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Hydrogen production by anaerobic digestion of pig manure: Effect of operating conditions

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ABSTRACT

Experiments were conducted in an Anaerobic Batch Reactor (ABR) to assess the influence of pH, organic load and retention time on hydrogen production using pig manure as substrate. The study was conducted in two stages: the first stage focused on the effect of pH and the second stage assessed the effect of retention time and organic load on hydrogen production. The pH values investigated were 5.0, 5.5 and 6.0. The retention times were 12, 24 and 36 h with organic loading rates of 96.4, 48.2 and 32.1 kg VS/m^3d, respectively. pH 5.5 had a maximum hydrogen concentration and production rate of 26.9% and 31.8 mL H_2/h, respectively. Meanwhile, the retention time and organic load of 12 h and 96.2 kg VS/m^3d produced a maximum hydrogen concentration and production rate of 23.6% and 102.1 mL H_2/h, respectively. The hydrogen concentration obtained by ABR of pig manure is limited. Methanogenesis was inhibited as concluded from the methane concentrations being below 1% during all experiments except pH 6.0 and a retention time of 36 h. At pH 6.0, an inverse linear relationship between methane and hydrogen concentration was found. Finally, a modified Gompertz model was used to fit hydrogen production at retention time of 12 and 24 h.

1. Introduction

Hydrogen has been studied as an alternative energy carrier which produces water as its final combustion product. It can be produced through a number of chemical processes such as steam reforming, gasification, electrolysis and pyrolysis, which use non-renewable sources as raw materials and demand high temperatures. Biological processes require less energy and use renewable biomass [1–3]. In this case, photofermentation and dark fermentation can use wastes for hydrogen production. However, the photofermentation process presents a number of disadvantages such as sunlight-dependence, which requires large surface areas. In addition, during photofermentation, hydrogen production is catalyzed by nitrogenases, which produces hydrogen at a lower rate than hydrogenases [1,3–5]. As a result, dark fermentation shows some advantages and could be used as a preliminary step to photofermentation in a sequential system. This configuration can increase the global hydrogen production to rates 1.4–4.6 folds higher than dark fermentation [3,4]. Dark fermentation generates less biomass, but maintaining acceptable growth rates for hydrogen-producing microorganisms [1,6]. Some studies in which dark fermentation was used for hydrogen production are listed in Table 1. In this case, the highest hydrogen production is obtained through the use of substrates rich in carbohydrates, nutrients, and selected or pretreated inoculum. However, the costs involved in maintaining these specific conditions remain a challenge.

There are many environmental parameters such as pH, temperature, retention time, organic load and nutrients that drive the anaerobic digestion required for hydrogen production. Under an acidic pH, it is possible to inhibit methanogenesis as methanogen activity requires a minimum pH of 6.5 [13,14]. In some studies, pH between 5.0 and 6.0 has been reported as a successful range for hydrogen production [15,16]. Even though high organic loads may increase the time response, high values of this parameter increase hydrogen production [17]. Organic shock loads inhibit hydrogen-consuming microorganisms and improve growth rates of hydrogen-producing microorganisms. As a result, the production of VFA, hydrogen and carbon dioxide is faster and stronger [18]. Therefore, pH and retention time decrease which, in turn, limit the reactions related to hydrogen consumers [19]. In addition, the reduction in retention time could limit the hydrolytic stage and acid formation decreasing hydrogen production. During dark fermentation, pure substrates such as glucose and starch require a minimum biomass contact time between 2 and 12 h to reach maximum hydrogen production [7,20]. Meanwhile, complex

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Table 1
Hydrogen production from simples and complex substrates by dark fermentation.

Substrate	Culture	H_2	Process features
Glucose	Mixed culture	300[a]	FC(20 g/L), UASB
Glucose	*Enterobacter aerogenes HO39*	850[a]	FC(10 g/L), fixed film
Sucrose	*Clostridium butyricum CGS5*	266–667.3[b]	FC(17.81 g/L), batch
Sugar factory wastewater	Mixed thermophilic culture	4.4[c]	Continuous
Sugar beet molasses	*Caldicellulosiruptor saccharolyticus*	200[b]	FC(15 g sucrose/L), batch
Sugar cane bagasse		19.6[d]	PF, 70 °C, batch
Sugarcane bagasse hydrolyzate	*Clostridium butyricum*	1.61[c]	PF, batch
Starch	*C. butyricum + E. aerogenes*	800[a]	FC(2%), CSTR
Cassava starch	Anaerobic mixed bacteria (*Clostridium* sp.)	334.8[b]	FC(10.4 g/L), batch
Corn starch cultures	Mixed mesophilic	2.57[c]	Continuous
Hydrolyzed cassava starch	Pre-heated activated sludge	262.4[b]	FC(25 g/L), batch
Ground wheat solution	Anaerobic sludge	69.3[b]	FC(6.7 g starch/L), batch
Sweet sorghum extract	Indigenous microbial mesophilic culture	8.52[c]	Continuous
Grass silage		6–16[d]	35–70 °C, batch
Maize leaves		18–42[d]	PF, 70 °C, batch
Palm oil mill effluent (POME)	Thermoanaerobacterium-rich sludge	4.2–6.5[e]	FC(85 g/L), 60 °C, ASBR
Molasses	Mixed mesophilic culture	4.8[c]	Continuous
Cheese whey	Mixed mesophilic indigenous microbial culture	2.51[c]	Continuous
Food waste		60–196[d]	PF, 35–36 °C, batch
OFMSW	Mixed mesophilic culture	27.8–180[f]	34–37 °C
Olive pulp	Mixed mesophilic culture	0.26[c]	Continuous
Dairy manure		14–18[d]	PF, 36 °C, batch
Cow feces and urine		0.7–29[d]	37–75 °C, batch

PF: Pretreatment of feedstock. FC: Feedstock concentration. OFMSW: Organic Fraction Municipal Solid Waste.
Adapted from:
[a] Kapdan and Kargi [7], (mL/L/h).
[b] Argun et al. [4], (mL/L/h).
[c] Ntaikou et al. [8], (L/L/d).
[d] Guo et al. [9], (mL/gVS).
[e] O-thong et al. [10], (L/L).
[f] Lay et al. [11], and Gomez et al. [12], (mL/gVS).

substrates such as organic wastes and sludge take about 12 h [21,22]. Similarly, the retention time required for fermentation of the Organic Fraction of Municipal Solid Waste (OFMSW) is 20 h [23,24]. There are other methods that inhibit hydrogen-consuming bacteria, such as the addition of exogenous agents and inoculum pretreatment which are widely used for microorganism selection [25,26].

In this context, a hydrogen production process that uses a complex substrate without the addition of a nutrient solution and specific inoculum was developed. The main objectives of this research project were to study the influence of pH, organic load and retention time on hydrogen production under dark fermentation using pig manure as only substrate, and to determine the values of these parameters, that can be used to optimize hydrogen production. The inhibition of hydrogen consumers related to methanogenesis was pursued through the variation of these parameters. The effect of studied parameters on VFA production, biogas composition and hydrogen production rate was evaluated, and additional analyses were undertaken using the information collected from the experiments.

2. Methods

2.1. Methodology

The study was developed in two stages: the first involved pH variation and the second evaluated the variation of retention time and organic load. The selected pH values were 5.0 ± 0.02, 5.5 ± 0.02 and 6.0 ± 0.02. The retention times evaluated were 12, 24 and 36 h. The feedstock for both stages maintained the same Volatile Solids (VS) content which resulted in an intrinsic organic load variation during the second stage. The organic loads related to the change in time were 96.4, 48.2 and 32.1 kg VS/m^3d for 12, 24 and 36 h respectively. The experiments with variation of retention time and organic load began under the best pH condition found during the first set of experiments. Each experiment lasted between eight and twelve days. The results were related to the number of batch cycles evaluated for each condition due to the change in retention time during the second stage. The initial values used at the beginning of the experiments corresponded to the highest acidity level, the longest retention time and the lowest organic load.

2.2. Seed microflora

The inoculum used in this study was obtained from a methanogenic reactor under mesophilic conditions (35 °C) and low organic load (6.9 kg VS/m^3d) using pig manure as substrate. The *Bacteroides*, *Eubacterium* and *Clostridium* bacteria contained in manure were used as a source of microorganisms [13,27]. The selection of microorganisms was undertaken by varying the operating conditions of the reactor. The temperature was set to thermophilic condition (55 °C) with a retention time of 24 h and pH was kept at 5.5 ± 0.5. These conditions improved the selection of hydrogen-producing bacteria including *Clostridium* which forms spores under adverse conditions. The selection process was completed when the hydrogen concentration in the biogas reached 4%.

2.3. Experimental procedure

Hydrogen production experiments were carried out in an Anaerobic Batch Reactor (ABR) with a working volume of 6 L and a total volume of 7.2 L. The substrate used was fresh pig manure suspension (4 L) with solids content between 8 and 10% (w/v). The reactor was operated as a semi-batch system with continuous output of biogas. Two liters of mixed liquor were left inside the reactor to retain the biomass. Each pH condition was established by adding either HCl (1.5 N) or NaOH (1.5 N) using automatic dosing