#### **BIO-HYDROGEN PRODUCTION ROUTES**

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DEPARTMENT OF RENEWABLE ENERGY ENGINEERING CAET,GODHRA Biohydrogen is now being commercially produced as a "Biofuel". It is the advanced biofuel, which makes the use of living biomass or organisms for its production. Biohydrogen is now considered best among all the biofuels as it accounts to fulfil all the energy demands as it can obtain from the sustainable resources like:

Biological splitting of the water molecule

By the conversion of biomass

By the solar thermal splitting of water

- Biohydrogen is a type of biofuel like others i.e. bioethanol, biodiesel, bio-oil etc. Hydrogen can produce by both chemical and biological method. The method, by which the hydrogen is produced biologically by the use of microorganisms, in a bioreactor will refer as Biohydrogen. In simple words, we can say the biological conversion of hydrogen into biohydrogen via microorganisms is known as biohydrogen.
- Biohydrogen is a biofuel which is the source of energy that uses living microorganisms for the conversion of hydrogen into biohydrogen via the fermentation and photolysis process in a specialized container or a bioreactor.

### Milestones in the discovery of Biohydrogen

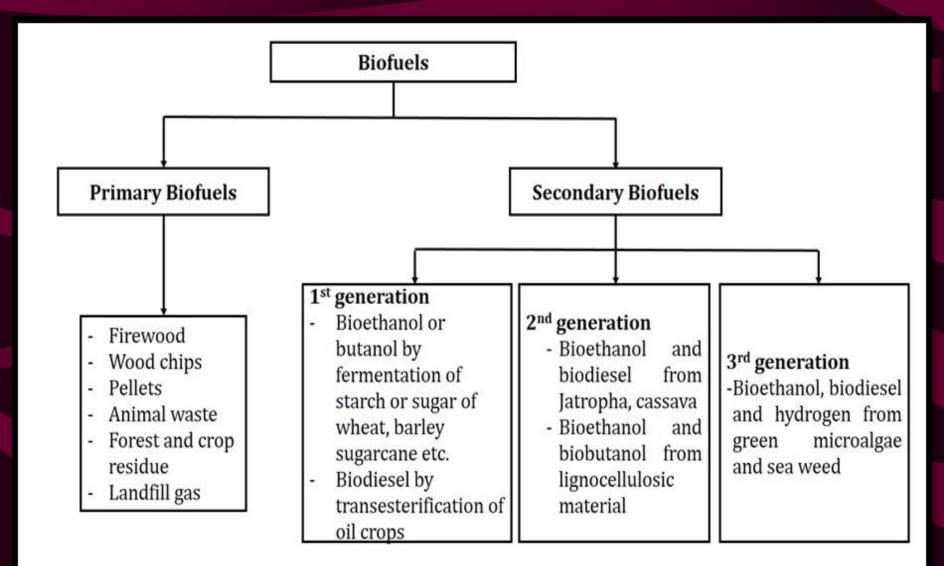
Year	Scientists	Discovery		
1939	Hans Gaffron	Discovered the switching of algae between		
		the production of H2 and O2		
1997	Ananstasios Malis	Discovered the cause of algae to switch from		
		producing H2 by the depletion of sulphur		
2006	Researchers from	Discovered large amount of hydrogen by		
	the University of	genetically modifying the single cell		
	Bielefeld	Chlamydomonas reinhardtiin		
2007	Ananstasios Malis	Discovered the conversion of solar energy to		
		chemical energy in tax X mutants of		
		Chlamydomonas reinhardtiin		

### **GENERATIONS OF BIOFUELS**

- Biofuels are referred to as solid, liquid or gaseous fuels derived from organic matter. They are generally divided into primary and secondary biofuels.
- 1. Primary biofuel: Primary biofuels such as fire wood, wood chips, pellets, animal waste, forest and crop residues, landfill gas etc are used in an unprocessed form primarily for heating, cooking or electricity production.
- 2. Secondary biofuel: Secondary biofuels such as bioethanol and biodiesel are produced by processing biomass and are able to be used in vehicles and various industrial processes. The secondary biofuels can be categorized into three generations: first, second and third generation biofuels on the basis of different parameters, such as the type of processing technology, type of feedstock or their level of development.

- **First generation biofuel:** The first generation production systems have considerable economic and environmental limitations. The most common concern related to the current first generation biofuels is that as production capacities increase, so does their competition with agriculture for arable land used for food production.
- Second generation biofuel: The advent of second generation biofuels is intended to produce fuels from lignocellulosic biomass, the woody part of plants that do not compete with food production. Sources include agricultural residues, forest harvesting residues or wood processing waste such as leaves, straw or wood chips as well as the non-edible components of corn or sugarcane.
- Third generation biofuel: Third generation biofuels derived from microalgae are considered to be a viable alternative energy resource that is devoid of the major drawbacks associated with first and second generation biofuels. Microalgae are able to produce 15–300 times more oil for biodiesel production than traditional crops on an area basis.

#### **WHAT ARE BIOFUELS?**



Among these three generations of biofuel, Biohydrogen comes in the category of third-generation biofuel or advanced biofuel. Third-generation biofuel has certain advantages over the first and second-generation biofuel.

The production of the first-generation biofuel has increased the price rates of the food items, whereas the third generation biofuels would not.

Second-generation biofuel required more surface area or land for the production of the biofuel, whereas advanced biofuel requires smaller areas for the production and are having the efficiency to capture solar energy 10 times to that of the second generation.

## Ideal properties of hydrogen as a Biofuel

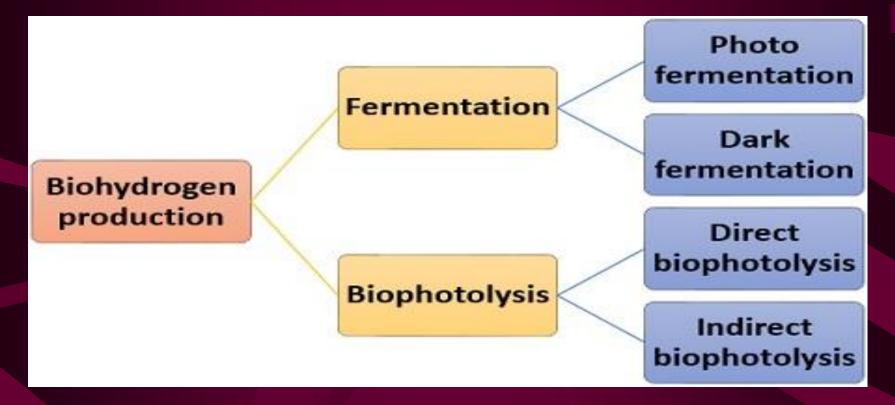
- Hydrogen has three times the high energy density than petrol and diesel.
- Hydrogen is highly combustible which can use as a fuel.
- Combustion of hydrogen only yields water which does not contribute to the gaseous pollutants.
- □ The efficiency of providing energy is more, with its little use.
- Acts as an energy carrier as hydrogen traps sunlight, wind, water as a renewable source.
- Hydrogen can be used as a transport fuel, by storing it as a "Metal hydride".
- □ It can be easily produced by the renewable source of energy like solar, wind, water etc.

## **Limitations of hydrogen as a Biofuel**

- Storage of hydrogen is difficult.
- There is a limitation of the cost of competitive technology for the production of biofuel.
- The utilization of hydrogen is quite difficult.
- Hydrogen can easily escape from the atmosphere to space.
- The presence of oxygen poisons the microbes, which produce hydrogen.

## **Production of Biohydrogen**

#### The production of biohydrogen is through two biological methods:



Through the fermentation process: It involves two methods namely photo fermentation and dark fermentation.
Through the photolysis: It also involves two methods namely direct photolysis and indirect photolysis.

### **Fermentation**

• Biohydrogen can produce by the process of fermentation. The fermentation of Biohydrogen is carried out by the use of microorganisms like bacteria. The process is either carried out in the presence of light i.e. photo fermentation or in the absence of light i.e. dark fermentation.

## **Photofermentation**

This process makes the use of photosynthetic organisms and the additional light source. The organisms used in the photo fermentation carry out the process of photosynthesis by the use of photosystem-I only for the production of hydrogen. For the splitting of water, these organisms not only requires an additional light source but also utilize organic acids like acetic acid to generate hydrogen, by donating its electron.

### $CH_3COOH + 2H_2O + Light \longrightarrow 4H_2 + CO_2$

In photofermentation, we can see in the equation, there is no evolution of oxygen, therefore it is a type of anoxygenic photosynthesis.

## **Dark fermentation**

- It is a process which makes the use of carbohydrate as an energy or carbon source. Dark fermentation does not require a source of light energy. Other than carbohydrate like glucose, it can also use other substrates like organic compounds, polymers (starch, cellulose etc.), algae biomass etc.
- Dark fermentation is a very complex process to carry out, which requires a series of biochemical reactions.

Breakdown of glucose into pyruvate and NADH: During this step, glucose converts into pyruvate by the phosphorylation of NAD into NADH.

 $C_6H_{12}O_6 + 2NAD^+ \longrightarrow 2CH_3COOH + 2NADH + 2H^+$ 

**Conversion of pyruvate to acetyl CoA**: The conversion of pyruvate into acetyl CoA can be catalysed by the use of two enzymes.

Catalysis by ferredoxin oxidoreductase

Pyruvate + CoA + 2Fd (ox.) Acetyl CoA + CO<sub>2</sub> + 2Fd (red.)

Catalysis by formate lyase

#### Pyruvate + CoA - Acetyl CoA + Formate

**Reoxidation of ferredoxin**: This step involves the reoxidation of ferredoxin by the Fe-fe hydrogenase enzyme.

 $\rightarrow$  H<sub>2</sub> + NAD<sup>+</sup>

### $2H^+ + Fd$ (red.) $\longrightarrow H_2^+ + Fd$ (ox.)

 $\frac{Production of hydrogen}{NADH + H^+}$ 

#### **Biophotolysis**

It makes the use of photoautotrophic organisms such as microalgae and cyanobacteria. These organisms use light as an energy source and carbon dioxide as a carbon source for the splitting of hydrogen.

$$4H_2O + Light energy \longrightarrow 2O_2 + 4H_2$$

Therefore in biophotolysis, the production of hydrogen is under anaerobic conditions.

## Direct photolysis

- It makes the use of solar light as a light source and photosynthetic algae to convert water into chemical energy or to produce hydrogen.
- Direct photolysis involves two steps for the generation of Biohydrogen:
- Absorption of sunlight by the photosystem-II of algae leads to the oxidation of water into electron, proton and oxygen molecules.

### $2H_2O \longrightarrow 4H^+ + 4e^- + O_2$

 Absorption of sunlight by the photosystem-I of algae leads to the transfer of an electron to the ferredoxin and to the hydrogenase enzyme through the electron transport chain. Recombination of proton and electron for the production of hydrogen gas.

$$4H^+ + 4e^- \longrightarrow 2H_2$$

• This process also refers as **One stage photolysis**, where hydrogen can be produced directly by the use of water, light energy and algae photosystem.

## Indirect photolysis

- This process makes the use of photosynthetic microorganisms like microalgae, cyanobacteria etc. Indirect photolysis also converts solar energy into the chemical energy by the series of two steps:
- In the first step, there is the production of biomass by the photosynthetic system. The second step involves the utilization of the biomass rich in carbohydrates to produce Biohydrogen.

 $6H_2O + 6CO_2 + Light \longrightarrow C_6H_{12}O_6 + 6O_2$ 

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

- Indirect photolysis involves the removal of both hydrogen and oxygen at different steps during the process just to avoid the sensitivity of the hydrogenase enzyme. It involves two stages to complete a reaction, so it refers as **Two-stage photolysis**.
- Cyanobacteria used in the process of indirect photolysis are Gloebacter sp., Synechocystic sp. Etc.

# Table showing different biological processes for the production ofBiohydrogen:

Biological processes for the production of hydrogen	Organisms used	Yield of hydrogen	End product
Photo fermentation	Phototrophic bacteria like purple sulfur and non-sulfur bacteria	0.16	$H_2$ and $CO_2$
Dark fermentation	Fermentative bacteria like Clostridium, Citrobacter and Enterobacter sp.	65-75	$H_2$ , $CO_2$ and VFA
Direct photolysis	Green algae	0.07	$H_2$ and $O_2$
Indirect photolysis	Cyanobacteria	0.36	$H_2$ and $O_2$

#### **Factors affecting Biohydrogen production**

There are several factors affect Biohydrogen production:

- □ **Temperature**: Thermophilic bacteria gives the maximum yield of hydrogen than the mesophilic bacteria. In simple words, the temperature is a factor which depends upon the type of microorganisms and substrate used for hydrogen production.
- □ pH: Hydrogen-producing microorganisms work well below the pH of 5.5-6.0.
- Hydraulic retention time: For, satisfactory hydrogen yields, the Hydraulic retention time should be in between 8-14 hours. Hydraulic retention time also influenced by several factors, like the composition of the substrate, type of substrate, type of microorganisms etc.
- □ The partial pressure of hydrogen: The partial pressure of the hydrogen should be low which can increase the yield of hydrogen production by 68%.

#### **Future prospects of Biohydrogen**

- Biohydrogen is considered to be a "Future fuel" because of its high energy density, zero-emission of carbon dioxide and other factors which we have discussed.
- In addition to this, several studies are also going on to improve the technology and the production of biohydrogen. There is a scope of development in each area, and our technology is improving day by day.
- Therefore, the use of oxygen-tolerant hydrogenase, increased production of hydrogen with the use of a minimal substrate, development of a cost-effective method for the commercial production of hydrogen etc. are the areas of improvement.

References: https://biologyreader.com/biohydrogen.html

