Science World Journal Vol 12(No 3) 2017
www.scienceworldjournal.org
ISSN 1597-6343

Full Length Research Article

CHELATING LIGANDS: ENHANCERS OF QUALITY AND PURITY OF BIOGAS

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ABSTRACT
The quality of biogas depends largely on the percentage of methane and hydrogen sulphide gas present. High concentration of hydrogen sulphide results in low quality biogas. This work employed the use of chelating ligands in scrubbing hydrogen sulphide gas while improving the yield of methane gas. Experimental analyses were carried out using Biogas 5000 analyser, Atomic Absorption Spectrophotometer and other classical analytical tools. Results from the analyses showed a 12 to 15 % improvement in the methane gas yield and reduction in the concentration of hydrogen sulphide gas from 80 to 30%. All digesters recorded pH within the optimum values. The cow dung (CD) digester shows significantly low volatile fatty acids concentrations which contributed to the increased methane gas yield. Trace metals like Iron, Cobalt and Nickel, found to be present within the digesters; reacted with the chelating ligands to form metal chelates which increased the bioavailability of essential nutrients; promoting the growth and stability of methanogens thus, improving methane production. The metal chelates equally undergoing a redox reaction with the hydrogen sulphide gas, produced elemental sulphur with the release of H^+ ions; thereby reducing the concentration of hydrogen sulphide. Generally, addition of ligands to substrate digesters increased methane production and significantly decreased hydrogen sulphide concentration.

Keywords: Biogas, Volatile fatty acids, Methane, Hydrogen sulphide and Ligands

INTRODUCTION

The sources of our fossil fuels are fast diminishing; therefore, the need for alternative sources of energy. Biogas is a bio-based renewable, environmentally friendly energy source as compared to non-renewable fossil fuels (Huttunen *et al*., 2014). Depending on the substrate, biogas is principally a mixture of methane (CH_4), carbon (IV) oxide (CO_2), hydrogen sulphide (H_2S) and traces of ammonia (NH_3). The biogas production via anaerobic digestion process is currently one of the most important routes in attaining environmental preservation and efficient utilization of natural resources (Sarvari *et al*., 2016). However, for profitable and safe use of its energetic potential, the biogas must satisfy certain standard which includes the purity and quality of biogas produced. H_2S is well known as one of the most common pollutants in the production of biogas. Biogas from anaerobic digestion of waste can contain up to 2000 ppm of H_2S (Osorio and Torres, 2009). Exposure to H_2S can be acutely fatal at concentrations between 500 and 1000 ppm or higher, bearing in mind that the maximum allowable daily exposure without appreciable risk of deleterious effects during a lifetime is 1.44 ppb (EPA, 2003). H_2S causes damage to electrical and mechanical equipment, and the combustion of H_2S results in the release of sulphur dioxide (SO_2), which is another gas pollutant.
In order to remove these pollutants, some classical processes have been put in place involving the use of activated carbon, zeolites, biofilters and packet towers (Bonnin, 1991),(Chen *et al*., 2001). Over the years, these technologies have yielded good results, but have also revealed high investment and working costs (Couvert *et al*., 2008b).
The percentage composition of methane in biogas, which is the main constituent of fuel affects its calorific value. Natural gas consists of 91 % methane, 5.1 % ethane, 4.8 % propane, 0.9 % butane, and about 0.61 % CO_2; while biogas consists mainly of 50-60 % CH_4 and 30-45 % CO_2 (Buratti *et al*., 2005). Based on the percentage of methane contained in it, natural gas has a higher calorific value of about 36.14 MJ/m^3 compared with biogas which has a calorific value of 21.48 MJ/m^3 (Dieter and Angelika, 2008). Therefore, improved percentage yield of CH_4 will increase biogas efficiency to a reasonable extent.

Presently, there exist few studies on the use of chemical additives as media for scrubbing biogas and improving the percentage yield of CH_4 gas. Thus, this research focuses on the use of ethylene diamine- N, N-diacetic acid (EDDA) and Nitrilotriacetic acid (NTA) chelating ligands at very low concentrations in improving the quality and purity of biogas produced from cow manure (CM).

MATERIALS AND METHODS

Sample Collection / Preparation

The EDDA and NTA used were purchased from Sigma Aldrich; while the cow manure waste sample (substrate) was obtained from Anguwan-Yusi, Hanwa New Extension, Zaria, Kaduna State. The waste sample was air-dried for 72 hours and ground to smaller particles sizes of about 30 nm with a mortar and pestle; properly labelled and stored in an air-tight plastic container. All reagents used were of analytical grade. EDDA and NTA salt (176.2 mg and 191 mg respectively) were both weighed using an analytical digital balance (Sartorius, USA) and each transferred into a separate 1000 cm^3 volumetric flask containing 500 cm^3 of deionized water. Both mixtures were continuously stirred with a glass rod till the salts completely dissolved forming a solution which was then diluted to the mark with deionized water.

Biogas sample analysis
The digester systems were operated at mesophilic temperature (27 – 30 °C). Two litres Pyrex digester bottles were used. Two hundred grams of the dry waste sample were loaded into the digesters and 1.5 litres of deionized water was added. This was sealed with a rubber bung having two bore holes to exclude air from getting into the digesters. One hole was used for temperature determination, while the other was connected to delivery tubing which was used to collect and measure the volume of biogas produced under water through the downward displacement of water method. The digesters were subjected to periodic agitation to ensure thorough mixing of the contents while maintaining intimate contact between the micro-organisms and the substrate to enhance the complete digestion of the substrate. The composition of the biogas produced was equally monitored using a biogas analyzer (Biogas 5000, UK) on a daily basis. The compositions of biogas generated within the digesters on addition of chelating ligands were also studied and the results recorded.

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, the samples from each digester were filtered through a 0.45 GM membrane filter. The filtered 20 cm3 samples were transferred into a 100 cm3 Pyrex beaker and the initial pH's of the filtrates determined using the pH meter (Jenway 3505, UK) with a pH range of -2 to 16 ± 0.001.

RESULTS AND DISCUSSION
Various studies have tried to draw correlation between the concentration of volatile fatty acids (VFA), CH_4 gas production and the health of the anaerobic digester system (Hill and Holmberg, 1988). A well working biogas digester is therefore characterized by CH_4 gas yields of above 50 %, low levels of fermentation intermediates and VFA concentration of less than 2000 mg/L (Hill and Holmberg, 1988). Results showing the VFA concentrations of the digester system studied are presented in (Figure 1). The results showed that the CM-digester recorded a final VFA concentration of 728.61 mg/L which was significantly lower than the threshold value of 2000 mg/L with an optimum pH ranging from 6.54-6.77. This stable biogas system performance was evident in the high CH_4 gas production level (64.7 %) observed from the CM-digester system (Figure 2).

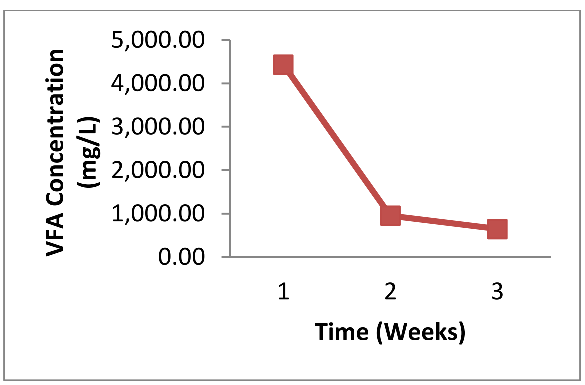

Figure 1: VFA Concentration in the CM-Digester

Table1: pH values of the CM, CM+EDDA and CM + NTA substrate

Week	CM	CM + EDDA	CM + NTA
3	6.54	6.04	6.00
6	6.90	7.37	7.38
9	6.77	7.50	7.37

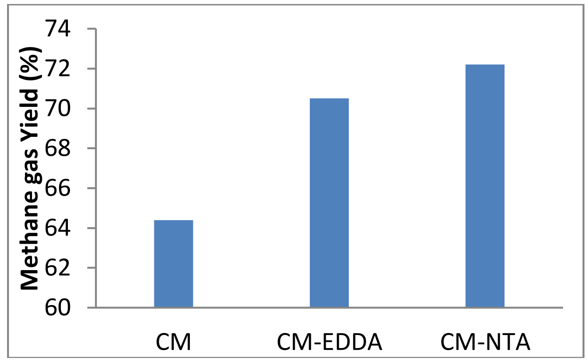

Figure 2: Percentage Methane Gas Yield

Another factor which determines the performance of an anaerobic digester system is the presence of trace metals most especially Iron (Fe) which serves as nutrients for the methanogens (Marvin, 1989). It is also assumed that these metals are only available for microbial uptake when they are present as free metal ions and as metal complexes in the soluble form (Saito *et al*., 2002; Worm *et al*., 2006). The amount of trace metals present in the digesters, as obtained via atomic absorption spectroscopy, is presented in Figure 3. Fe is particularly important for the growth of bacteria; results from Figure 3 shows that Fe was present at a higher concentration compared to those of the other metals present in the CM-substrate.
Also, researchers have reported (Mosey *et al*., 1971) that bioavailability of the necessary nutrients (i.e. the availability for microbial uptake and growth) within the substrates is controlled by the total metal concentration. High concentrations of some of these trace metals like cobalt (Co) and nickel (Ni) usually have an inhibitory effect on the anaerobic digester system. Thus, the presence of these metal ions within the minimum acceptable range is necessary to enhance CH_4 gas production. Results from Figure 3 show the presence of these metal ions at the acceptable range (0.001 - 0.050 mg/L) for samples taken out of the CM digester system. This further explains the reason for the high CH_4 gas yield obtained within the CM-digester system.

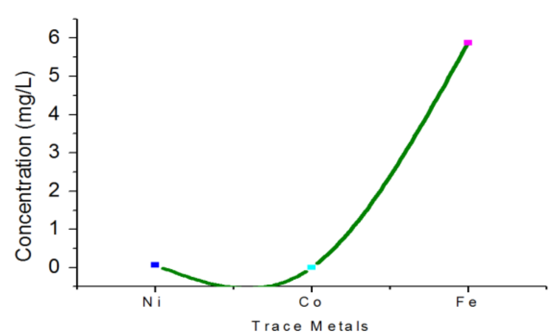

Figure 3: Concentration of Trace Metals in CM Substrate Digester

On addition of the chelating ligands EDDA and NTA into the CM-digester the anaerobic digester performed appreciably above average with a 12 and 15 % increase in the CH_4 gas yield respectively (Fig. 2). Also, a final VFA concentration was given as 476.05 mg/L and 671.96 mg/L respectively (Figure 4).

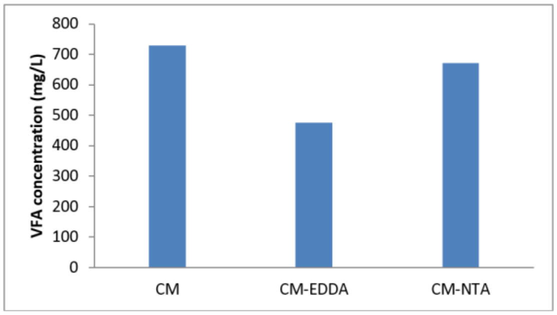

Figure 4: VFA Concentration within Anaerobic Digesters

In summary, the VFA concentrations were significantly lower than 2000 mg/L with pH ranging from 6 to 7.5 (Table 1), indicating that the CM - digesters containing chelating ligands, performed appreciably above average. This low VFA concentration / optimum pH values (Table 1) is implicated in the 12 and 15 % improvement in methane gas yield observed within these EDDA and NTA digesters respectively (Figure 2). Other variables like the number of heterocyclic rings formed in chelate and presence of the metals as metal chelates also contributes to the bioavailability of ions serving as nutrients within the digester (Anderson, 1999). In addition, EDDA and NTA chelating ligands form lipophilic complexes (Hartwig *et al*., 1993) which permeate the plasma membrane of an organism (methanogen), allowing them to reach the sites of metal storage and thus form stable soluble complexes with these metal ions thereby leading to the significant improvement in CH_4 production observed within these digesters (Klaassen, 2006).

Figure 5a and 5b, shows the effect of addition of EDDA and NTA chelating ligands on H_2S concentration within the CM-digester. The results showed a general decrease in H_2S concentration from 80 to 30 % on addition of chelating ligands at a concentration of 10µM. On further increase in the concentration of the chelating ligands, a noticeable decrease in the H_2S concentration by about 20 % was equally observed in both digesters.
A redox reaction process is responsible for the desulphurization observed within the digesters. Metals serving as nutrients already present within the system (Figure 4) react with the various chelating ligands introduced, to form metal chelates. These metal chelates then react with the H_2S gas produced, absorbing the gas from the system (Gary, 2003).

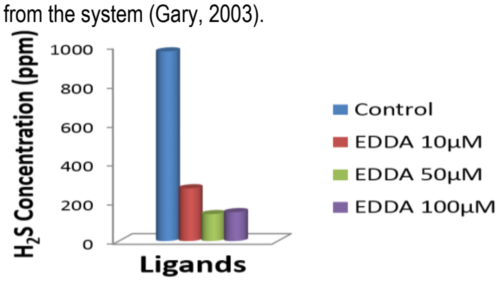

Figure 5a: H_2S gas concentration from CM-EDDA digester

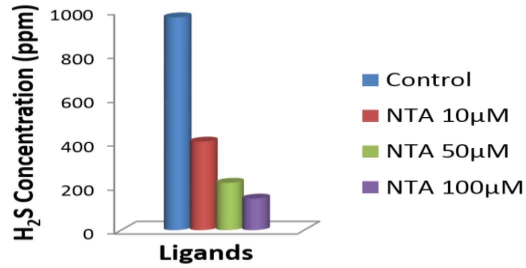

Figure 5b: H_2S gas concentration from CM-NTA digester

$H_2S_{(g)} \leftrightarrow {}_2S_{(aq)}$...(1)
$H_2S_{(aq)} + M^{x+}\ Chelant^{y-} \rightarrow S\downarrow + 2H^+ + 2M^{(x-1)}\ Chelant^{y-}$.............(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 reaction, 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; thus reducing the H_2S concentration within the digester (Gary, 2003). This implies that the addition of chelating ligands has served as a scrubber, helping to reduce the concentration of H_2S as well as improve the quality of the methane gas produced.

Conclusion

In summary, stimulation of digester systems by addition of EDDA and NTA chelating ligand has been used to improve the percentage yield of methane and is equally effective in reducing the concentration of H_2S gas in the digesters.

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