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Hydrogen and ethanol production in anaerobic fluidized bed reactors: Performance evaluation for three support materials under different operating conditions

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ABSTRACT

The objective of this study was to evaluate the influence of different support materials (polystyrene – R1, grounded tire – R2 and polyethylene terephthalate (PET) – R3) on producing hydrogen and ethanol using three anaerobic fluidized bed reactors. Each reactor had a total volume of 4192 cm^3 and was fed with media containing glucose as the carbon source (4000 mg L^{-1}) with an influent pH around 5.0 and an effluent pH of about 3.5, a hydraulic retention time (HRT) of 8–1 h at a temperature of 23 ± 2 °C, with thermal treatment of the inoculum. For hydrogen production, the best performance was achieved with R2 (2.11 mol H_2 mol^{-1} glucose), providing the highest H_2 content in biogas (60%). In all reactors, the predominant soluble metabolites were acetic acid, butyric acid, lactic acid and ethanol, with small amounts of propionic acid. The reactor R2 produced more acetic and butyric acid (434.74 and 1013.61 mg L^{-1}, respectively). However, reactor R3 showed a better performance for ethanol concentration (1941.78 mg L^{-1}).

1. Introduction

Anthropogenic climate changes and the decreasing availability of fossil fuels have led scientists all over the world to look for alternative sources of energy [1]. One alternative to fossil fuels that is drawing international attention is the employment of biological processes to produce biofuels, such as hydrogen and ethanol. Ethanol and hydrogen can be produced simultaneously and in significant amounts [2], which makes them promising alternative energy sources [3].

Hydrogen has the highest energy content per unit weight of all known fuels (142 kJ g^{-1} or 61,000 Btu lb^{-1}) and can be easily transported for domestic and industrial use. Today, it is regarded as an environmentally safe and renewable source of energy, i.e., one that does not contribute to the greenhouse effect [4].

A promising area of technological development is the production of hydrogen and ethanol by microorganisms from a wide variety of renewable sources, such as beet sugar plant residues, potato and wheat starches, and cellulose, e.g., *Miscanthus* [2]. The main species identified as responsible for the biological production of hydrogen during acidogenesis of carbohydrates are *Enterobacter*, *Bacillus*, and *Clostridium* [5] as well as *Clostridium* for the simultaneous production of H_2 and ethanol [2].

According to Ren et al. [6], three types of fermentation may occur: (1) butyric acid-type fermentation, (2) ethanol-type fermentation, and (3) propionic acid-type fermentation. *Butyric acid-type fermentation* occurs when most of the products generated by acidogenic fermentation consist of acetic and butyric acid. This type of fermentation is suitable for hydrogen production because four moles of hydrogen are produced when generating one mole of acetic acid from glucose fermentation, and two moles of hydrogen are produced in the generation of one mole of butyric acid. In *ethanol-type fermentation*, the liquid products are derived mainly from ethanol and acetic acid. Lastly, in *propionic acid-type fermentation*, the propionic acid is converted to methane and accumulates in the reactor during fermentation.

Among the high-rate anaerobic reactors used for biological production of hydrogen is the anaerobic fluidized bed reactor (AFBR). In AFBRs, the microbial film is retained by natural adherence of microorganisms to particles of a solid support medium, which is its most influential variable [7]. It is therefore important to use support materials that are simultaneously lightweight, inexpensive, easy to purchase and that can also contribute to solving the serious environmental problems caused by today's generation and inappropriate disposal of solid wastes. Polymeric support materials, such as polystyrene, polyethylene terephthalate (PET), and grounded tire, are lightweight, easy to purchase, and reusable, and their use as support medium may reduce the amount of waste in landfills and minimize the energy required for fluidization in AFBRs.

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Some studies have shown that the products of fermentation depend on the type of substrate used and the operating conditions of the reactor, e.g., the hydraulic retention time (HRT), temperature, and pH. In particular, pH has the greatest influence on the composition of the acidogenic reactor effluent [8]. According to Wang and Wan [9], it influences hydrogen production because it can affect the hydrogenase activity as well as the metabolic pathway. As indicated by van Ginkel et al. [10], Fang and Liu [11], Li et al. [12], and Aceves-Lara et al. [13], the optimum pH value for hydrogen production is between 5.5 and 6.0. A pH between 6.0 and 6.5 can produce an excessive amount of propionic acid. However, pH values lower than 4.5 are conducive to the production of H_2, CO_2, acetic acid, butyric acid, and ethanol [8]. The literature presents contradictory results in regard to the optimum pH value for hydrogen production. Possible reasons for this lack of consensus are the type of inoculum and substrate used in these studies as well as the pH range under investigation [9].

Another important aspect of AFBRs is whether the pH should be controlled because the use of alkalis to achieve this control increases the cost of the process. Contradictory results have been described in the literature. For example, Barros et al. [14] achieved a high hydrogen yield (HY) (1.90 and 2.59 mol H_2 mol^{-1} glucose, respectively) and a low ethanol concentration (1.96 and 4.35 mM, respectively) with glucose as the carbon source, polystyrene and expanded clay as the support materials, and alkalis for pH control. Amorim et al. [15] and Shida et al. [16] also achieved a high HY (2.49 and 2.29 mol H_2 mol^{-1} glucose, respectively) and a low ethanol concentration (1.86 and 1.18 mM, respectively) with glucose as the carbon source and expanded clay as the support material, but without using alkalis. Abreu et al. [17] reported a low HY (0.8 mol H_2 mol^{-1} arabinose) and a high ethanol concentration (197.43 mM) with arabinose as the carbon source and a batch reactor and the use of an alkalizing agent for pH control. However, Wu et al. [3] achieved a high HY (1.04 mol H_2 mol^{-1} hexose) and ethanol concentration (20.43 mM) with polyethylene-octane elastomer as the support medium, pH control, and glucose as the carbon source, despite the fact that the production pathways of these biofuels compete with one another.

Thus, the purpose of this study was to investigate the simultaneous biological production of hydrogen and ethanol in an AFBR with synthetic wastewater used as the substrate (4000 mg L^{-1} of glucose as the carbon source), an HRT reduction from 8 to 1 h at a temperature between 20 °C and 25 °C, different support materials (polystyrene, grounded tire, and PET) and an effluent pH around 3.5, without the addition of alkalis.

2. Materials and methods

2.1. Anaerobic fluidized bed reactors

Fig. 1 shows a schematic of the three identical jacketed reactors used for H_2 production in this study. The reactors were constructed of transparent acrylic with the following dimensions: a height of 190 cm, an internal diameter of 5.3 cm, and a total volume of 4192 cm^3. The temperature in the AFBRs was maintained at 23 ± 2 °C.

2.2. Synthetic wastewater and support materials

The synthetic wastewater contained glucose as the main carbon source (4000 mg L^{-1}) and was supplemented with nutrients as described by LEITE et al. [18].

Particles of polystyrene (R1), grounded tire (R2) and PET (R3) were used in the AFBRs as support materials for biomass immobilization. The support materials were submitted to prior chemical treatment to increase their surface roughness [19]. The basic characteristics of the support materials are shown in Table 1.

2.3. Heat treatment of inoculum and AFBRs start-up

The inoculum used in this study was obtained from the anaerobic sludge of an upflow anaerobic sludge blanket (UASB) reactor treating effluent from swine wastewaters. The H_2 productivity of the sludge was enhanced by heat treatment according to the methodology of Kim et al. [20]. This treatment consisted of preheating the sludge for 10 min at 90 °C to inhibit the methanogenic activity.

The three AFBRs were fed with a medium containing glucose (4000 mg L^{-1}) and heat-treated sludge (10%, v/v). Reactor R1 was filled with 930 g of polystyrene, reactor R2 was packed with 621 g of grounded tire, and reactor R3 was filled with 1375 g of PET, thus creating an initial fixed bed of 73 cm, 50 cm and 80 cm in depth for the reactors, respectively. Due to use of different particle sizes and densities, we made the experimental determination of the minimum fluidization velocitiy for each particle, in order that the reactors reach similar heights when they were fluidized. The total liquid flow (Q) was adjusted at 76, 122 and 139 L h^{-1}, for the reactors R1 (polystyrene), R2 (grounded tire) and R3 (PET), respectively. These flow rates produced a superficial velocity 1.30 times greater than the minimum fluidization velocity for each particle. After fluidization, the reactors R1, R2 and R3 reached an average initial height of 106 cm, 92 cm and 96 cm. Nitrogen gas was used to sparge the fermentation medium to create an anaerobic environment. The bioreactors were initially operated on batch mode for 48 h to activate the H_2-producing sludge. Afterward, they were switched to a continuous mode at a designated hydraulic retention time (HRT = 8 h). When a steady state condition was reached (based on a constant H_2 production rate with a variation of within 5–10% for 5–10 days), the HRT was decreased progressively from 8 h to 1 h. The three reactors were operated for 175 days in five experimental phases. A gas–liquid separator was used at the effluent outlet to collect gaseous and soluble products separately. A gas meter (TG1; Ritter Inc., Germany) was used to quantify the amount of hydrogen generated.

2.4. Chemical and biomass analyses

The pH, chemical oxygen demand (COD), and solids (total solids, TS; volatile suspended solids, VSS; and total volatile solids, TVS) were measured in accordance with Standard Methods [21]. The glucose concentration was measured with an enzymatic GOD-PAP [18]. Biomass adhesion to the polystyrene, grounded tire and PET particles was determined according to the methods of Chen and Chen [22].

The biogas hydrogen content was determined by gas chromatography (GC-2010, Shimadzu, Japan) using a thermal conductivity detector (TCD) with argon as the carrier gas and a column packed with Supelco Carboxen 1010 Plot (30 m × 0.53 mm i.d.) [23].

Concentrations of volatile fatty acids (VFA) and alcohols were also measured by gas chromatography (GC-2010, Shimadzu, Japan) using a device equipped with FID (flame ionization detector) and COMBI-PAL headspace injection (AOC 5000 model) as well as a HP-INNOWAX column (30 m × 0.25 mm i.d. × 0.25-μm film thickness) [23].

3. Results and discussion

3.1. Glucose conversion and hydrogen production

The pH remained stable throughout the system operation within the operating range of acidogenic anaerobic systems, i.e., between