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Review

Bio-hydrogen production by different operational modes of dark and photo-fermentation: An overview

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ABSTRACT

This article overviews reported studies on bio-hydrogen production from different raw materials by dark and photo-fermentations operated with different modes. Sequential and combined dark and photo-fermentations operated in batch, continuous and fed-batch modes were compared. Operating conditions and modes resulting in the highest hydrogen yield and formation rate were revealed. Relative advantages of sequential and combined dark and photo-fermentations were discussed. Sequential fermentation was found to be preferable due to high H_2 yields and productivities. High cell density fed-batch culture with controlled feeding and simultaneous product removal was concluded to be the most suitable operation mode at the optimum environmental conditions.
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1. Introduction

Hydrogen (H_2) is considered to be one of the most promising fuels of the future [1] due to high energy content (122 kJ/g) as compared to hydrocarbon fuels [2–4]. Hydrogen gas is also a clean fuel with no CO_x, SO_x and NO_x emissions. Besides, H_2 is an important energy carrier and can be used in fuel cells for generation of electricity [5,6]. However, hydrogen gas is not readily available in nature like fossil fuels and natural gas, but can be produced from renewable materials such as biomass [2,7] and water [3]. Hydrogen gas production technologies has gained special attention during the last fifty years due to the increasing energy demand, rapid consumption of non-renewable fossil fuel reserves and hydrocarbon fuel based atmospheric emissions [7–9].

Steam reforming of natural gas and water electrolysis are the most commonly used processes for H_2 gas production [1]. Due to energy intensive nature of those processes more energy efficient H_2 production methods are searched for [6]. Hydrogen gas production from renewable resources (e.g. biomass) and carbohydrate rich waste materials by bio-processes offers distinct advantages over energy intensive methods used [2,10]. Major drawbacks in bio-hydrogen production are low yields and productivities requiring large reactor volumes and long residence times [2,11].

Main bio-hydrogen production processes are direct/indirect bio-photolysis, dark and photo-fermentations [1,6,10,11]. A brief comparison of those processes is depicted in Fig. 1. Bio-photolysis of water under sunlight is considered as the cleanest approach for bio-hydrogen production. However, low

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H_2 gas productivity [12], strict light requirement and oxygen inhibition are the main problems in bio-photolysis of water [2,12]. Fermentative hydrogen gas production from carbohydrates is a much faster process than bio-photolysis [8,10,13] with volatile fatty acids (VFAs) and H_2 gas formation [14,15]. However VFAs need to be fermented for further H_2 gas production [16,17]. Photo-fermentative bacteria have the ability to use VFAs for H_2 production under light irradiation [2,6,13] for which dark fermentation effluent can be used as feedstock [14,15,18–20]. Hydrogen gas formation can be enhanced by integration of dark and photo-fermentations in the form of sequential or combined fermentations [8,14,15,18–21]. Both the dark and photo-fermentations can be realized by using suspended and immobilized-cell reactors operating in batch, continuous and fed-batch modes. Major mechanisms for bio-hydrogen production by dark and photo-fermentations have been elucidated. However, development of an effective bio-hydrogen production process at industrial scale is still a challenge. Recent reviews published on fermentative hydrogen gas production summarized studies using different raw materials, bacterial cultures, operating conditions (T, pH, ORP) and pre-treatment methods [1–3,6,10,11,13]. The reported rates and the yields of fermentative hydrogen gas production were not high enough to make the process economically viable. The most suitable raw materials, pre-treatment methods, bacterial cultures, operating conditions, cultivation types, operating modes and processing schemes are yet to be determined for an effective and economically viable fermentative hydrogen production process.

Operating modes of bioreactors affect the rate and the yield of hydrogen gas formation during dark and photo-fermentations by affecting the biomass, substrate and product concentrations in the reactor. None of the published review articles considered the effects of operating modes and processing schemes as factors affecting hydrogen production rate and the yield. Therefore, the main objective of this study is to overview the reported studies on bio-hydrogen production by different operating modes. Sequential and combined dark and photo-fermentations operated in batch, continuous and fed-batch mode were compared in terms of hydrogen gas formation rates and yields. Some conclusions were drawn to identify the most suitable cultivation type (suspended or immobilized cultures) and operation mode (batch, continuous, fed-batch) for effective bio-hydrogen production.

2. Dark fermentation

A wide variety of heterotrophic bacteria have the ability to ferment carbohydrates under anaerobic conditions to produce H_2 gas, volatile fatty acids (VFAs) and CO_2 [8,22–24]. In general, spore forming *Clostridium* species, facultative *Enterobacter* sp, *Bacillus* sp [2,13,25], some thermophilic bacteria [22,24,26,27] and anaerobic acidogenic sludge [2,22,28–30] are the most widely used cultures for this purpose. Hydrogenase is the key enzyme catalyzing molecular H_2 formation by combining protons and electrons in dark fermentation [31,32]. Usually, monosaccharides are main carbon sources [22,33–35] which can be generated by acid or enzymatic hydrolysis of polysaccharides like starch or cellulose [23].

Dark fermentative conversion of glucose to H_2, acetic acid and CO_2 is presented in (Eq. (1) [10]). Negative free energy indicates that the reaction proceeds toward product formation spontaneously with no external energy requirement. Theoretically, a maximum of 4 mol of H_2 can be produced per mole glucose when acetic acid is the only VFA product. However, lower yields are obtained in practice since part of the glucose is used for microbial growth and maintenance [34]. Butyric acid formation is accompanied with formation of 2 mol of H_2 per mole of glucose and propionic acid formation consumes 1 mol of H_2 per mole of propionic acid [36,37]. Lactic acid and ethanol fermentations do not result in H_2 formation or consumption. When both acetic and butyric acids are produced in dark fermentation of glucose, theoretically 2.5 mol H_2 is formed per mole glucose [38].

$$C_6H_{12}O_6 + 2\,H_2O \rightarrow 2\,CH_3COOH + 4\,H_2 + 2\,CO_2 \quad \Delta G^o = -206\ kJ \tag{1}$$

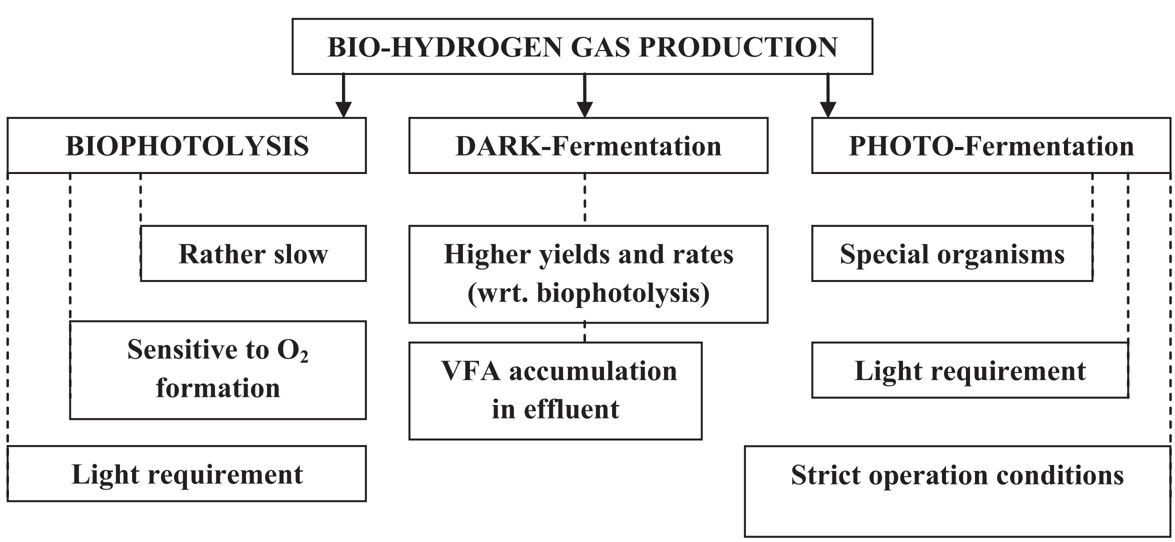

Fig. 1 – Comparison of bio-hydrogen production by algal and bacterial bioprocesses.

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