Bioresource Technology xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Review

Hydrogen production from algal biomass – Advances, challenges and prospects

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ARTICLE INFO

Keywords:
Algal biomass
Biohydrogen
Bioreactor
Hydrogen pathway
Fermentation

ABSTRACT

Extensive effort is being made to explore renewable energy in replacing fossil fuels. Biohydrogen is a promising future fuel because of its clean and high energy content. A challenging issue in establishing hydrogen economy is sustainability. Biohydrogen has the potential for renewable biofuel, and could replace current hydrogen production through fossil fuel thermo-chemical processes. A promising source of biohydrogen is conversion from algal biomass, which is abundant, clean and renewable. Unlike other well-developed biofuels such as bioethanol and biodiesel, production of hydrogen from algal biomass is still in the early stage of development. There are a variety of technologies for algal hydrogen production, and some laboratory- and pilot-scale systems have demonstrated a good potential for full-scale implementation. This work presents an elucidation on development in biohydrogen encompassing biological pathways, bioreactor designs and operation and techno-economic evaluation. Challenges and prospects of biohydrogen production are also outlined.

1. Introduction

Extensive global effort is being made to explore renewable energy sources that could replace fossil fuels in mitigating global warming and other environmental issues. Hydrogen is a promising alternative fuel to conventional fossil fuels, because it releases energy explosively without air pollutants in combustion. Currently most of the hydrogen is produced through thermo-chemical processes via electricity generation from non-renewable fossil fuels. A major issue of conventional hydrogen production is sustainability.

Hydrogen production via biological processes production is deemed a key development to a sustainable energy supply and a promising alternative to fossil fuels. Biohydrogen production is carried out largely at ambient temperatures and pressures, and hence is less energy intensive than chemical or electrochemical ones. As a desired green energy product of natural bioconversion, biohydrogen metabolism is primarily the domain of bacteria and microalgae. Within these microorganisms, it involves many taxonomically diverse species, a variety of enzymes and metabolic pathways and processes (Vignais et al., 2001). Biological processes use enzyme hydrogenase or nitrogenase as hydrogen producing protein. This enzyme regulates hydrogen-metabolism of prokaryotes and some eukaryotic organisms including green algae. The function of nitrogenase as well as hydrogenase is linked with the utilization of metabolic products of photosynthetic reactions that generate reductants from water.

Earlier development of algal hydrogen production was focusing on biophotolysis and photosynthesis-hydrogen production using various microbial species. Subsequent development in dark fermentation or heterotrophic fermentation led to production of hydrogen under anaerobic environment without the need of light energy. Work has been conducted in improving algal photosynthetic capacity using molecular engineering approach. Encouraging work indicated that genetic engineering might offer a feasible approach in developing oxygen-tolerant algal mutant. Multi-stage bioreactor systems have been tested to tap the energy stored in metabolites and products in order to maximize hydrogen yield and productivity rate. This paves the way to making compact energy generators for large-scale applications. This review examines the perspectives and state-of-the-art of algal hydrogen research in the context of pathways of hydrogen metabolism, bioreactor design and operation and techno-economic considerations. Prospects and Challenges in algal hydrogen production are also outlined.

2. Pathways of hydrogen metabolism

Biohydrogen can be generated by microorganisms such as microalgae and cyanobacteria (or called blue-green algae) through

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https://doi.org/10.1016/j.biortech.2018.02.105
Received 18 December 2017; Received in revised form 20 February 2018; Accepted 22 February 2018

biophotolysis, catabolism of endogenous substrate and dark fermentation by anaerobes. Biophotolysis occurs due to the effect of light on the microbial systems that results in dissociation of water into molecular hydrogen and oxygen. The light-dependent biophotolysis metabolic pathways can be differentiated into two distinct categories: direct-biophotolysis and indirect-biophotolysis. While electrons derived from water lead to photosynthetic hydrogen production in biophotolysis, electrons from catabolism of endogenous substrate result in hydrogen production in a distinct mechanism. Deriving energy from sunlight, green algae generate electrons for the photosynthetic systems through catabolism of endogenous substrate and the associated oxidative carbon metabolism in heterotrophic fermentation. On the other hand, dark fermentation by anaerobes as well as some microalgae, such as green algae on carbohydrate-rich substrates, can produce hydrogen via heterotrophic fermentation under anaerobic environment without the need of light energy.

2.1. Light-dependent pathways

2.1.1. Direct biophotolysis

Light-dependent direct biophotolysis occurs in two basic steps: splitting of water molecule in photosynthesis (Eq. (1) and hydrogen production catalyzed by hydrogenases (Eq. (2)) in green algae and cyanobacteria.

$$\text{Photosynthesis: } 2H_2O \rightarrow 4H^+ + 4e^- + O_2 \quad (1)$$

$$\text{Hydrogen Production: } 4H^+ + 4e^- \rightarrow 2H_2 \quad (2)$$

Direct biophotolysis involves water-oxidation and a light-dependent transfer of electrons to the [Fe]-hydrogenase, leading to the photosynthetic hydrogen production. Electrons are derived from water upon the photochemical oxidation by photosystem II (PSII or water-plastoquinone oxidoreductase) which is an enzyme located in the thylakoid membrane of algae and cyanobacteria. PSII uses photons from sunlight to energize electrons that are then transferred through the thylakoid membrane electron-transport chain and, via photosystem I (PSI or ferredoxin oxidoreductase) and ferredoxin (Fd), to the hydrocarbon cluster of [Fe]-hydrogenase (Florin et al., 2001). Plastoquinone is reduced to plastoquinol from the electrons transferred which are used to reduce $NADP^+$ to NADPH or are used in cyclic photophosphorylation. The energized electrons are replaced by oxidizing water to form hydrogen ions and molecular oxygen as shown in Fig. 1. By obtaining these electrons from water, PSII provides the electrons needed for the photosynthesis. The hydrogen ions (protons) generated by the oxidation of water help to create a proton gradient that is used by ATP synthase to generate ATP. Protons are the terminal acceptors of these photo-synthetically generated electrons in the algal chloroplast. The process results in simultaneous production of oxygen and hydrogen gases (Greenbaum et al., 1983).

Direct biophotolysis capitalizes on the photosynthetic capability of microalgae and cyanobacteria to split water directly into oxygen and hydrogen. Cyanobacteria, also known as blue-green algae, belong to a phylum of bacteria that obtain their energy through photosynthesis. Microalgae have evolved the ability to harness solar energy by extracting protons and electrons from water via water–splitting reactions. The biohydrogen production takes place via direct absorption of light and transfer of electrons to two groups of enzymes – hydrogenases and nitrogenases (Manis and Banerjee, 2008). Under anaerobic conditions or when too much energy is captured in the process some microorganisms vent the excess electrons by using a hydrogenase enzyme which converts the hydrogen ions to hydrogen gas (Turner et al., 2008). It has been reported that the protons and electrons extracted via the water-splitting process are recombined by a chloroplast hydrogenase to form molecular hydrogen gas with a purity of up to 98% (Hankamer et al., 2007).

The merit of direct biophotolysis is that the principal feed is water and the driver energy is derived from sunlight, both are readily available. While this technology has significant promise, it is also seeing tremendous challenges. A major challenge is the incompatibility in the simultaneous molecular hydrogen and oxygen production. In addition to producing hydrogen, the microorganisms also produce oxygen, which in turn suppresses hydrogen production (Kapdan and Kargi, 2006). Hence, photosynthetic hydrogen can only be produced transiently, as oxygen is a strong suppressor of hydrogenate reactions, and a powerful inhibitor of the [Fe]-hydrogenase. Research work has been carried out to engineer algae and bacteria so that the majority of the solar energy is diverted to hydrogen production, with bare energy diverted to carbohydrate production to solely maintain cells. Researchers are attempting to either, identify or engineer less oxygen sensitive microorganisms, isolate the hydrogen and oxygen cycles, or change the ratio of photosynthesis to respiration to prevent oxygen buildup (U.S. DOE, 2007). Addition of sulfate has been found to suppress oxygen production. However, the hydrogen production mechanisms are also inhibited (Turner et al., 2008). Methods to overcome the shortcomings of simultaneous production of oxygen and hydrogen will be further discussed in Section 5.1.

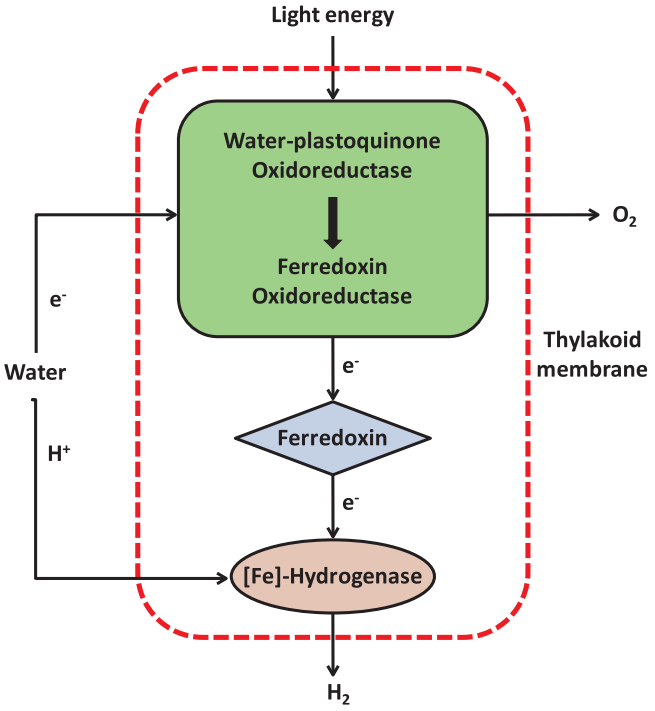

Fig. 1. Scheme of hydrogenase-mediated direct biophotolysis (adapted from Show and Lee (2013b)).

2.1.2. Indirect biophotolysis

Other than direct biophotolysis, photosynthetic hydrogen can be produced through the use of green algae that can produce hydrogen under the condition of sulfur deprivation (Manis and Banerjee, 2008). Deprivation of sulfur-nutrients in the growth medium causes a reversible inhibition in the activity of oxygenic photosynthesis in green algae. Protein biosynthesis is impeded in the absence of sulfur, and the green algae are unable to perform the required turnover of the D1/32-kD reaction center protein of PSII (known as the psbA chloroplast gene product) in the thylakoid membrane of algae (Melis et al., 2000). Under sulfur deprivation, the photochemical activity of PSII declines, and the absolute activity of photosynthesis becomes less than that of respiration. As a result, the rates of photosynthetic oxygen evolution drop below those of oxygen consumption by respiration. Such imbalance in the photosynthesis–respiration relationship by sulfur deprivation resulted in net consumption of oxygen by the cells causing anaerobic