

Biogas Potentials of Maize Cob Co-Digested with Animal and Plant Waste under the Effect of Bentonite Catalyst

Mohammed Abubakar Clarkson

Department of Agricultural & Bio-Environmental Engineering, School of Engineering, Federal Polytechnic Bali, P.M.B. 05, Taraba State, Nigeria.

Corresponding author: mcaclarkson455@gmail.com

Abstract

This paper evaluates the effect of various contents of bentonite catalyst (B-cat) on biogas production from lignocellulosic biomass (maize cob), cow dung and food waste. It was hypothesised that the pore and the negatively charged B-cat may likely have a reducing effect on the production of inhibition in the digester. The experiment involved milling of the maize cob and determining some of its chemical composition prior and after the pretreatment. The milled maize cob was co-digested with cow dung and food waste in an airtight digester. The results indicated that highest cumulative biogas production of 561 ml was documented with digester where 2.5 g B-cat was applied one week after the commencement of the experiment. However, when the catalyst was applied at the onset of the experiment, application of 3.5 g B-cat became the most appropriate content with highest cumulative biogas production of 452 ml throughout the entire experiment in that category. ANOVA analysis revealed that the effects of the application doses is statistically significant ($P < 0.05$) at 95% level of confidence irrespective of the time of application. Moreover, when application time of B-cat was delayed by a week, higher biogas out was obtained with lower dose (2.5 g) of B-cat. It is concluded that the introduction of B-cat in the digester one week after the commencement of digestion involving maize cob, cow dung and food waste is appropriate.

Keywords: Maize Cob, Catalyst, Biogas, Lignocellulose, Digestion.

Introduction

Biomass is hydrocarbon material consisting of carbon, hydrogen, oxygen, small traces of sulphur, nitrogen and significant quantities of inorganic species (Yaman, 2004). Agricultural wastes (plant residues and by-products) are collectively referred as lignocellulosic biomass. They have cell walls containing organic components: cellulose, hemicellulose and lignin making-up 75% of the biomass dry matter (Van Acker *et al.*, 2016; Xie *et al.*, 2011). Lignocellulosic building blocks are naturally developed to block their microbial and enzymatic deconstruction. This collective resistance is identified as biomass recalcitrance. It is a result of a sophisticated combination of the crystalline cellulose in microfibrils, heteropolysaccharides, and lignin. This combination varied in different types of lignocelluloses, various compartment of the cell wall, different ages of the plants, and is also affected by the natural and processing phenomena, such as drying and heating. It is therefore important to understand these factors in order to have effective pretreatment and digestion (Taherzadeh & Jeihanipour, 2008).

Bioconversion of agricultural lignocelluloses into biofuels is significantly impeded by their chemical and structural complexities. This challenged the use of lignocelluloses as feedstock in biogas production. Cellulose and hemicellulose transformed into sugars are easily converted to biofuels through established technologies, by adjusting the surrounding matrix before enzymatic conversions of the polymers (Zheng *et al.*, 2009). The anaerobic degradation (AD) process is also described as the biological oxidation of organic matter by the action of specific microorganisms (in the absence of atmospheric oxygen). Organic matter is converted into established end products and at the same time, the process produces biogas (mainly methane and carbon dioxide) that can be valorised energetically. Lately, there has been an outstanding escalation in the variability of the substrates treated by anaerobic digestion (Mudhoo, 2012).

Lignocellulosic pretreatment is a process which converts biomass from its recalcitrant form into cellulose enzyme systems, and makes hydrolysis more effective (Zheng *et al.*, 2009). It could be any process that modifies indirect factors and improve direct factors which increase the availability of cellulose and hemicellulose for microbial activities (Zhao *et al.*, 2012b). Structural complexities are the main factors limiting hydrolysis of lignocelluloses (Zhao *et al.*, 2012b). Esteghlalian *et al.* (2001), Yejun and Hongzhang (2007), Chang and Holtzapple (2000), Himmel *et al.* (1994) and Alvira *et al.* (2010) concluded that digestibility of lignocellulosic substrates is a function of factors such as contents of lignin, hemicelluloses, acetyl group and cell wall proteins. Thus, Zhao *et al.* (2012a) described pretreatment as the process which disrupts the compact structure of lignocellulosic biomass and exposes cellulose fibres, attainable through mechanical comminution, chemical alterations of biomass compositions, biological decomposition, or a combination of these methods. Fundamentally, pretreatment methods used in biomass bioconversions are associated with a number of bottlenecks which include the formation of inhibitory products such as acids, furans, phenols, high particle load, high energy input, and efficient separation of soluble sugars from solid residues (Bajpai, 2016). This brings the need to minimize the extent of these inhibitions on the biogas output and introduction of catalyst (B-cat) is hypothesised to be one of the suitable alternatives.

Objective

The purpose of the present study is to examine the effect of early and late application of B-cat into digester to determine which is appropriate, capable of minimizing digester inhibition.

Materials and Methods

Pretreatment

The biomass samples were milled and passed through 2 mm sieve mesh. Exactly 150 g of milled biomass was mixed with 0.15 L of pretreatment substances (dilute NaOH) at room temperature. The samples were heated to 100°C without stirring in an oven for 1 hours. At

the completion of pretreatment, the samples were be washed in hot water to precipitate the dissolved biomass. The biomass was washed with water at least four times to remove the pretreatment substances. The pretreatment process was performed in triplicate. This is according to the method of (Qiu *et al.*, 2012).

Inoculation of Substrates in the Digester

Inoculum was cultured from fresh cow dung prepared according to the method of Lawal *et al.* (2015). About 500 g of cow dung will be collected from Animal Farm of the Federal Polytechnic Bali and was taken to the laboratory. A sample of 200 g was diluted in distilled water to 10% dry matter and transferred into 2 litre glass bottles. The headspace of the diluted cow dung was flushed with nitrogen gas and closed with a rubber cork and resin. The solution was incubated at 35°C. During the incubation, the solution was degassed by allowing the build-up gas to escape through valve controlled tube. The completely degassed solution was used as inoculum.

Preparation and Introduction of Catalyst into Digesters

The catalyst was prepared from natural clay mined within the premises of the Federal Polytechnic Bali. It was characterised using XRF machine. The clay sample was dried under the sun at an ambient temperature of 35°C to make them amenable to grinding and was reduced to fines by grinding with a laboratory mortar and pestle (Usman *et al.*, 2012). The particulates was sieved with a standard sieve of 80 micrometre and 100 g of sample was placed in a crucible and heated at 650°C for 45 minutes in a furnace and allowed to cool slowly to an ambient temperature. After the slow cooling, the catalyst was introduced into the digesters.

Analytical Methods

Biomass was analysed for extractives, ash content and total solids. Extractives was analysed using LAP (NREL/TP-510-42619), ash content was determined by LAP (NREL/TP-510-42622), total solids of the biomass was determined with LAP (NREL/TP-510-42621) standard analytical procedures.

Compositional Analysis and Determination of Solid Matter

About 2.5 g of raw dried biomass was loaded into the cellulose thimble. 150 ml of acetone was used as solvent for extraction using Soxhlet. Residence times for the boiling and rising stages was carefully adjusted 70°C and 25 minutes on heating mantle for a 4-hour run period. After extraction, the sample was air dried at room temperature for few minutes. Constant weight of the extracted materials was achieved in a convection oven at 105°C. The %(w/w) of the extractives content was evaluated as the difference between the raw extractive-laden biomass and extractive-free biomass. Similar to extractives, the

determination of hemicellulose, cellulose, and lignin followed the method of Adeeyo *et al.* (2015).

Analysis for Biogas

Biogas was measured daily until when no gas is produced using Liquid Displacement method as shown in Figure 1.

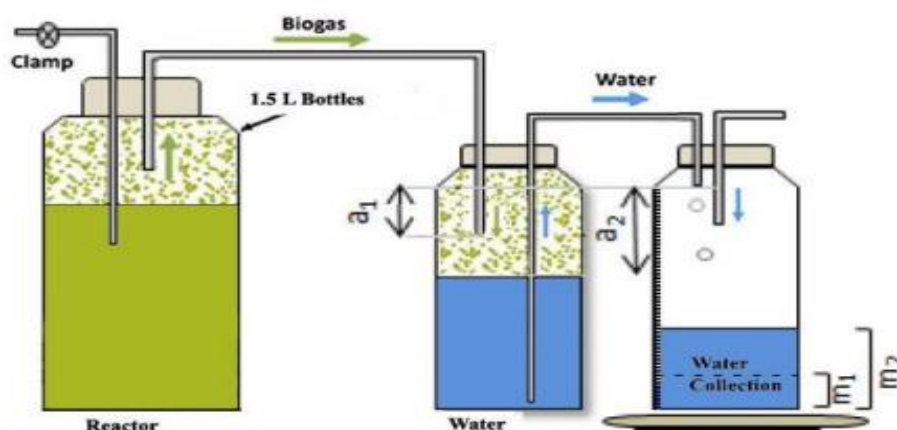


Figure 1. Digester set up showing quantification by positive displacement method (Najafi *et al.*, 2019).

Results and Discussion

Influence of Pretreatment on Biomass Chemical Composition

The information in Table 1 is the result of chemical composition of treated and untreated lignocellulosic biomass. The data illustrated that there is substantial depolymerisation of the lignocellulosic biomass due to pretreatment.

Table 1. Some chemical properties of treated and untreated biomass

Parameters	Maize cob samples	
	Treated	Raw
Total solids (%)	96.27±1.11	94.84±0.23
Volatile solids (%)	64.65±3.24	32.33±1.28
Hemicellulose (%)	27.12±0.69	33.73±1.04
Cellulose (%)	38.03±0.90	43.57±1.49
Lignin (%)	7.01±0.08	9.56±0.40
Ash (%)	33.35±3.24	67.67±1.28

From the table, about 6% of hemicellulose in maize cob was solubilised while about 5.5% of cellulose was degraded. Also, about 26.7% delignification was achieved for maize cob after pretreated. The ash content in the treated biomass was 50.7% lower than the content in the

raw maize cob. This disparity is large and could be explained by high reactivity between the biomass constituents and the pretreatment substance. This may partly be responsible for improvement of biogas production.

Effects of Application Time of B-cat on Biogas Production

Application at the Beginning of the Experiment

In a study on catalyst effect on biogas and biomethane production from maize cob and soybean straw, Clarkson (2023) recommended for studies that will look at the effects of the introducing catalyst at different times into digester to determine whether interesting output may emerge. Here, B-catalyst was introduced at the beginning and at one week of the experiment to determine if this difference in application time could cause significant change in the biogas production. The information in Figure 1 is the results of biogas production from maize cob co-digested with cow dung and food waste under the influence of B-cat introduced at the beginning of the experiment at the rates of 2.5, 3.5 and 4.5 g. Findings revealed that the digester where maximum production rate of 39 m/day biogas was produced is also the digester with highest gas output compared to all other treatments and the control as shown in Figure 2.

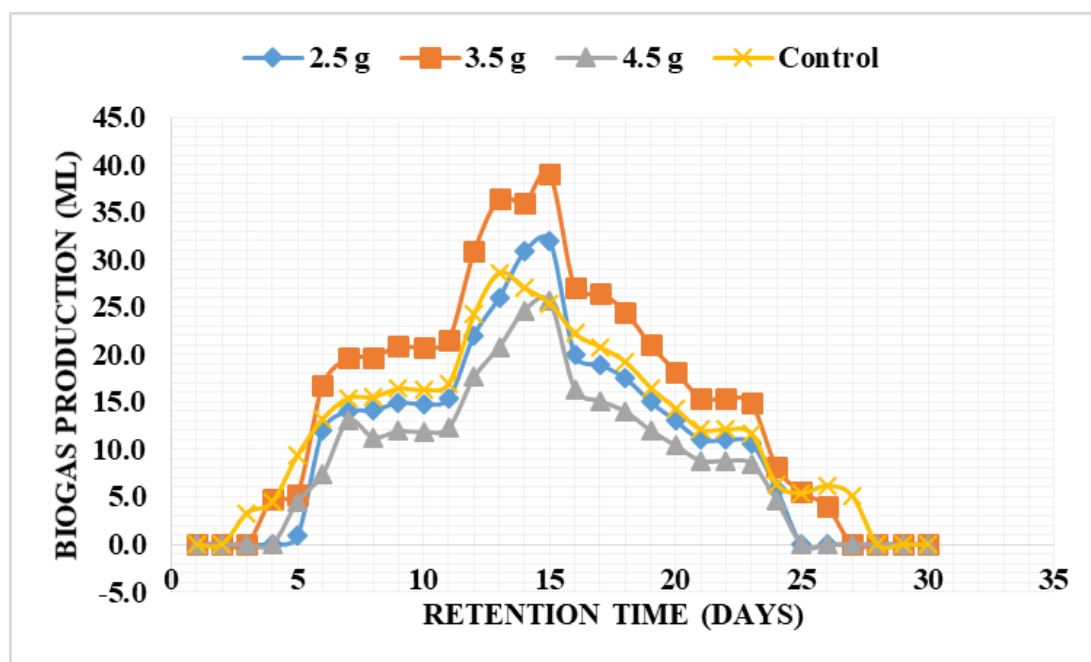


Figure 2. The results of daily biogas production for digesters where B-cat was introduced earlier into the digesters at different rates.

The difference of biogas produced by the digesters is statistically significant at 95% level of confidence. Moreover, biogas produced by control digesters is interestingly higher than the gas outputs from the two treatment digesters where 2.5 and 4.5 g of B-cat was applied. The significant production of biogas from the control digester suggested that, even though, the

biogas out from the control was 22.8% lower than the digester with 3.5 g B-cat, the effect of this catalyst did not seem to be significant (Figure 2). Addition of clay mineral have delayed onset of ammonia inhibition and process recovery after initial inhibition. The effects was not through direct antagonistic effect towards ammonia but an increased process resistance to toxic compounds (Borja *et al.*, 1996). Bentonite was found to counteract the inhibitory effect of ammonia during thermophilic anaerobic digestion of cattle manure (Angelidaki & Ahring, 1992).

However, the catalyst at some contents (2.5 and 4.5%) have retrogressed digester performances. Together, these results suggest that the application of 3.5 g B-cat is the most appropriate content for improvement of biogas production from cow dung co-digested with maize cob and food waste. However, the economics of using this finding for practical applications need to properly appraised, probably on a pilot scale.

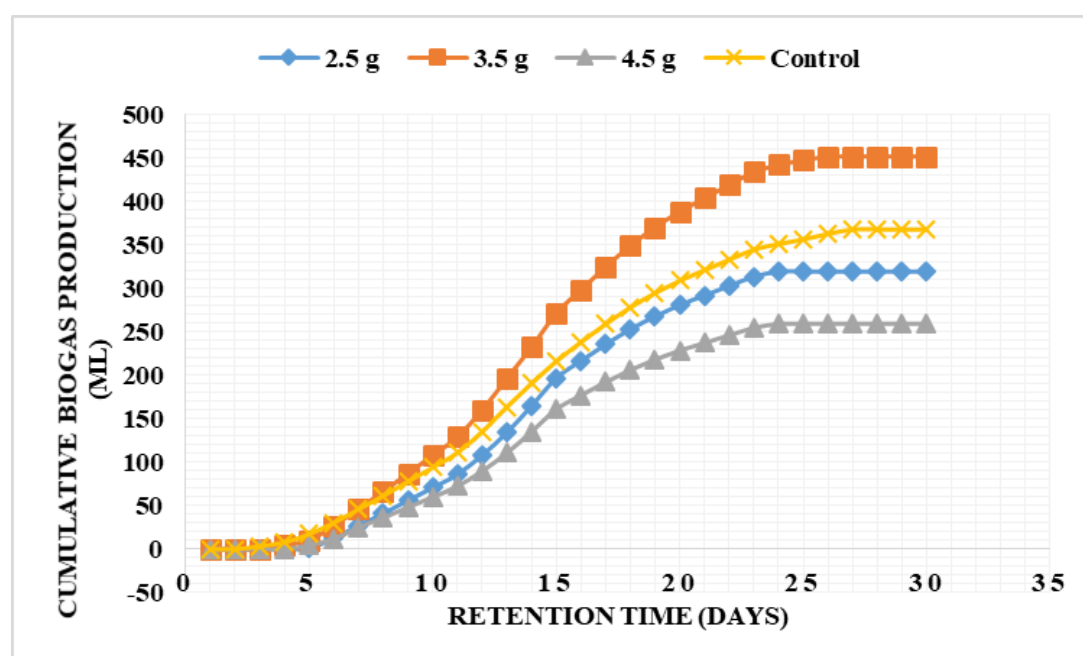


Figure 3. The results of cumulative biogas production for digesters where B-cat was introduced earlier into the digesters at different rates.

Looking at the cumulative biogas curves, it can be argued that the effect of 3.5 g B-cat was about 22.8% higher than the gas output from control digester. On the overall, the application of 3.5 g catalyst appeared to be the best treatment because it is the treatment where highest daily and cumulative biogas was obtained.

Application at One Week into the Experiment

The data in Table 3 is the results of biogas production from maize cob co-digested with cow dung and food waste subjected to B-cat, a substance hypothesised to have the capacity to minimize adverse effects of digestion involving lignocellulosic substrates.

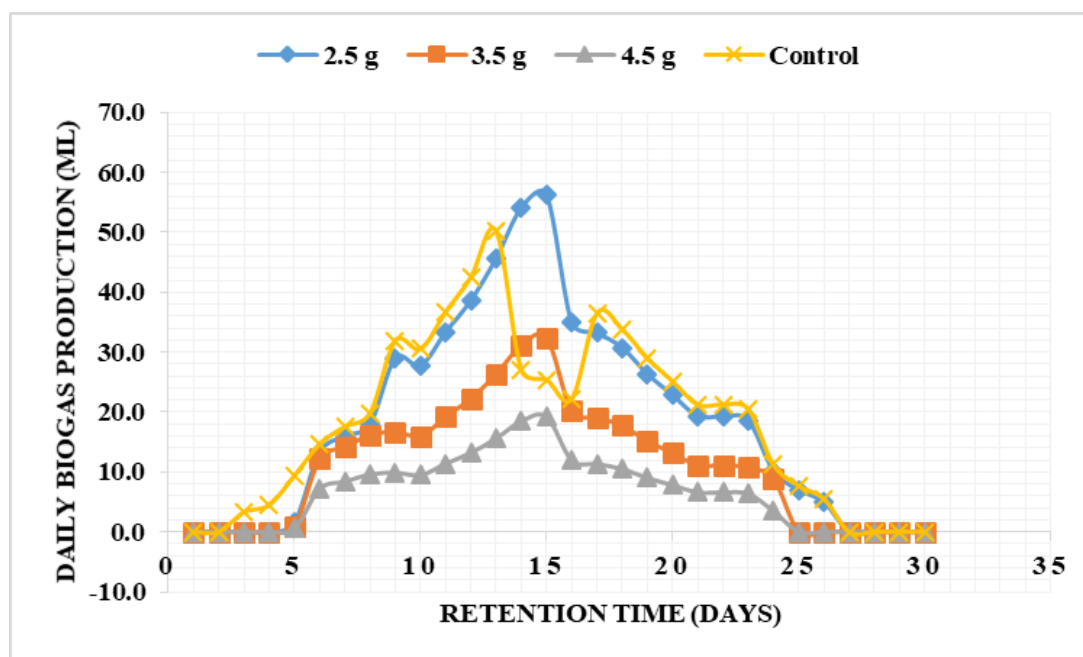


Figure 4. The results of daily biogas production for digesters where B-cat was lately introduced into the digesters at different rates.

Findings revealed that highest biogas output during the entire experiment was observed on 15th day of the experiment at a rate of 56.2 m/day and this was observed with the digester where 2.5 g of B-cat was applied. It was found that the gas production in digester with 2.5g B-cat was 75% and 192% higher than when 3.5 and 4.5 g of B-cat were applied respectively. Biogas production from 2.5 g B-cat digester was also about 12% higher than the control. The implications of this findings is that lower doses of B-cat is appropriate for use in digestion involving maize cob, cow dung and food waste. Natural clay mineral has a synergistic effect on the Ca^{2+} supply as well on the NH_4^+ removal during anaerobic digestion, which is effective for the mitigation of NH_4^+ inhibition against methane production (Tada *et al.*, 2005). However, increasing the doses have substantially impeded digester performance which also suggested that inhibition has been increased.

The information in Figure 4 is the results of cumulative biogas production for the experiment whose daily gas production was reported in Figure 3. The result illustrated that the cumulative biogas production from the best treatment (561.2 ml) was only 2.5% higher than that of control (547.6 ml) suggesting that the performance of this catalyst need to be re-evaluated to determine whether the effect of the catalyst may become clearer at this point of application.

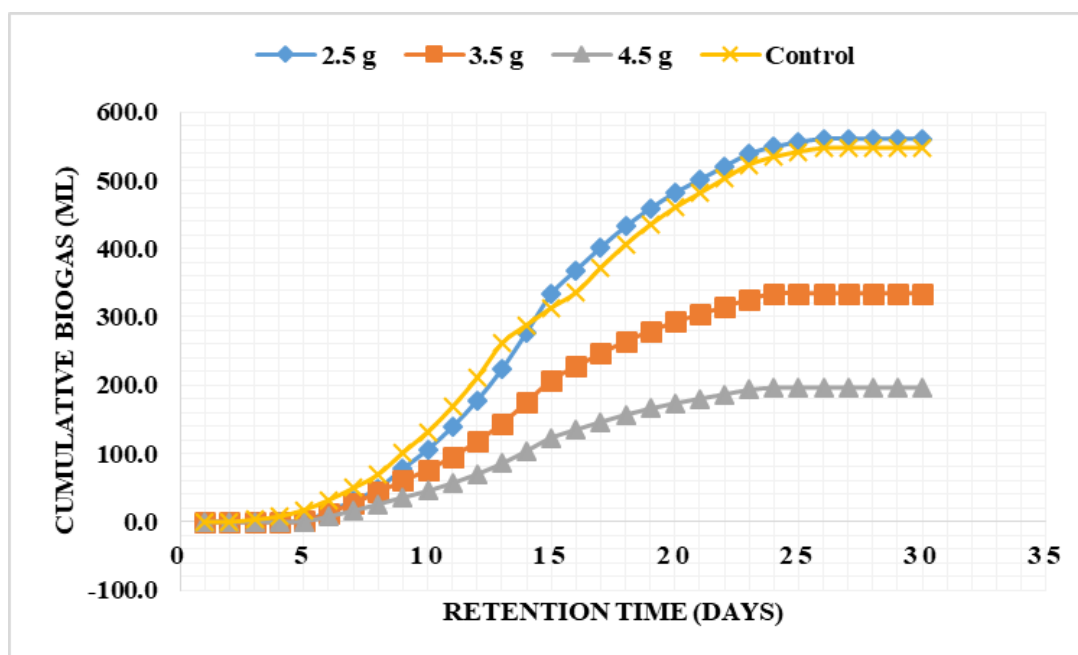


Figure 5. The results of cumulative biogas production for digesters where B-cat was lately introduced into the digesters at different rates.

It will be interesting to re-appraise the effects of 2.5 g B-cat at a different point of application during digestion and probably better outputs may be recorded.

Conclusion

This study aimed to determine the effect of different contents B-catalyst and different time of application on the performance of digesters and biogas outputs. It is found that application of 3.5 g catalyst at the onset of the experiment is an appropriate content but when the application time was delayed by a week, 2.5 g catalyst became more appropriate. It is also found that highest cumulative biogas production was obtained from 2.5 g B-cat applied one week after the commencement of the experiment.

Recommendations

1. Based on the findings of this study, processing the catalyst in a much different manner such as chemical treatment to improve void space and basicity is recommended.
2. Higher temperature for catalyst preparation is recommended.

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