4. conversion of acetate which has been produced in third stage
these four steps can takes place inside a microalga or cyanobacteria cell[22]. The schematic of indirect biophotolysis, illustrated in Figure 4[15].

![Figure 4. Schematic flow diagram of indirect biophotolysis hydrogen production process](image)

The following reactions are summarized series reactions for production of biohydrogen from indirect biophotolysis for instance in Cyanobacteria photosynthesis may generate glucose then the carbohydrate is converted to hydrogen; the reactions are stated as follows:

\[
\begin{align*}
H_2O + CO_2 + \text{light energy} & \rightarrow C_6H_{12}O_6 + O_2 \\
C_6H_{12}O_6 + H_2O + \text{Light energy} & \rightarrow H_2 + CO_2
\end{align*}
\]

The required substrates for cyanobacteria for hydrogen production is light as source of energy for producing biomass, air as a source of O\(_2\), water and mineral salts[23]. In this process three enzymes are involved namely: nitrogenases, uptake hydrogenases and bi-directional hydrogenases. These enzymes catalyze the production of H\(_2\) via reduction of nitrogen to ammonia; while catalyzing the H\(_2\) oxidation, the oxidation and synthesis of H\(_2\) [24]. Number of investigations conducted on optimization of hydrogen production by indirect biophotolysis process. Beside the strain of cyanobacteria, the most influential parameters are temperature, pH, gaseous substrate [24, 25], culture age, biomass density and composition of growth medium. For instance increasing the temperature from 30 to 40 °C can enhance (even double) the hydrogen production rate, and optimal pH value in the range of 6.8-8.3 may enhance the hydrogen production [26-28].

### 2.5. Photo-fermentation

Photosynthetic bacteria have the ability to produce hydrogen with the aid of nitrogenase while utilizing biomass or organic acids as carbon source. A schematic diagram of hydrogen production via photo fermentation is shown in Figure 5 [15]. In this process hydrogen production has some drawbacks such as high energy demand, low energy conversion of sun light and demanding large areas for the location of anaerobic photobioreactors [29-31]. Various type of biomass such as lactic acid [30], lactate feedstock wastewater [32, 33], sugar refinery wastewater [34] are used for production of hydrogen by photo fermentation. Disadvantage of photo fermentative process is known as an impractical hydrogen production process.

![Figure 5. Hydrogen production by photo fermentation process](image)
3. Potential hydrogen producing microorganisms

Four types of microorganisms can produce hydrogen: green algae, cyanobacteria, photosynthetic bacteria and fermentative bacteria. These microorganisms can produce hydrogen in different manner and each organism has its advantage and disadvantages[35]. Table 1 summarized advantages and disadvantages of these potent microorganisms.

### Table 1. Summary of variety of potential hydrogen producer microorganisms

| Type of microorganism | Name of microorganism | Advantages | Disadvantages | Ref. |
|----------------------|------------------------|------------|---------------|------|
| **Green algae**      | *Scenedesmus obliquus* | Hydrogen production from water | Light requirement for hydrogen production | [36] |
|                      | *Chlamydomonas moewusii* | High sun energy conversion | Sensitive to oxygen presence | [37] |
| **Cyanobacteria**    | *Anabaena azollae*     | Hydrogen production from water by nitrogenase enzyme | Inhibitory of O₂ for nitrogenase | [38, 39] |
|                      | *A. variabilis*        | | Presence of O₂ in the product gas | [40, 25] |
|                      | *Nostoc muscorum*      | | | [41] |
|                      | *N. spongiaeforme*     | | | [25] |
|                      | *Westiellopsis prollica* | | Sun light requirement | [25] |
| **Photosynthetic bacteria** | *Rhodobacter sphaeroides* | Can use different substrate for hydrogen production | Light requirement for hydrogen production | [42, 43] |
|                      | *R. capsulatus*        | Uses a wide range of light for hydrogen production | Water pollution problem by fermented broth | [44] |
|                      | *R. sulidophilus*      | | | [45] |
|                      | *Rhodopseudomonas sphaeroides* | | | [46] |
|                      | *R. palustris*         | | | [47] |
|                      | *R. capsulate*         | | | [48] |
|                      | *Rhodospirillum rubrum* | | | [49] |
|                      | *Chromatium sp.*       | | | [49] |
|                      | *Miami PSB 1071*       | | | [50] |
|                      | *Chlorobium limicola*  | | | [50] |
|                      | *Chloroexu aurantiacus*| | | [50] |
|                      | *Thiocapsa roseopersicina* | | | [51] |
|                      | *Halobacterium halobium* | | | |
| **Fermentative bacteria** | *Enterobacter aerogenes* | Producing hydrogen without light demand | Water pollution problem by fermented broth | [52] |
|                      | *E. cloacae*           | Can use a wide variety of substrates as carbon source | Presence of CO₂ in product gas | [19] |
|                      | *Clostridium butyricum* | | | [53] |
|                      | *C. pasteurianum*      | | | [54] |
|                      | *Desulfovibrio vulgaris* | No need to oxygen | | [54] |
|                      | *Magashaera eldenii*   | Produces valuable byproducts such as butyrate | | [53] |
|                      | *Citrobacter intermedius* | | | |
|                      | *Escherichia coli*     | | | |
Table 2. Hydrogen production from renewable sources

| Microorganism                        | Type                        | Substrate                           | maximum H₂ production (mmol H₂/h) | Products of process                        | Ref.       |
|-------------------------------------|-----------------------------|-------------------------------------|-----------------------------------|--------------------------------------------|-----------|
| Oscillatoria sp. Miami BG7          | Photosynthetic bacteria     | Medium A expect NH₄                 | 0.4                               | H₂, CO₂, O₂, biomass                       | [56, 57]  |
| Anabaena cylindrica                 | Photosynthetic bacteria     | Nitrogen-starved medium             | 1.2                               | H₂, O₂, biomass                            | [58]      |
| Rhodopseudomonas capsulate          | Photosynthetic bacteria     | Lactate and nitrogen sources        | 5.3                               | H₂, CO₂, O₂, biomass, fatty acids          | [59, 60]  |
| Rhodospirillum rubrum               | Photosynthetic bacteria     | Organic compounds                   | 3.0                               | H₂, CO₂, O₂, biomass, fatty acids          | [61, 60]  |
| Citrobacter intermedius            | Facultative anaerobic       | Cellulose, starch, glucose          | 11                                | H₂, CO₂, biomass, fatty acids with high concentration | [54]      |
| Enterobacter aerogens               | Facultative anaerobic       | Sugar cane                          | 11.36                             | H₂, CO₂, biomass, fatty acids with high concentration | [60]      |
| Enterobacter cloacae IIT BT-08      | Facultative anaerobic       | Sucrose containing medium           | 37.03                             | H₂, CO₂, biomass, fatty acids with high concentration | [19]      |

4. Enzymes role in hydrogen production

Fe-nitrogenase and Mo-nitrogenase are the most important enzymes involved in pathway of anaerobic organisms liberate hydrogen. In fact protons are reduced to hydrogen while nitrogenase can catalyze nitrogen fixation to generate ammonia. Three types of enzymes are having significant role in hydrogen production in algae and Cyanobacteria: the acting enzymes are Hydrogenase [62, 36], uptake hydrogenase and nitrogenase [63].

4.1 Hydrogenase

Hydrogenase is a family of enzymes which catalyze the hydrogen production reaction; the following reaction is catalyzed in presence of hydrogenase enzyme:

\[ 2H^+ + 2e^- \rightarrow H_2 \] (10)

Most prokaryotic microorganisms and some of eukaryotes can liberate Hydrogenase enzyme. These microorganisms can produce or even utilize hydrogen. Equation (10) shows the reaction occurs in presence of hydrogenase enzyme. The reaction is reversible and can goes in both directions. Production or consumption of hydrogen depends on presence of metallic compounds in hydrogenase enzymes. Iron and nickel are two metallic elements which are responsible for leading cells to produce or uptake hydrogen. The hydrogen producer microorganism enzymes usually contains iron and the hydrogen consumer organism contains both iron and nickel [64]. Chlamydomonas reinhardtii is a well-known algae species in hydrogen production which is able to liberate hydrogenase [65, 66].
Activity of hydrogenase enzyme was extensively investigated. Also comparison between activities of Hydrogenase in different species was conducted by number of researchers. Winkler et al. [67] reported that the activity of hydrogenase in \textit{C. reinhardtii} was higher than \textit{Scenedesmus sp}.

4.2 \textit{Nitrogenase}

Nitrogenase in photosynthetic microorganism has significant role in production of hydrogen. High N/C ratio, presence of oxygen and ammonia may inhibit nitrogenase activity [68]. That is due to sensitivity of nitrogenase to photosynthetic microorganisms inhibitors need an oxygen free and ammonia limited media for hydrogen production [69, 70]. Effect of inhibiting materials on hydrogen production of photosynthetic microorganisms has been investigated. Yokoi et al.[71] conducted an investigation on \textit{Rhodobacter} sp. M-19. It has been reported that presence of ammonia completely stopped hydrogen production; that was most probably due to significant changes made in pathway of organism for nitrogen fixation and ammonia generation. In addition, effect of presence of different proteins [72, 69], high nitrogen concentration [72] and high ammonia concentration [69] was investigated.

5. \textit{Bioreactors for hydrogen production}

Several bioreactor configurations such as: large pounds and tubular photobioreactors for microalgae strains were experimented in hydrogen production. Benemann et al.[63] studied the feasibility of photobiological hydrogen production in large pounds and tubular photobioreactor. They have reported that the production rate of biomass in large pound was higher than tubular photobioreactor. Kumar et al.[73] investigated the effect of bioreactor on biohydrogen production they reported that rhomboid and tapered bioreactors resulted in higher hydrogen production rate than tubular bioreactors. In fact the gas hold up in rhomboid bioreactors was 67% lower than tubular bioreactor.

6. \textit{Conclusion}

Based on evaluation of various carbon sources; hydrogen is evolved in bioconversion of syngas while utilization of suitable of organic substrate may lead to molecular hydrogen. In evaluation of organic compound through the cell active pathway, it was found that light sources may enhance production of hydrogen in anaerobic processes. Dark fermentation may result in active hydrogen production while biological pigments were synthesized when the light sources available to adsorb light energy for the synthesis of active biological molecules.

7. \textit{References}

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