State of the art of biological hydrogen production processes

N. LOUBETTE, M. JUNKER
ALPHEA Pôle de Compétences sur l'Hydrogène, Parc d'Activités Forbach-Ouest, rue Jacques CALLOT, F-57600 FORBACH, France (www.alphea.com)
nicolas.loubette@alphea.com, Phone : +333.87.84.76.50.

Our study gives an overview of the state of the art of biological hydrogen production research and development activities.
Despite biological hydrogen production phenomena have been observed for more than one hundred years, related R&D is of growing interest since the 1970's. Attention was first paid to photosynthetic processes, while fermentation processes were relatively neglected. During the last twenty five years, a great number of publications dealing with biological hydrogen production were published, but only few progresses in practical applications were performed.
Different biological processes can be distinguished depending on the possible involvement of light as primary energy and depending on the implicated microorganisms (algae or bacteria). Four main biological hydrogen production processes are described:

1. water biophotolysis ;
2. decomposition of organic compounds by photosynthetic bacteria (photofermentation) ;
3. hydrogen production with the "water gas shift reaction " by bacteria;
4. dark fermentation of organic compounds by fermentative bacteria.

All biological hydrogen production processes are basically dependant on the presence of enzymes. Hydrogenases and nitrogenases are the known enzymes which catalyze biological hydrogen production.

Organisms that use light as energy source are called phototrophic. We can distinguish photoautotrophic and photoheterotrophic organisms, depending on the carbon source used.
The use of light is possible thanks to photosynthesis which is mainly based on two photosystems called photosystems I and II. Absorption of light energy by these photosystems results in the decomposition of water in protons and oxygen. Protons are catalytically reduced in hydrogen at enzyme active sites. Required electrons are transferred from the photosystems to the enzyme using a transporters chain. Today, photosynthetic production processes still need important R&D efforts in various fields (genetic engineering, improvement and cost reduction of reactor materials…). Both light conversion efficiencies and production yields are low.

Fermentation process does not need light to produce hydrogen. Raw materials such as carbon hydrates (sugar, cellulose, starch…) are best suited for hydrogen production in a fermentative way. These reactions can occur in a wide temperature range, depending on bacteria strains: 25-40°C, 40-65°C, 65-80°C or even more. Hydrogen production by fermentative bacteria is very dependent on experimental conditions. The fermentative hydrogen production paths are very sensitive to the hydrogen partial pressure. Judicious strains and substrates combination is of major concern for an optimized hydrogen production yield.

Comparing the actual performances of different hydrogen production processes, production of hydrogen by fermentation and water gas shift reaction with bacteria show the most interesting production rates. Respective production rates of 121 and 96 mmol H_2. $L^{-1}.h^{-1}$ can be reached. Photosynthetic processes show rates below 1 mmol H_2. $L^{-1}.h^{-1}$.
These experimental results have however to be confirmed in larger scale experimentations.

In order to improve the hydrogen yield per mole of substrate, some processes which integrate two stages are studied today.

As a conclusion, biological hydrogen production processes still need important R&D efforts. All are still at the lab scale. Only few pilot scale experimentations have been carried out.
“Dark fermentation” and “water gas shift” processes seem to have the better hydrogen production rates. Photosynthetic processes have to face several major issues: light energy conversion, oxygen sensibility of hydrogenases …
We can imagine that optimised biological hydrogen production processes could lead in the future to small or medium scale hydrogen production units.
The study of natural enzymes that catalyse the hydrogen production reaction could lead to bio mimetic catalyst that can have great potential for hydrogen production.