

The Effect of The Initial pH on The Energy Gain from The Dark Fermentation of Vinasse

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Abstract—The effect of the initial pH on the thermophilic dark fermentation of the sugarcane vinasse was studied. Two initial pH values were investigated (4.5 and 5.5). The maximum volumetric hydrogen production and hydrogen yield were 3.85 L H₂.L⁻¹ vinasse and 52.2 mL.g⁻¹ COD applied at an initial pH of about 4.5. The maximum electrical energy that can be obtained was 4.6 KWh. M³vinasse⁻¹ (16.5 MJ.m³vinasse⁻¹) after a day of the dark fermentation of vinasse at an initial pH of 4.5.

Keywords—vinasse, biohydrogen, pH, energy, dark fermentation

Introduction

Nowadays, fossil fuels are considered the world's dominant energy source. The environmental problems such as climate change and global warming associated with their use as well their depletion have prompted researchers all over the world to look for environmentally-friendly sustainable alternatives [1]. In similar fashion, the agro-industrial wastes, if not properly handled can cause significant environmental problems affecting the climate, ecosystem, and overall health. Thus, there was a paradigm shift in the research to study the production of the energy from these wastes to achieve a pollution control and generate bioenergy and value-added products [2]. Among the agro-industrial wastes, the molasses-based vinasse is considered one of the most contaminant wastewater during the production of the bioethanol from the sugarcane molasses. The molasses generally goes along three stages viz. the preparation, the fermentation by yeast, and the distillation. The vinasse is the waste derived from the first distillation column. It is estimated that a pollution of 1.43 humans equals the pollution of a liter of vinasse [3]. On average, 10–15 liters of vinasse are produced for every liter of the bioethanol produced, with low acidity (pH 3–5), high organic matter in terms of COD (100–190 g/L), BOD (31–43 g/L), high temperature (70 – 90 °C), dark brown color, and unpleasant odor [4]–[6].

Biohydrogen is regarded as the cleanest biofuel as the water is the only resultant of its combustion. The biohydrogen extracted from wastes is a sustainable and environmentally safe fuel with a three-fold higher energy density (122 kJ/g) than hydrocarbon fuels [1]. Some of the benefits of dark fermentation of vinasse over the other biohydrogen production

methods could be the higher hydrogen rate and content, the light independency, and the simple and cost-effective design [7]. Since vinasse is produced with a high temperature, the thermophilic dark fermentation of the vinasse could be a cost-effective method. The high temperature decreases the solubility of the hydrogen allowing for higher production [7]. The effect of the pH on the dark fermentation was studied by several researches as it is considered one of the main parameter affecting the fermentation pathway and therefore the main products [8]–[10]. A study on the dark fermentation of a sugarcane vinasse by [9] revealed that the highest hydrogen production was at a pH range of 5.0 – 5.5, while a pH of less than 5.0 encouraged the lactate fermentation and a value of more than 6.0 encouraged the propionate fermentation. However, the maximum hydrogen production obtained by [10] was at a pH of 6.0.

Thus, this paper investigated the initial pH effect on the batch fermentation of the sugarcane vinasse at 55 °C. In addition, the energy potential of a m³ vinasse was computed to present the energy gain from the fermentation.

Materials and Methods

A. Seeding Sludge and Substrate

A granular anaerobic sludge was obtained from a full-scale anaerobic reactor located in Al-Hawamdia integrated sugar industries distillation-factory located in Giza, Egypt. The sludge was heat-pretreated at 90° C for 10 min to inhibit the hydrogen utilizing bacteria. The pretreated sludge was then stimulated to produce the biohydrogen from glucose in a continuous thermophilic anaerobic operation for 17 days before used in this experiment. The total solids (TS), volatile solids (VS), and their ratio (VS/TS) were 79.8, 69.15 g/L, and 0.87, respectively.

The raw sugarcane vinasse was collected from Al-Hawamdia integrated sugar industries distillation-factory located in Giza, Egypt. It was allowed to cool to room temperature before being stored at 4 °C until use, allowing a natural sedimentation process. The characteristics of the vinasse used in this experiment were as follows: 103 g.L⁻¹ COD, 4.46 pH, 6.0 g.L⁻¹ VFA, and 20 g.L⁻¹ total carbohydrates.

B. Experimental Procedure and Operational Conditions

To investigate the effect of the initial pH on the thermophilic dark fermentation of the vinasse using the acclimated anaerobic sludge, two batch tests were conducted with three serum bottles with 200 mL working volume (2 tests and control) were used. Experiments were done in duplicate with an initial substrate to biomass ratio (S/X) of 4 g COD.g⁻¹ VS which was noticed to be within the reasonable range for hydrogen production [11], [12]. The first test was conducted without pH adjustment (initial pH of 4.46), while the second was tested with an initial pH of 5.5. Each batch was supplemented with 0.1 mM NaHCO₃ as a buffer. N₂ gas was purged into serum bottles for 5 minutes to ensure the presence of anaerobic conditions. The sets were incubated at 55 °C for 24 h.

C. Analytical Methods

1) Analytical Measurements

The hydrogen-containing biogas production was determined every hour by passing it through a saturated acidified saline solution to prevent CO₂ dissolution, while the biohydrogen production was determined by passing the biogas through a 3 – 5 % (w/v) NaOH solution to extract the CO₂ and trace gases [13]. The pH was measured at the end of the test by a waterproof tri-meter. The Total COD was determined at the end of the experiment using a Hach (DR 2010) device. TS and VS were determined according to the standard methods [14]. The statistical analysis was performed using Minitab 19.

2) Kinetic Model

The produced volumetric biohydrogen can be modeled using the well-known modified Gompertz equation as follows:

$$VH = VP \exp[-\exp(VR_m \cdot e / VP \cdot (\lambda - t) + 1)] \quad (1)$$

Where VH is the volumetric cumulative hydrogen production at time (t in h) (mL.L⁻¹), VP is the volumetric hydrogen potential (mL.L⁻¹), VR_m is the maximum volumetric hydrogen production rate (mL.L⁻¹.h⁻¹), and λ is the lag period (h).

3) COD Mass Balance

The COD mass balance can be calculated based on the effluent COD, the COD of the generated biomass, and the COD of the hydrogen gas produced as shown in (2).

$$R = (\text{COD}_{\text{out}} + \text{biomass} + \text{H}_2) / \text{COD}_{\text{in}} \quad (2)$$

Where R is the COD recovery (%), COD_{out} is the COD after the fermentation period (g.L⁻¹), biomass is the COD content of the generated sludge using a conversion of 1.42 gCOD.g⁻¹ VS (gCOD.L⁻¹), H₂ is the COD equivalent of the produced hydrogen (gCOD.L⁻¹), and COD_{in} is the applied COD.

4) Energy Calculations

The energy that could be obtained from the dark fermentation of the vinasse can be calculated according to (3) and (4) [15], [16].

$$\text{SEP} = \text{HY} \cdot \text{S} \cdot \text{LHV} \quad (3)$$

$$\text{SE} = \text{SEP} \cdot \eta / k \quad (4)$$

Where SEP is the specific energy potential (MJ/m³vinasse or KWh/m³vinasse), HY is the hydrogen yield (L H₂.g⁻¹ COD applied), S is the applied COD (g.L⁻¹), LHV is the lower heating value of the hydrogen (10.71 KJ.L⁻¹ H₂), η is the electrical conversion (40%), and k is a unit conversion factor from MJ to KWh (3.6).

Results and Discussion

A. The Effect of Initial pH on the Biohydrogen Production

The biohydrogen produced from the two batches (minus the control) along with the fitted model are shown in Fig. 1. It can be seen from Figs. 1 and 2 that the difference in the production was insignificant. The maximum cumulative hydrogen production within 24 h was 3.85 L.L⁻¹ vinasse at an initial pH of 4.46. This was higher than that obtained from [17] who studied the biohydrogen production of vinasse with 30 % leachate at 37 °C and an initial pH of 7.0. However, the maximum mean of 1.54 ± 1.27 L-H₂.L⁻¹ vinasse was obtained from the batch with an initial pH of 5.5 comparing to 1.3 ± 1.53 L-H₂.L⁻¹ vinasse when fermenting at an initial pH of 4.46.

Table 1 presented the kinetics of the modified Gompertz model and the final pH of the two batches. According to the model, the initial pH of 5.5 had the maximum hydrogen potential (6.97 L.L⁻¹), a minimum lag time of 7.3 h, and corresponding production rate of 186.6 mL.L⁻¹.h⁻¹, while the maximum production rate was 272 mL.L⁻¹.h⁻¹ at an initial pH of 4.46 corresponding to VP and lag time of 5.6 L.L⁻¹ and 10.3 h, respectively. The changes in the pH during the fermentation were 0.32 and 0.22 unit at an initial pH of 4.46 and 5.50,

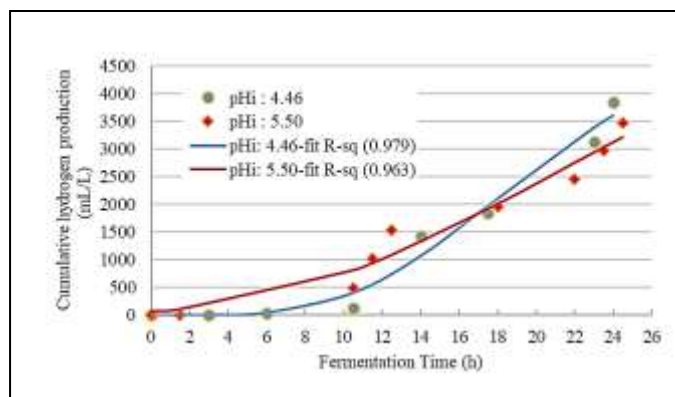


Figure 1. Cumulative thermophilic hydrogen production at different initial pH fitted by the modified Gompertz equation

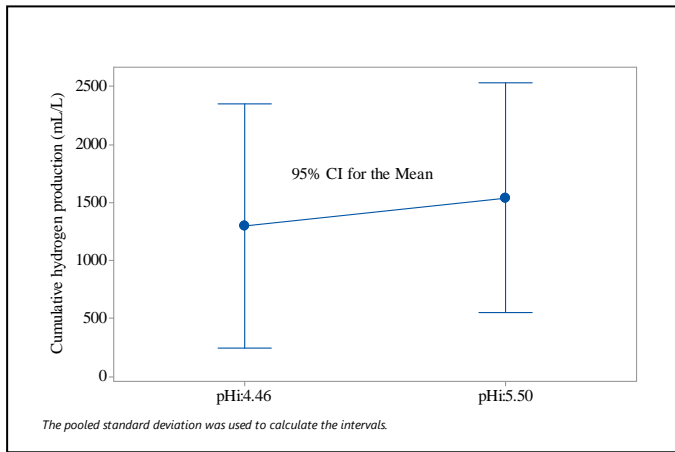


Figure 2. The ANOVA analysis of the hydrogen production from two anaerobic fermentations (at pH of 4.46 and 5.5), pHi: initial pH

respectively. The detected small changes were consistent with that was reported by [12].

Fig. 3 shows the hydrogen production rate and content profiles along the fermentation period. The production rate profiles of the two batches were similar with a highest rate of $722 \text{ mL}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$ at an initial pH of 4.46. Several studies reported an ethanol-type fermentation at such low pH (<4.5) as the cells produced ethanol to resist the low pH [18]. This type of fermentation could surpassed the other types such as butyrate-type fermentation (preferred at pH 5.0 – 5.5) in terms of hydrogen production [19]. It can be noticed from the figure that the fermentation of the vinasse with an initial pH of 5.50 peaked twice and reached 528 and 500 $\text{mL}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$ after 11.5 and 24 h, respectively. Whereas, the Peaks of the hydrogen rate at the initial pH of 4.46 were 370 and $722 \text{ mL}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$ at 14 and 24 h, respectively. The hydrogen content in the biogas at a pH of 4.46 was higher than that of the pH of 5.5 with a maximum value of 86 % reached after 10.5 h of the fermentation. In general, the average hydrogen contents were 75 ± 6 and 57 ± 10 % found in the vials with initial pH of 4.46 and 5.50, respectively.

Considering the hydrogen yield, Fig. 4 shows the relation between the HY and the VS/TS ratio at each initial pH. It can be deduced from the figure that there was a positive correlation between the two parameters i.e. the hydrogen yields at initial pH of 4.46 and 5.50 were 52.21 and $46.98 \text{ mL}\cdot\text{g}^{-1}$ COD-applied at VS/TS ratios of 0.749 and 0.724, respectively. These yield values in the range reported by [20] who found HY of 27.72 and $64.06 \text{ mL}\cdot\text{g}^{-1}$ COD-applied when fermenting raw and diluted vinasse, respectively.

TABLE I. KINETICS OF THE MODIFIED GOMPERTZ MODEL DESCRIBED THE 24-H THERMOPHILIC HYDROGEN PRODUCTION FROM UNDILUTED VINASSE AT DIFFERENT INITIAL pH

Batch	Initial pH	Final pH	Kinetics of the modified Gompertz model			
			VP (mL/L)	VR _m (mL/L.h)	λ (h)	R ²
A	4.46	4.14	5622.32	272.31	10.25	0.979
B	5.5	5.28	6974.59	186.62	7.29	0.963

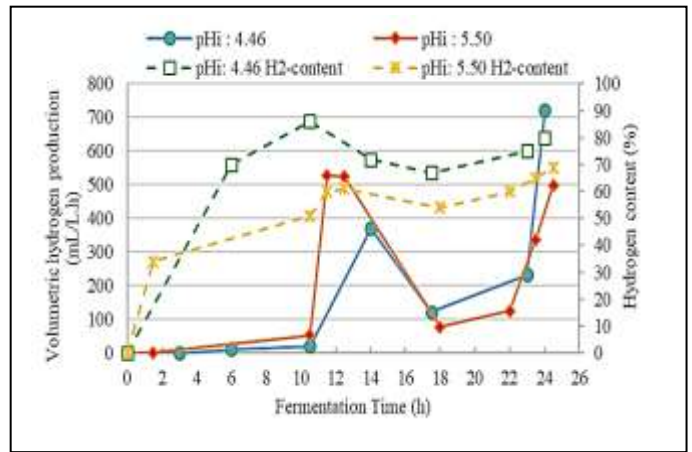


Figure 3. Volumetric hydrogen production and contents in the fermentation vials

B. The COD Mass Balance

The COD mass balance is shown in Table 2. The COD recovery values were 93.32 and 92.73 at initial pH of 4.46 and 5.5, respectively. This was consistent with that found by [11]. The high recovery values confirmed the data reliability. The generated biomass in the batch with 5.50 initial pH was five times greater than that of the batch with 4.46 initial pH. The higher produced biomass could be an evidence of using more energy in the assimilation and growth process [21].

C. The Energy Gain from The Process

The energy analysis is an important tool to assess the viability of the fermentation process. Fig. 5 illustrates the specific energy potential of the dark fermentation of the vinasse. The SEP values that could be obtained per a cubic meter of vinasse at pHi_{in} of 4.46 and 5.50 were 41.2 and 37.1 MJ, respectively, corresponding to specific electricity production per a m³ of vinasse of 16.5 and 14.8 MJ (4.6 and 4.1 KWh), respectively. Ren et al. [22] obtained a highest energy of 12.89 MJ/m³ from the ethanol-type fermentation comparing to the butyrate-type. Moreover, Garcia-Depraect et al. [23] reported an electricity potential from the biohydrogen produced through the dark fermentation of the tequila vinasse of 4.36 KWh per a cubic meter of the vinasse.

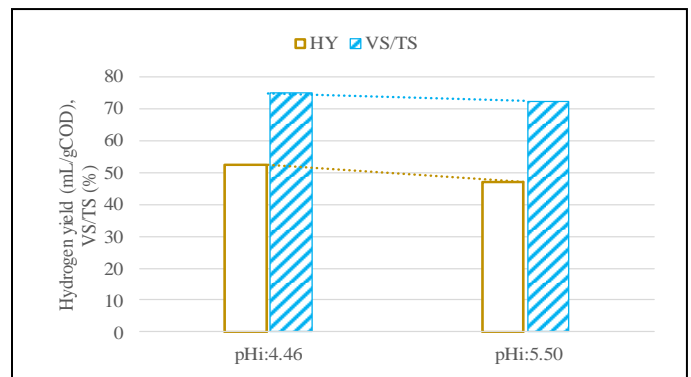


Figure 4. Hydrogen yield and the VS/TS ratio of the sludge after fermentation at different initial pH

TABLE II. COD MASS BALANCE

Batch	Initial pH	COD Mass Balance				
		COD_{in} (g/L)	COD_{out} (g/L)	H_2 (gCOD/L)	Biomass (gCOD/L)	Recovery (%)
A	4.46	73.65	65.70	2.75	0.29	93.32
B	5.5	73.65	64.37	2.47	1.46	92.73

References

Locally, the Egyptian Al-Hawamdyia distillation factory generates about 1500 – 2000 m³ vinasse.d⁻¹. Consequently, the factory can daily produce about 6.863 – 9.151 MWh. According to [24], the average electricity consumption per capita in Egypt in 2018 was 1.6 MWh.

Conclusion

The biological hydrogen production through the thermophilic dark fermentation of the sugarcane vinasse could be remarkable when applying the suitable environmental parameters such as the pH. Thus the effect of two initial pH values were studied i.e. the inherent vinasse pH of 4.46 and the pH of 5.50 (by adding NaOH). In most cases, the initial pH of 4.46 had the better performance since the fermentation pH range (4.46 – 4.14) was reported to be suitable for the ethanol-type fermentation and the corresponding highest hydrogen production [19]. The maximum volumetric hydrogen production rate, hydrogen yield, and content were 3.85 L.L⁻¹, 52.9 mL.g⁻¹ COD_{in}, and 86%, respectively at the initial pH of 4.46. However, the thermophilic dark fermentation of the vinasse with an initial pH of 5.5 achieved a higher COD removal efficiency of 12.6 %. On the other hand, the highest energy yield in the form of electrical power that could be obtained from the fermentation process at an initial pH of 4.46 was about 4.6 KWh per a cubic meter of processed vinasse which might render the process economically feasible in terms of the energy gain and the chemical saving. In brief, the obtained results clarify the potential of using the thermophilic dark fermentation in treating the raw vinasse for the purpose of producing biohydrogen gas without using chemicals to raise the vinasse initial pH. In addition, the high COD acidogenic effluent can be valorized through subsequent biogas production unit.

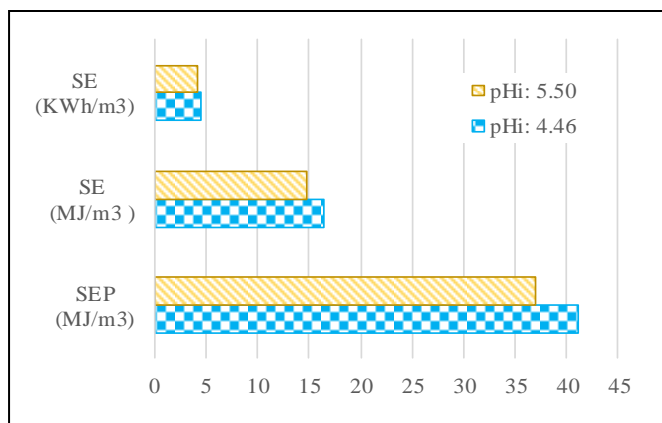


Figure 5. Energy Potential of the produced hydrogen

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