Available at www.sciencedirect.com

ScienceDirect

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

Photo-fermentative hydrogen gas production from dark fermentation effluent of ground wheat solution: Effects of light source and light intensity

*Hidayet Argun, Fikret Kargi**

Department of Environmental Engineering, Dokuz Eylul University, Buca, Izmir, Turkey

ARTICLE INFO

Article history:
Received 9 November 2009
Received in revised form
7 December 2009
Accepted 8 December 2009
Available online 29 December 2009

Keywords:
Bio-hydrogen
Light fermentation
Light intensity
Light source
Rhodobacter sphaeroides-RV

ABSTRACT

Dark fermentation effluent of wheat powder solution was subjected to light fermentation for bio-hydrogen production using different light sources and intensities. Tungsten, fluorescent, infrared (IR), halogen lamps were used as light sources with a light intensity of 270 Wm^{-2} along with sunlight. Pure culture of *Rhodobacter sphaeroides*-RV was used in batch light fermentation experiments. Halogen lamp was found to be the most suitable light source yielding the highest cumulative hydrogen formation (CHF, 252 ml) and yield (781 ml $H_2\,g^{-1}$ TVFA). In the second set of experiments, light fermentations were performed at different light intensities (1–10 klux) using halogen lamp. The optimum light intensity was found to be 5 klux (approx. 176 Wm^{-2}) resulting in the highest CHF (88 ml) and hydrogen yield (1037 ml $H_2\,g^{-1}$TVFA). Hydrogen formation was limited by the availability of light at low light intensities below 5 klux and was inhibited by the excess light above 5 klux.

1. Introduction

Due to considerable environmental problems arising from utilization of coal, petroleum and natural gas as major energy sources, research on development of clean fuels has been given special attention for the last fifty years. Among the clean fuels, hydrogen gas has significant advantages over other alternatives. Hydrogen is a carbon, nitrogen, and sulfur free fuel and energy carrier with much higher energy content (122 kJ g^{-1}) as compared to fossil fuels. Besides hydrogen gas can be used in fuel cells for electricity generation and is considered to be the major energy carrier of the future. However, unlike fossil fuels hydrogen gas is not readily available in nature and requires expensive production methods. Hydrogen gas is already traded worldwide with a rate of 50 million tones/year and with a growth rate of nearly 10% per year [1].

The most common method used for hydrogen gas production is steam reforming of natural gas and hydrocarbons requiring high temperatures and energy inputs [2]. Hydrogen gas production by fermentation of carbohydrate rich raw materials has considerable advantages over chemical processes due to operation under mild conditions (30–35 °C, 1 atm). Low hydrogen yields and formation rates are the major problems in bio-hydrogen production requiring considerable improvements [2–5].

Renewable resources (biomass) and wastes (industrial, agricultural and domestic) constitute attractive raw materials for bio-hydrogen production at large scale. Usually sequential dark and light anaerobic fermentations are used for bio-hydrogen production from carbohydrate rich biomass or

* *Corresponding author*. Tel.: +90 232 4127109.
E-mail address: fikret.kargi@deu.edu.tr (F. Kargi).

0360-3199/$ – see front matter © 2009 Professor T. Nejat Veziroglu. Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.ijhydene.2009.12.040

waste materials [2]. The first step is the acid or enzymatic hydrolysis of biomass to highly concentrated sugar solution. Dark fermentation of hydrolyzed biomass by acetogenic–anaerobic organisms is the next step for production of volatile fatty acids (VFA), hydrogen and CO_2 [2–4]. The last step is the light fermentation of organic acids produced by dark fermentation by the photo-heterotrophic bacteria (*Rhodobacter* sp) to produce CO_2 and H_2 [2–4].

Dark fermentation of starch and cellulose containing biomass for hydrogen gas production has been reported in literature [6–11]. Heat treated anaerobic sludge was used for dark fermentation of starch, cellulose and other carbohydrate rich raw materials along with some pure cultures of *Clostridia* sp. and *Enterobacter* sp. Hydrogen yields in dark fermentation of carbohydrates are reported to be between 1 and 3 mol H_2 mol^{-1} glucose [2,6–11]. Due to formation of a mixture of volatile fatty acids (VFAs) and utilization of carbohydrate source for growth and maintenance, the experimental yields are lower than the maximum theoretical yield (4 mol H_2 mol^{-1} glucose) which is based on formation of acetic acid as the sole product in dark fermentation.

Light fermentation of VFAs present in dark fermentation effluent for bio-hydrogen production is more problematic than the dark fermentation due to complexity of nutritional requirements of the bacteria used, light requirement, strict control of environmental conditions, substrate (VFA and NH_4^+) inhibitions and susceptibility for contamination. *Rhodobacter* species have been the most widely used bacteria for bio-hydrogen production by light fermentation of VFAs [12–16]. Maximum theoretical hydrogen yield from light fermentation of acetic acid is 4 mol H_2 mol^{-1} acetate. When acetic acid is the only VFA produced and used by the dark and light fermentations, the total hydrogen yield is 12 mol H_2 mol^{-1} glucose, 4 moles of which are from the dark and 8 moles are from the light fermentation [2]. The maximum total hydrogen yield was reported to be between 6 and 7.2 mol H_2 mol^{-1} glucose for the sequential dark and light fermentations [2].

Pure VFAs such as acetic or butyric acids and pure *Rhodobacter* cultures were used in most of the light fermentation studies [12–16]. Acid hydrolyzed wheat starch was used for hydrogen production by light fermentation using different *Rhodobacter* species [17]. Limited number of light fermentation studies was reported on dark fermentation effluents for bio-hydrogen production [10,18–24]. Effects of light intensity on hydrogen formation performance of light fermentation bacteria have been studied using pure VFAs and mainly tungsten lamp [25–29]. Different optimum light intensities were reported for different light sources under different conditions [25–31]. Uyar et al. [25] used tungsten lamp with the light intensities between 88 and 405 Wm^{-2} for light fermentation and reported 270 Wm^{-2} as the optimum light intensity. Obeid et al. [26] used sodium vapor lamp for light fermentation and reported 50 klux as the optimum light intensity. Ding et al. [30] reported 8 klux as the optimum light intensity for tungsten lights when immobilized bacteria were used for combined dark and light fermentations. Miyake et al. [31] used halogen lamp with light intensities between 0 and 1 kWm^{-2} and reported 0.5 kWm^{-2} as the optimum light intensity. However, no systematic studies were reported on comparison of different light sources in light fermentation of dark fermentation effluent for bio-hydrogen production.

Therefore, the major objective of this study is to investigate the effects of the light source and intensity on the rate and the yield of hydrogen production in light fermentation of dark fermentation effluent. Dark fermentation effluent of wheat powder solution and pure culture of *Rhodobacter sphaeroides*-RV were used in batch light fermentation experiments. Tungsten, fluorescent, infrared and halogen lamps were used as different light sources at a constant light intensity. After selecting the most suitable light source, batch experiments with different light intensities were carried out. The most suitable light source and intensity resulting in the highest rate and yield of hydrogen production were determined.

2. Materials and methods

2.1. Experimental set up and procedure

Dark fermentation effluent (DFE) containing volatile fatty acids (VFA) was used as substrate in light fermentations. In dark fermentation, 20 gL^{-1} ground wheat powder solution (WPS) was boiled for 1.5 h, settled for 16 h and the supernatant was filtered to obtain particle-free wheat starch solution which was inoculated with the heat treated anaerobic sludge. Dark fermentation lasted for about 70 h and the effluent contained 3250 ± 30 mgL^{-1} TVFA, 20 ± 10 mgL^{-1} NH_4–N, respectively. Since high NH_4–N concentrations was reported to be inhibitory for the light fermentation organisms [20,23], pH of the effluent was adjusted to pH = 10 and aerated overnight to remove ammonia from the solution. The aerated effluent was centrifuged for 30 min at 7000 g to remove the solids. The supernatant was diluted to reduce the TVFA to nearly 2000 mgL^{-1} since this was reported to be the most suitable VFA concentration for the light fermentation [32–34].

Two sets of batch experiments were performed to determine the most suitable light source and light intensity yielding the highest rate and extent of bio-hydrogen formation in light fermentations. The experiments were conducted in 310 ml serum bottles (Isolab-Germany Boro 3.3) equipped with silicone rubber stoppers and screw caps to avoid gas leakage. Height and diameter of serum bottles were 8.5 cm and 7 cm, respectiveley with 2.5 mm glass wall thickness and surface/volume ratio of 0.75 cm^2 cm^{-3}. Anaerobic conditions were maintained by passing Argon gas from the head space of the bottles for 3 min at the beginning of the experiments. A control experiment without any inoculation under fluorescent lamp and an experiment with the sunlight illumination were also performed for comparison. Experiments were performed in a temperature controlled room at 30 ± 1 °C.

Light intensities and irradiation were measured using a light meter LX-1108 LT Lutron (LT Lutron, Taiwan) and an Apogee Pyronometer Sensor-PYR-P 3587 (Apogee, USA), respectively. The serum bottles were mixed manually several times a day. pH, ORP, and hydrogen gas measurements were done everyday.

In selection of the most suitable light source, the bottles were illuminated with halogen (Kengo Lighting, PAR 30 75W E27), tungsten (Tung, Philips A55 E27 ES 75W), Infrared (IR, Philips BR 125 IR 150W), tungsten and infrared (Tung & IR), and fluorescent lamps (Phillips LTD 36W/54) with 270 Wm^{-2}