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Analysis of the physicochemical process in the production of biogas from equine manure

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Abstract. The present research aims to evaluate the physicochemical variables involved in the anaerobic digestion process to produce methane from manure on an agricultural farm; the farm has 2 equines that generate 12 Kg of manure per day. A manure sample was collected, and the following physicochemical parameters were determined: total solids, volatile solids, chemical oxygen demand, and pH. A tubular household biodigester was then implemented, consisting mainly of a polyethylene geomembrane that stores the organic matter and in which anaerobic digestion takes place. The performance of the biodigester was determined by the removal of organic matter quantified by volatile solids and chemical oxygen demand in the biodigester influent and digestate, of which removal of 82% of volatile solids and 74% of chemical oxygen demand was achieved. The average biogas production was 0.5 m³/day, and its lower heating value was 26,000 kJ/m³. The pH level of the biodigester was within the range of 6-7, in order to keep the methanogenic bacteria active, in charge of carrying out physicochemical process that guarantees anaerobic digestion and thus, the production of biogas.

1. Introduction

According to statistics from the “Instituto Colombiano Agropecuario (ICA)”, Colombia, there are currently 1.6 million equines, being one of the most abundant species in the Colombian countryside [1]. An equine can weigh between 400 Kg and 700 Kg and can generate daily about 7 Kg of manure for every 100 Kg of weight of the sow [2]. Currently, manure from livestock activities is used as fertilizer without any treatment. This incorrect disposal of manure can generate problems such as bad odors, the attraction of vectors, emission of greenhouse gases (GHG), contamination of water bodies with pathogenic microorganisms, and soil acidification [3].

An alternative for the stabilization of organic matter present in horse manure is anaerobic digestion (AD) since this waste is characterized by a moisture content of approximately 25 wt%, pH of 8.2 and a carbon to nitrogen ratio (C/N) of 23:1 [4]. AD is a complex physicochemical and biochemical reaction carried out in an oxygen-free environment by several types of microorganisms [5] where bacteria decompose organic matter to produce energy in the form of biogas, generally used in rural areas to replace firewood, natural gas or propane gas, and digestate, used as biofertilizer.



The "Tierra Guane" farm is located in the municipality of Girón, Colombia, at 959 m.a.s.l. and has an area of 2 hectares. The farm is mainly dedicated to agricultural activities, has 2 horses and its manure is used as fertilizer in the planting of cut grass. The organic waste produced by this livestock activity causes negative environmental impacts associated with manure management. Concerning the geosphere, the permanent disposal of any type of manure on the soil exceeds its nutrient assimilation capacity, which causes infiltration into groundwater and soil acidification [6]. The main effect of manure on the hydrosphere is contamination caused by the content of pathogenic microorganisms such as *Escherichia coli* that cause different diseases in the human population [6]. Finally, one of the effects produced by unstabilized manure in the atmosphere is the emission of GHG such as methane (CH₄), carbon dioxide (CO₂), and hydrogen sulfide (H₂S), which cause global climate change [7]. CH₄ is a GHG 23 times more potent than CO₂, and manure contributes 16% of global emissions [6].

The "Tierra Guane" farm lacks natural gas supply because it is in an area of difficult access and as for the use of fertilizers, the owners must purchase chemical fertilizers to meet the nutritional requirements of the crop. Therefore, to meet the needs of the farm, this research seeks to take advantage of the equine manure to generate gas and obtain organic fertilizer, product, and a by-product of anaerobic digestion, respectively; similarly, this paper aims to demonstrate the contribution of physicochemical processes in the transformation of agricultural biomass into renewable energy, presenting results that can serve as a basis for future research by the academic-scientific community

2. Methodology

The livestock practice of the farm consists of 2 equines that have a daily feeding period of 8 hours, they are boarded 16 hours a day. The manure produced in the stables was collected and weighed daily for one month. The manure was sampled and characterized for total solids (TS), volatile solids (VS), chemical oxygen demand (COD), and pH. VS were measured according to the protocols described by the standard methods published by the American Public Health Association, the American Water Works Association and the Water Environment Federation [8]. COD was measured by the calorimetric method. volatile fatty acids (VFA), and total alkalinity (TA) were quantified by titration according to the protocol proposed by Jobling Purser, *et al.* [9]. The pH was determined using a pHmeter Metrohm 691.

The biodigester was designed with the most important criteria: (a) temperature, which was measured with a sensor that recorded its value every 12 hours for 30 days; (b) hydraulic retention time (HRT), which was determined using the table reported by Martí-Herrero [2]; (c) flow rate (Q), which is the mixture fed to the biodigester and is composed of manure and water, in a 1:3 dilution as reported by Castro, *et al.* [10] for working with equine manure; (d) volume, Martí-Herrero [2] indicates that the total volume (V_T) of the digester should house a liquid part (75%) and a gaseous part corresponding to the gas hood (25%), the volume of liquid (V_L) is the product of two known variables as shown in the Equation (1), and from the total volume, the dimensions of the biodigester can be found, considering that it is cylindrical, using Equation (2). The length (L) depends on the perimeter of the coil, which is generally 4 m, and lastly r corresponds to the radius of the digester.

$$V_L = \text{HRT} * Q, \quad (1)$$

$$L = (V_L/0.75)/(3.1415 * r^2). \quad (2)$$

The installation was carried out following the recommendations described by Martí-Herrero [2]. It was installed near the manure disposal site, close to the availability of water and the use of sunlight. Once the biodigester was installed, the start-up and stabilization of the process began. To start up the digester, an initial load of 4 m³ of the 1:3 mixture was made. Then the load was allowed to stabilize until the biogas production was verified (35 days approx.) and the daily feeding of the determined flow was started.

After the start-up and stabilization of the biodigester, the volume of biogas produced was quantified with a G1.6 diaphragm gas meter. Once stable biogas production was achieved, the anaerobic digestion

process was monitored for two months. pH, TS, VS, COD, VFA, and TA were measured in the influent and digestate to determine reactor performance and evaluate the stability of the process. One of the important parameters was pH, since this value directly affects the biochemical and physicochemical functioning of the DA, since its variations have an impact on the activity of the microorganisms.

The lower calorific value (LCV) of biogas was calculated as shown in Equation (3). Finally, the energy savings represented by the use of biogas were determined using the following Equation (4).

$$\text{LCV}_{\text{biogas}} = \text{LCV}_{\text{methane}} * \frac{\% \text{ methane}}{100}, \quad (3)$$

$$\% \text{ Energy savings} = \frac{\text{Energy supplied by biogas}}{\text{Farm energy consumption}} * 100, \quad (4)$$

where, the energy supplied by the biogas corresponds to the theoretical energy contribution of the biogas produced, and the energy consumption of the farm was determined from the consumption of propane gas for one month. The energy contribution was estimated based on the LCV of each gas.

3. Results and discussion

After quantifying the equine manure, it was determined that between 19 Kg/day and 24 Kg/day were available to feed the biodigester. It was also established that this manure has the following organic matter and stability characterization: 242.44 g VS/Kg and 6.9 pH, respectively. The organic matter available for degradation is shown in the VS concentrations, which allows identifying the equine manure as a source of carbon available for AD. The pH is in the appropriate range for the AD process without the risk of digester acidification [11].

In the first month of stabilization, the 1:3 dilution reported in the literature with the best biomethanization potential caused clogging in the feed pipe, therefore, it was changed to guarantee the proper operation of the digester. Thus, different dilutions were tested, and it was obtained that the ratio 1:7 manure:water was adequate since no clogging in the piping occurred. Subsequently, the feed flow rate was modified so as not to affect the volume of the installed digester. The operating parameters were a temperature of 23 °C - 25 °C, HRT of 45 days-55 days, availability of manure of 10 Kg/day -12 Kg/day, a dilution ratio of 1:7 manure:water, an inlet flow rate of 80 L/day - 96 L/day, a total volume of 5.8 m³, low-density polyethylene material for the digester and general dimensions of 4.5 m length and diameter of 1.3 m.

The performance of the biodigester was determined by the removal of organic matter quantified by VS and COD in the biodigester influent and digestate; removal of 82% of VS was achieved as shown in Figure. It is important to highlight that this high removal is partly influenced by the retention of solids inside the biodigester, this phenomenon generally occurs in domestic digesters without agitation [12]. Furthermore, the results obtained are comparable with those reported by Lansing, *et al.* [13], who obtained 80% and 83% removals for domestic digesters fed with bovine and swine manure, respectively [12].

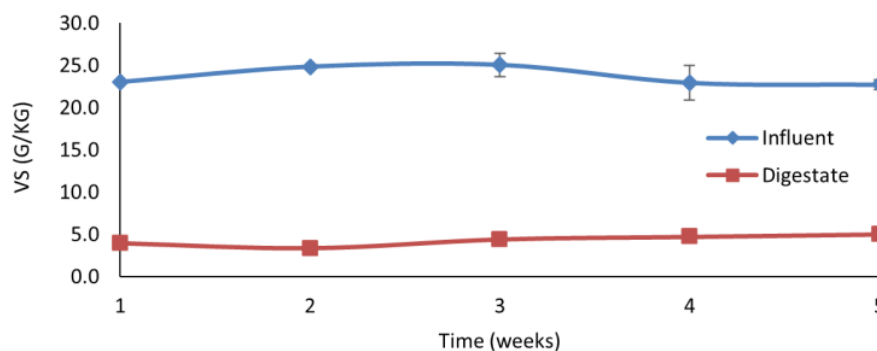


Figure 1. Behavior of VS in the process.

The VS/TS parameter indicates the percentage of biodegradable matter. According to the literature, for rural digesters fed with cattle manure at mesophilic conditions, the percentage of biodegradability is between 43% and 66% [12-14]. This wide range is mainly due to variations in organic load fed to the digester. In this study the VS/TS ratio was 66%, indicating that the stability of the digestate is somewhat low due to its concentration of biodegradable material.

As shown in Figure, a 74% COD removal was achieved when the biodigester was operated at a temperature of 23 °C - 25 °C. Lansing, *et al.* [13] obtained a COD removal of 86% and 92% for bovine and swine manure, respectively, when the digesters operated at 26 °C. However, the results of this study show a high transformation of the organic matter present in equine manure when fed to a domestic biodigester.

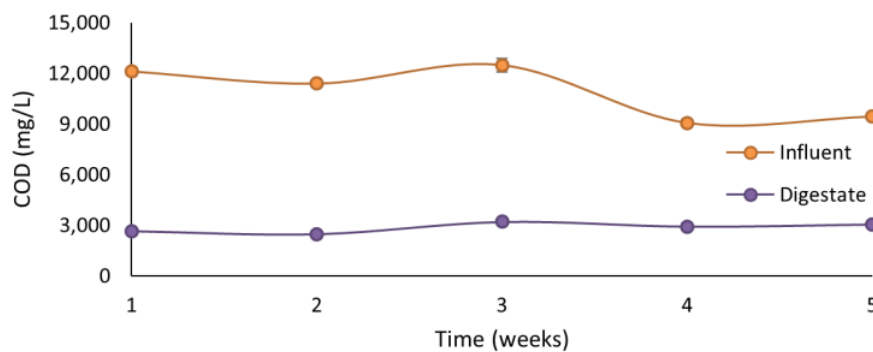


Figure 2. Behavior of COD in the process.

The anaerobic digestion process that occurs in the digester has three variables that are related to stability: VFA, pH, and buffer capacity (VFA/TA). VFA represents readily biodegradable soluble organic matter. Figure shows that the acid concentration in the digestate from the biodigester was between 1200 mg/L - 1500 mg/L. These values remain within the acidification inhibition limit of 1500 mg/L for continuous reactors [15]. For their part, Risberg, *et al.* [16] stated that higher values around 500 mg_{acetic acid}/L can have inhibitory effects on the soil. Therefore, the digestate should be stabilized and diluted, if necessary, before its application, in case it is used for agricultural purposes.

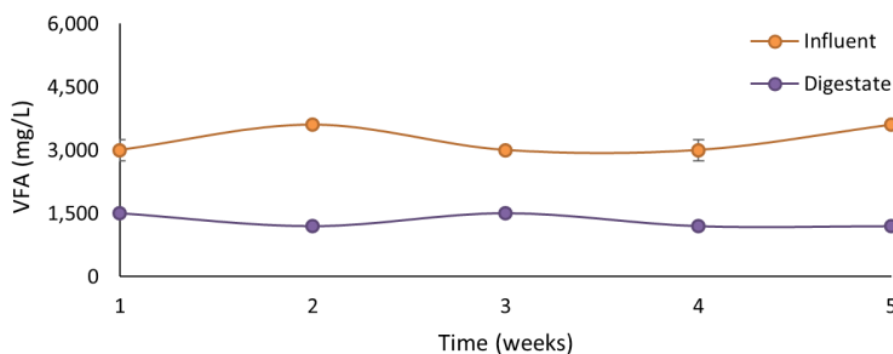


Figure 3. Behavior of VFA in the biodigester.

In this study, the pH of the influent and digestate is maintained in a range of 6-7, as shown in Figure 4. Behavior of pH, recommended values for the anaerobic digestion process [11]. This pH value indicates that the process in the digester is proceeding properly. In addition, if the digestate is used in agriculture, the pH is compatible with common acidity measurements reported for agricultural soils [12]. On the other hand, the VFA/TA ratio for the influent and digestate during the 5 weeks of the study remained in the stability range of an anaerobic process between 0.2-0.8 [17].

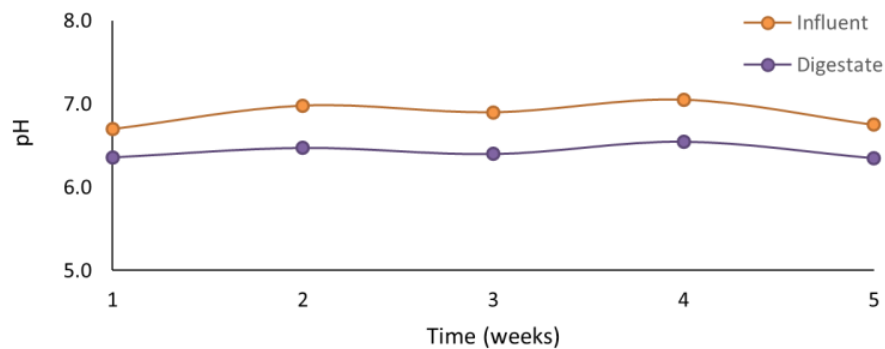


Figure 4. Behavior of pH in the biodigester.

Finally, the behavior of biogas production from horse manure in a domestic digester is shown in Figure. The first 45 days reported in the figure correspond to the start-up of the digester from the moment biogas production was verified. Stabilization is not reached at this stage because the HRT is not exceeded. However, the methanogenesis process is being developed, since it is the last biochemical stage, in which the different groups of methanogenic bacteria participate to produce methane, through the microorganisms that digest the organic matter of the effluent. After 45 days, an average production of 0.5 m^3 of biogas per day is reached.

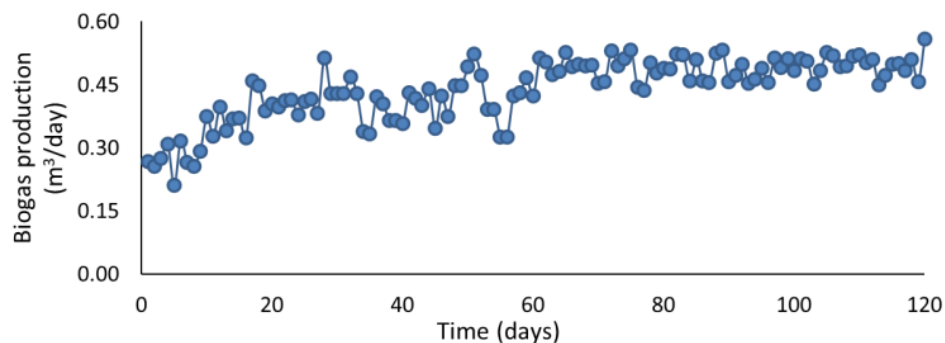


Figure 5. Biogas production from equine manure.

The efficiencies of the digester and the anaerobic digestion process are defined by the biogas production rate (BPR) and the specific biogas production (SBP), respectively [18]. In this study, an SBP of $0.19 \text{ m}^3_{\text{biogas}}/\text{Kg VS}$ and a BPR of $0.10 \text{ m}^3_{\text{biogas}}/\text{m}^3_{\text{digester}} \text{ day}$ were obtained by feeding the digester an organic loading rate (OLR) of $0.5 \text{ Kg VS}/\text{m}^3_{\text{digester}} \text{ day}$.

Castro, *et al.* [10] reported efficiencies of $0.13 \text{ m}^3_{\text{biogas}}/\text{m}^3_{\text{digester}} \text{ day}$ for the digester and $0.15 \text{ m}^3_{\text{biogas}}/\text{Kg VS}$ for the anaerobic digestion process obtained from bovine manure with 35 days of HRT and an OLR of $0.7 \text{ Kg VS}/\text{m}^3_{\text{digester}} \text{ day}$. In comparison, the current study presented a higher efficiency in the anaerobic digestion process, indicating that the equine manure presented an adequate response for biogas production. However, a lower efficiency was presented in the digester, the latter because the organic load fed is also lower.

On the other hand, Garfí, *et al.* [12] located the digester at 2800 m.a.s.l. and had a higher HRT (90 days) and lower OLR ($0.34 \text{ Kg VS}/\text{m}^3_{\text{digester}} \text{ day}$), which led to efficiencies of $0.12 \text{ m}^3_{\text{biogas}}/\text{m}^3_{\text{digester}} \text{ day}$ and $0.32 \text{ m}^3_{\text{biogas}}/\text{Kg VS}$. In comparison, the current study had lower efficiencies in the digester and the anaerobic digestion process, due to the shorter retention time.

As can be seen, the efficiencies are expressed as a function of the design variables such as temperature, HRT, and OLR. However, it can be concluded that the horse manure was adjusted to the anaerobic digestion process in a domestic digester and that the efficiencies are comparable with those reported in the literature working with other types of manure.

The biodigester installed in the "Tierra Guane" farm valorized the organic matter present in the equine manure, reaching a daily biogas production of 0.5 m³ on average. This biogas was used for cooking food, replacing the propane gas used before the biodigester was installed.

The biogas obtained in a low-cost biodigester operated at mesophilic conditions generally reaches a methane content between 55% and 65% [10,12,13]. According to Hernández [19], biogas with a methane content higher than 55% upon combustion can have a lower heating value (LHV) of approximately 26,000 kJ/m³. Therefore, the energy supplied by biogas is approximately 390,000 kJ/month. As for propane gas, it has an LHV of 46,367 kJ/m³ [10], and the consumption of the farm before the implementation of the biodigester was 14 m³/month. According to the above, an average energy saving of 60% is achieved with the production of biogas.

The installation cost of the biodigester was US\$ 273.13 considering installation materials, feed tank, biogas reservoir, and rainwater collection tank. Operating costs are not taken into account because the feed is diluted with collected rainwater, and the system does not require agitation, heating, or maintenance. The implementation of the biodigester results in an economic saving of US\$ 7.02/month, which corresponds to the reduction in the purchase of commercial propane gas. Considering that the useful life of a low-cost polyethylene biodigester is 10 years [20], the payback period for the investment is 3.25 years.

4. Conclusions

The domestic biodigester with a total volume of 5.8 m³ for the anaerobic stabilization of the equine manure generated at the "Tierra Guane" farm, reduced the environmental problems caused by the manure and obtained an organic load removal of 82% and 74% in terms of volatile solids and chemical oxygen demand, respectively. As for the stability variables, the volatile fatty acids in the digestate remained between 1380 mg/L and 1500 mg/L and the pH between 6 and 7, remaining between the adequate ranges for anaerobic digestion.

The organic matter present in the equine manure was valorized, obtaining an average biogas production of 0.5 m³ (*i.e.*, 0.041 m³/Kg manure). Similarly, the efficiencies of the digester and the anaerobic digestion process of 0.10 m³_{biogas}/m³_{digester} and 0.19 m³_{biogas}/Kg volatile solids, respectively, were obtained. The energy supplied by this biogas was 390,000 kJ/month, achieving an average monthly energy saving of 60%, which is equivalent to an economic saving of US\$ 7.02/month and the payback period for the biodigester investment is 3.25 years.

Finally, the results of the present study show the importance of controlling the physicochemical variables to achieve a high conversion of the organic matter present in the equine manure into biogas, which demonstrates that anaerobic digestion is a technically and economically viable alternative for the use of equine manure, which could be implemented in similar farms, allowing the recovery of energy and nutrients from this livestock waste.

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