Monitoring Anaerobic Digester Parameters of Biogas Production from Corn (Zea mays) Leaf and Stalk Residual Biomass

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Abstract

Anaerobic digestion (AD) is a well-known technology with recognized environmental benefits for renewable energy generation from organic wastes. This work is focused on monitoring key variables widely considered in AD as volatile fatty acids (VFA), total alkalinity (TA), pH, and total reducing sugars (TRS) in order to study process stability. Corn leaf and stalk biomass were selected as substrate with particle size higher than 2 mm and with an inoculum to substrate (I:S) ratio of 3:1. Alkaline pretreatment was also carried out to evaluate its effects on biogas production and anaerobic digester stability. Experimental results for corn stalk biomass indicated an improvement in buffering capacity of substrate due to the total alkalinity data was in desirable range. The VFA/TA ratio exhibited values between 3.11-4.55 and 3.11-3.47 for control and pretreated biomass, respectively. For corn leaf biomass, it was found VFA/TA ratio in the range 2.7-4.13 and 2.16-3.12 for pretreated and control sample, respectively, which suggested that pretreatment with NaOH affects anaerobic digester stability. In general, corn residual biomass showed promising results allowing high biogas production by a stable AD process without significant VFA accumulation and variations in pH.

Keywords: anaerobic digestion, alkaline pretreatment, biomass, biogas
1. Introduction

Biogas has been emerging as energy source that can lessen the greenhouse gases emissions in comparison with traditional fossil fuels [9]. The production of this biofuel from AD is known to be the most cost-effective and environmentally-friendly alternative [13]. AD of agricultural waste has long been investigated and implemented in full-scale facilities [12]. Residues from many traditional crops are considered feedstock for this purpose such as coffee husk, corn stover, wheat and rice straw, among other lignocellulosic materials [7, 4]. They have the advantage of high availability and non-competition against food crops for land and fresh water [8]. In addition, these residual biomasses create an integrated waste management system which reduces the water pollution [3]. One of the major challenges for biogas from lignocellulosic feedstocks is its complex chemical composition that resists hydrolysis stage and conversion by anaerobic microorganisms [15]. On the other hand, the amount of biogas produced in AD may be altered by digester stability, which is affected by sudden changes in temperature, hydraulic or organic overloading and the presence of inhibitory substances [10]. The aim of this work was to measure key variables as VFA, pH, TA, and TRS that exhibit an important role for the anaerobic digester stability in order to evaluate the suitability of this technology to produce biogas from corn residual biomass.

2. Materials and Methods

Corn stalk and leaf are lignocellulosic by-products of the agroindustrial processes which were the focus materials for this study. The corn stover was obtained in the rural area of Bolivar department and separated into stalks and leaves. The substrates were prepared by means of a wash with water, solar energy drying and milling to reduce particle size above 2 mm. The inoculum was a mixture (80:20) of rumen liquid and pig manure, containing a variety of anaerobic microorganisms in a suitable medium (water and minerals). The I:S ratio was set to 3:1 according to the study developed by Parra-Orobio [11].

Anaerobic digestion: The AD assay was performed during 15 days at room temperature (28°C). The bioreactor consisted of 500 mL glass bottle with 350 mL of reaction volume. To ensure an anaerobic environment inside the reactor, a purge with nitrogen was necessary. Biogas production in the recipient was quantified by daily measurement using liquid displacement method. The TRS were measured by 3, 5-dinitrosalicylic acid (DNS) colorimetric method based on reducing DNS by reducing sugar as glucose detectable in absorbance lecture with 540 nm wavelength. VFA and TA were determined according to methodology described in the literature [6]. To accelerate the hydrolysis step in AD process, several approaches for organic substrates pretreatment have been proposed. In this study, alkaline pretreatment was carried out by adding 1% wt. NaOH solution (15 mL per g substrate) into an autoclave during 30 minutes at 121 °C.
3. Results and Discussion

Regulation of VFA, TA, TRS, and pH allow to study anaerobic digester stability. It has been pointed out that AD process efficiency is strongly affected by operational and environmental conditions such as temperature, pH, VFA, among others [9]. The VFA/TA ratio and pH provides information about process stability in order to achieve an efficient methanogenesis [5]. It has been reported suitable values of 0.1-0.4 for VFA/TA ratio and neutral pH. VFA above 6,000 mg/L causes inhibitory effects during AD. In addition, common values for total alkalinity are in the range 1,500-7,500 mg CaCO₃/L.

Corn stalk biomass: Figure 1 shows that VFA concentration increased gradually after 3 days when pretreated biomass is used. These results suggested that hydrolytic stage occurred slowly over time, which enhances system stability and limits global degradation rate reducing accumulation of VFA in reactor. The concentration of CaCO₃ was in the desirable range of 2,500-5,000 mg CaCO₃/L, which provided a higher buffering capacity for which a much larger increase in VFA can be obtained with a minimum drop in pH [14].

![Figure 1. Production of VFA and TA from pretreated and control corn stalk biomass against time](image)

For biomass without alkaline pretreatment (control), the stages in AD lasted longer in comparison to pretreated biomass. Although acidogenesis was observed between 6-9 days, the acid production was carried out since the setting up for biomass pretreated with NaOH. Lignin protects cellulose and hemicelluloses for enzyme attack that affects TRS production, hence, pretreatment is required to improve this biodegradability [13]. As is shown in Figure 2, TRS concentration for pretreated biomass is higher than control biomass, indicating than alkaline pretreatment facilitates the hydrolysis stage, maximizing substrate accessibility [16].
The VFA/TA ratio varied in the range 3.11–4.55 and 3.11–3.47 for control and pretreated biomass, respectively, as is shown in Figure 3. These results indicated that TA exhibited lower values in comparison to VFA, which affected pH buffering (pH values below 6). AD process is very sensitive to pH fluctuations in the system [9]. The decrease of pH suggested an accumulation of VFA at high organic loading [2]. However, it was not observed significant variations over time that hinders methanogenesis stage. Figure 4 shows that the highest amount of methane (209.75 and 205.6 mL) was reached on the 15th day. After 10 days, pretreated biomass exhibited greater biogas production than control biomass, which can be attributed to pH and VFA concentration that strongly affect process efficiency.
Figures 4 and 5 illustrate the biogas production and the production of volatile fatty acids (VFA) and total acidity (TA) from pretreated and control corn stalk and leaf biomass, respectively.

**Corn leaf biomass**: The concentration of VFA increased over time reaching the maximum amount (5,190 mg VFA/L) on the 9th day as shown in Figure 5. A reduction in pH was inevitable due to the low concentration of CaCO₃. The hydrolytic stage is more stable for biomass with pretreatment enhancing biogas production kinetic. Figure 6 shows that higher amounts of TRS were obtained for corn leaf biomass without pretreatment than pretreatment biomass, which differed from results obtained with corn stalk biomass. As is shown in Figure 7, VFA/TA ratio varied between 2.7-4.13 for pretreated corn leaf biomass. Control biomass also exhibited a decrease in pH and VFA/TA ratio of 2.16-3.12. However, TA was higher than pretreated biomass enhancing process stability. The instability of AD process induces an overflow of protons that decompose the bicarbonates in the liquid phase to produce CO₂ and decreases the digester pH [10]. Hence, acetogenesis and methano-
genesis steps get hindered due to acidity [1]. Figure 8 shows that the highest amount of methane (271 mL) was obtained for biomass with alkaline pretreatment. In addition, corn leaf was selected as suitable substrate for biogas production due to its satisfactory results in AD.

Figure 6. Production of TRS from pretreated and control corn leaf biomass

Figure 7. VFA/TA ratio and pH against time for pretreated and control corn leaf biomass.

Figure 8. Biogas production from corn leaf biomass against time
4. Conclusions

In this work, monitoring of VFA, TA, TRS, and pH was carried out over time to study anaerobic digester stability for biogas production from corn residual biomass. For corn stalk biomass, it was found that TA exhibited values in desirable range of 2500-5000 mg CaCO3/L, which improve buffering capacity of substrate. The VFA/TA ratio varied in the range 3.11-4.55 and 3.11-3.47 for control and pretreated biomass, respectively. The insignificant variation in pH indicated reducing in VFA accumulation. For corn leaf biomass, it was observed values for VFA/TA ratio in the range 2.7-4.13 and 2.16-3.12 for pretreated and control sample, respectively, which pointed out that AD is more unstable when pretreated biomass is used. The highest biogas production was reached for corn leaf pretreated biomass because of maximization of substrate accessibility in hydrolysis stage. In brief, these results suggested that alkaline pretreatment affects anaerobic digester stability to produce biogas from corn residual biomass.

Acknowledgements. Authors would like to thank financial support provided by University of Cartagena.

References


Received: March 21, 2018; Published: May 2, 2018