Biotechnology Reports 15 (2017) 63–69

Contents lists available at ScienceDirect

Biotechnology Reports

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

Review

Hydrogen from algal biomass: A review of production process

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ARTICLE INFO

Keywords:
Hydrogen
Algae
Biofuels
Immobilization
Bioreactors

ABSTRACT

Multifariousness of biofuel sources has marked an edge to an imperative energy issue. Production of hydrogen from microalgae has been gathering much contemplation right away. But, mercantile production of microalgae biofuels considering bio-hydrogen is still not practicable because of low biomass concentration and costly down streaming processes. This review has taken up the hydrogen production by microalgae. Biofuels are the up and coming alternative to exhaustible, environmentally and unsafe fossil fuels. Algal biomass has been considered as an enticing raw material for biofuel production, these days photobioreactors and open-air systems are being used for hydrogen production from algal biomass. The formers allow the careful cultivation control whereas the latter ones are cheaper and simpler. A contemporary, encouraging optimization access has been included called algal cell immobilization on various matrixes which has resulted in marked increase in the productivity per volume of a reactor and addition of the hydrogen-production phase.

1. Introduction

Forthwith, the world is bearing the challenges of high energy demands as well as escalating fuel prices because of breakneck growth of world population and hasty industrialization. So there is a need of an hour to cope up with such challenges and for this researchers are now paying much appreciable attention by recommending sustainable and cost-effective methods for energy production [1,2]. Fossil fuels are associated with the environmental pollution and thus, more efforts have been evolved in renewable energy sources being economic and environmental friendly [2]. Governments are now proactive in addressing secured supply of raw materials with limiting climate change and many potential candidate fuels have been studied in the energy area, subsequently [3,4]. Biomass is one of the most encouraging renewable resources being used to bring about different types of biofuels, serving as biodiesel, bioethanol, biogas and biohydrogen. Energy from biomass would contribute to a stable energy supply and to local society due to an increase in commercial activities [5]. Biomass can be derived from cultivation of dedicated energy crops; by harvesting forestry and other plant residues; and from biomass wastes [6]. Hydrogen is extensively being seen as a clean fuel, environmentally safe, renewable energy resource and an excellent substitute of fossil fuels and a potential candidate with highest energy density with many of the technical, socio-economic and environmental benefits to its credence among all other known fuels (143 GJ per tonne) and is the only acknowledged fuel that does not produce carbon dioxide as a by-product when used in fuel cells for electricity generation [2,6]. The bulkiest users of hydrogen are the fertilizer and petroleum industries with approximately 50% and 37% respectively [6]. Hydrogen production has been determined only at the laboratory scale with yield still low for commercial application and so, the optimization of design and operating parameters for maximum hydrogen production is a must step while addressing the subject of hydrogen production rate. The optimization basically counts on the microalgae strain along with the available growth conditions [7]. For biofuels to be broadly authorized in the energy merchandise, spotlight must be on acclimatizing and improving photosynthetic organisms for biofuel production [8].

By the time mentioned, the sucrose and starch crops, for instance, sugarcane and corn as well as lignocellulosic materials like rice straw and switchgrass are being used as biofuel feedstock's. But, high cost in the hydrolysis of lignocellulosic materials is a matter of concern. Sugars come in several forms, containing approximately four calories per gram. Simple sugars like monosaccharides like glucose, fructose and galactose. Biohydrogen production offers a sustainable alternate and by utilizing renewable carbon sources can be considered as carbon dioxide offset. This can utilize various carbon sources including wastewater. Glucose, sucrose are readily degradable and hence preferred as model substrates for hydrogen production. Because of complex composition and polymeric structure complex carbon must released or converted to simple sugars. Complex polymer consists of tightly bound lignin, cellulose and hemicelluloses. Cellulose and hemicelluloses can be degraded under same conditions and add up the cost factor which is a matter of concern [2,9]. A lot of microorganisms are involved in the production of biofuels like hydrogen, but most accepted are

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http://dx.doi.org/10.1016/j.btre.2017.06.001
Received 15 February 2017; Received in revised form 20 May 2017; Accepted 1 June 2017
Available online 14 June 2017

cyanobacteria and green microalgae freshly considered as third generation feedstock's being more efficient at converting sunlight into the chemical energy and require a smaller footprint and less water for cultivation [7,10,11].

Diverse pretreatment methods and physic-chemical pretreatments have been revised for the hydrogen production. It is necessary step to breach the algal cell wall along with the complex carbohydrate to release simple sugars. Pretreatment methods such as physical (sonication, milling, grinding, pyrolysis), chemical (acid, alkali, thermal) and biological methods (enzymatic) is being employed to break algal cell wall, to hydrolyze the complex carbohydrates and to release fermentable sugars [9].

An immobilized cell means a cell by natural or artificial paths is being prevented independent movement from its neighbouring environment to all parts of the system which is under consideration [12]. Basically, there are six different types of cell immobilization methods. They are covalent coupling, affinity immobilization, adsorption, confinement in the liquid–liquid emulsion, capture behind semi-permeable membrane and entrapment. Utilization of immobilization technique contributes more resilience while designing a reactor comparing conventional suspension systems. Furthermore, increase in cell density, increase in cell wall permeability, no washout of cells and better system stability are certain additional merits of cell immobilization technique. Out of all, entrapment of cell within polymeric matrices and self adhesive attachment of cells onto surfaces of solid support are usually more common. Important criteria for successful entrapment are to set algal cells from within their partition, while pores inside gel matrix allow diffusion of substrates and metabolic products towards and from cells [13].

In these, bioreactors which are being considered for hydrogen production from algal biomass are matter of concern. Biohydrogen production by microorganisms has attracted our increasing worldwide attention, having its potential for inexhaustible, low-cost and a renewable source of energy. They are categorically pre-requisite for large scale hydrogen production by microorganisms. Certain microorganisms have been evolved for hydrogen production either from organic materials like sugar or biomass. Bioreactors are closed systems that have varied size from the small (5 mL–10 mL) to the larger scale or more than 500,000 L industrial scale. Photobioreactors are made up of an array of tubes, tanks bags, where photosynthetic microorganisms including algae are being cultivated and later monitored as light is the essential component for growing photosynthetic microorganisms. Bioreactors that have been mentioned later in this are photobioreactors, continuous stirred tank reactor (CSTR), fixed bed bioreactors, membrane bioreactors, multi-stage bioreactors and hybrid bioreactors [69].

2. Hydrogen production

2.1. Principle

Hydrogen makes up about three quarters of all matter and thus the most plentiful element of universe. Compelling hydrogen sources includes fossil fuels (95–99%) and water [14]. Dealing with future hydrogen demands independent of fossil fuels, it is necessary to appreciate all available renewable resources [15].

The classical methods for hydrogen production consists of steam reforming of natural gases, coal gasification and electrolysis of water are energy intensive processes that requires high temperatures (> 840 °C) and are not environmental friendly as such. Electrolysis of water being the cleanest technology for hydrogen production, can only used in sectors with cheap electricity as adds up to 80% of the operating cost [3]. Fig. 1 explains hydrogen production processes with examples.

2.2. Mechanism

With the noteworthy merits, the low production rates, low substrate conversion efficiencies are certain practical hindrances need to overcome for the successful hydrogen production.

2.2.1. Direct photolysis

There is a dissociation of water into hydrogen and oxygen in the presence of light, that is, $H_2O \rightarrow H_2 + ½O_2$ [16,17]. Green microalgae can use light to carry out photosynthesis as they possess chlorophyll a and the photosynthetic systems: Photosystem (PS) II and Photosystem (PS) I, respectively [18,19]. Disadvantages are the enzyme hydrogenase is very sensitive to oxygen so when a certain amount of oxygen is present, will inhibit hydrogenase activity and will stop it from producing hydrogen. Also, it requires high intensity of light. The advantages include tenfold more solar conversion in green microalgae.

2.2.2. Indirect photolysis

There is two step processes, firstly there is a splitting of water molecules in the presence of sunlight and protons and oxygen is formed. Secondly carbon dioxide fixation occurs storage carbohydrate is being produced, followed by the production of hydrogen gas by hydrogenase [20].

$$12H_2O + 6CO_2 + \text{light energy} \rightarrow C_6H_{12}O_6 + 6O_2$$

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

Blue-green algae (cyanobacteria) are promising microorganisms for this. Advantages are hydrogen evolution is separated from oxygen evolution. It can also produce relatively higher hydrogen yields. Furthermore, by-products can be efficiently converted to hydrogen. Disadvantages are like significant adenosine triphosphate (ATP) requirement of nitrogenase. Also, this requires continuous light source which is difficult for large scale processes [21–24].

2.2.3. Dark fermentation

Hydrogen production in a dark environment without the presence of sunlight, water and oxygen. Fermentative microorganisms hydrolyze complex organic polymers to monomers that are further converted to a mixture of lower molecular weight organic acids and alcohols by necessary hydrogen producing bacteria [24–26]. Advantages consist of use of a variety of carbon sources and production of hydrogen without light. It produces valuable by-products like butyric acid, lactic acid and acetic acid etc. Disadvantages are relatively lower hydrogen yields. Also the product gas mixture contains carbon dioxide which has to be separated [3]. Fig. 2 explains different types of microorganisms capable of dark fermentation with examples.

2.2.4. Photo-fermentation

It is a fermentative conversion of organic substrates into hydrogen and carbon dioxide by use of sunlight as an energy source.

$$CH_3COOH + 2H_2O + \text{light} \rightarrow 4H_2 + 2CO_2$$

Using light as the energy source, the organic acid substrates are oxidized using the tricarboxylic acid cycle (TCA), producing electrons, protons and carbon dioxide. Example includes purple non sulfur bacteria (PNS) [11,17]. Advantages in removal of environmental pollutants, use of industrial waste and use of organic acids produced from dark fermentation. Disadvantages are need to nitrogen limit condition and pretreatment of industrial effluent as it may be toxic [23].

3. Hydrogen production from algal biomass

The renewable energy sources play crucial role in decreasing the greenhouse effect but also provides an alternative approach regarding increasing global energy demands resulting into depletion of energy reserves [27]. Many algal species show potential to produce hydrogen under certain conditions [28]. Nonetheless, certain technical barriers