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Microbial Disintegration of Bio-Waste for Hydrogen Generation for Application in Fuel Cell

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Abstract - *With gradual decrease in our conventional energy resources and the grave threat of global warming, there is a need to find sources that are long lasting. Hydrogen as fuel provides a very good option. Fuel cell converts hydrogen directly into electricity, with water as the only byproduct. No greenhouse gases are produced during this process. But Hydrogen production uses Natural gas and electrolysis of water, thus directly or indirectly creating pollution. As per this, we cannot say Hydrogen as a clean energy.*
So, we need to categorize clean Hydrogen production techniques. In this review paper, we will look into methods of Hydrogen production by microbial action on wastewater or biomass. It provides a renewable path and reduces CO_2 emission. Also, we will look into Microbial Fuel Cells, which can be used to produce electricity from water containing glucose or lactate.

Key Words: *Biological H_2 production, Aerobic Reaction, Anaerobic reactions, Waste Disposal, Fuel cell*

1. INTRODUCTION

Energy is the need for every generation. Any technological advancement is supported by continuity of power. With gradual depletion of conventional resources, the world is looking towards clean and green energy sources to satisfy the demand of the present generation. The scientific world is providing us with solutions but their use is restricted due to lack of funds or technology. In this scenario, Fuel Cells possess the potential for its use on large scale. Fuel Cells are now being introduced commercially for large scale domestic use, revolutionizing the way we produce power. Presently Fuel Cells uses Hydrogen as fuel, offering us a clean sustainable power source, with water as byproduct. Hydrogen Fuel Cell is seen as a possible replacement for conventional power production in many applications, especially on-site/off-grid power production.

But the problem with hydrogen is that it is an inert gas, and extracting & packing hydrogen for usage is a difficult & costly process. In majority, Hydrogen is produced from natural gas and its production is accompanied by CO_2 emission, which is a greenhouse gas. Also, hydrogen production by electrolysis consumes large amount of power which indirectly comes from conventional power plants. So newer methods of H_2 production are being worked on with, which reduces the emissions caused in conventional methods. Biological methods of H_2 production by the action of microbes on wastewater and biomass wastes is very important as it consumes waste helping the reduction of garbage volume, it can be applied on wastewater which results in wastewater treatment and the process is free of greenhouse gas emissions. Biological hydrogen production delivers clean hydrogen with an environmental-friendly technology and is very suitable for the conversion of wet biomass in small-scale applications, thus having a high chance of becoming an economically feasible technology.

2. BIOLOGICAL HYDROGEN GENERATION

Hydrogen is considered as a clean fuel because on combustion it generates water. So, basically Hydrogen is renewable, as it can be reformed from by-products. [1] It has high a very high energy content per unit mass. Presently, only 40 % of hydrogen is produced from natural gas, 30 % from heavy oils and naphtha, 18 % from coal, and 4 % from electrolysis and about 1 % is produced from biomass.[2] The methods used today uses Natural gas as input, thus producing CO_2 and other waste gases. Electrolysis of water looks like a clean method but the electrical power required to drive electrolysis process comes from thermal or nuclear power plants, that is indirectly creating pollution. In coal gasification process, large amount of waste gases are produced containing sulphur compounds, thus highly polluting. [3] To meet the emission levels of CO_2 as imposed by the Kyoto protocol, hydrogen should be produced from renewable energy sources. [4] Indirect hydrogen production by electrolysis using electricity from renewable resources, such as sunlight, wind and hydropower, is also possible to incorporate the tag of pollution free hydrogen generation.

Hydrogen is a natural, though transient, by-product of several microbial driven biochemical reactions, mainly in anaerobic fermentation processes. In addition, certain microorganisms can produce enzymes that can produce H_2 from water if an outside energy source, like sunlight, is provided to them. Many microorganisms are able to produce hydrogen from mono-saccharides and disaccharides, starch and hemicellulose under anaerobic conditions. The anaerobic production of hydrogen is a common phenomenon, occurring during the process of anaerobic digestion.

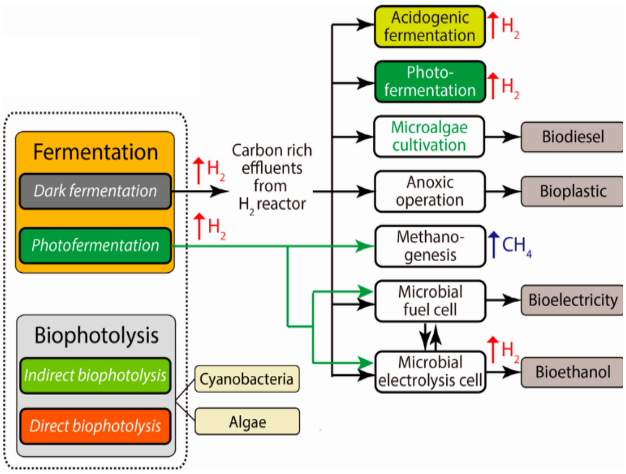

Fig 1 – Hydrogen Production Methods

Here, hydrogen producing microorganisms are in syntrophy with methanogenic bacteria which consume the hydrogen as soon as it is produced. In this way, hydrogen production remains obscure and methane is the end-product. By uncoupling H_2 production from methane production, H_2 becomes available for recovery and exploitation.

The selection of extreme thermophilic bacteria is due to its higher hydrogen production efficiency as compared to mesophilic bacteria, for the production of hydrogen from renewable resources. For this purpose the feedstock can range from crop wastes of high sugar content and waste streams of domestic organic waste, paper sludge and potato steam peels etc. Hydrogen production can be achieved by certain microbes like *Caldicellulosiruptor saccharolyticus*, *Thermotoga elfii* and *Thermotoga neapolitana* are observed in various research experiments. [5] Nutrient requirements and inhibitory effects differed depending on the strain and the feedstock applied. Specific ways in which microbes can produce H_2 are described below:

- Biophotolysis of water using green & blue-green algae (cyanobacteria)
  - Direct biophotolysis
  - Indirect bio-photolysis
- Photo-fermentation
- Dark fermentation
- Hybrid systems (Using dark fermentative and Photo-fermentative bioreactors)
- Bio-electrochemically assisted microbial bioreactors.

3. DIRECT BIOPHOTOLYSIS

A direct biophotolysis of H_2 production is a biological process which utilizes solar energy and photosynthetic systems of algae to convert water into chemical energy. [6]

$$2H_2O + \text{solar energy} \rightarrow 2H_2 + O_2$$

The two photosynthetic systems (PS) responsible for photosynthesis process are:

1. Photo-system I (PS I)
   This produces reductant for CO_2.
2. Photo-system II (PS II)
   This splits water to evolve O_2.

In the above process, two protons (H^+) are released. In the presence of 'Hydrogenase' enzyme, these two protons can produce one molecule of H_2. Hydrogenase enzyme is present in green algae and cyanobacteria, thus they possess the ability of generating hydrogen.[7]

$$H_2O \rightarrow PSII \rightarrow PSI \rightarrow Fd \rightarrow \text{Hydrogenase} \rightarrow H_2$$
$$\downarrow$$
$$O_2$$

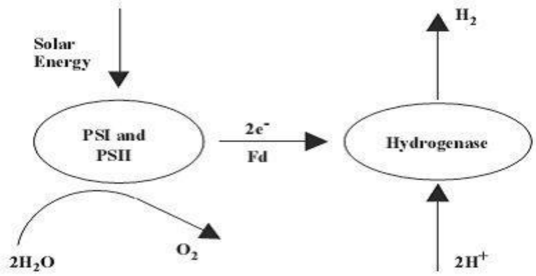

Fig 2- Direct Bio-photolysis

Since hydrogenase is sensitive to oxygen, it is necessary to maintain the oxygen content at a low level (under 0.1 %) so that the hydrogen production can be sustained. This condition can be obtained by the use of green algae, *Chlamydomonas reinhardtii*, which can deplete oxygen during the oxidative respiration. However, the reaction is very short-lived and the rate of the hydrogen production is very low, less than one-tenth than that of other photosynthetic reactions.[8]

4. INDIRECT BIO-PHOTOLYSIS

In indirect bio-photolysis, the problem of sensitivity of the H_2 evolving process to O_2 is usually circumvented by separating O_2 and H_2. In this process, CO_2 is intermittently fixed and released serving as the electron carrier between the O_2 producing (water splitting) reaction and the O_2 sensitive hydrogenase reactions. In such concepts the algae undergo a cycle of CO_2 fixation into storage carbohydrates (starch, glycogen) followed by its conversion to H_2 by dark anaerobic fermentation processes. In a typical indirect bio-photolysis H_2 is produced as follows: [9]

$$12H_2O + 6CO_2 \rightarrow C_6H_{12}O_6 + 6O_2$$
$$C_6H_{12}O_6 + 12H_2O \rightarrow 12H_2 + 6CO_2$$

4.1 Photo-fermentation

H_2 production by purple non-sulphur bacteria is mainly due to the presence of nitrogenase under oxygen-deficient conditions using light energy and reduced compounds (organic acids). The reaction is as follows:

$$C_6H_{12}O_6 + 12H_2O + \text{Light energy} \rightarrow 12H_2 + 6CO_2$$

The overall biochemical pathways for the photo-fermentation process can be expressed as follows:

$$(CH_2O)_2 \rightarrow (NADPH)\ \text{Ferredoxin} \rightarrow \text{Nitrogenase}$$
$$\uparrow ATP \qquad \downarrow$$
$$H_2$$

Many types of green algae and cyanobacteria, besides having the ability to fix CO_2 via photosynthesis, also have the ability to fix nitrogen from the atmosphere and produce enzymes that can catalyse the second H_2 generating step. Since these nitrogen fixing enzymes, nitrogenase, are localized within the heterocyst, they provide an O_2 free environment to carry out the H_2 evolution reactions. [10]

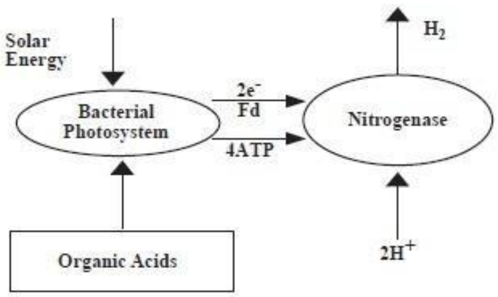

Fig 3- Photo-fermentation

The advantage of this method is in the versatile metabolic capabilities of these organisms and the lack of Photo-system II (PSII), which automatically eliminates the difficulties associated with O_2 inhibition of H_2 production. Major bottlenecks of the process involve low photochemical efficiencies (3-10 %). Moreover, inhomogeneity of the light distribution in the reactor also contributes to lowering of the overall light conversion efficiency. This may be overcome by using co-cultures having different light utilization characteristics. The improvement of a photo-bioreactor design with the increased light diffusing capability may also improve photo-conversion efficiency rates. By this process, H_2 yields may further be improved by maintaining a maximal activity of nitrogenase and a minimal activity of hydrogenase, a favorable molar ratio of the carbon source to nitrogen source and the availability of a uniform distribution of light through the culture.

4.2 Dark fermentation

Dark fermentation is a ubiquitous phenomenon under anoxic or anaerobic conditions. The oxidation of the substrate by bacteria generates electrons which need to be disposed off in order to maintain the electrical neutrality. Under the aerobic conditions O_2 serves as the electron acceptor while under the anaerobic or anoxic conditions other compounds, such as protons, act as the electron acceptor and are reduced to molecular H_2. Carbohydrates, mainly glucose, are the preferred carbon sources for this process, which predominantly give rise to acetic and butyric acids together with H_2 evolution. [11]

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

$$C_6H_{12}O_6 + 2H_2O \rightarrow CH_3CH_2COOH + 2CO_2 + 2H_2$$

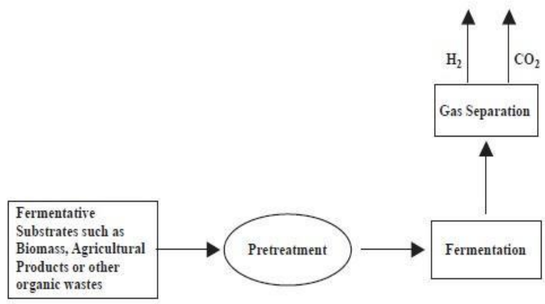

Fig 4- Dark Fermentation

In this process, glucose is initially converted to pyruvate by the glycolytic pathway.[13] Pyruvate is further oxidized to acetyl-CoA, which can be converted to acetyl phosphate and results in the generation of ATP and the excretion of acetate. This oxidation to acetyl-CoA requires a ferredoxin (Fd) reduction. Reduced Fd is oxidized by hydrogenase which regenerates Fd (ox) and releases electrons as molecular H_2. The overall reaction of the processes can be described as follows: [13]

$$\text{Pyruvate} + \text{CoA} + 2\text{Fd (ox)} \rightarrow \text{Acetyl-CoA} + 2\text{Fd (red)} + CO_2$$

$$2H^+ + \text{Fd (red)} \rightarrow H_2 + \text{Fd (ox)}$$

5. HYBRID FERMENTATION TECHNOLOGY

Hybrid fermentation technology might be one of the promising routes for the enhancement of H_2 production yields. The synergy of the process lies in the maximum conversion of the substrate which otherwise fails to achieve a complete conversion due to thermodynamic limitations. Thus, in this system the light independent bacteria and photosynthetic bacteria provide an integrated system for maximizing the H_2 yield. In such a system, the anaerobic fermentation of carbohydrate (or organic wastes) produces intermediates, such as low molecular weight organic acids, which are then converted into H_2 by the photosynthetic bacteria in the second step in a photo-bioreactor. The overall reactions of the process can be represented as [14]:

Dark fermentation *(facultative anaerobes)*

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

Photo-fermentation *(photosynthetic bacteria)*

$$2CH_3COOH + 4H_2O \rightarrow 8H_2 + 4CO_2$$

In a bio-electrochemically assisted microbial reactor (BEAMR), H_2 is evolved at the cathode using any biodegradable material, including glucose, acetate, proteins, starch and cellulose.[15]

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

Anode:

$$CH_3COOH + 2H_2O \rightarrow 2CO_2 + 8e^- + 8H+$$

Cathode:

$$8H+ + 8e^- \rightarrow 4H_2$$

Each of the processes defined above have their own advantages and disadvantages, however none of the technologies have achieved the level of perfection required for commercial purposes. On the other hand, the basic sciences on which bio-hydrogen technologies and process development must be based have greatly advanced over the past two decades, with an ever more intimate understanding of the genetics, biochemistry, and physiology of the microbial H_2 metabolism. This fundamental scientific information must now be applied to the development of H_2 production processes that could deliver bio-hydrogen at acceptable costs.

6. CONCLUSIONS

In this study we have seen that there are many processes are available that can be used to generate hydrogen by completely organic process based on microbial activities. The direct result of these methods the utilisation of organic wastes and water as raw material. Adaptation of these technique can ensure a completely renewable hydrogen generation. The alternate use of the process could be made in waste disposal methods, where the microbes can be used to work on organic waste to generate hydrogen.

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