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Analysis of the cyanobacterial hydrogen photoproduction process via model identification and process simulation

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HIGHLIGHTS

- Dynamic simulation models for cyanobacterial hydrogen production process.
- Parameter estimation via dynamic optimisation.
- Proposed modified models exhibit higher accuracy for real process simulation.
- Interpretation of higher performance of CSTR over PFR for this process.
- Fed-batch processes are proposed as the optimal reactor operation.

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ABSTRACT

Cyanothece sp. ATCC 51142 is considered a microorganism with the potential to generate sustainable hydrogen in the future. However, few kinetic models are capable of simulating different phases of *Cyanothece* sp. ATCC 51142 from growth to hydrogen production. In the present study four models are constructed to simulate *Cyanothece* sp. batch photoproduction process. A dynamic optimisation method is used to determine parameters in the models. It is found that although the piecewise models fit experimental data better, large deviation can be induced when they are used to simulate a process whose operating conditions are different from the current experiments. The modified models are eventually selected in the present study to simulate a two-stage continuous photoproduction process. The current simulation results show that a plug flow reactor (PFR) shows worse performance compared to a continuous stirred-tank reactor (CSTR) in the current operating conditions since it lowers the total hydrogen production. The finding is that nitrate and oxygen concentration change along the direction of culture movement in PFR, and hydrogen is only generated in the zone where both of them are low. The reactor area thereby is not well utilised. Additionally, as hydrogen production rate is primarily influenced by biomass concentration, which increases initially and decreases eventually along the direction of culture movement, the overall hydrogen production rate in a PFR may be lower than that in a CSTR. Finally, in this study fed-batch photoproduction processes are proposed containing only one photo-bioreactor based on the current simulation.

1. Introduction

1.1. Introduction of biohydrogen production from different microorganisms

Molecular hydrogen (H_2) is considered as one of the fuels of the future with greatest potential and environmental friendliness. At present, the conventional industrial hydrogen production process almost totally relies upon the utilisation of carbon-based resources which are limited and not renewable (Cooke et al., 2011). In order to fulfill the world's long-term energy needs, it is essential to find low cost, sustainable and environmentally friendly resources for future hydrogen production. Recently biohydrogen, the hydrogen produced by microorganism biosynthesis, has been extensively investigated due to its outstanding advantages. For example, the energy source of biohydrogen is solar energy, which is always plentiful and has a low investment cost (Catalanotti et al., 2013). Although biohydrogen can be generated by different microorganisms, two groups, photosynthetic green algae and nitrogen-fixing cyanobacteria, are particularly of interest, since they can photosynthetically

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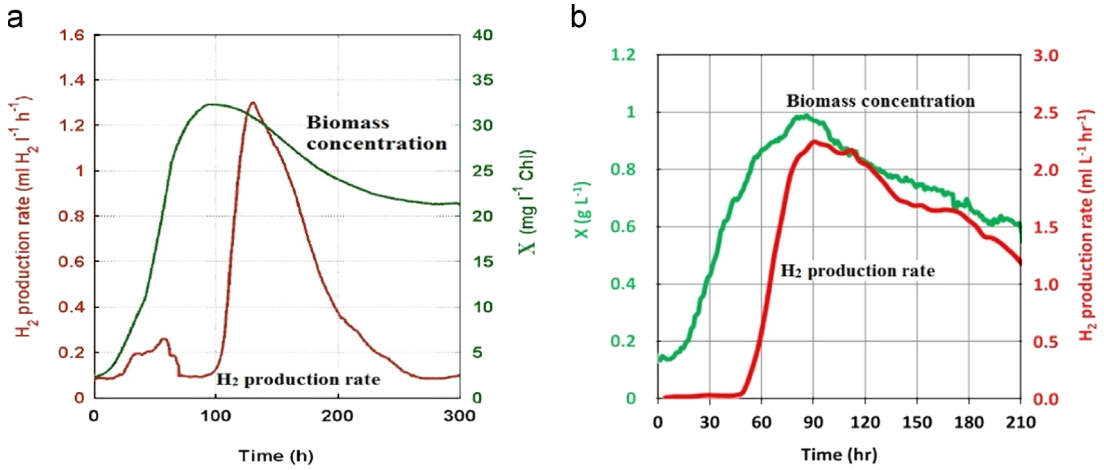

Fig. 1. Comparison of green algal and cyanobacteria hydrogen production rate. (a) Hydrogen production rate and biomass concentration during the time course of photoproduction reported by Tamburic et al. (2012) in green algae. (b) Hydrogen production rate and biomass concentration during the time course of photoproduction reported by Dechatiwongse et al. (2015) in cyanobacteria.

derive H_2 from sunlight (Catalanotti et al., 2013; Min and Sherman, 2010).

Chlamydomonas reinhardtii, an outstanding representative of green algae, has been extensively explored. Previous research demonstrated that in *C. reinhardtii* hydrogen is generated by hydrogenase (Melis et al., 2000). Electrons for hydrogen reduction are originally provided by water through photosynthesis with the generation of oxygen. As the activity of hydrogenase is completely inhibited by oxygen, *C. reinhardtii* can only produce hydrogen in anaerobic conditions (Antal et al., 2011). Different methods have been used to remove oxygen in algal culture, while the generally accepted method in recent research is to cultivate *C. reinhardtii* in a sulphur-free culture (Melis et al., 2000). As algal photosynthetic activity is significantly inhibited without the replenishment of sulphur, oxygen production rate is significantly reduced and even drops lower than algal respiration rate. Hence, oxygen produced by oxygenic photosynthesis is totally consumed by algae respiration and anaerobic conditions are achieved.

In addition to hydrogenase, Bandyopadhyay et al. (2010) finds that cyanobacteria also process nitrogenase for hydrogen production. *Cyanothece* sp. ATCC 51142 is mainly selected as the typical cyanobacteria in the current research because its remarkably high rate of H_2 production has never been observed before in any other hydrogen-producing strains. In spite of having two distinct biological enzymes, previous research has demonstrated that the hydrogen generation rate catalysed by nitrogenase is much higher (Min and Sherman, 2010). In cyanobacteria, hydrogen reduction by nitrogenase is directed by the nitrogen-fixing metabolic pathway instead of photosynthesis, and electrons for hydrogen production are usually provided by the carbohydrate reserved during photosynthesis, or by an additional carbon source such as glycerol (Tripp et al., 2010; Bandyopadhyay et al., 2010). As cyanobacterial nitrogenase activity is inhibited by oxygen and nitrogen source such as nitrate, hydrogen is usually generated in oxygen and nitrogen deprived cultures. Once the activity of nitrogenase is stimulated, hydrogen reduction by nitrogenase can last for a long period even in the absence of nitrogen gas (Kufryk, 2013; Min and Sherman, 2010).

Compared to green algae, cyanobacteria are given more attention in current research because of their distinctive advantages. For example, the profile of cells growth and hydrogen production of both green algae and cyanobacteria are presented in Fig. 1. It is found that because of the dramatic damage of photosynthesis activity in green algae, the decreasing tendency of hydrogen production and cell growth rates in *C. reinhardtii* is much sharper than that in *Cyanothece* sp. ATCC 51142 (Dechatiwongse et al., 2015; Tamburic et al., 2012, 2013). Furthermore, hydrogen production in cyanobacteria is much higher than that in green algae. For example Dechatiwongse et al. (2015) compared the capacity of different microorganisms on hydrogen production, and it is found that the maximum hydrogen productivity of *C. reinhardtii* is only 6.4 μmol mg Chl^{-1} h^{-1}, which is much less than 225 μmol mg Chl^{-1} h^{-1} of *Cyanothece* sp. ATCC 51142. Apart from the higher H_2 production rate cyanobacteria can also utilise nitrogen gas as the nitrogen source, which offers the benefit in terms of significant reduction in nutrient cost. As a result, cyanobacteria are more suitable for industrial biohydrogen production processes.

Extensive research has been conducted to improve the performance of cyanobacteria hydrogen production. For instance, effects of different nutrients and illumination duration on cyanobacterial growth rate and hydrogen productivity have been widely explored (Min and Sherman, 2010; Bandyopadhyay et al., 2010). However, problems such as the influence of light intensity and light wavelength, optimal ratio of nitrogen source to biomass concentration and photobioreactor configuration are still unsolved and restrict the application of hydrogen production by cyanobacteria.

One way to understand the source of these problems is to construct an accurate kinetic model for cyanobacteria photoproduction process simulation and optimisation. Although various kinetic models have been developed such as the Monod model and the logistic model (Xie et al., 2012; Bezerra et al., 2008; Dechatiwongse et al., 2014), most of them are unable to simulate the entire growth phase of cyanobacteria. For example, the Monod model cannot be used to simulate the decay phase of green algae and cyanobacteria where hydrogen is mainly generated (Antal et al., 2011; Melis et al., 2000). The logistic model assumes that bacterial growth is only a function of bacterial biomass concentration, which makes it impossible to explore the influence of limiting nutrients on bacterial growth (Bezerra et al., 2008).

This study aims to construct an accurate kinetic model capable of simulating different cyanobacterial growth phases for hydrogen production. Based on the kinetic model the current research studies the capacity of different cyanobacterial photoproduction processes, including batch operation, fed-batch operation and continuous operation. In order to maximise hydrogen production in different modes of photobioreactor operation, future work will also optimise the operating conditions of each photoproduction process and the configuration of the photobioreactor.

1.2. Growth phases of cyanobacteria

As green algae and cyanobacteria can only generate a significant amount of hydrogen in sulphur or nitrogen deprived cultures,