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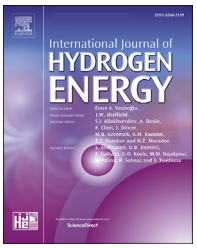

Continuous production of biohydrogen from oil palm empty fruit bunch hydrolysate in tubular photobioreactors

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ABSTRACT

Production of hydrogen by the photosynthetic bacterium *Rhodobacter sphaeroides* was compared in continuously operated tubular photobioreactors illuminated by natural outdoor sunlight (0.15–66 klux; diurnal cycle) and constant indoor artificial light (10 klux; tungsten lamps). In both cases the operating temperature was 35 °C and the organic carbon source was an acid hydrolysate of oil palm empty fruit bunch (EFB), an agroindustrial waste. In the outdoor photobioreactor, under the best production conditions, the daytime feeding rate of the mixed carbon substrate was 48 mL h^{-1} and the average pseudo-steady state hydrogen production rate was 36 mL H_2 L^{-1} medium h^{-1}. The cumulative hydrogen production was 430 mL H_2 L^{-1} medium. For the indoor photobioreactor fed at the same rate as the outdoor system, the steady state average hydrogen production rate was 43 mL H_2 L^{-1} h^{-1} and the cumulative hydrogen production was 517 mL H_2 L^{-1} medium. Reducing the feed rate to less than 48 mL h^{-1}, enhanced the biomass concentration, but reduced hydrogen production in both bioreactors. The sunlight-based cumulative hydrogen production was only about 17% less compared to the artificially lit system, but required only 22% of the electrical energy.

Introduction

Hydrogen is a potential nonpolluting fuel as it burns cleanly to produce only water. On a mass basis, combustion of hydrogen has an energy yield of 122 kJ g^{-1}, around 2.75-fold higher than the energy content of fossil fuels [1,2]. In 2016, the global hydrogen production exceeded 63 million metric tons [3]. Of this, nearly 96% was obtained by steam reforming [4,5] of fossil fuels and the remaining 4% was sourced through electrolysis. In principle, hydrogen can be produced renewably through microbial action on organic waste such as lignocellulosic agroindustrial waste. Microbial methods of producing hydrogen from organic waste include dark fermentation [6–10] and photofermentation [11–14]. Photofermentations of food waste [12] and certain crop residues [13] to hydrogen have been reviewed. Integrated production relying on sequential dark fermentation and photofermentation is also potentially feasible [15]. Here the focus is on photofermentation [16].

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In a photofermentation, photosynthetic bacteria use sunlight (or artificial light) and organic matter to produce a mixture of hydrogen and carbon dioxide under ambient operating conditions [17]. Purple nonsulfur anaerobic bacteria such as *Rhodobacter sphaeroides* carry out a nonoxygenic photosynthesis to generate hydrogen from protons (H^+). This process is powered by the energy-rich adenosine triphosphate (ATP) [17,18] generated via photosynthesis. The electrons and protons needed for hydrogen production are derived from organic matter [19]. The hydrogen production reaction follows the following stoichiometry:

$$2H^+ + 2e^- + 4ATP \rightarrow 4ADP + H_2 \quad (1)$$

Biomass production or growth competes with hydrogen production. As a consequence, the hydrogen yield during growth does not usually exceed 25% of theoretical value. In the absence of growth, hydrogen yield may approach nearly 90% of theoretical [20]. Growth of bacteria such as *R. sphaeroides* requires fixed nitrogen, generally provided in the form of ammonium salts although too much ammonium in the culture medium inhibits the production of hydrogen [21].

Although hydrogen production by photofermentation using artificial light and various organic carbon substrates has been extensively reported [22–30], it is impractical in view of the expense of artificial lighting and the overall poor energetics of the process. In contrast, a photofermentation relying on freely available sunlight and waste organics, is more likely to be viable. In an outdoor culture, seasonal variations in light level affect hydrogen production with higher light levels improving production [31].

In certain tropical regions sunlight is plentiful throughout the calendar year and cheap carbon substrates in the form of agroindustry waste are abundant. For example, large amounts of oil palm empty fruit bunch (EFB) fiber is available in palm oil producing regions [32]. Production of palm oil globally generates nearly 40 million tons of waste EFB fiber. EFB, a lignocellulosic material, is readily hydrolyzed to simple organic substrates suitable for photofermentation [30], offering an inexpensive raw material for sustainable production of hydrogen. Photofermentative hydrogen production from EFB hydrolysates has been demonstrated using both batch [27] and repeated batch operations [21]. Continuous production of hydrogen using pure carbon sources (succinic acid, malic acid and glucose) has been reported [33–36], but the use of pure carbon sources is impractical in view of their high cost.

This study reports on production of hydrogen using continuous cultures in tubular loop photobioreactors. In view of their high surface area to volume ratio, tubular photobioreactors are superior to other types of culture systems [29]. Sunlight driven outdoor production is compared with indoor production based on artificial light in otherwise identical photobioreactors. In both cases, EFB hydrolysate is used as a cheap carbon substrate. In addition to being energetically attractive and potentially affordable, the integration of sunlight and a low-cost waste carbon source offers opportunities for reducing the adverse environmental impact of EFB. Earlier work on hydrogen production by photofermentation of EFB hydrolysates focussed only on artificially illuminated indoor cultures [21,27,29,30].

Materials and methods

The EFB raw material and preparation of the medium

Mechanically crushed EFB fibers were provided by Southern Palm Co., Ltd (1978), Surat-Thani province, Thailand. On receipt the EFB fibers had a moisture content of 22% by weight. The as received EFB fibers (5 kg) were washed twice with tap water (~10 L per wash) and then dried to a moisture content of around 13% by weight in an oven (model UM-500; Memmert, Germany) at 105 °C. The dried EFB fibers were ground and sieved (number 10 sieve, 2.0 mm aperture, ASTM E11, the International ISO 565 scale) as previously described [32]. This ground material was further dried to a constant weight in an oven at 105 °C and stored at room temperature (35 ± 3 °C) until used. The particle size of the dried fibers was <2 mm.

The ground EFB fibers were subjected to an acid-thermal hydrolysis treatment [27]. Briefly, the ground EFB fibers (80 g) were mixed with 640 mL of 6% H_2SO_4 (6 mL concentrated sulfuric acid made up to 100 mL with distilled water) and autoclaved (120 °C) for 15 min. The slurry was cooled to room temperature and suction filtered (Whatman no. 1 filter paper, 11 μm pore nominal size). The clear filtrate contained 10.4 mM glucose, 129.6 mM xylose, 96.5 mM acetic acid, 7.08 mM furfural and 0.48 mM hydroxymethylfurfural (HMF). As EFB is a natural material, its composition can vary depending on many factors including the maturity status of the fresh fruit bunches used to recover the EFB; the geographic region where the source plant was grown; and the season of collection of the fruit [32]. In the present study, the impact of such factors was excluded by using a single batch of EFB throughout.

The Modified Ormerod 3 (MO3) culture medium was used in all hydrogen production experiments. The carbon source used in this medium was the EFB hydrolysate, as prepared above. The 1-fold concentrated MO3 medium was prepared by mixing three different stock solutions (Stocks 1–3). The Stock solution 1 consisted of 77 mL EFB hydrolysate, 0.76 g glucose, 1.29 g xylose, 735.6 mg L-glutamic acid, 0.6 g KH_2PO_4, and 0.9 g K_2HPO_4 dissolved in 800 mL distilled water. (Glucose and xylose were added to the medium to obtain an optimal glucose-to-xylose mole ratio of 5:18 [30].) Stock solution 2 consisted of 0.3 g yeast extract, 2.46 g $MgSO_4 \cdot 7H_2O$, 0.075 g $CaCl_2 \cdot 2H_2O$, 1.45 mg $Na_2MoO_4 \cdot 2H_2O$ and 100 mL distilled water. Stock solution 3 contained 0.011 g $FeSO_4 \cdot 7H_2O$, 0.02 g EDTA and 100 mL distilled water. All stock solutions had been adjusted to pH 7.0 prior to separate sterilization (121 °C, 15 min) [30]. The 3-fold concentrated medium contained all the MO3 components at 3-fold the concentration compared to the 1-fold concentrated medium specified above. The measured concentrations of the carbon sources in the 3-fold concentrated feed medium were as follows: 15.63 ± 0.12 mM glucose, 37.65 ± 0.16 mM xylose and 36.57 ± 0.63 mM acetic acid. These values were somewhat different to the concentrations actually added to Stock solution 1 because sterilization degraded some of the components.

The glutamic acid-malic acid (GM) medium used for maintaining the bacterium and preparation of the starter culture was formulated as previously described [30]. GM agar contained the GM medium and 15 g Bacto-agar L^{-1}.

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