Supported by tetfund TERTIARY EDUCATION TRUST FUND

IMPROVING THE QUALITY AND EFFICIENCY OF BIOGAS PRODUCTION PROCESSES BY THE USE OF CHELATING LIGANDS

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Received: December 05, 2017 **Accepted:** May 14, 2018

Abstract: The need for alternative renewable energy sources has resulted in the use of methane gas as a renewable and environmentally friendly energy source as compared to non-renewable fossil fuels. Methane gas, which is the main constituent of biogas with fuel value, was generated from cow manure digester systems. In an attempt to improve methane gas yield; reduce hydraulic retention time, and decrease the concentration of hydrogen sulphide produced within the digester systems, ethylene diamine-N, N-diacetic acid, nitrilotri-acetic acid and diethylenetriamine-pentaacetic acid were introduced as chelating ligands. Several experiments and analyses were carried out which involved the use of the Biogas 5000 analyser, Flame Atomic Absorption Spectrophotometer; and other analytical tools. The results from these analyses showed that on addition of the chelating ligands, ethylene diamine-N, N-diacetic acid, nitrilotri-acetic acid and diethylenetriamine-pentaacetic acid, there was an increase in the methane gas yield ranging from 2 to 15% and a reduction in the production of hydrogen sulphide gas from 80 to 30%. Also, a reduction in hydraulic retention time was recorded from 50 to 25 days; and on further increase in chelating ligand concentration, the hydraulic retention time reduced from 25 to 19 days. Trace metals of Iron, Cobalt, and Nickel were present at a concentration that ranged from 0.001- 0.050 mg/L; these metals reacted with the chelating ligands introduced to form metal chelates. The formation of these metal chelates resulted in an increased bioavailability of essential nutrients, promoting growth and stability of the methane producing bacteria and the formation of elemental sulphur with the release of H^+; thus, reducing hydrogen sulphide concentration. Also, the metal chelate formation resulted in the metal catalysis of the hydrolysis stage. Generally, the addition of chelating ligands to anaerobic digesters, decreases hydrogen sulphide concentration and hydraulic retention time, with a significantly increased in methane gas production.

Keywords: Methane gas, hydraulic retention time, chelating ligand, anaerobic digester

Introduction

The negative impact of fossil fuels on the environment has increased the levels of pollution in the land, air, and water. Also, the increasing depletion of the fossil fuel sources has put pressure on societies to develop renewable alternative energies sources (Midilli *et al*., 2006); with a focus on mitigation of environmental pollution.

Biogas is a renewable and an environmentally friendly alternative compared to our non-renewable fossil fuels with great potentials; such as use as transportation or automobile fuels and in the generation of power and heat (Teodorita *et al.*, 2008). It is obtained as a byproduct of anaerobic treatment processes of organic waste materials and consist mainly of methane (CH_4; 55-65%), carbon (IV) oxide (CO_2; 30-40%), and Hydrogen sulphide (H_2S; 0-6%); depending on the nature of the waste material.

Several countries have already setup large scale biogas technologies making use of a variety of waste materials arising from industries, communities, households, plants and animals waste. Animal wastes are one of the most common wastes readily available for the production of biogas. But, with a major disadvantage of generating a very high concentration of H_2S up to about 4000 ppm depending on the type of animal waste.

H_2S is a major pollutant in fossil fuel based industries, sulphur based chemical industries and biogas based units (Kenneth *et al*., 2001). Improvement of biogas quality is essential because of the toxicity of this gas which affects the environment and its highly corrosive nature which causes corrosion of metallic parts, like boiler tube engines, coming in contact with it in a few hundred hours of operation (Popoola *et al.*, 2013; Mohd *et al*., 2014). Also, internal combustion (IC) engines application requires H_2S concentration to be less than 1000 ppm for a better engine life (Gary, 2003).

Another problem with the production of biogas is the prolonged hydraulic retention time (HRT). With the use of the batch digestive systems, the most probable retention time will vary from 50 – 80 days at an optimum operating temperature of about 36°C (Lfu, 2007). Therefore, improving the biogas production efficiency by reduction in this long HRT will lead to an equal reduction in the industrial production cost (Singh *et al*., 1995; Zennaki *et al*., 1996).

Different techniques have been employed for the enhancement of biogas production. These include: recycling of digested slurry, variation of operational parameters and the use of biological and/or chemical additives (Kobayashi *et al*., 1998). From these methods, few studies have been carried out on the use of chemical additives to improve biogas production efficiency. Thus, this research focuses on the use of ethylene diamine-N, N-diacetic acid (EDDA), nitrilotri-acetic acid (NTA) and diethylenetriamine-pentaacetic acid (DTPA) in cow manure (CM) waste digester systems to improve the quality and efficiency of biogas production.

Materials and Methods

Sample collection/preparation

The EDDA, NTA, DTPA chelating ligands used, were purchased from Sigma Aldrich, while the cow manure waste sample (substrate) were obtained from the Anguwan - Yusi, Hanwa N/Extension, Zaria, Kaduna State. The waste sample was air dried for 72 h and ground to smaller particles sizes of about 30.0 nm with a mortar and pestle. The waste sample was then properly labelled and stored in an air-tight plastic container until the time of use. All reagents used were of analytical grade.

Stock solutions of EDDA, NTA and DTPA were prepared at a concentration of 1000 µM, out of which standard solutions of 10, 50 and 100 µM for the chelating ligands were prepared by serial dilution and stored in sterilized amber-coloured bottles.

Method for monitoring system performance

The performance of the various digester systems was assessed by monitoring the CH_4 -production, pH, VFA-concentration and VS-reduction as recommended by Pind *et al*. (2003). The three digesters labelled CM-EDDA, CM-NTA, and CM-DTPA were operated over a period of 50 days at a mesophilic temperature range of 29-31^{o}C and an optimum weight of 250 g.

Biogas sample analysis

Production of biogas was carried out using lab-scale anaerobic digesters fabricated from 2 L aspirator bottles according to Song *et al*. (2012) method; while the composition of the biogas produced was equally monitored on a daily basis using a biogas analyser (Biogas 5000, UK).

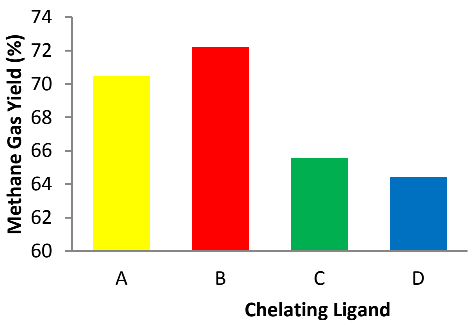
The concentration of Iron (Fe), Cobalt (Co) and Nickel (Ni) in the CM sample were determined by Flame Atomic Absorption Spectrophotometer (AAS) version AA240FS. Before analysis, small portions of the samples for each digester were filtered through a 0.45 µM membrane filter; 20 cm^3 of the filtered samples were then transferred into a 100 cm^3 pyrex beaker and the initial pH of the filtrates determined using the pH meter Jenway 3505, UK with a pH range of -2 to 16± 0.001.

Analysis of data

Data collected at the end of the study were analysed using Statistical Package for Social Sciences (SPSS) version 15.0 (SPSS Inc. Chicago, IL, USA).

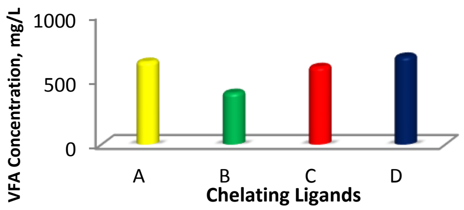
Results and Discussion

The addition of the chelating ligands to the CM digester systems brought about a general increase in the production of CH_4 gas compared to the control (Fig. 1). In the CM- EDDA digester systems, a 12% improvement in the percentage CH_4 gas yield was observed. For the CM-NTA digester system, a 15% improvement in the percentage CH_4 gas yield was equally recorded. Also, in the CM-DTPA digester system, a 2% improvement in the CH_4 gas yield was observed. Several factors are for the responsible for the performance indicted within these digester systems; some of which are the VFA concentration, presence of trace metals and formation of soluble metal chelates.



A=EDDA, **B**=NTA, **C**=DTPA, **D**=Control

Fig. 1: Effect of chelating ligand addition on methane gas yield



A=Control, **B**=EDDA, **C**=NTA, **D**=DTPA

Fig. 2: Effect of chelating ligand addition on VFA concentration

Figure 2 shows the concentrations of VFA within the respective digesters. Various studies have tried to draw a correlation between the concentration of VFA, CH_4 gas yield and the health of an anaerobic digester system (Hill and Holmberg, 1988). A well working biogas digester is characterised by low levels of fermentation intermediates and VFA concentration's of less than 2000 mg/L (Hill and Holmberg, 1988). In Fig. 2, VFA concentration within the CM-EDDA, CM-NTA and CM-DTPA digester systems were found to be: 476.05, 671.96 L and 737.63 mg/L, respectively. These values of the VFA concentration are less than the threshold value of 2000 mg/L; therefore, the low values of VFA concentration compared to the controls are implicated in the high CH_4 gas yield observed within these digester systems.

Figure 3 shows the presence of certain trace metals within the various digesters. The uptake of these trace metals Fe, Co, and Ni, which serve as nutrients within the digester systems, depends on the metal speciation and bioavailability of these metals (Marvin, 1989). It is assumed that these metals, which most often than not are present as metal sulphides within the digester, are available for microbial (methanogenic) uptake when they are present as free metal ions and as metal complexes in the soluble form (Saito *et al*., 2006).

The presence of organic and inorganic chelates will affect these metals bioavailability by the formation of metal chelates with high stability constants (Table 1). Thus, the large stability constants of EDDA, NTA and DTPA formed with the trace metals Fe, Co and Ni implies a higher proportion of these metal chelates in solution. This implies that, with the formation of metal chelates, the availability of these nutrients to the methanogens (which are the micro-organisms responsible for the production of CH_4 gas) increases, resulting in the growth and stability of the methanogenic population with an equal increase in the CH_4 gas yield (Marvin, 1989) (Fig. 3).

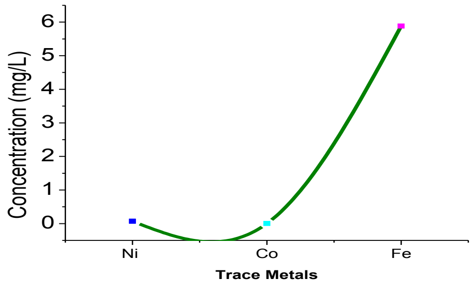


Fig. 3: Concentration of trace metals within the digester systems

Table 1: Logarithm stability constants of chelating ligands employed in this study

Chelating Ligand	Fe^{3+}	Co^{2+}	Ni^{2+}
EDDA	8.63	11.25	13.60
NTA	15.87	10.38	11.54
DTPA	28.60	18.40	20.32

Table 2: pH values within the digester systems CM, CM-EDDA, CM-NTA and CM-DTPA

WEEK	CM	CM-EDDA	CM-NTA	CM-DTPA
1	6.54	6.04	6.00	6.15
2	6.90	7.37	7.38	7.95
3	6.77	7.50	7.37	7.43

Also, the pH values in the digester systems CM-EDDA, CM-NTA and CM-DTPA ranged between 6.0- 8.0 (Table 2). This indicates that all digester systems performed appreciably above average; since the pH range of 7.0 - 8.0 signifies a stable biogas system with an optimal performance and methanogenic population (Lay *et al*., 1997).
Figure 4 shows the effect of the addition of chelating ligands on percentage yield of H_2S. The introduction of Chelating ligands EDDA, NTA and DTPA into the digester systems at a concentration of 10 µM resulted in a general decrease in H_2S concentration from 80-30% (Fig. 4). Also, on further increase in the concentration of the chelating ligands, a noticeable decrease in H_2S by about 20% was equally observed in all digester systems.

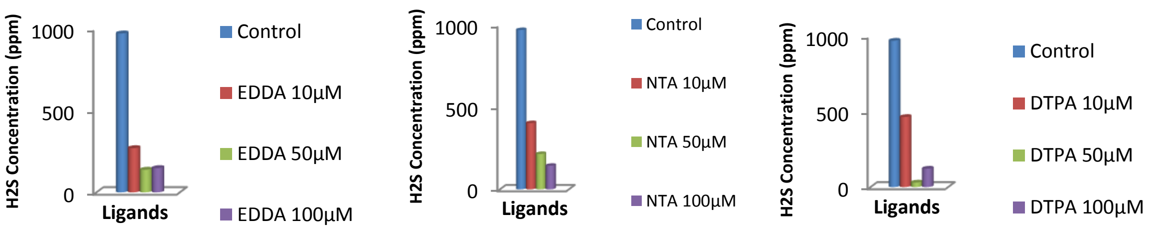


Fig. 4: Effect of increasing chelating ligand concentration on H_2S produced

The results in Fig. 4 shows that the addition of the chelating ligands served as a scrubber; helping to reduce the concentration of H_2S and thereby improving the quality of the biogas produced.
A redox reaction process is responsible for the desulphurisation observed within these digester systems. The trace metals (Fe, Co, and Ni; already confirmed to be present within the digesters), reacted with the various chelating ligands introduced to form metal chelates. These metal chelates then reacted with the H_2S gas produced absorbing the gas from the system. The reaction sequence for the absorption of the H_2S by the metal chelates is presented in the equation below:

$$H_2S_{(g)} \leftrightarrow H_2S_{(aq)} \quad \ldots\ldots\ldots\ldots 1$$

$$H_2S_{(aq)} + M^{x+}\,Chelant^{y-} \rightarrow S\downarrow + 2H^+ + 2M^{(x-1)}\,Chelant^{y-} \quad \ldots.2$$

Where; "x" denotes the charge of the metal cation
"y" denotes the charge of the chelant anion and
"M" represents the metal ion

In the absorption/redox reaction presented, H_2S comes in contact with the metal chelate to bring about the reduction of M^{n+} to $M^{(n-1)+}$ and the oxidation of H_2S to form elemental sulphur with the release of H^+ ions; thereby reducing the concentration of H_2S gas produced within the digesters (Gary, 2003).
The HRT was equally reduced with the addition of chelating ligands (Fig. 5). For the control, the HRT was 50 days but on addition of EDDA, NTA, and DTPA, the HRT reduced to 25 days. A significant production of CH_4 gas observed between the 1st and 2nd day for all digester systems containing chelating ligands. Production continued to improve until peak values were attained on the 9th, 10th and 18th day for the CM-EDDA, CM-NTA and CM-DTPA digester systems, respectively.

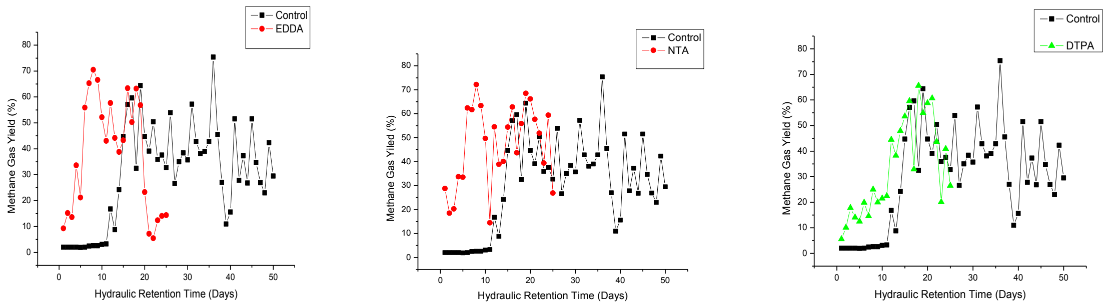


Fig 5: Effect of chelating ligand addition on HRT

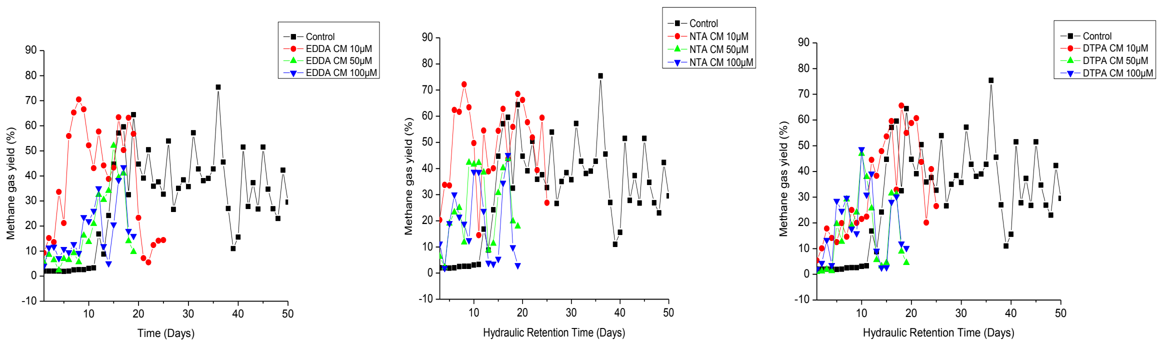


Fig. 6: Effect of increasing chelating ligand concentration on HRT

A further decrease in HRT was observed, from 25 to 19 days on increase in chelating ligand concentration from 10 µM to 100 µM for all digester systems (Figure 6).
This decrease in HRT is due to the metal chelate catalysis of the hydrolysis stage (which is the rate determining step) of the anaerobic digestion process. The metal chelate formation is a result of the reaction occurring between metals serving as nutrients within the digester system and the chelating ligands introduced. This serves as a driving force in the solvolysis process (Kroll, 1952); thus, helping to speed up the anaerobic digestion process.

Conclusion

In summary, stimulation of the digester systems by the addition of chelating ligands EDDA, NTA and DTPA, resulted in a 2 - 15% improvement in the CH_4 – production within the digester systems. A general decrease in H_2S concentration from 80 - 30% was also observed on increasing chelating ligand concentration within the CM-EDDA, CM-NTA and CM-DTPA digester systems. Also, a significant reduction in HRT was obtained on addition of the chelating ligands from 50 – 25 days. On increasing the chelating ligand concentration, further reduction in HRT was observed from 25 – 19 days. Thus, the addition of EDDA, NTA and DTPA has been shown to result in faster digester start up, reduced HRT, increased CH_4 gas yield and a reduction in H_2S gas concentration.

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