ARTICLE IN PRESS

INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2016) 1–8

Available online at www.sciencedirect.com

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

A compact tubular photobioreactor for outdoor hydrogen production from molasses

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ARTICLE INFO

Article history:
Received 2 May 2016
Received in revised form
28 July 2016
Accepted 3 August 2016
Available online xxx

Keywords:
Photofermentation
Molasses
Rhodobacter capsulatus
Biohydrogen
Photobioreactor
Stacked U-tube reactor

ABSTRACT

Hydrogen can be produced sustainably by photofermentation of biomass. For an economically feasible operation, the process should be implemented outdoors using low-cost organic material. In the current study, molasses from a sugar factory was utilized for photofermentative hydrogen production. The experiment was run with *Rhodobacter capsulatus* YO3 (hup^-) in fed-batch mode under outdoor conditions in Ankara between July 12, 2015 and July 24, 2015. The stacked U-tube photobioreactor (9 L) designed for outdoor photobiological hydrogen production by our group was used. The design consists of 4 stacked U-tubes and 2 vertical manifolds. During the operation, the sucrose concentration in the reactor was adjusted to 5 mM daily by diluting the molasses. Maintaining pH at the desired level (around 7.0) was the main challenge of the operation. The pH value was eventually stabilized at 5.9 and hydrogen production was sustained for 8 days with continuous feeding of molasses. The maximum productivity was found as 0.31 mol H_2/(m^3 h). In this study, a long term photobiological hydrogen production from molasses under outdoor conditions was demonstrated for the first time.

Introduction

The escalating global energy demand cannot be met by fossil fuels alone in the long-term, due to the depletion of these finite resources and the associated adverse environmental effects resulting from their use. With its carbon-free combustion products and high energy content, hydrogen is a promising alternative. In order to be sustainable, hydrogen has to be produced from renewable energy sources. Biological hydrogen production methods have the potential to produce hydrogen with an economically feasible operation from renewable energy sources [1]. The advantages of photofermentation can be listed as high theoretical yield, lack of O_2 evolution, which inhibits enzymes responsible for H_2 production, the ability to utilize various organic substrates including wastewaters and the ability to capture a wide range of the solar spectrum (from 300 to 1000 nm) [2,3].

Purple non sulfur bacteria (PNSB), which are the members of the *Rhodobacter* species, are the most commonly used microorganisms in photofermentation [4]. There is an optimum biomass concentration (0.5–0.7 gdcw/L_c) for hydrogen production, whereas the optimum temperature range is 30 to 35 °C. Buffering solutions are employed to keep pH within the range of 6.5–9 [5]. There have been different approaches on the modification of the microorganism so that higher hydrogen productivities could be obtained. Hydrogen production has been improved by deletion of the gene encoding for the uptake hydrogenases (hup^-), which is responsible for hydrogen consumption [6].

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http://dx.doi.org/10.1016/j.ijhydene.2016.08.014

Please cite this article in press as: Kayahan E, et al., A compact tubular photobioreactor for outdoor hydrogen production from molasses, International Journal of Hydrogen Energy (2016), http://dx.doi.org/10.1016/j.ijhydene.2016.08.014

PNSB can produce hydrogen from a wide variety of organic substrates such as short chain organic acids (acetate, butyrate, propionate and lactate), and sugars (glucose and sucrose). The initial organic acid and sugar concentrations affect the hydrogen productivity and the biomass growth rate. Real feedstocks that are used in the photofermentation are generally dark fermenter effluents (DFE) of different wastes obtained from pulp and paper industry, sugar processing industry, cheese manufacturing and olive mill factories [4]. Single stage photofermentation of sugar industry wastes and by-products have also been studied. Productivity was found as 0.41 mol $H_2/(m^3$ h) utilizing *Rhodobacter capsulatus* YO3 on 5 mM sucrose-containing molasses [7]. In another study, hydrogen production was improved with single stage photofermentation of molasses compared to molasses DFE. Sugar concentrations of 1, 2, 5, 10, 15 and 20 g/L were studied, with beet molasses containing 51% sucrose and black strap molasses containing a total of 32% sucrose, 14% glucose and 16% fructose. The highest productivity from 2 g/L sugar-containing black strap and 20 g/L sugar-containing beet molasses was found as 1.57 and 2.82 mol $H_2/(m^3$ h). However, pH started to decrease rapidly after20 h and reached values as low as 4.5–5.0 for beet molasses and 4.5–5.5 for black strap molasses after 120 h. In general, pH decrease was much higher in higher concentrations. Though a high hydrogen productivity was observed for 20 g/L sugar-containing molasses [8], high sugar content is hard to maintain in large scale without a proper pH control.

The nitrogenase enzyme, which is responsible for hydrogen production, contains Fe and Mo. In one study, Fe and Mo addition was found to improve the hydrogen productivity. The productivity of the control experiment which was performed with 2% olive mill wastewater was 0.09 mol $H_2/(m^3$ h), whereas this value increased to 0.18 mol $H_2/(m^3$ h) upon Mo addition. Fe addition improved the productivity to 0.29 mol $H_2/(m^3$ h) [9].

The ultimate goal of photofermentation is to operate such systems under outdoor conditions and natural sunlight. However, because of the fluctuating temperature and light conditions, the operation becomes complicated and an optimized reactor design becomes crucial. An ideal photobioreactor should have a good light and flow distribution, low gas permeability, high surface to volume ratio and a high illuminated surface area to occupied ground area ratio. The reactor material should be transparent to the useful wavelength region of the solar spectrum, and have a low gas permeability to avoid loss of hydrogen. In one study with Roux bottles, hydrogen produced was observed mainly at depths smaller than 1.5 cm [10]. Therefore, a 3 cm diameter seems appropriate for outdoor operation. Glass has been found as the least permeable material for hydrogen and air compared to other transparent materials such as polyurethane, PVC and LDPE [11]. Besides, glass is more durable compared to materials such as LDPE tubes, which had to be replaced annually due to structural failure and overall wear [12].

Commonly, two reactor types have been preferred for outdoor hydrogen production: panel [13] and tubular [14]. Panel type photobioreactors have the advantage of a high illuminated surface area to the occupied ground area ratio; 8:1, compared to 1:1 for tubular reactors [15]. On the other hand, scale-up and mixing in panel reactors is difficult to achieve due to mechanical limitations of the design and tubular reactors are therefore preferred for pilot to large scale applications.

Up to now, dark fermenter effluents of various industrial wastes and other complex feedstocks have been utilized in photofermentation [16]. Most of the pilot scale photobioreactors were operated with dark fermenter effluents in outdoor conditions. In a previous study, a panel type photobioreactor was operated under outdoor conditions with molasses dark fermenter effluents. The highest productivity was found as 0.67 and 0.50 mol $H_2/(m^3$ h) when *R. capsulatus* YO3 and *R. capsulatus* wild type strains were utilized, respectively [13]. A horizontal tubular type reactor was operated under outdoor conditions with thick juice dark fermenter effluents. The highest productivity was found as 0.27 mol $H_2/(m^3$ h) [14]. When *R. capsulatus* YO3 on molasses DFE was utilized in a plastic horizontal tubular pilot scale reactor (90 L) in outdoors (August, 2010), the average and the maximum productivities were found as 0.05 and 0.12 mol $H_2/(m^3$ h), respectively [17]. In another study, a horizontal tubular type photobioreactor was operated with malate and the maximum productivity of 1.21 mol $H_2/(m^3$ h) was observed [18]. The main problem with horizontal, tubular manifold type photobioreactors are high ground area requirement and non-uniform flow distribution.

In our previous study, a stacked U-tube photobioreactor was designed, built and tested for hydrogen production. The design contains 2 vertical glass manifolds and 4 glass U-tubes connected to the manifolds. With this design, the illuminated surface area to the occupied ground area ratio was increased to 5:1. Besides, a good light and velocity distribution were obtained. The details of the design can be found elsewhere [19].

The aim of this work was to operate a pilot scale stacked U-tube photobioreactor under outdoor conditions using molasses as the feedstock. In our previous study [19], a proper feeding strategy was suggested for the utilization of molasses in outdoor conditions. In the present study, the proposed feeding strategy was applied for the first time and continuous hydrogen production was observed. To the best of our knowledge, this is the first outdoor study which utilized molasses as the feedstock for long term biological hydrogen production in fed-batch mode.

Materials and methods

Pilot-scale stacked U-tube photobioreactor

The stacked U-tube photobioreactor (9 L) was designed by our group and the glass pieces were custom-built. The tube diameter was 3 cm, the manifold diameter was 6 cm and the length of the tubes was 4 m. The heights of the distribution and collection manifolds were 0.595 m and 0.515 m, respectively. The produced gas was collected by water displacement. The reactor was cooled by means of spiral coils within the manifolds. The reactor contents were held below 40 °C by a temperature controller, which manipulated the circulation rate of the coolant water, the temperature of which was between 5 and 10 °C. The reactor temperature was monitored by the two