ARTICLE IN PRESS

INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2018) 1–13

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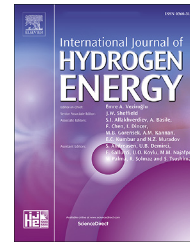

# Effect of hydraulic retention time on a continuous biohydrogen production in a packed bed biofilm reactor with recirculation flow of the liquid phase

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ARTICLE INFO

Article history:
Received 26 May 2018
Received in revised form
22 July 2018
Accepted 13 August 2018
Available online xxx

Keywords:
Dark fermentation
Anaerobic packed bed reactor
Mesophilic sludge
Hydraulic retention time
Homoacetogenic bacteria

ABSTRACT

The present paper reports on results obtained from experiments carried out in a laboratory-scale anaerobic packed bed biofilm reactor (APBR), with recirculation of the liquid phase, for continuously biohydrogen production via dark fermentation. The reactor was filled with Kaldnes® biofilm carrier and inoculated with an anaerobic mesophilic sludge from a urban wastewater treatment plant (WWTP). The APBR was operated at a temperature of 37 °C, without pH buffering. The effect of theoretical hydraulic retention time (HRT) from 1 to 5 h on hydrogen yield (HY), hydrogen production rate (HPR), substrate conversion and metabolic pathways was investigated. This study indicates the possibility of enhancing hydrogen production by using APBR with recirculation flow. Among respondents values of HRT the highest average values of HY (2.35 mol $H_2$/mol substrate) and HPR (0.085 L $h^{-1}L^{-1}$) have been obtained at HRT equal to 2 h.



## Introduction

Currently, sustainable production of fuels is important due to global demand for energy, uncertainty in the supply of petroleum resources and environmental concerns bound up with petrochemicals processing. Biohydrogen, a high energy clean fuel, is considered as a promising alternative to conventional fossil fuels. Hydrogen gas is a recyclable, efficient (energy density equal to 122 kJ/g) and clean fuel with no $CO_2$ emissions [1–4]. In addition, $H_2$ can be used as a reactant in hydrogenation processes (in order to produce lower molecular weight compounds), as well as an $O_2$ scavenge. Due to increasing need for hydrogen energy, in the recent years much progress has been made to determine effective and efficient methods of biohydrogen production.

Many methods to produce biohydrogen have been studied, but most of them are energy intensive and it makes hydrogen production expensive. Currently, about 96% of hydrogen comes from processes based on fossil fuels [5]. Alternative methods of hydrogen generation include electrolysis of water, biophotolysis and biological production. Biological hydrogen production offers the benefits of clean gas, simple technology and is a more attractive potential than the current chemical methods. Hence, generate biohydrogen from renewable source is a promising method, which allows to make

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https://doi.org/10.1016/j.ijhydene.2018.08.094

hydrogen a clean and cheap energy carrier. Among the various pathways able to produce hydrogen from biomass, dark fermentation seems to be one of the most attractive processes [6–9]. During dark fermentation biohydrogen and others products are produced via an heterotrophic mechanism in anaerobic conditions, in which carbohydrates are used as the energy and carbon source [10]. It is recognized as an emerging way ahead, because it does not require external energy to drive the process or large surface area to capture the necessary light, it also can use a wide range of substrates, and different pure and mixed cultures [11]. Production of biohydrogen by mixed cultures is preferred from an engineering point of view, because it can be integrated with wastewater treatment systems. Using organic wastes reduces waste disposal problems [12] and it can minimize hydrogen production cost in scaled-up systems [13]. Furthermore, the acids produced during this process (mainly butyric, acetic and propionic acids) can be used for many industrial purposes. Basis dark fermentation provides an economically feasible and environmental friendly process.

Several studies have investigated various sources of carbon, including: sucrose [7,14–21], glucose [20,22–27], galactose [28] and fructose [16] as well as different feedstock such as: municipal wastewater [17], yeast factory [3], cheese whey [18,29,30] and oat straw hydrolysate [31]. Mix cultures are characterized by better degradation of organic matter and efficiently consume carbon sources compared to pure microbial species [32]. Moreover, hydrogen production using anaerobic organic waste or wastewater can be done without sterilization, which has large economic benefits. Hydrogen yield obtained from mixed culture is generally lower than from pure cultures, due to hydrogen consumption by microorganisms [33]. Thus, inoculum pretreatment is needed and it is one of the most debated issues nowadays. Effective methods of pre-treatment allow to inhibit the methane-producing bacteria activity, sulfidogenic microorganisms, as well as harvest anaerobic spore-forming bacteria. In general, pretreatment methods include: heat [34,35] and acid shock [35,36], mechanical pretreatment [37], ultrasonic [38] and electric field [39]. However, the most commonly used method for treatment of mixed culture is heat-shock, which obtains the best performance and higher $H_2$-production rates than acid shock [40,41]. Furthermore, thermal treatment is simple, inexpensive and effective. It requires temperatures around 100 °C for durations of 15–120 min in order to suppress non-spore-forming bacteria [23,42–45]. However, the pretreatment at 90 °C for 10 min has also been used [46–48].

In general, hydrogen yield is related to the dominant microorganisms and operating parameters used for fermentation process. It has been demonstrated, that the performance of hydrogen production via dark fermentation is influenced significantly by factors such as pH [23,49,50], temperature [50,51], HRT [3,14,17,18,23,24,27] and hydrogen partial pressure [52]. Specifically, pH has the great influence on hydrogen production, because of it affects on the hydrogenase activity, microbial communities, their structure and metabolism. Therefore, in order to keep medium pH at the optimum value (between 5.5 and 7.8), dark fermentation process has been commonly carried out with pH control systems and buffers such as sodium hydroxide (NaOH), sodium bicarbonate ($NaHCO_3$), hydrochloric acid (HCl) and phosphoric acid ($H_3PO_4$) [14–17,19,21–27]. However, from an industrial application point of view, hydrogen production without a pH buffer addition offers the major economic and environmental advantages.

Although many efforts have been made to produce hydrogen in dark fermentation, obtained values of hydrogen yield are still low (Table 1). Therefore, improving the efficiency of $H_2$ production poses a major challenge, because it determines the economic viability of the process. Moreover, the improvement in yields of hydrogen production from dark fermentation is a key step towards its commercialization.

Among biological reactors employed in biohydrogen production, anaerobic packed bed reactors (APBRs) are one of the most commonly used. Reactors employing immobilization systems generally show large volumes of biomass accumulation on the support medium [53]. Moreover, maintaining a high biomass inventory in biofilm reactors gives robustness against product inhibition [3]. In comparison to conventional anaerobic treatment systems, biofilm reactors could significantly reduce start-up time and increase organic loading rates up to fivefold [49]. In addition, one of the major advantages of immobilized cell technology is that there is no cell washout at high dilution rates, whereas in continuous stirred-tank reactor, since biomass has the same retention time as the liquid phase, washout of microorganisms can occur at short values of HRT [54]. Also, the construction and operation of packed bed reactors are relatively simple. However, a disadvantage of APBRs is that mixing is not completely achieved, leading to higher mass transfer resistance [55]. Therefore, pH gradient distribution along a reactor column leads to a heterogeneous distribution of microbial activity and thus high hydrogen yield cannot be maintained consistently [56]. To overcome this disadvantage, recirculation flow of a liquid phase can be used. A review of the literature has indicated that studies focused on a long-term hydrogen production via dark fermentation in ABPRs, equipped with the system for back-mixing, are limited to only few papers [19,22,27]. Fontes Lima and Zaiat [19] have demonstrated the positive effect of a liquid recirculation on $H_2$ production via dark fermentation in APBRs. The aforementioned authors have found that the optimum value of the recycle ratio is equal to 0.5–0.6. Based on this, in Ref. [22] a packed bed biofilm reactor with a liquid recycle (at 60% of the feed flow rate) was applied. In turn, dos Reis and Silva [27] have investigated the impact of HRT (in the range from 1 to 8 h) on hydrogen and ethanol coproduction in anaerobic packed bed reactors equipped with effluent recycling. However, in mentioned papers [19,22,27], in order to improve biohydrogen production, pH control systems have been used.

In response to the state of the existing literature, the aim of this study was to evaluate the effect of theoretical hydraulic retention time on hydrogen yield (HY), hydrogen productive rate (HPR) and composition of soluble microbial products in an anaerobic packed bed biofilm reactor equipped with recirculation flow of soluble products, inoculated with a mesophilic sludge, without pH buffer addition.

Please cite this article in press as: Tomczak W, et al., Effect of hydraulic retention time on a continuous biohydrogen production in a packed bed biofilm reactor with recirculation flow of the liquid phase, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.08.094