

Bio-hydrogen production from waste materials: A review

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Abstract. When hydrogen burns in air, it produces nothing but water vapour. It is therefore the cleanest possible, totally non-polluting fuel. This fact has led some people to propose an energy economy based entirely on hydrogen, in which hydrogen would replace gasoline, oil, natural gas, coal, and nuclear power. Hydrogen is a clean energy source. Therefore, in recent years, demand on hydrogen production has increased considerably. Electrolysis of water, steam reforming of hydrocarbons and auto-thermal processes are well-known methods for hydrogen gas production, but not cost-effective due to high energy requirements. As compare to chemical methods, biological production of hydrogen gas has significant advantages such as bio-photolysis of water by algae, dark and photo-fermentation of organic materials, usually carbohydrates by bacteria. New approach for bio-hydrogen production is dark and photo-fermentation process but with some major problems like dark and photo-fermentative hydrogen production is the raw material cost. By using suitable bio-process technologies hydrogen can be produced through carbohydrate rich, nitrogen deficient solid wastes such as cellulose and starch containing agricultural and food industry wastes and some food industry wastewaters such as cheese whey, olive mill and baker's yeast industry wastewaters. Utilization of aforementioned wastes for hydrogen production provides inexpensive energy generation with simultaneous waste treatment. This review article summarizes bio-hydrogen production from some waste materials with recent developments and relative advantages.

1. Introduction

The energy need has been increasing exponentially all over world-wide, the reserves of fossil fuels are going to deplete very soon in near future, and serious negative effects of the combustion of fossil fuels are spreading throughout because of CO₂ emission is growing day by day in the atmospheric air. For such types of reasons, motivating the researchers to find some kind of new sustainable energy sources those should be capable to substitute the conventional energy sources with less emissions.

The major demerits in utilization of hydrogen as a gaseous fuel is its availability in nature is nil or can say not easy and expensive production methods are required. It has been reported that 50 million tonnes of hydrogen are traded annually worldwide with a growth rate of nearly 10% per year for the time being [1]. Based on the National Hydrogen program of the United States, the contribution of hydrogen to total energy market will be 8–10% by 2025 [2]. It was reported by the US Department of Energy (US-DOE) that H₂ power and transport systems will be available in all regions of the United States by the year 2040 [3]. Due to this level of increasing need for hydrogen energy, in recent years there is urgent need to pay attention on finding the cost-effective development and efficient hydrogen production technologies.

Some methods are developed to improve the existing technologies like, membrane processes, selective oxidation of methane and oxidative dehydrogenation [2]. Biomass and water can be used as renewable resources for hydrogen gas production. Utilization of wide variety of gaseous, liquid and solid carbonaceous wastes was

investigated by Kim [4] as renewable sources for formation of hydrogen gas by steam reforming. Despite the low cost of waste materials used, high temperature requirement (T = 1200 °C) is still the major limitation for this process. Electrolysis of water may be the cleanest technology for hydrogen gas production. However, electrolysis should be used in areas where electricity is inexpensive since electricity costs account for 80% of the operating cost of H₂ production. In addition, feed water has to be demineralized to avoid deposits on the electrodes and corrosion [2].

Photosynthetic processes include algae which use CO₂ and H₂O for hydrogen gas production. Some photo-heterotrophic bacteria utilize organic acids such as acetic, lactic and butyric acids to produce H₂ and CO₂. However, the rate of H₂ production is low and the technology for this process needs further development [5].

With the use of sustainable technologies production of clean energy source and utilization of waste materials make biological hydrogen production a novel and promising approach to meet the increasing energy needs.

2. Types of waste materials

Availability, cost, carbohydrate content and biodegradability are the major concern for the selection of waste materials from which bio-hydrogen is going to be produced. Pure carbohydrate sources are expensive raw materials.

2.1. Carbohydrate industrial wastewaters

Some biodegradable carbohydrate containing and non-toxic industrial effluents such as dairy industry, olive

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mill, baker's yeast and brewery wastewaters can be used as raw material for bio-hydrogen production [6]. To remove undesirable components and for nutritional balancing, pre-treatment of waste waters may require. Fig. 1 shows schematic diagram for bio-hydrogen production from food industry wastewaters by two stage anaerobic dark and photo-fermentations.

2.2 Waste sludge of WTP

For production of methane or hydrogen gas, large quantities of carbohydrate and proteins are useful which can be available from waste sludge generated in wastewater treatment plants.

2.3. Agricultural or food industry wastes (Starch and cellulose)

Biodegradability may be affected badly due to the complex nature of these types of wastes. Cellulose containing agricultural wastes requires further pre-treatment. Agricultural wastes should be ground and then de-lignified by mechanical or chemical means before fermentation.

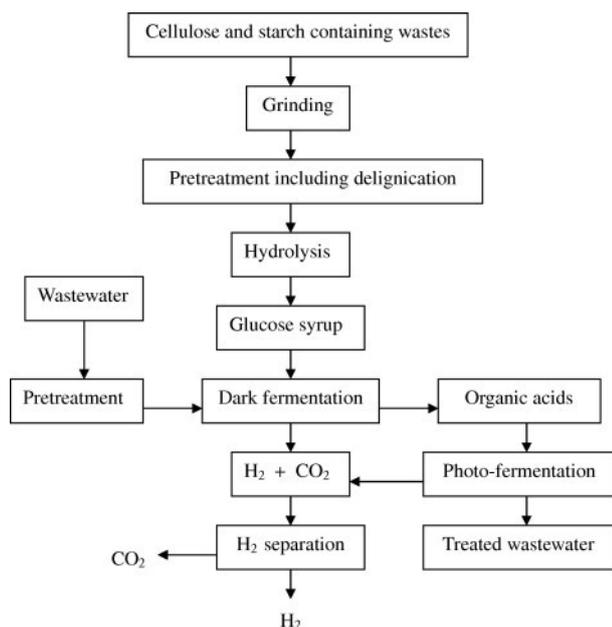


Fig. 1: Bio-hydrogen production from agriculture and food industry wastewaters by two stage anaerobic dark and photo-fermentations

3. Bio-processes for hydrogen gas production

For hydrogen gas production, three major categories can be classified:

1. Bio-photolysis of water through algae.
2. Dark/photo-fermentative (two stage) hydrogen production.
3. Dark-fermentative hydrogen production during acidogenic phase of anaerobic digestion of organic matter.

3.1. Bio-photolysis of water through algae

Generally, the work of algae is division of water molecules into hydrogen ion and oxygen via photosynthesis process. By the use of hydrogenase enzyme, hydrogen ions can be converted in hydrogen gas. *Chlamydomonas reinhardtii* is one of the well-known hydrogen producing algae [7,8]. Hydrogenase activity has been detected in green algae, *Scenedesmus obliquus* [9], in marine green algae *Chlorococcum littorale* [10,11], *Playtmonas subcordiformis* [12] and in *Chlorella fusca* [13]. The hydrogenase activity of different algae species was compared by Winkler et al. [14] and it was reported that enzyme activity of the *Scenedesmus* sp. (150 nmol/_g Chl a.h) is lower than *C. reinhardtii* (200 nmol/_g Chl a.h). It was reported that *Anabaena* sp. have higher hydrogen evolution potential over the other cyanobacter species [15]. Four to 18% CO₂ concentrations were reported to increase cell density during growth phase resulting in higher hydrogen evolution in the later stage [16].

3.2. Hydrogen gas production through photo-fermentations (two stage)

3.2.1. Types of organisms with conditions

Hydrogen gas production capabilities of some purple photosynthetic bacteria such as *Rhodobacter spheroides* [17,18-27], *Rhodobacter capsulatus* [29], *Rhodovulum sulfidophilum* W-1S and *Rhodospseudomonas palustris* have been investigated. Photoproduction of hydrogen from CO or other organic acids by carbon-monoxide dependent dehydrogenase (CODH) enzyme containing cultures such as *Rhodospirillum rubrum* and *Rhodospseudomonas palustris* P4 has also been investigated.

Therefore, the process requires ammonium limited and oxygen free conditions. Hydrogen gas production was lower in the presence of ammonia salts, while proteins such as albumin, glutamate and yeast extract as a nitrogen source enhanced the production. The metabolism shifts to utilization of organic substance for cell synthesis rather than hydrogen production in the presence of high nitrogen concentrations resulting in excess biomass growth and reduction in light diffusion [27]. It was reported that presence of carbonate enhanced ammonia removal and stimulated hydrogen production. Light intensity is one of the parameters which affects the performance of photofermentation. Increasing light intensity has a stimulatory effect on hydrogen yield and production rate, but has an adverse effect on the light conversion efficiency [29]. Light intensity might also affect the consumption rates of organic acids. Similarly, Wakayama reported that hydrogen production rate during 30 min dark/light cycle was 22 L/m² d which was twice as much as that obtained by illuminated culture during a 12 h cycle under the same condition.

3.2.2. Substrates

Utilization of industrial effluents for hydrogen gas production by photosynthetic bacteria is possible although, these cultures prefer organic acids as carbon sources. Color of wastewaters is the one of the effluents, which could reduce the light penetration. Hydrogen gas production from potato starch, sugar cane, juice and whey by using *Rhodospseudomonas* sp. Was investigated by Singh Among the three substrates sugar cane juice yielded the maximum level of hydrogen production (45 mL/mg DWh) as compared to potato (30 mL/mg DWh) and whey (25 mL/mg DWh)[29].

3.2.3. Bio-hydrogen production via Photo-bioreactors

Tubular, flat panel and bubble column reactors are the major types of photo-bioreactors developed for hydrogen production. A mutant type photosynthetic bacteria have been developed to increase the light conversion efficiency and hence hydrogen production rate.

El-Shishtawy reported 9.23% maximum light conversion efficiency by using light-induced and diffused photo-bioreactor (IDPBR) at 300 W/m² light intensity. The width of the culture significantly affected the productivity which reached to 7577 mL H₂/m² h hydrogen production rate with 1 cm culture width was investigated by Nakada in a photo-bioreactor composed of four compartments aligned along the light penetration axis. In addition, a delay of 2–4 h was observed in maximum hydrogen production rate (3.4 L H₂/m² h) after the highest light intensity at noon with an average light conversion efficiency of 1.4%.

3.3. Dark-fermentative hydrogen production during acidogenic phase of anaerobic digestion of organic matter

3.3.1. Type of organisms with conditions

Hydrogen can be produced through many anaerobic organisms from carbohydrate containing organic wastes. Investigations on microbial diversity of a mesophilic hydrogen producing sludge indicated the presence of *Clostridia* species as 64.6%. By mixed acid or the 2–3 butanediol fermentation, CO₂ and H₂ are produced from formic acid in addition to ethanol and the 2–3 butanediol. Recently, researchers identified hydrogen producing aerobic cultures such as *Aeromonas* spp., *Pseudomonas* spp. and *Vibrio* spp. Under anaerobic conditions when the cultures were cultivated, the hydrogen yield varied between 1 and 1.2 mmol/mol glucose. Hydrogen production by *Thermotogales* species and *Bacillus* sp. were detected in mesophilic acidogenic cultures.

Medium pH affects biogas content, hydrogen production yield, the specific hydrogen production rate, and type of the organic acids produced. pH range for the maximum hydrogen yield or specific hydrogen production rate is reported between pH 5.0 and 6.0. However, the optimum pH range is reported by some investigators in between 6.8 and 8.0. Most of the studies indicated that final pH in anaerobic hydrogen production is around 4.0–4.8

regardless of initial pH. Due to production of organic acids which depletes the buffering capacity of the medium results in decrease in pH. Gradual decreases in pH inhibit hydrogen production since pH affects the activity of iron containing hydrogenase enzyme.

When lactose and molasses (sucrose) were used as the substrates, formation of lactic acid was observed. pH also affects the type of organic acids produced. Concentration of acetate and butyrate could be almost equal at pH 6.5–7.0. Ethanol production was observed depending on the environmental conditions. Methane was not detected in most of the hydrogen production studies because of elimination of methane producers by heat digestion of sludge. However, long retention times may cause methane formation by the mesophilic cultures. Methane production was also observed when sewage sludge was used as the substrate.

3.3.2. Substrates

3.3.2.1. Use of simple sugars

An easily biodegradable carbon source is Glucose which is present in most of the industrial effluents and can be obtained abundantly from agricultural wastes. The highest hydrogen yield obtained from glucose is around 2.0–2.4 mol/mol. Though, even when more than 95% glucose was degraded, the yield could be less than 1.7 mol H₂/mol glucose. Therefore, utilization of substrate as an energy source for bacterial growth is the main reason for obtaining the yields lower than theoretical estimations. Similarly, cumulative hydrogen production from sucrose was 300mL while it was only 140mL from starch. These studies showed that the higher hydrogen yields could be obtained from sucrose compared to other simple sugars.

3.3.2.2. Use of starch containing wastes.

As a carbohydrate source for hydrogen production, starch containing materials are abundant in nature and have great potential to be used. As per the reaction stoichiometry, a maximum of 553mL hydrogen gas is produced from one gram of starch with acetate as a by-product.

3.3.2.3. Use of cellulose containing wastes.

The major constitute of plant biomass and highly available in agricultural wastes and industrial effluents such as pulp/paper and food industry is Cellulose. If cellulose concentration increases, it resulted in lower yields with the maximum value of 2.18 mol H₂/mol cellulose with 12.5 g/L cellulose concentration.

During an 81 h period of stationary culture, the organisms consumed 0.92 mmol glucose/h and produced 4.10 mmol H₂/h. The hydrogen yield from the hydrolysate was higher than that of carbohydrates as 19.6 and 18.6 mmol H₂ per gram of substrate consumed, respectively.

3.3.2.4. Use of food industry wastes and wastewater.

The conventional approaches for the solid waste management are landfilling, composting and

incineration. The variations in carbohydrate and protein types and concentrations in the mixture is the problem with the food waste. Each component requires different environmental and bio-processing conditions for hydrogen gas production.

Addition of sewage sludge onto food waste as a rich protein source did not improve the production rate. Similarly, hydrogen production potential of carbohydrate rich high solid organic waste (HSOW) was 20 times larger than those of fat rich HSOW and protein rich HSOW because of the consumption of hydrogen gas to form ammonium using nitrogen generated from biodegradation of protein rich solid wastes.

3.3.2.5. Use of waste sludge.

Biosolids (sludges) from waste water treatment plants contain large amounts of polysaccharides and proteins. Hydrogen yields of 1.2 mg H₂/g COD and 0.6 mol/kg COD_i were reported when sludge was used as the raw material. However, higher hydrogen yields (15 mg H₂/g COD) were obtained from the filtrate.

3.4. Hydrogen gas production by sequential dark and photo-fermentation

A new approach in biological hydrogen gas production is sequential dark and photo-fermentation. The limitation by the organic acid availability would be removed. Higher hydrogen production yields can be attained when two systems are combined. Further, utilization of organic acids by photo-fermentative bacteria could offer better effluent quality in terms of COD. The ammonia concentration and C/N ratio in the effluent of anaerobic fermentation should not be at the inhibitory level for the photosynthetic bacteria. Dilution and neutralization of dark fermentation effluents are required before photo-fermentation to adjust the organic acid concentration and the pH for the optimal performance of photosynthetic bacteria.

4. Conclusions

Hydrogen is considered as the 'energy for future' since it is a clean energy source with high energy content as compared to hydrocarbon fuels. Therefore, new processes need to be developed for cost-effective production of hydrogen. Chemical methods such as steam reforming of hydrocarbons and partial oxidation of fossil fuels operate at high temperatures, and therefore are energy intensive and expensive.

Biological methods offer distinct advantages for hydrogen production such as operation under mild conditions and specific conversions. However, raw material cost is one of the major limitations for bio-hydrogen production. Utilization of some carbohydrate rich, starch or cellulose containing solid wastes and/or some food industry wastewaters is an attractive approach for bio-hydrogen production.

Among the various methods used for bio-hydrogen production are: (a) water splitting by photosynthetic algae, (b) dark fermentation of carbohydrate rich wastes

and (c) photofermentation of organic acid rich wastewaters. Organic acids produced during the dark fermentation of carbohydrate rich wastes may be converted to hydrogen and CO₂ by photoheterotrophic bacteria. The process requires special organisms, light and strict control of the environmental conditions. Sequential or combined bio-processes of dark and photo-fermentations seem to be the most attractive approach resulting in high hydrogen yields for hydrogen production from carbohydrate rich wastes.

The major problems in bio-hydrogen production from wastes are the low rates and yields of hydrogen formation. Large reactor volumes are required for bio-hydrogen production due to low hydrogen production rates. Low yields and the rates of hydrogen formation may be overcome by selecting and using more effective organisms or mixed cultures, developing more efficient processing schemes, optimizing the environmental conditions, improving the light utilization efficiency and developing more efficient photo-bioreactors. Considerable research and development studies are needed to improve the 'state of the art' in bio-hydrogen production.

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